

Diphenolic Acid-Derived Hyperbranched Epoxy Thermosets with High Mechanical Strength and Toughness

Laihui Xiao, Wenbin Li, Shuai Li, Jie Chen,* Yigang Wang, Jinrui Huang, and Xiaoan Nie

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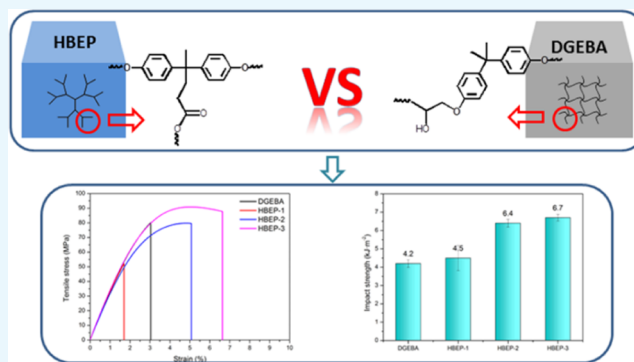


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Supporting Information

ABSTRACT: Diglycidyl ether of bisphenol A (DGEBA) is a kind of widely used epoxy resin, but its thermosets normally show high brittleness and poor impact resistance due to the intrinsic rigid aromatic rings, which limit its application greatly. To avoid this drawback, we proposed a method to prepare a series of hyperbranched epoxies (HBEPs) with different molecular weights. After HBEPs were cured with methyl tetrahydrophthalic anhydride (MTHPA), characterizations were carried out to evaluate the properties of the cured HBEP samples. Testing results indicate that the hyperbranched thermosets can achieve excellent mechanical strength and toughness (tensile strength: 89.2 MPa, bending strength: 129.6 MPa, elongation at break: 6.1%, toughness: 4.5 MJ m⁻³, and impact strength: 6.7 kJ m⁻²), which are superior to those of the thermosets of commercial DGEBA (tensile strength: 81.2 MPa, bending strength: 108.2 MPa, elongation at break: 3.0%, toughness: 1.5 MJ m⁻³, and impact strength: 4.2 kJ m⁻²). In addition, HBEP with the highest molecular weight and degree of branching shows the best comprehensive mechanical properties. All hyperbranched thermosets exhibit high glass-transition temperatures (T_g) and thermostability, which further illustrates the potential application value of HBEPs.



1. INTRODUCTION

Epoxy resin is one of the most important thermosetting resins, which has been widely used as coatings, adhesives, matrix resins, and so on.^{1,2} In particular, the diglycidyl of bisphenol A (DGEBA), a commercial epoxy resin, exhibits high mechanical strength, excellent thermodynamic properties, and favorable stability after being cured with curing agents.³ However, the rigid benzene structure of DGEBA and the high cross-linking density of its thermosets normally result in brittleness and poor impact strength, limiting its application to a large extent.^{4–6}

Previous research has demonstrated that epoxy thermosets incorporated with a hyperbranched structure may enhance mechanical strength and toughness simultaneously.^{7,8} Because a hyperbranched structure has a high density of cross-linkers, it may increase the cross-linking density of the whole thermosets once this structure was incorporated and further increase mechanical strength. On the other hand, hyperbranched polymers have a higher content of free volume than their linear counterparts, which is beneficial to improve the toughness of the epoxy resin.^{9–11} Fei et al. used a hyperbranched tannic acid derivative to toughen the DGEBA/methylhexahydrophthalic anhydride (MeHHPA) curing system, and the results indicated that tensile strength, modulus, and impact strength of DGEBA thermosets can be improved simultaneously at a certain adding amount.¹² Similar results were also achieved in our previous study, in which we

toughened the DGEBA/polyetherdiamine D230 curing system with a tung oil-based hyperbranched polyester.¹³

However, most studies are focused on the toughening effect of hyperbranched polymers used as modifiers for DGEBA thermosets rather than the properties directly used as matrix resins. Even though a few studies have been reported, the mechanical properties of the prepared hyperbranched thermosets still need to be enhanced.^{14–17} Karak and De prepared different kinds of hyperbranched epoxies by a one-pot polycondensation reaction, while the tensile strengths of all the cured thermosets were less than 50 MPa, which may be due to a high proportion of flexible chains in the hyperbranched structure.^{14–16} Liu et al. reported a way to prepare hyperbranched epoxies from DGEBA, but their cured samples broke before yield and showed low elongations at break, which indicated the low toughness.¹⁷ Therefore, it is still a challenge to prepare hyperbranched epoxy resins with high mechanical strength and toughness.

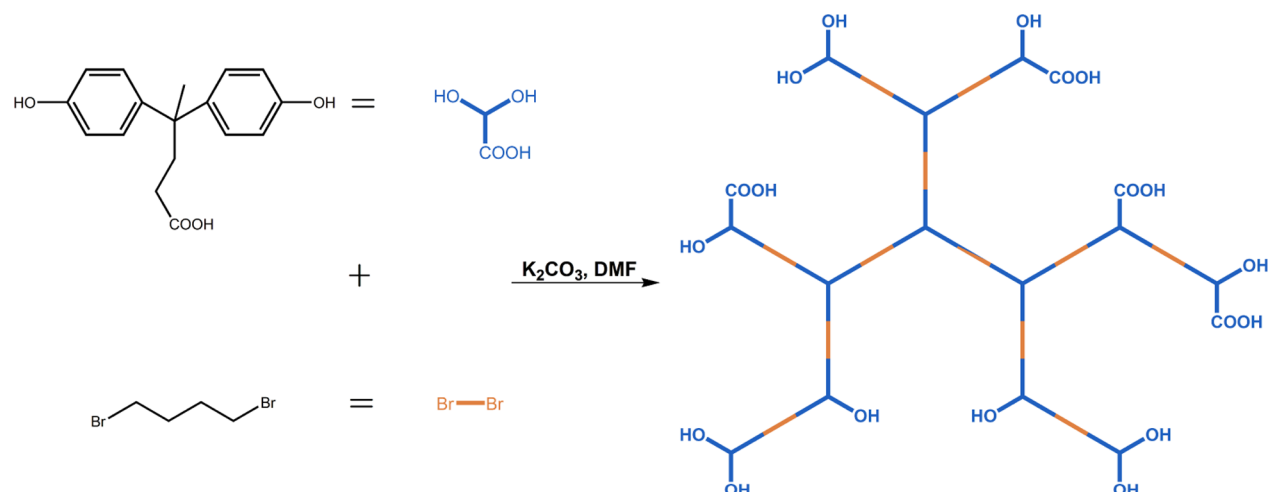
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Scheme 1. General Synthetic Routes of HBPs



Herein, we proposed a two-step process to prepare hyperbranched epoxy resins from diphenolic acid and dibromobutane, which were expected to be with high mechanical strength and toughness. An A3 + B2 strategy was carried out to synthesize hyperbranched frameworks, and then ending functional groups were epoxidized by epichlorohydrin to prepare epoxies. In this way, diphenolic acid is used as the branching unit, and its aromatic rings may endow products with high mechanical strength, while dibromobutane serves as the flexible unit, which can absorb energy through the movement of its flexible chains.¹⁸ Besides, by controlling the ratio of bisphenol acid and dibromobutane units, hyperbranched epoxies with various molecular weights and the degree of branching (DB) were prepared. After all the hyperbranched samples were fully cured, a series of tests were conducted to determine the performances of the final thermosets and to reveal the mechanisms.

2. EXPERIMENTAL SECTION

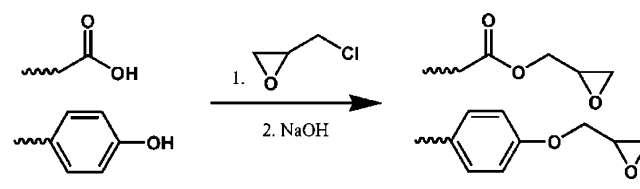
2.1. Materials. Diphenolic acid [DPA, Saen Chemical Technology (Shanghai) Co., Ltd.], 1,4-dibromo butane (DBB, Shanghai Aladdin Biochemical Technology Co., Ltd.), *N,N*-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd.), potassium carbonate (K_2CO_3 , Sinopharm Chemical Reagent Co., Ltd.), acetone (Nanjing Chemical Reagent Co., Ltd.), ethyl acetate (Shanghai Titan Scientific Co., Ltd.), anhydrous magnesium sulfate ($MgSO_4$, Shanghai Macklin Biochemical Co., Ltd.), epichlorohydrin (ECH, Shanghai Lingfeng Chemical Reagent Co., Ltd.), benzyltriethylammonium chloride (TEBAC, Shanghai Aladdin Biochemical Technology Co., Ltd.) sodium hydroxide (NaOH, Shanghai Aladdin Biochemical Technology Co., Ltd.), calcium oxide (CaO, Sinopharm Chemical Reagent Co., Ltd.), methyl tetrahydrophthalic anhydride (MTHPA, Chengdu Ai Keda Chemical Reagent Co., Ltd.), 2,4,6-tris(dimethylaminomethyl)phenol (TAP, Saen Chemical Technology (Shanghai) Co., Ltd.), and ethylene glycol diglycidyl ether [EGDGE, epoxy value: $0.7 \text{ mol (100 g)}^{-1}$, Shanghai Rin Technology Development Co., Ltd.] were used as received without any further purification.

2.2. General Procedures of Preparation. **2.2.1. Hyperbranched Polymers (HBPs).** The general synthetic method for HBPs is shown in Scheme 1. Diphenolic acid, 1,4-dibromo

butane, potassium carbonate, and DMF were charged into a round-bottomed flask, and the mixture was stirred at 60°C for 20 h. After cooling to room temperature, the mixture was transferred into a separating funnel, and deionized water was added to it. Then, ethyl acetate was added to extract the product, and brine and anhydrous $MgSO_4$ were used to wash and dry the solution. After ethyl acetate was evaporated with a rotary evaporator, hyperbranched polymers were obtained. Then, the ratio of diphenolic acid and 1,4-dibromo butane was changed to prepare HBPs with various molecular weights. The detailed stoichiometric ratio of reactants for HBPs, yields, and functional group contents are presented in Table S1.

2.2.2. Hyperbranched Epoxy Resins (HBEPs). The general epoxidation reaction of HBPs is illustrated in Scheme 2. To be

Scheme 2. General Epoxidation Reaction of HBPs



specific, HBP (1 equiv functional group), epichlorohydrin (10 equiv), and benzyltriethylammonium chloride (0.01 equiv) were added into a flask equipped with a condenser and a thermometer. The reaction system was heated to 117°C and stirred for 3 h in a N_2 atmosphere. After it was cooled to 60°C , sodium hydroxide (1 equiv) and calcium oxide (1 equiv) were added into the flask, and the system reacted for another 4 h. Then, the precipitate was removed by filtration, and excess epichlorohydrin was evaporated by a rotary evaporator. Finally, orange hyperbranched epoxy resins were obtained, decoded HBEP-1, HBEP-2, and HBEP-3. The detailed stoichiometric ratio of reactants for HBEPs, yields, and epoxy values are presented in Table S2.

2.2.3. Preparation of Thermosets. According to Table S2, HBEPs are cured by mixing with ethylene glycol diglycidyl ether and methyl tetrahydrophthalic anhydride at 50°C , and 2,4,6-tris(dimethylaminomethyl)phenol was incorporated as a catalyst. After the mixtures became homogeneous, they were degassed by vacuum. Then, samples were transferred into stainless molds preheated at 80°C , and the curing process was

conducted at 120 °C for 2 h and 160 °C for 4 h. In the meantime, DGEBA, which was set as the control, was cured through the same method.

2.3. Characterization. Fourier transform infrared (FTIR) spectra were recorded by a Thermo Scientific Nicolet iS10 spectrometer in the wavenumber range of 600–4000 cm^{-1} . A Bruker 400 MHz spectrometer was used to record the nuclear magnetic resonance (NMR) spectra by using dimethylsulfoxide as the solvent and tetramethylsilane as the internal standard. A Waters1515 gel permeation chromatography (GPC) (Waters Corporation, Milford, MA, USA) was used to determine different kinds of molecular weight and their dispersity (\bar{D}). The tests were carried out at room temperature, and tetrahydrofuran and polystyrene were used as the solvent and the standard, respectively.

An Instron 4201 machine equipped with a 30 kN electronic load cell was used to conduct the tensile test and three-point bending test, which are according to standards of GB13022-91 and GB/T9341-2008, respectively, and their corresponding cross-head speeds are 5 mm min^{-1} and 3 mm min^{-1} . According to the standard of GB/T1043.1-2008, the notched impact strength was conducted to evaluate the toughness of the sample, and the depth of the notch in samples is 1 mm. All mechanical tests were carried out at room temperature (20 °C).

Dynamic thermomechanical properties of all samples were characterized by dynamic mechanical analysis (DMA) Q800 instruments. A dual cantilever mode with an oscillating frequency of 1 Hz was applied and test temperature was controlled from -50 to 180 °C at 3 °C min^{-1} .

Thermal stability was detected through a TG209F1 TGA (Netzsch) instrument, and the temperature was increased from 30 to 800 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere.

A 3400 N-I scanning electron microscope (Hitachi) was used to investigate the surface morphology, and the acceleration voltage is 15 kV. Fractured surfaces were obtained from tensile tests and were coated with gold before the examination.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. In this study, HBEPs were prepared by a two-step process. First, HBPs were synthesized through an A3 + B2 condensation polymerization, and FTIR, NMR, and GPC were performed to characterize their structures. Characterization results indicate that all HBPs have a similar structure; thus, HBP-3 was presented as an example, and other figures of structural characterization are shown as the Supporting Information. In Figure 1, the peaks at 3374 and 1702 cm^{-1} correspond to the phenolic group and carboxyl acid, respectively, and a shoulder peak appears at 1727 cm^{-1} , which is assigned to the ester group, suggesting that carboxyl acids are involved in condensation polymerization.⁴ The ^1H NMR spectrum of HBP-3 is shown in Figure 2a, the chemical shifts at 3.7–4.2 and 1.7–2.1 ppm indicate the formation of the ether bond.¹⁰ These results indicate the successful preparation of HBPs.

The molecular weights of HBPs were determined by GPC, and the test results are presented in Table 1 and Figure 3. As we all know, the molecular weight and polydispersity are higher as the stoichiometric ratio of the two monomers is closer to 1.¹⁹ Therefore, HBP-1 has the minimum M_n , M_w , and \bar{D} , while these parameters of HBP-3 are the highest.

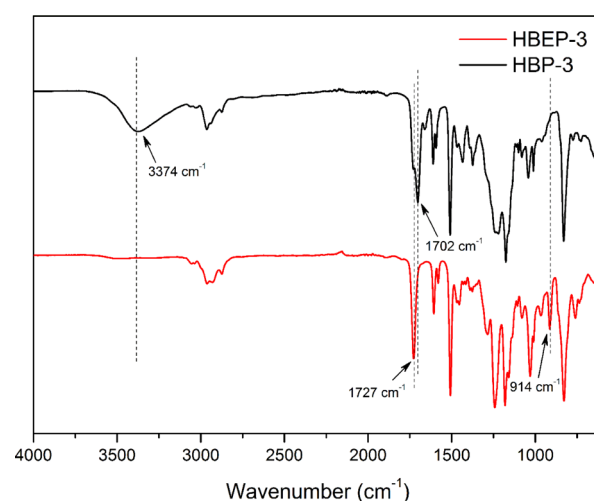


Figure 1. FTIR spectra of HBP-3 and HBEP-3.

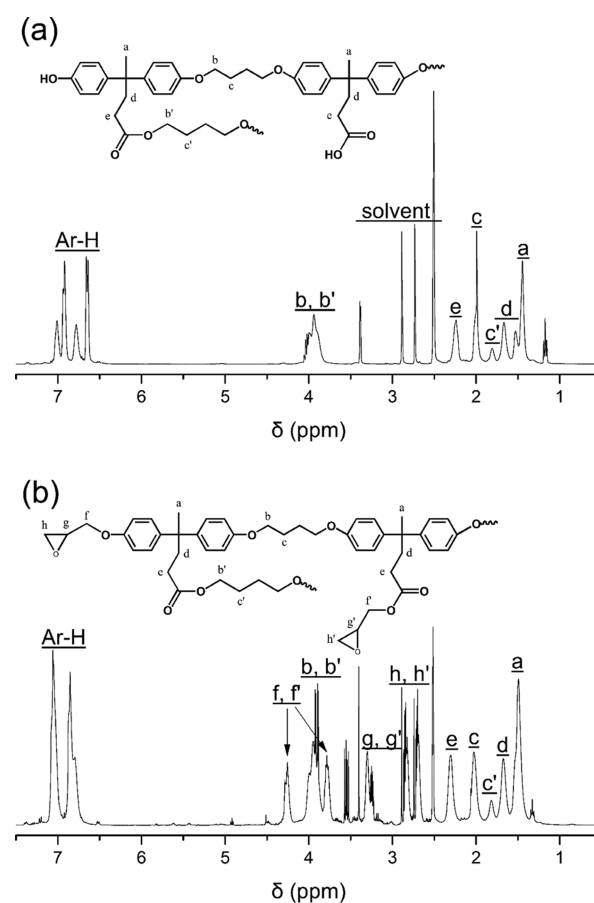


Figure 2. ^1H NMR spectra of HBP-3 (a) and HBEP-3 (b).

Table 1. Physical Properties of HBPs

code	M_n (g mol^{-1})	M_w (g mol^{-1})	\bar{D} (M_w/M_n)	DB
HBP-1	2177	4301	1.98	0.28
HBP-2	2648	6971	2.63	0.39
HBP-3	3810	14361	3.77	0.43

According to previous reports,¹³ ^{13}C NMR was used to determine the DB. Because the molecular weights of HBPs were relatively low, the value of DB was calculated by the modified equation^{20,21}

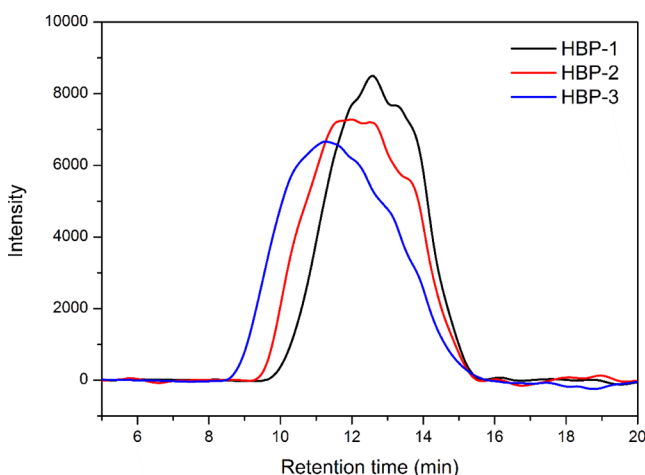


Figure 3. GPC curves of HBPs.

$$DB = \frac{2D}{2D + L} \quad (1)$$

where D and L are the contents of dendritic units and linear units, respectively, which can be obtained by integrating the ^{13}C NMR spectra (Figure S2). As shown in Figure S3, the monosubstituted, disubstituted, and trisubstituted diphenolic acid, corresponded to the terminal, linear, and dendritic units, peaks at 44.24, 44.33, and 44.42, respectively.²² The detailed values of DB calculated according to the formula are listed in Table 1. Just as we expected, a higher amount of DBB consumes more functional groups of DPA, contributing to more dendritic units and a higher DB (Table 1).

In the second step, HBEPs were synthesized via the epoxidation reaction between HBPs and epichlorohydrin. The changes of the functional groups can be observed intuitively in the FTIR spectra (Figure 1), where peaks assigned to phenolic and carboxyl groups disappear, while instead, a peak at 914 cm^{-1} appears, which corresponds to the epoxy group.^{23,24} Besides, the ^1H NMR spectra of HBEPs can prove the successful preparation as well. As the spectrum of HBEP-3 shown in Figure 2b, the chemical shifts at 2.6–2.9 and 3.2–3.4 ppm are attributed to the epoxy group, and the signals peak at 4.3 and 3.7 ppm correspond to the methylene adjacent to the epoxy group.^{23,25}

The epoxy values of HBEPs are determined via the acetone–hydrochloride titration method. Epoxy values of HBEP-1, HBEP-2, and HBEP-3 are 0.347, 0.340, and 0.338 mol $(100\text{ g})^{-1}$, respectively. Because there are fewer phenolic and carboxyl groups left as the stoichiometric ratio of the two monomers in polycondensation is closer to 1, then fewer epoxy groups can be grafted, thus epoxy values show a decreasing tendency.

3.2. Dynamic Mechanical Analysis. DMA was carried out to analyze the viscoelastic properties of HBEP thermosets. As the result curves are shown in Figure 4, all samples exhibit only one glass transition. The temperature corresponding to the peak of $\tan \delta$ was defined as the glass-transition temperature (T_g), and the exact values are listed in Table 2.

Table 2. DMA Parameters of the Neat and Toughened Epoxy Resin Thermosets

sample	T_g ($^{\circ}\text{C}$)	E' (MPa)	V_e ($10^{-3}\text{ mol cm}^{-3}$)
DGEBA	99.45	6.37	0.63
HBEP-1	92.91	16.76	1.70
HBEP-2	87.36	15.12	1.55
HBEP-3	85.86	15.05	1.55

Obviously, DGEBA has the highest T_g value, which is $99.45\text{ }^{\circ}\text{C}$, and T_g 's for HBEP samples show a downward tendency from 92.91 to $85.86\text{ }^{\circ}\text{C}$. That is because HBEPs incorporate a large number of linear chains, which are more likely to move at a low temperature. Thus, the more linear chains incorporated, the lower the T_g is.

Besides, cross-linking density (ν_e) is calculated according to the following formula

$$\nu_e = \frac{E'}{3RT} \quad (2)$$

where R is the gas constant [$8.314\text{ J (mol k)}^{-1}$], T is the absolute temperature at $T_g + 30\text{ }^{\circ}\text{C}$, and E' is the storage modulus at $T_g + 30\text{ }^{\circ}\text{C}$.^{25,26} It is obvious that HBEPs show much higher ν_e values than that of DGEBA, which is due to the high branching degree in HBPE. The branching point in HBEPs is formed by diphenolic acid; thus HBEP-1, which has the highest content of diphenolic acid, shows the maximum ν_e among the three hyperbranched samples.

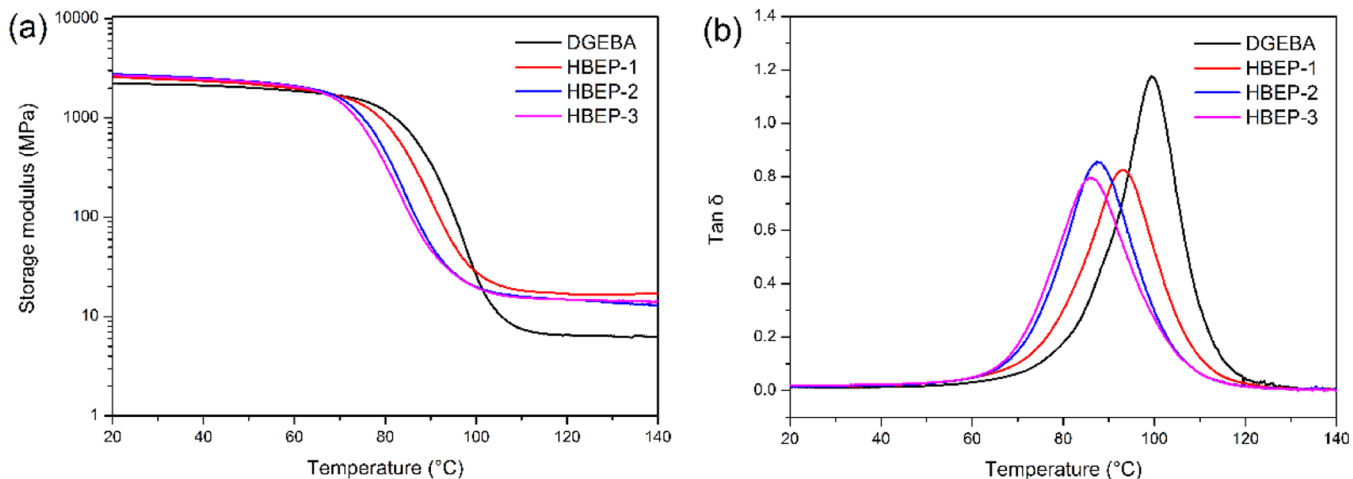


Figure 4. DMA results: (a) curves of storage modulus and (b) curves of the $\tan \delta$.

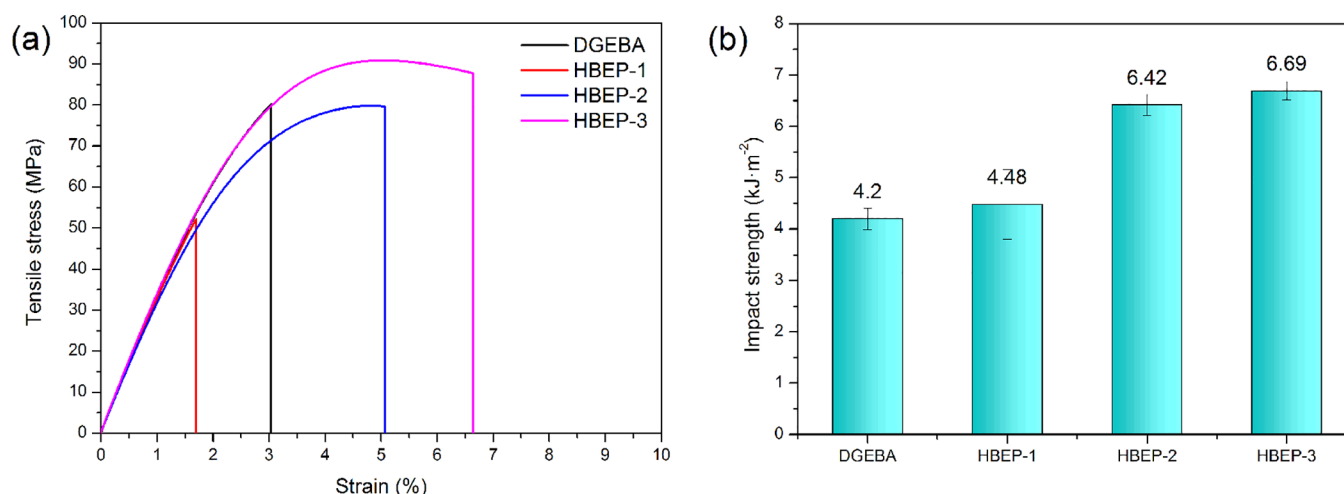


Figure 5. Comparison of mechanical properties: (a) representative curves from tensile tests and (b) results from the notched impact tests.

Table 3. Mechanical Properties of Cured Epoxy Samples

properties	DGEBA	HBEP-1	HBEP-2	HBEP-3
tensile strength (MPa)	81.2 ± 1.0	50.1 ± 2.1	80.1 ± 0.3	89.2 ± 1.2
elongation at break (%)	3.01 ± 0.1	1.6 ± 0.1	5.1 ± 0.1	6.1 ± 0.6
Young's modulus (MPa)	3567.5 ± 40.7	3452.4 ± 22.36	3582.7 ± 243.7	3529.6 ± 34.3
toughness ^a (MJ m ⁻³)	1.5 ± 0.1	0.4 ± 0.1	3.0 ± 0.1	4.5 ± 0.2
impact strength (kJ m ⁻²)	4.2 ± 0.2	4.5 ± 0.7	6.4 ± 0.2	6.7 ± 0.2
bending strength (MPa)	108.2 ± 0.6	116.2 ± 1.6	127.3 ± 0.6	129.6 ± 1.0
bending modulus (MPa)	2804.2 ± 174.5	2980.5 ± 16.2	2906.3 ± 67.7	3433.3 ± 10.2
hardness (HD)	76.0 ± 1.6	88.3 ± 1.7	89.0 ± 0.8	88.3 ± 0.5

^aCalculated by integrating the area under stress–strain curves.

3.3. Mechanical Properties. Mechanical tests were used to illustrate the practicability of HBEPs. In the tensile test (Figure 5a), the samples of DGEBA and HBEP-1 break before yield; thus, they exhibit low values of elongation at break and poor toughness. By contrast, thermosets of HBEP-2 and HBEP-3 yield before the break and show great improvement in terms of elongation at break, suggesting good toughness. On the other hand, although thermosets of HBEPs and DGEBA share a similar value of Young's modulus at about 3500 MPa, the tensile strength of HBEP-3 is 89.2 MPa, which is higher than that of DGEBA. In addition, bending strengths and moduli of HBEPs show a simultaneous upward tendency from HBEP-1 to HBEP-3, and all values are higher than that of DGEBA (Figure S5). Besides, the values of hardness for all HBEPs are about 88 HD, while that for DGEBA is 76 HD. Thus, these results indicate the excellent mechanical strength of HBEPs.

To better evaluate the comprehensive mechanical properties of thermosets, toughness, which is the integral value from the stress–strain curve, was introduced in this study. As shown in Table 3, HBEP-1 breaks at low stress and strain; thus, it has the minimum toughness value, while HBEP-2 and HBEP-3 break after yield, contributing to higher toughness values (3.0 and 4.5 MJ m⁻³, respectively), which are significantly higher than that of DGEBA (1.5 MJ m⁻³). The excellent toughness of HBEP-2 and HBEP-3 can be determined by the notched impact test as well. As shown in Figure 5b and Table 3, HBEP-2 and HBEP-3 exhibit higher impact strengths than DGEBA and HBEP-1. Therefore, these results from mechanical tests demonstrate that the thermosets of HBEPs have excellent toughness and mechanical strength simultaneously, and their

comprehensive mechanical performances are superior to those reported previously.^{14,15,27–29}

These results may be interpreted in terms of cross-linking density and hyperbranched structure. As we all know, fabricating a hyperbranched structure in thermosets may improve cross-linking density and incorporate more free volume, which can enhance strength and toughness simultaneously.¹⁰ Besides, the flexible chains in the hyperbranched framework are beneficial in consuming energy through chain movement. Therefore, HBEP-2 and HBEP-3 show excellent mechanical strength, toughness, and impact strength. However, HBEP-1 has the lowest DB, while showing the highest cross-linking density, and both of the two factors have an adverse impact on toughness. Besides, in the framework of HBEP-1, the content of the flexible segment that derives from DBB is the least, which may be the other factor leading to poor toughness.

3.4. Morphology Analysis. SEM was used to study the fracture surfaces from tensile tests and further illustrate the microstructures of HBEP thermosets. As shown in Figure 6, DGEBA, HBEP-2, and HBEP-3 have a similar fracture surface, where many cracks are radially distributed, while HBEP-1 has a smooth fracture surface. These indicate the lowest toughness of HBEP-1, which is in line with the conclusions drawn from mechanical tests. Just as explained above, HBEP-1 has the highest cross-linking density, but the lowest DB and content of flexible chains; thus, it is unable to prevent crack propagation and leads to a smooth fracture surface. Although DGEBA has no hyperbranched structure, its cross-linking density is lower than that of any other sample, which endows the thermoset with the ability to induce plastic deformation. However, the

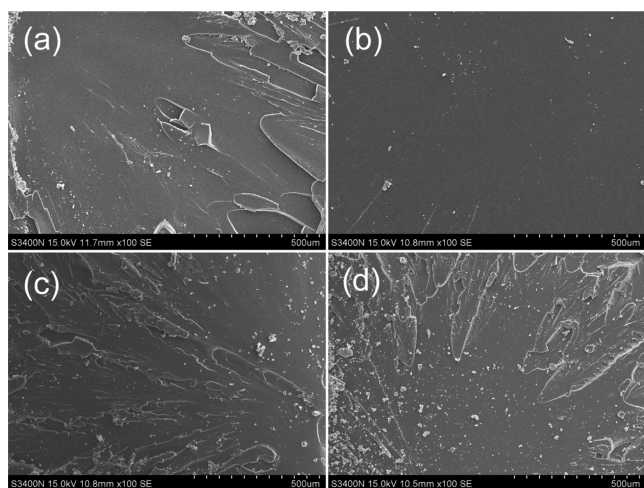


Figure 6. SEM images of the fracture surface from tensile tests: (a) DGEBA, (b) HBEP-1, (c) HBEP-2, and (d) HBEP-3.

fracture surface of DGEBA still has a larger smooth area when compared with HBEP-2 and HBEP-3, which suggests a lower toughness. HBEP-2 and HBEP-3 show a high degree of density, which can provide enough free volume for chain movement, and the high content of flexible chains is easy to produce plastic deformation through chain movement; thus, a large amount of plastic deformation can be observed.

3.5. Thermogravimetric Analysis. TG was conducted to evaluate the thermal stability of samples. As shown in Figure 7, there is only one pyrolysis process for DGEBA because only peaks can be detected in its DTG curve.^{30,31} However, all thermosets of HBEPs show two peaks in their DTG curves, indicating two pyrolysis processes. All important parameters of pyrolysis are listed in Table 4. According to Figure 7a, these thermosets perform a similar process of weight loss at the initial stage, and DGEBA, HBEP-2, and HBEP-3 share an approximate $T_{10\%}$ value, which is around 338 °C. Maybe owing to the highest cross-linking density, HBEP-1 shows a slightly higher $T_{10\%}$ value. On the other hand, T_{p1} values for HBEPs are similar to that of DGEBA, and the second pyrolysis process for HBEP peaks at a higher temperature (around 430 °C), which may be corresponding to the pyrolysis of the hyperbranched framework.^{18,27} Besides, due to the high

Table 4. Values of Characteristic Data from Thermogravimetric Plots

sample	$T_{10\%}^a$ (°C)	T_{p1}^b (°C)	T_{p2}^b (°C)	char residue at 800 °C(%)
DGEBA	338.9	399.3		3.1
HBEP-1	349.5	394.9	429.5	10.6
HBEP-2	337.0	389.2	425.8	8.0
HBEP-3	336.9	391.8	436.6	9.5

^aThe temperature corresponding to 10% loss of weight. ^bThe temperature corresponding to the peak degradation rate.

cross-linking density, HBEPs show much more char residue at 800 °C than DGEBA. In a word, all these results prove the good thermal stability of HBEPs.

4. CONCLUSIONS

In this study, a series of hyperbranched epoxies were synthesized from diphenolic acid, and NMR, FTIR, and GPC tests indicate its successful preparation. After being fully cured, the properties of the thermosets are characterized systematically. Mechanical tests show that the cured samples of HBEPs can achieve high mechanical strength and toughness simultaneously, which is even better than commercial DGEBA. Besides, the higher molecular weight and the DB of HBEP contribute to higher tensile and bending strengths, elongation at break, toughness, and impact strength. Although the incorporation of flexible chains into the hyperbranched framework leads to a lower T_g than that of DGEBA, all T_g 's of HBEP thermosets are higher than 85 °C. The thermal stability of the HBEP samples is similar to that of DGEBA, but their high cross-linking density leads to more char residue. Therefore, all results demonstrate that diphenolic acid-derived hyperbranched epoxies are potential high-performance materials, which can be commercially used in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05812>.

¹H NMR spectra of HBP-1 and HBP-2, ¹³C NMR spectra of HBPs, enlarged ¹³C NMR spectra of HBPs, ¹H NMR spectra of HBEP-1 and HBEP-2, representa-

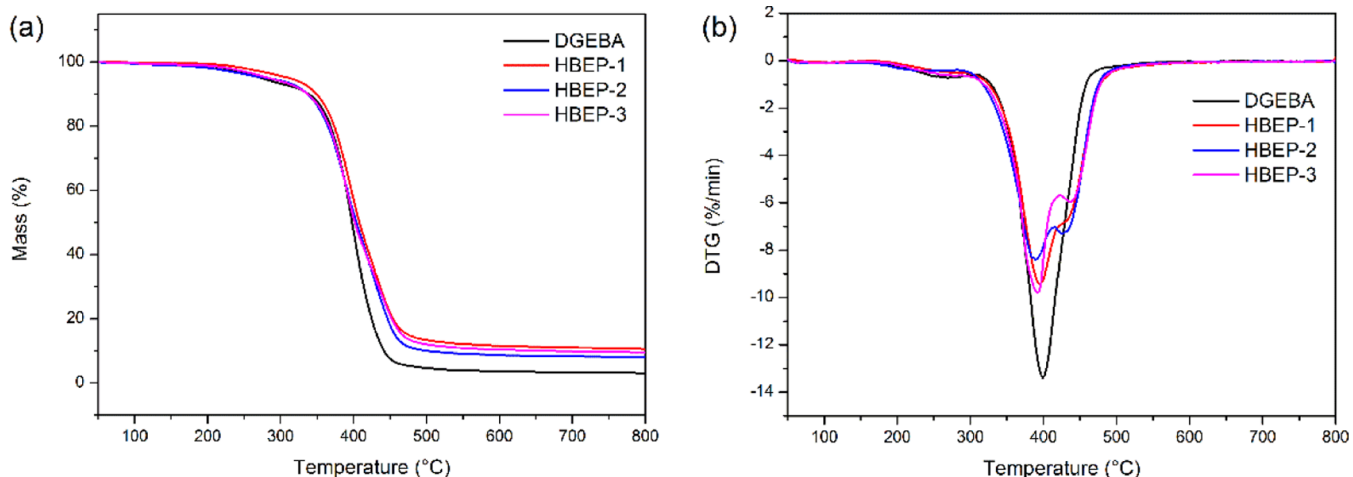


Figure 7. Thermogravimetric plots of the curing system: (a) T_g curves and (b) DTG curves.

tive curves from tensile tests, stoichiometric ratio of reactants for HBPs, stoichiometric ratio of reactants for HBEPs, and fabrication ratios of different thermosets (PDF)

AUTHOR INFORMATION

Corresponding Author

Jie Chen – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China; orcid.org/0000-0002-7796-4444; Email: chenjie_hi@126.com

Authors

Laihui Xiao – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China; orcid.org/0000-0002-3412-0954

Wenbin Li – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China

Shuai Li – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China

Yigang Wang – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China

Jinrui Huang – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products,

Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China; orcid.org/0000-0001-9040-230X
Xiaoan Nie – Key Laboratory of Biomass Energy and Material, Jiangsu Province, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province, Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, National Engineering Laboratory for Biomass Chemical Utilization, Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042 Jiangsu Province, P. R. China

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Huang, J.; Nie, X. A simple and novel method to design flexible and transparent epoxy resin with tunable mechanical properties. *Polym. Int.* **2016**, *65*, 835–840.
- (2) Ai, Y.-F.; Xia, L.; Pang, F.-Q.; Xu, Y.-L.; Zhao, H.-B.; Jian, R.-K. Mechanically strong and flame-retardant epoxy resins with anti-corrosion performance. *Composites, Part B* **2020**, *193*, 108019.
- (3) Jian, R.; Wang, P.; Duan, W.; Wang, J.; Zheng, X.; Weng, J. Synthesis of a Novel P/N/S-Containing Flame Retardant and Its Application in Epoxy Resin: Thermal Property, Flame Retardance, and Pyrolysis Behavior. *Ind. Eng. Chem. Res.* **2016**, *55*, 11520–11527.
- (4) Xiao, L.; Huang, J.; Wang, Y.; Chen, J.; Liu, Z.; Nie, X. Tung Oil-Based Modifier Toughening Epoxy Resin by Sacrificial Bonds. *ACS Sustainable Chem. Eng.* **2019**, *7*, 17344–17353.
- (5) Xiao, L.; Li, S.; Wang, Y.; Li, W.; Chen, J.; Huang, J.; Nie, X. Toughening epoxy resin by constructing π - π interaction between a tung oil-based modifier and epoxy. *Ind. Crops Prod.* **2021**, *170*, 113723.
- (6) Mi, X.; Wei, F.; Zhong, L.; Zeng, L.; Zhang, J.; Xu, Z.; Zhang, D.; Miao, M. Epoxidation of agricultural byproduct konjac fly powder and utilization in toughening and strengthening epoxy resin. *Ind. Crops Prod.* **2020**, *146*, 112161.
- (7) Chen, S.; Xu, Z.; Zhang, D. Synthesis and Application of Epoxy-Ended Hyperbranched Polymers. *Chem. Eng. J.* **2018**, *343*, 283–302.
- (8) Chen, S.; Zhang, J.; Zhou, J.; Zhang, D.; Zhang, A. Dramatic toughness enhancement of benzoxazine/epoxy thermosets with a novel hyperbranched polymeric ionic liquid. *Chem. Eng. J.* **2018**, *334*, 1371–1382.
- (9) Zhao, Y.; Huang, R.; Wu, Z.; Zhang, H.; Zhou, Z.; Li, L.; Dong, Y.; Luo, M.; Ye, B.; Zhang, H. Effect of free volume on cryogenic mechanical properties of epoxy resin reinforced by hyperbranched polymers. *Mater. Des.* **2021**, *202*, 109565.
- (10) Liu, T.; Nie, Y.; Chen, R.; Zhang, L.; Meng, Y.; Li, X. Hyperbranched polyether as an all-purpose epoxy modifier: controlled synthesis and toughening mechanisms. *J. Mater. Chem. A* **2015**, *3*, 1188–1198.

- (11) Mashouf Roudsari, G.; Mohanty, A. K.; Misra, M. Green Approaches To Engineer Tough Biobased Epoxies: A Review. *ACS Sustainable Chem. Eng.* **2017**, *5*, 9528–9541.
- (12) Fei, X.; Wei, W.; Zhao, F.; Zhu, Y.; Luo, J.; Chen, M.; Liu, X. Efficient Toughening of Epoxy–Anhydride Thermosets with a Biobased Tannic Acid Derivative. *ACS Sustainable Chem. Eng.* **2016**, *5*, 596–603.
- (13) Xiao, L.; Liu, Z.; Li, N.; Li, S.; Fu, P.; Wang, Y.; Huang, J.; Chen, J.; Nie, X. A hyperbranched polymer from tung oil for the modification of epoxy thermoset with simultaneous improvement in toughness and strength. *New J. Chem.* **2020**, *44*, 16856–16863.
- (14) De, B.; Karak, N. Novel high performance tough hyperbranched epoxy by an A2 + B3 polycondensation reaction. *J. Mater. Chem. A* **2013**, *1*, 348–353.
- (15) Barua, S.; Dutta, G.; Karak, N. Glycerol based tough hyperbranched epoxy: Synthesis, statistical optimization and property evaluation. *Chem. Eng. Sci.* **2013**, *95*, 138–147.
- (16) De, B.; Gupta, K.; Mandal, M.; Karak, N. Bio-degradable Hyperbranched Epoxy from Castor Oil Based Hyperbranched Polyester Polyol. *ACS Sustainable Chem. Eng.* **2014**, *2*, 445–453.
- (17) Han, J.; Liu, T.; Hao, C.; Zhang, S.; Guo, B.; Zhang, J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* **2018**, *51*, 6789–6799.
- (18) Wang, X.; Zong, L.; Han, J.; Wang, J.; Liu, C.; Jian, X. Toughening and reinforcing of benzoxazine resins using a new hyperbranched polyether epoxy as a non-phase-separation modifier. *Polymer* **2017**, *121*, 217–227.
- (19) Chen, J.-Y.; Smet, M.; Zhang, J.-C.; Shao, W.-K.; Li, X.; Zhang, K.; Fu, Y.; Jiao, Y.-H.; Sun, T.; Dehaen, W.; Liu, F.-C.; Han, E.-H. Fully branched hyperbranched polymers with a focal point: analogous to dendrimers. *Polym. Chem.* **2014**, *5*, 2401.
- (20) Khalyavina, A.; Schallausky, F.; Komber, H.; Al Samman, M.; Radke, W.; Lederer, A. Aromatic–Aliphatic Polyesters with Tailored Degree of Branching Based on AB/AB₂ and ABB*/AB₂ Monomers. *Macromolecules* **2010**, *43*, 3268–3276.
- (21) Chen, H.; Kong, J. Hyperbranched polymers from A₂ + B₃ strategy: recent advances in description and control of fine topology. *Polym. Chem.* **2016**, *7*, 3643–3663.
- (22) Liu, D.; Wang, H.; Jiang, H.; Zhou, D. Improving the heat-resistance and toughness performance of phenolic resins by adding a rigid aromatic hyperbranched polyester. *J. Appl. Polym. Sci.* **2016**, *133*, 42734 DOI: 10.1002/app.42734.
- (23) Chen, J.; Wang, Y.; Huang, J.; Li, K.; Nie, X. Synthesis of tung oil based triglycidyl ester plasticizer and its effects on poly(vinyl chloride) soft films. *ACS Sustainable Chem. Eng.* **2017**, *6*, 642–651.
- (24) Huang, K.; Liu, Z.; Zhang, J.; Li, S.; Li, M.; Xia, J.; Zhou, Y. A self-crosslinking thermosetting monomer with both epoxy and anhydride groups derived from tung oil fatty acids: Synthesis and properties. *Eur. Polym. J.* **2015**, *70*, 45–54.
- (25) Huang, K.; Zhang, P.; Zhang, J.; Li, S.; Li, M.; Xia, J.; Zhou, Y. Preparation of biobased epoxies using tung oil fatty acid-derived C₂₁ diacid and C₂₂ triacid and study of epoxy properties. *Green Chem.* **2013**, *15*, 2466–2475.
- (26) Xiao, L.; Liu, Z.; Hu, F.; Wang, Y.; Huang, J.; Chen, J.; Nie, X. A renewable tung oil-derived nitrile rubber and its potential use in epoxy-toughening modifiers. *RSC Adv.* **2019**, *9*, 25880–25889.
- (27) Saikia, A.; Karak, N. Renewable resource based thermostable tough hyperbranched epoxy thermosets as sustainable materials. *Polym. Degrad. Stab.* **2017**, *135*, 8–17.
- (28) Xia, M.; Yang, H.; Ling, J.; Yao, Q.; Li, G.; Luo, Y. The mechanical behaviors of epoxy-terminated hyperbranched polyester (E-HBP) as toughener in different epoxy resins. *Adv. Compos. Hybrid Mater.* **2018**, *1*, 310–319.
- (29) De, B.; Karak, N. Ultralow dielectric, high performing hyperbranched epoxy thermosets: synthesis, characterization and property evaluation. *RSC Adv.* **2015**, *5*, 35080–35088.
- (30) Li, X.-L.; Zhang, F.-H.; Jian, R.-K.; Ai, Y.-F.; Ma, J.-L.; Hui, G.-J.; Wang, D.-Y. Influence of eco-friendly calcium gluconate on the intumescent flame-retardant epoxy resin: Flame retardancy, smoke suppression and mechanical properties. *Composites, Part B* **2019**, *176*, 107200.
- (31) Jian, R.-K.; Ai, Y.-F.; Xia, L.; Zhao, L.-J.; Zhao, H.-B. Single component phosphamide-based intumescent flame retardant with potential reactivity towards low flammability and smoke epoxy resins. *J. Hazard. Mater.* **2019**, *371*, 529.