A novel bio-based epoxy resin from oligomer: Excellent processability, high heat resistance, and intrinsic flame retardancy

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Abstract. Preparing an epoxy resin with biomass resources as an alternative for bisphenol A is significant for sustainable and renewable development under great pressure of limited fossil resources and urgent environmental issues. Herein, we synthesized an epoxy oligomer P-DBP-EP-n derived from biomass magnolol through an efficient one-step glycidylation. P-DBP-EP-n exhibited a low viscosity of 11.7 Pa·s at room temperature, endowing it with excellent processability as diglycidyl ether of bisphenol A (DGEBA) and magnolol-based epoxy monomer EDBP. Then P-DBP-EP-n was cured with a diamine curing agent, 4,4'-diaminodiphenyl methane (DDM), and following thermal addition polymerization of allyl units. Compared with DGEBA/DDM and EDBP/DDM, P-DBP-EP-n/DDM possessed a higher glass transition temperature (T_g) (304 to 167 and 226 °C), implying distinguished heat resistance. Furthermore, the tensile properties and notched impacted strength of P-DBP-EP-n/DDM were better than EDBP/DDM (20.7 to 19.4 MPa, 2.0 to 1.6 GPa, and 2.5 to 2.0 kJ/m²). The initial degradation temperature and char residue of P-DBP-EP-n/DDM were 421 °C and 35.2%, with a 13.5 and 101% increase compared with those of DGEBA/DDM, respectively. Additionally, P-DBP-EP-n/DDM displayed outstanding flame retardancy with V-0 rate for the vertical burning test and limiting oxygen index value of 47.7%, which was almost twice as much as that of DGEBA/DDM. This study offers a promising and feasible pathway to obtain a fully bio-based epoxy resin substituted for petroleum-based DGEBA with distinguished processability, heat resistance, and flame retardancy. Comprehensive properties of the bio-based thermosets are expected to be further regulated by the thermal addition polymerization of allyl units.

Keywords: thermal properties, biomass, oligomer, low viscosity, intrinsic flame retardancy

1. Introduction

Epoxy resin, an important thermoset, is extensively used in constructions, composites, electrical engineering, and electronics for its high corrosive resistance, low curing shrinkage, and excellent mechanical, thermal, and electrical properties. Currently, petroleum-based DGEBA which originates from bisphenol A (BPA) and epichlorohydrin takes up dominance [1]. Not only is BPA strongly dependent on the chemical industry, but it also acts as an endocrine disruptor [2] due to the similar structure to

estrogens. It is harmful to human immune and reproductive systems because BPA and its derivatives will leach from plastic packaging [3]. In terms of the negative impact of BPA on humans, some countries and organizations such as Canada and the EU have banned BPA as raw materials for food packaging products, especially infant bottles [4]. Therefore, with the concern of accelerating consumption of fossil fuel and increasing awareness of the health of humans, it is necessary to find biomass to replace BPA to prepare epoxy resins.

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With a large stock and wide range of sources, renewable biomass has attracted increasing attention in designing bio-based epoxy resins [1, 3, 5–7]. It has been reported that biomass like soybean oil [8], tung oil [9], linseed oil [10] and cardanol [11] can be easily epoxidized to obtain corresponding epoxy resins. They generate extremely low viscosity [9, 12, 13] at room temperature due to strong chain mobility from the long flexible aliphatic chains. However, such a long flexible aliphatic chain always results in relatively low T_g compared with conventional BPA-based one [14]. Consequently, the epoxies mentioned above tend to be used for diluting viscous systems and toughening brittle system [12, 15, 16] rather than be used alone where high-performance is required.

In terms of drawbacks arising from the aliphatic chain, the introduction of rigid and aromatic structures is expected to improve the T_g of the bio-based resins [3, 17, 18]. Renewable materials such as lignin [19], vanillin [20, 21], and eugenol [22, 23] have attracted much attention for their fascinating aromatic structures and high reactivity from phenolic hydroxyl groups. For example, Wan *et al.* [4] synthesized a novel epoxy based on eugenol with a rigid core of cyanuric chloride. The T_g of the resin cured by 3,3'-DDS was 207 °C, 18.9% higher than that of the DGEBA-based one. Moreover, Tian *et al.* [24] demonstrated that T_g also had a close tie with the crosslinking density of the cured network. The cured trifunctional resveratrol-based epoxy resin with a high crosslinking density of 6900.6 mol/m³ (DGEBA 2087.4 mol/m³) possessed a corresponding high T_g of 210.8 °C, with a 39% increase compared with DGEBA-based. However, the above bio-based epoxies always yield powder even crystal [3] at room temperature owing to the rigid aromatic backbone and the accompanying poor chain mobility. Hence, they need to be melted under high temperature or diluted with solvent before molding. But it is difficult to remove all the solvent during degassing process and the remaining solvent will influence the performance of the final product.

Magnolol, which is extracted from biomass *magnolia officinalis* and confirmed safe and low toxicity [25], is widely used in herbs and make-up for its unique anti-bacterial, anti-tumor effect. It contains symmetrical and reactive allyl groups and phenolic hydroxyl groups. Hence, it is easy to be modified, obtaining bio-based derivatives [26] and thermosets with excellent thermal properties [27]. It has been

reported that the introduction of allyl groups can improve processability, using in various epoxy systems [28, 29]. The symmetrical biphenyl structures not only enhance the thermal stability but also promote char formation during combustion, therefore possessing intrinsic flame retardancy [30]. A previous study has demonstrated that magnolol-based epoxy monomer DGEM exhibited better thermal properties compared with DGEBA-based ones whereas tensile and impact properties were still mysterious [31]. Furthermore, DGEM was an epoxy monomer, which was quite different from most of the commercial epoxy resins with a series of degrees of polymerization. The properties of epoxy oligomers can be controlled by regulating the degree of polymerization [32]. Unfortunately, there are few relative reports, and the properties of resulting epoxy oligomers could not compete with the DGEBA-based one, especially T_g values [33, 34].

The increasing focus on bio-based epoxy resins has motivated us to design an inherent fascinating molecular structure, achieving balanced performances. In this study, we designed and synthesized a bio-based glycidyl ether oligomer (P-DBP-EP-n) using biomass magnolol and epichlorohydrin through a one-step glycidylation reaction. It is desirable to address the contradiction between processability and thermal properties with the combination of flexible allyl groups and rigid biphenyl structures of magnolol moieties. Oligomer P-DBP-EP-n was cured with the diamine curing agent DDM and following thermal addition polymerization. Tensile and notched impact properties were determined. Dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), vertical burning test (UL94), and limiting oxygen index (LOI) were carried out to investigate the thermal and flame-retardant properties of the thermosets P-DBP-EP-n/DDM. To further ascertain the mechanism of intrinsic flame retardancy, scanning electron microscopy (SEM) was used to observe the morphology of the residual char collected from flame retardancy tests. It will be a promising and feasible method to synthesize a bio-based epoxy oligomer as a BPA-free substitute for DGEBA for a wider application.

2. Experimental section

2.1. Materials

Magnolol was purchased from Guangzhou Seye Biological Technology Co., Ltd (Guangzhou, China).

DGEBA (epoxy value = 0.48~0.54 mol/100g) was provided from Hangzhou Wuhuigang Adhesive (Hangzhou, China). Epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB), tetraethylammonium bromide (TEAB), 4,4-diaminodiphenyl methane (DDM), crystal violet, and perchloric acid (0.1 M in glacial acetic) were obtained from Sigma-Aldrich. Analytical ethyl acetate and glacial acetic acid, sodium hydroxide (NaOH), sodium chloride (NaCl), and anhydrous magnesium sulfate (MgSO_4) were supplied from Tianjin Zhiyuan Chemical Reagent Co., Ltd (Tianjin, China). All the reagents were used as received without any further purification.

2.2. Synthesis of magnolol-based epoxy oligomer (P-DBP-EP-n)

Magnolol (5 g, 18.7 mmol), ECH (6.9 g, 74.8 mmol), and TBAB (0.06 g, 0.5 wt%) were added into a three-necked round-bottomed flask, which was equipped with a mechanical stirring bar and reflux unit. The mixture was continuously and homogeneously stirred at 50 °C for 2 h. An aqueous solution of NaOH (40 wt%, 5 ml) was added dropwise using a constant flow pump to the mixture. Afterward, the mixture further reacted for another 3 h with vigorous stirring at 80 °C. Subsequently, excess ethyl acetate was added to dilute the mixture and then washed three times with distilled water and once with saturated NaCl solution. Then the organic phase was dried with anhydrous MgSO_4 overnight. After that, the organic phase was concentrated under vacuum to remove excess ECH and ethyl acetate and further dried at 50 °C in a vacuum oven to yield the target product P-DBP-EP-n as a pale yellow liquid.

2.3. Synthesis of magnolol-based monomer (EDBP)

Magnolol (5 g), ECH (17.3 g, 5 eq.), and TBAB (0.6 g, 0.05 eq.) were charged into a three-necked round-bottomed flask, which was equipped with a magnetic stirring bar and reflux unit. The mixture was allowed to be stirred at 80 °C for 3 h. Subsequently, NaOH (3 g, 2 eq) and TBAB (0.6 g, 0.05 eq.) was added into 15 ml of distilled water, and the solution was added into the mixture. Then the mixture reacted for another hour at room temperature with stirring. After that, ethyl acetate was used to dilute the mixture and then rinsed three times with distilled water and once with saturated NaCl solution. The organic phase was dried with anhydrous MgSO_4

overnight. Next, the organic phase was concentrated under vacuum to remove excess ECH and ethyl acetate and further dried at 50 °C in a vacuum oven to yield the final product EDBP as a light yellow liquid.

2.4. Thermal curing of P-DBP-EP-n and EDBP

The curing agent DDM was employed in this work to obtain cured epoxy resins, taking P-DBP-EP-n as an example. Firstly, DDM was added into P-DBP-EP-n with a molar ratio of epoxy groups to N–H as 1:1. The mixture was stirred vigorously at 90 °C until DDM completely dissolved. Subsequently, the mixture was degassed in a vacuum oven at 50 °C to remove trapped air and then poured into a silica gel mold. The curing behavior was monitored by differential scanning calorimetry (DSC) and Fourier Transform Infrared (FTIR). According to results of DSC and FTIR (discussed in Curing network of P-DBP-EP-n/DDM Section), the sample was cured at 100 °C for 1 h, 140 °C for 1 h, 180 °C for 2 h in the oven, and 320 °C for 8 h in a tube furnace to get a completely cured resin, denoted as P-DBP-EP-n/DDM. For comparison, DGEBA/DDM and EDBP/DDM were cured with a similar procedure, respectively.

2.5. Characterization

^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker 400 (Switzerland) nuclear magnetic resonance spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was performed on a Bruker Ultraflex extreme MALDI-TOF (Germany) with a positive ion mode.

The epoxy value of the epoxy oligomer was titrated according to ASTM D1652. 0.4 g epoxy oligomer was dissolved in 10 ml of methylene chloride, and then 10 ml of tetraethylammonium bromide in glacial acetic acid solution (250 mg/ml) and 6~8 drops of 0.1% crystal violet indicator in glacial acetic acid solution were added. The mixed solution was titrated to a green color with 0.1 M perchloric acid in glacial acetic acid solution.

The epoxy-amine reaction was monitored by DSC (METTLER TOLEDO DSC 3, Switzerland) with a heating rate of 10 °C /min ranging from 25 to 370 °C under 50 ml/min nitrogen gas flow. The polymerization of allyl units was determined by FTIR using a Nicolet IS-50 FTIR spectrometer (Thermo Fisher Scientific, USA) with the wavenumber range of

4000–500 cm^{-1} . All the samples were mixed with KBr pellets to press into small flakes, and the area of the characteristic peaks was integrated using the Origin 8.5 software package. The degassed mixture was cured in Jinghong XMTD-8222 (China) oven first and then a tube furnace (GSL-1400X, Hefei Kejing Technology Co., Ltd, China.).

Viscosity was investigated using an Anton Paar Modular Compact Rheometer (Austria) as a function of shear rate from 1 to 100 1/s and temperature from 25 to 40 °C fitted with 25 mm-cone parallel plates, respectively. A separation of 0.051 mm between the plates was used for all the samples. Dynamic mechanical analysis (DMA) was performed using an Anton Paar Modular Compact Rheometer (Austria) under torsional mode with a constant frequency of 1 Hz, amplitude of 0.1%, and a heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was conducted on a NETZSCH STA449F5 (Germany) thermogravimetric analyzer with a temperature range from 30 to 700 °C and a heating rate of 10 °C/min under 40 ml/min nitrogen gas flow.

Tensile properties of the cured epoxy resins were determined by Gotech testing machines inc. AI-7000M micro-tensile tester (China). The measurements were performed on standardized dog-bone samples at a speed of 1 mm/min according to GB/T 1040-92. The notched impact properties of the cured epoxy resins were investigated using Guangce Automation Digital IZOD impact tester (China) according to GB/T 1843-2008.

Limiting oxygen index (LOI) values were characterized by a PDF-60B oxygen index meter (Shandong Derek Instruments Co., Ltd., China) according to ASTM D 2863-97 with the specimen measured 130 mm $\times$ 6.5 mm $\times$ 3 mm. Vertical burning tests (UL94) were conducted on a ZCF-5 horizontal and vertical instrument (Nanjing Jionglei Instrument Equipment Co., Ltd., China) according to ASTM D 3801 with the samples measured 130 mm $\times$ 13 mm $\times$ 3.2 mm.

The morphology of the residual char was observed using scanning electron microscopy (SEM) on a Hitachi S-3400 N-II scanning electron microscope (Japan) with the accelerating voltage of 15 kV.

3. Results and discussion

3.1. Synthesis of P-DBP-EP-n

As shown in Figure 1, P-DBP-EP-n was synthesized through a one-step glycidylation reaction using magnolol, excess ECH, and a small amount of phase transfer initiator TBAB under alkaline conditions. Excessive ECH is always employed in glycidylation reaction, which can minimize the formation of higher molecular oligomers, obtaining monomers or low molecular oligomers. The average chain length can be controlled by varying the excess of ECH. In the current study, 4 and 10 times ECH were applied for the preparation of oligomer P-DBP-EP-n and monomer EDBP, respectively. The chemical structure of P-DBP-EP-n and EDBP was confirmed by ^1H NMR (Figure 2a, 2c) and ^{13}C NMR (Figure 2b, 2d). In

Figure 1. The synthetic route of P-DBP-EP-n and EDBP from magnolol.

Figure 2. The ^1H NMR spectrum of a) P-DBP-EP-n, c) EDBP, and ^{13}C NMR spectrum of b) P-DBP-EP-n, d) EDBP.

Figure 2a, chemical shifts of 5.06 (H_6, H_6') and 5.98 (H_5) ppm were ascribed to the allyl groups of magnolol, and 3.19 (H_8), 2.73 (H_9), and 2.57 (H_9') ppm were attributed to epoxy rings. Both of the chemical shifts of ^1H NMR and ^{13}C NMR were consistent with the statement in the literature [31]. Interestingly, compared with monomer EDBP (Figure 2d), a new chemical shift at ~ 69 ppm, which was ascribed to $\text{C}_{13}, \text{C}_{14}$, and C_{15} was observed in ^{13}C NMR spectrum (Figure 2b), indicating the successful synthesis of P-DBP-EP-n. Additionally, the average repeating unit of P-DBP-EP-n was characterized by ^1H NMR, comparing allyl groups integrations ($3(2n + 2)$ H per molecule, 3.05) with epoxide groups integrations (6 H) per molecule, 1.65) [32]. The ratio was 1.84, implying that the average polymerization degree (n)

was 0.92. To further determine the composition of the oligomer P-DBP-EP-n, MALDI-TOF was carried out, and the results are listed in Table 1. As shown in Figure 3, the strongest signal peak at 723.412 m/z was observed, which was corresponding to P-DBP-EP-n with a polymerization degree of 1. From data of Table 1, P-DBP-EP-n was a mixture of magnolol-based epoxy with different n values ranging from

Table 1. The MALDI-TOF Mass results of P-DBP-EP-n.

Degree of polymerization, n	Calculated $[\text{M} + \text{Na}^+]$	$[\text{M} + \text{Na}^+]$	Percent [%]
0	401.46	401.12	11.6
1	723.86	723.41	47.3
2	1046.27	1045.62	27.8
3	1368.67	1367.85	9.6
4	1689.10	1690.10	3.6

Figure 3. The MALDI-TOF spectrum of P-DBP-EP-n.

0 to 4, in which $n = 1$ came into prominence, accounting for 47.3%. Components with polymerization of $n = 0, 2, 3$ and 4 took up 11.6, 27.8, 9.6 and 3.6% respectively. Furthermore, the epoxy value of the oligomer P-DBP-EP-n was titrated to be 0.31 mol/100 g according to ASTM D1652. All the results above indicate that the magnolol-based oligomer was successfully synthesized, and the average polymerization degree was approximately 1.

3.2. Processability of P-DBP-EP-n

With numerous rigid and compact aromatic structures and accompanying low chain mobility, aromatic bio-based epoxies tend to yield powder with high

melting points [3, 22], which need to be melted before molding. However, P-DBP-EP-n was a liquid at room temperature, which was totally different from most of the aromatic bio-based epoxy resins. In order to characterize the processability of P-DBP-EP-n, a viscosity test was carried out, and results are shown in Figure 4. As shown in Figure 4a, all the epoxies acted as Newtonian fluids with a constant viscosity of 11.7, 12.9, and 1.5 Pa·s for P-DBP-EP-n, DGEBA, and EDBP, respectively. It is noteworthy that the viscosity of P-DBP-EP-n was slightly lower than that of DGEBA, resulting in excellent processability at room temperature. The reason why P-DBP-EP-n exhibited a relatively low viscosity was that aliphatic

Figure 4. The viscosities of DGEBA, EDBP and P-DBP-EP-n. a) Viscosity as a function of shear rate from 1 to 100 1/s at 25 °C for DGEBA, EDBP and P-DBP-EP-n without curing agents. b) Viscosity as a function of temperature from 25 to 40 °C for DGEBA, EDBP and P-DBP-EP-n without curing agents.

allyl groups increase chain mobility, which is widely used for reducing the viscosity of polymer systems and broadening process window [28, 29]. Rich, flexible allyl units promoted chain motion, improving the free volume and reducing the high aromaticity and rigidity arising from the compact backbone of biphenyl. Moreover, the epoxy needs to be mixed with the curing agent before molding, so we determined the viscosities under variable temperatures with a steady shear rate of 50 1/s, and the results are shown in Figure 4b. It was discovered that the viscosities of both DGEBA and P-DBP-EP-n reduced with increasing temperature and ultimately reached ~ 1 Pa·s at 40 °C, which was closed to that of monomer EDBP. From the results collected from the rotational rheology approach, we conclude that P-DBP-EP-n exhibits excellent processability, meeting the target of the following molding procedure.

3.3. Curing network of P-DBP-EP-n/DDM

The oligomer P-DBP-EP-n has two types of reactive groups and can react under suitable conditions at different temperature ranges, forming distinct cross-linked polymer networks. Figure 5 shows the curing route of P-DBP-EP-n and the probable crosslinked structure of P-DBP-EP-n/DDM. Firstly, epoxy rings of P-DBP-EP-n reacted with amino groups of DDM, opening epoxy rings and obtaining the first cured network, and the resulting thermoset was denoted as P-DBP-EP-n/DDM-180. Secondly, thermal addition polymerization of allyl groups was triggered at higher temperatures [35], forming the second cured network as illustrated in Figure 5b.

To confirm the suitable curing process, DSC and FTIR were carried out to monitor the epoxy-amine

reaction and thermal addition polymerization of allyl units, respectively. A broad exothermic peak from ~ 80 to ~ 275 °C, with a temperature of exothermal peak (T_p) of ~ 150 °C was observed in the DSC curve, which was corresponding to the epoxy-amine reaction. It is suggested that epoxies started to react with amines at ~ 80 °C and the fastest reaction occurred at ~ 150 °C. According to reports, a higher temperature could trigger thermal addition polymerization [35], but unfortunately, DSC failed to determine the reaction within a limited experimental time. Therefore, FTIR was carried out to investigate the optimum curing temperature using a series of cured resins with different second curing temperatures (denoted as P-DBP-EP-n/DDM-T). As we all know, characteristic peaks of allyl groups appear at ~ 1637 , ~ 995 , and ~ 914 cm^{-1} , which can be used as a symbol of the extent of thermal addition polymerization. In this study, the characteristic peak at 911 cm^{-1} was chosen as an index, and its area integration was used to estimate whether allyl groups reacted completely during the second curing procedure. Detailed results are listed in Table 2. For comparison, EDBP/DDM was prepared with a similar curing procedure, and the FTIR spectra are shown in Figure 6b. As for P-DBP-EP-n/DDM, it was observed that the intensities of characteristic peaks of allyl groups were gradually weaker and finally disappeared with increasing second curing temperature, as shown in Figure 6a. From data in Table 2, it was found that the ratio of the integrated area of peaks at 911 cm^{-1} decreased vastly after 280 °C, indicating that thermal addition polymerization accelerated over 280 °C and gradually got completed at higher curing temperature and ultimately finished at 320 °C. Hence, the whole curing

Figure 5. The curing route of P-DBP-EP-n with DDM and the probable crosslinked structure of the cured resins. a) Epoxy rings opening reaction and the probable crosslinked structure for P-DBP-EP-n-180. b) Allyl groups thermal addition polymerization reaction and the probable crosslinked structure for P-DBP-EP-n/DDM-320.

Figure 6. The FTIR spectra of samples with different second curing process. a) P-DBP-EP-n/DDM, I) P-DBP-EP-n/DDM-180, II) P-DBP-EP-n/DDM-280, III) P-DBP-EP-n/DDM-300, IV) P-DBP-EP-n/DDM-320. b) EDBP/DDM, I) EDBP/DDM-180, II) EDBP/DDM-290.

Table 2. Integration of characteristic peak in FTIR spectra for cured resins P-DBP-EP-n/DDM with different second curing process.

	Area of peak at 912 cm ⁻¹	A_T/A_{180}^*
P-DBP-EP-n/DDM-180	1259	1.00
P-DBP-EP-n/DDM-280	1004	0.80
P-DBP-EP-n/DDM-300	156	0.12
P-DBP-EP-n/DDM-320	—	—

*T represents 180, 280, 300 and 320, respectively.

process was confirmed as follows: 100 °C 1 h, 140 °C 1 h, 180 °C 2 h in the oven, and 320 °C 8 h in a furnace. The obtained dual-cured network with a high crosslinking density might endow the cured resin with a high T_g .

3.4. Thermomechanical properties of cured P-DBP-EP-n/DDM

To further confirm our hypothesis, DMA was carried out to evaluate the thermomechanical properties of the cured resins, and the results are shown in Figure 7. As could be seen in Figure 7a, storage modulus increased from 5295.8 MPa (P-DBP-EP-n/DDM-180) to 9413.7 MPa (P-DBP-EP-n/DDM-320), with a tremendous increase of 77.8%. As we discussed above, P-DBP-EP-n/DDM-180 only conducted an epoxy ring-opening reaction at 180 °C, indicating that the cured network was not completed yet. However,

higher curing temperature promoted thermal addition polymerization of allyl groups which provided extra crosslinking sites [36], thereby significantly improving the storage modulus of P-DBP-EP-n/DDM-320, close to that of DGEBA/DDM (10 494 MPa). Remarkably, it was observed that the storage modulus of DGEBA/DDM decreased sharply from 7713 MPa (~134 °C) to 198 MPa (~175 °C), whereas P-DBP-EP-n/DDM-320 remained a storage modulus higher than 6000 MPa before 200 °C. It was suggested that multiple compact biphenyl structures in P-DBP-EP-n/DDM-320 had an advantage in resisting heat and deformation compared with bisphenol A, which can be qualified for application where high temperature is required. As we know, T_g value has a close tie with the crosslink density of the cured resins, and the higher the crosslinking density is, the higher the T_g is [37, 38]. Distinct T_g values were observed for epoxy systems (Figure 7b), suggesting that they exhibited different crosslinked polymer networks. In order to estimate the influence of crosslinking density on T_g , the average molecular weight between crosslinking points (M_c) of different epoxy systems was calculated according to the Equation (1) and (2) [37, 39]:

$$M_c = \frac{n_{EP}M_{EP} + n_{DDM}M_{DDM}}{n_{DDM}} \quad (1)$$

$$M_c = \frac{n_{\text{reacted allyl groups}}M_{\text{reacted allyl groups}} + n_{EP}M_{EP} + n_{DDM}M_{DDM}}{n_{\text{reacted allyl groups}} + n_{DDM}} \quad (2)$$

Figure 7. Thermomechanical properties of the cured resins. a) DMA spectra for the storage modulus and b) $\tan \delta$ against temperature of DGEBA/DDM and P-DBP-EP-n/DDM with different second curing procedure. c) the dashed red rectangle area in image (b) with higher magnification. d) DMA spectra for the storage modulus and e) $\tan \delta$ against temperature of EDBP/DDM.

where n and M represent the molarity and molar mass of the corresponding component in the epoxy formulations, respectively. Calculated M_c and results from DMA tests of the cured resins were summarized in Table 3. As shown in Figure 7b and Table 3, it can be clearly seen that P-DBP-EP-n/DDM-180 exhibited a M_c of 1488, with a corresponding T_g of 102, 65 °C lower than that of DGEBA/DDM ($M_c = 982$), indicating that a much lower crosslinked polymer network was obtained. Lower crosslinking density

Table 3. Comparison of properties from DMA testing for cured resins.

	T_g^* [°C]	M_c
DGEBA/DDM	167	982
P-DBP-EP-n/DDM-180	102	1488
P-DBP-EP-n/DDM-280	213	644
P-DBP-EP-n/DDM-300	263	236
P-DBP-EP-n/DDM-320	304	217

* T_g : Glass transition temperature define by the peak value temperature of $\tan \delta$ against temperature curve.

and abundant allyl groups in P-DBP-EP-n/DDM-180 provided the biphenyl backbone with free volume and increased chain mobility, which was responsible for lower T_g value compared with DGEBA/DDM. However, it is noteworthy that T_g value is enhanced with increasing second-curing temperature accounting for increasing crosslinking density (decreasing M_c). Interestingly, P-DBP-EP-n/DDM-320 exhibited an extremely low M_c of 217 and corresponding high T_g value of 304 °C, with an 82% improvement compared with DGEBA/DDM. Similarly, T_g value of EDBP/DDM increased from 132 to 226 °C after the second curing process (Figure 7e). Such a high T_g value was attributed to the distinguished cured network as discussed in the section Curing network of P-DBP-EP-n/DDM. On the one hand, a highly crosslinked network where polymer chains were ‘frozen’ by extra crosslinking sites of allyl groups resulted in low free volume and hindered the mobility of segments [40]. On the other hand, high crosslinking density aggravated rigidity and stiffness caused by numerous biphenyl structures, rendering cured network able to resist heat and deformation.

3.5. Mechanical properties of P-DBP-EP-n/DDM

Figure 8 and Table 4 show the tensile and notched impact properties of P-DBP-EP-n/DDM, EDBP/DDM, and DGEBA/DDM for comparison. P-DBP-EP/DDM-180 and EDBP/DDM-180 showed lower tensile strength (42.9 and 44.5 MPa) than that of DGEBA/DDM (69.6 MPa). After the second curing process, the tensile strength of P-DBP-EP/DDM-320 and EDBP/DDM-290 reduced vastly to 20.7 and 19.4 MPa, with a decrease of 51.7 and 56.4%, respectively. It was attributed to the high aromaticity of biphenyl structures which were more rigid than that of BPA, reducing chain mobility and weakening the ability to resist deformation. However, the higher stiffness originated from the rod-like rigid components made the molecular structure more stable, endowing P-DBP-EP-n/DDM-320 with a tensile modulus as high as DGEBA/DDM (2.0 GPa). The notched impact strength was tested to determine the toughness of materials, and as shown in Figure 8b, DGEBA/DDM is a typical brittle material with a low notched impact strength of 3.6 kJ/m². As expected, EDBP/

Table 4. Tensile properties and notched impact strength for cured resins.

	Tensile strength [MPa]	Tensile modulus [GPa]	Notched impact strength [kJ/m ²]
DGEBA/DDM	69.6±1.2	2.0±0.1	3.6±0.7
EDBP/DDM-180	44.5±1.1	1.5±0.2	2.1±0.7
EDBP/DDM-290	19.4±1.7	1.6±0.1	2.0±0.6
P-DBP-EP-n/DDM-180	42.9±4.0	2.0±0.3	1.9±0.3
P-DBP-EP-n/DDM-320	20.7±2.1	2.0±0.3	2.5±0.4

Figure 8. Mechanical properties of DGEBA/DDM, EDBP/DDM and P-DBP-EP-n. a) tensile and b) notched impact properties.

DDM-180, EDBP/DDM-290, and P-DBP-EP-n/DDM-180 containing multiple biphenyl aromatic structures exhibited high aromaticity and poor capacity for absorbing impact energy [41], resulting in corresponding lower impact strength, which is 41.6, 44.4, and 47.2% lower than that of DGEBA/DDM, respectively. Noticeably, P-DBP-EP-n/DDM-320 with the highest crosslinking density and aromaticity showed a slight increase of notched impact strength (2.5 kJ/m^2) compared with the EDBP/DDM-290. It was probably due to extra aliphatic segments between two biphenyl structures and flexible aliphatic chain caused by thermal addition polymerization of allyl units improved toughness for the cured resin.

3.6. Thermal stability of P-DBP-EP-n/DDM

The thermal stability of cured resins was investigated by TGA, and results are shown in Figure 9 and summarized in Table 5. Initial decomposition temperature, defined as the temperature at 5% weight loss ($T_{d5\%}$) is used to evaluate the thermal stability of the cured resins. As shown in Figure 9, DGEBA/DDM exhibited a one-stage decomposition with a $T_{d5\%}$ of 371°C and char yield of 17.5% at 700°C . For P-DBP-EP-n/DDM-180, a two-stage decomposition was observed, with an earlier $T_{d5\%}$ of 347°C compared with DGEBA/DDM. It might be assigned to the breakage of liable aliphatic allyl groups because less energy was needed compared with aromatic rings with unsaturated C=C bonds [42, 43]. However, it achieved a char residue of 28.6%, with an increase of 11.1% in comparison with DGEBA/DDM, suggesting that symmetric biphenyl structure reduced liable combustible gas [4], resisted pyrolysis [44, 45], and promoted charring. Contrary to DGEBA/DDM and P-DBP-EP-n/DDM-180, P-DBP-EP-n/DDM-320

Table 5. Comparison of properties from TGA testing for cured resins.

	$T_{d5\%}$ [$^\circ\text{C}$]	T_{max} [$^\circ\text{C}$]	Char yield at 700°C [%]
DGEBA/DDM	371	384	17.5
P-DBP-EP-n/DDM-180	347	460	28.6
P-DBP-EP-n/DDM-280	396	460	32.1
P-DBP-EP-n/DDM-300	409	457	33.2
P-DBP-EP-n/DDM-320	421	458	35.2

yielded the highest $T_{d5\%}$ of 421°C and char residue of 35.2%, with an improvement of 13.5 and 101.1% compared with that of DGEBA/DDM, respectively. It is well known that thermal stability is not only affected by molecular structure but also by crosslink density. As discussed in the Thermomechanical properties of cured P-DBP-EP-n/DDM section, P-DBP-EP-n/DDM-320 yielded the highest crosslinking density ($M_c = 217$). The improvement of crosslinking density arising from the thermal addition polymerization of allyl units [35, 42] contributed to the heat resistance of the cured resins. With higher aromaticity and extra crosslinking density, segments motion was restricted [46], rendering a more stable and perfect crosslinked network and thereby obtaining outstanding thermal stability.

3.7. Flame retardancy and morphology of char residue of P-DBP-EP-n/DDM

High char residue is a good indication of flame-retardant performances of the materials and confirms our prediction; LOI and the UL 94 were carried out to investigate the flame retardancy of P-DBP-EP-n/DDM, and results are summarized in Table 6. DGEBA/DDM exhibited an LOI value of 25.5% due to the combustible flexible aliphatic chain. Similarly, P-DBP-EP-n/DDM-180 with abundant allyl groups,

Figure 9. a) TGA and b) DTG curves of the cured resins.

Table 6. Flame retardancy properties of cured resins.

	LOI%	UL94
DGEBA/DDM	25.5	NR
P-DBP-EP-n/DDM-180	26.5	NR
P-DBP-EP-n/DDM-320	47.7	V-0

showed a slight increased LOI value of 26.5%. In contrast, P-DBP-EP-n/DDM-320 behaved differently, with an extremely high LOI value of 47.7%, which was approximately twice as much as DGEBA/DDM. It implied that P-DP-EP-n/DDM-320 is a nonflammable material in air [22] that has the potential to be used in cutting edge where high flame retardancy is required. The large margin increase of LOI value was ascribed to the highly crosslinked network resulting from extra crosslinking sites of allyl units and the compact biphenyl structure. A much higher crosslinked polymer network was obtained through thermal addition polymerization of allyl units. Polymer segments were wrapped tightly to form a stable and regular structure by the second cured network,

restricting chain motion and thereby increasing structure stability as illustrated in Figure 5b. Moreover, higher aromaticity originated from multiple symmetrical biphenyl moieties endowed the cured resins with better heat resistance and ability of charring promotion, as stated above.

To further investigate the burning behavior of different cured resins, the UL 94 was performed, and the representative moments of the burning process were captured, as shown in Figure 10. As shown in Figure 10a, DGEBA/DDM was ignited quickly and burned vigorously with rapid flame propagation, and some melt dripping occurred owing to the gaseous combustible segment (Figure 10a₆). Such a flourishing combustible failed to pass the V rating, and therefore just a little char residue was left, as shown in Figure 11. For P-DBP-EP-n/DDM-180, it burned more fiercely because it contained more aliphatic segments compared with DGEBA/DDM and was qualified for no rating as well. However, there was no melt dripping for the entire combustion, predicting that the

Figure 10. Video screenshots of UL94 test at representative time. a) DGEBA/DDM, b) P-DBP-EP-n/DDM-180, c) P-DBP-EP-n/DDM-320.

Figure 11. Digital photos taken from the residual char for DGEBA/DDM, P-DBP-EP-n/DDM-180 and P-DBP-EP-n/DDM-320.

structural stability and complete char residue as protective layer were assigned to it [47] as displayed in Figure 11. Conversely, P-DBP-EP-n/DDM-320 self-extinguished within about 5 s, and then a second ignition (Figure 10c₄) was applied immediately, but it behaved in the same way, passing the V-0 rating. As shown in Figure 11, P-DBP-EP-n/DDM-320 was kept intact, and only the bottom where it was exposed to fire was burned and carbonized after the test. It is indicative that the highly crosslinked network and stable biphenyl structures of P-DBP-EP-n contribute to the outstanding flame-retardant properties.

Figure 12. SEM images taken from the residual char collected from UL94 tests for DGEBA/DDM (a), P-DBP-EP-n/DDM-180 (b) and P-DBP-EP-n/DDM (c) (Outer layer 1,2 and inner layer 3.).

As for the distinct burning behaviors for different cured resins, SEM was carried out to investigate the morphologies of the residual char collected from the UL94, and the SEM images for different samples are shown in Figure 12. For DGEBA/DDM (Figure 12a), it was found that residual char was loose and porous, letting heat and oxygen penetrate the inner matrix through numerous holes [48]. Meanwhile, the combustible aliphatic fracture was easily exposed to heat through these broken holes (Figure 12a₃), leading to melting drop and combustion acceleration [24]. In contrast, P-DBP-EP-n/DDM-180 (Figure 12b) yielded denser and more compact and continuous residual char, which was beneficial for flame retardancy in theory [49, 50]. Such a complete and continuous char layer could retard the exchange of heat and low molecular fragments, obtaining complete char residue (Figure 11). It is indicative that P-DBP-EP-n/DDM has the potential to exhibit more excellent flame retardancy with further suitable curing procedures. As speculated, the morphology of char residue of P-DBP-EP-n/DDM-320 was vastly distinct from the former samples. As shown in Figure 12c, the outer layer char residue seemed loose and discontinuous, whereas the underlying matrix was smooth. It could be found that only the surface exposed to fire was carbonized and the matrix was well protected. Dense and compact holes were observed in the inner layer, suggesting fewer combustible fragments released owing to the stable aromatic structure and highly crosslinked network. Furthermore, the combustible gas was enveloped by the continuous matrix, blocking the spread of combustion effectively. All the results above indicate that P-DBP-EP-n/DDM-320 exhibits satisfactory flame-retardant effects.

4. Conclusions

In the current study, we successfully synthesized an epoxy oligomer derived from biomass magnolol through one-step glycidylation. The chemical structure of P-DBP-EP-n was systematically characterized by ¹H NMR, ¹³C NMR, and MALDI-TOF. The oligomer P-DBP-EP-n was a mixture with different polymerization degrees where $n = 1$ came to prominence. The viscosity of P-DBP-EP-n was 11.7 Pa·s, which was slightly lower than that of DGEBA, exhibiting excellent processability at room temperature. Then the cured P-DBP-EP-n was prepared with curing agent DDM and following thermal addition

polymerization of allyl units at a higher temperature. FTIR was carried out to determine the extent of reaction, and an 8 h-second-curing process at 320 °C was considered as optimum. The tensile and notched impact tests showed that P-DBP-EP-n/DDM-320 could not compete with DGEBA/DDM and even EDBP/DDM due to the highly crosslinked aromatic network with weak segments mobility. However, P-DBP-EP-n/DDM-320 exhibited an extremely high T_g value of 304 °C, which increased by 82% compared with that of DGEBA/DDM owing to higher crosslinking density ($M_c = 217$). In terms of thermal stability, $T_{d5\%}$ increased to 421 °C with a residual mass of 35.2% at 700 °C owing to the introduction of rigid biphenyl structures, which promoted charring. Furthermore, P-DBP-EP-n/DDM-320 was nonflammable, passing V-0 rating for the UL 94 test and achieving an 80% increase of LOI value (47.7 to 23.5%). This distinguished flame retardancy was ascribed to more dense morphology of char residue, which prevented heat and oxygen from penetrating the inner matrix. In conclusion, the magnolol-based oligomer is found as a renewable and promising substitute for DGEBA toward heat resistance and flame retardancy, satisfying the high application requirements.

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