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Novel biobased epoxy resin thermosets derived from eugenol and vanillin.

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Abstract

Novel renewable bisepoxide 2, 2'-diglycidyl ether-3, 3'-dimethoxy-5, 5'-diallydiphenylmethane (BEF-EP) and its hardener 3-methoxy-4-hydroxy-phenylbenzimidazole (VBZMI) were prepared from 1-allyl-3-methoxy-4-hydroxybenzene (eugenol) and 2-methoxy-4-formylphenol (vanillin), respectively. The chemical structures of two monomers were confirmed by their ^{1}H NMR spectra. Estrogenic activity test revealed that biobased bisphenol monomer 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-diallydiphenylmethane (BEF) as the precursor of BEF-EP showed extremely lower estrogenic activity than commercial bisphenol (BPA and BPF). This biobased, safe and green epoxy (BEF-EP) and commercial epoxy diglycidyl ether of bisphenol F (BPF-EP) were then cured with conventional and renewable hardener (benzimidazole BZMI and VBZMI), respectively, for comparison. The result showed the biobased epoxy thermoset (BEF-EP/BZMI) possessed excellent thermal stability ($T_{d5\%}$ =372 ^oC), almost reaching the properties of commercial epoxy thermoset (BPF-EP/BZMI, $T_{d5\%}$ =385 ^oC). Furthermore, BEF-EP/BZMI showed good hydrophobic properties, which exhibited a higher contact angle (79.53^o) than BPF-EP/BZMI (75.16^o). In addition, for the comparison between VBZMI and BZMI, the epoxy resins using VBZMI as the curing agent displayed higher performance than the epoxy resins using BZMI as the curing agent. Especially, BEF-EP/VBZMI showed a higher thermal stability ($T_{d5\%}$ =395 ^oC), a higher glass transition temperature (T_g=97 ^oC) and a higher contact angle

(94.07) than BEF-EP/BZMI. The result could be attributed to the existence of hydroxyl groups in the side chain of VBZIMI, which enhanced the crosslinking density and then improved the rigid of epoxy material. Herein, we believe the novel biobased epoxy resin (BEF-EP) and hardener (VBZMI) has wide application as the alternative of conventional petroleum-based epoxy resin and hardener.

Keywords: Eugenol; vanillin; epoxy resin; biobased; alternative

1. Introduction

Nowadays, energy crisis of the world is undoubtedly confirmed due to the excessive exploitation and immoderate depletion of human. Fossil fuels as nonrenewable resources will be certainly replaced by renewable feedstocks. Therefore, biomass as one of the abundant, renewable and high output resources should be paid more attention to meet the requirement of sustainable development and energy exhaustion [1-8].

Epoxy resin, as one of the most important thermosetting materials, has been widely used in coating, adhesives, aerospace and electronics industry due to its outstanding adhesion, lower density, high strength, good durability, excellent chemical resistance [9-14]. As is well known, almost all of the epoxy resin are produced from fossil resources. Among them, diglycidyl ether of bisphenol A (BPA-EP) and diglycidyl ether of bisphenol F (BPF-EP) as two kinds of conventional epoxy resins via the reaction between bisphenol monomers and epichlorohydrin (ECH), which are strongly dependent on fossil resources [15]. In addition, bisphenol A (BPA) as the precursor of epoxy resins possess the estrogenic activity because of the similar structure to estrogens, which has been recognized as the endocrine disruptor. According to the report [16], small amount of BPA can still release from the epoxy resin with time due to the existence of unstable chemical bonds. Thus, BPA could be detected in foods and liquids that were stored in the containers made from or lined with BPA-containing materials. This could increase the risk of reproductive disorder and cancer of humans [17-18]. Unfortunately, bisphenol F (BPF) as an analogue of BPA has the similar estrogenic activity to BPA [19]. As the result, their applications have been restricted in many countries.

In recent years, many researchers attempted to prepare the biobased epoxy resin instead of petroleum-based product. Various biomasses have been used for designing the structure of bio-based epoxy resins such as cardaol [20], rosin [21], itaconic [22-23], eugenol [24-26] and vanillin [27]. Miao et al [28]. prepared a novel biobased epoxy monomer with the extremely high biomass content via the reaction of eugenol and 2,5'-furandicarboxylic acid After curing with methyl hexahydrophthalic anhydride (MHHPA), the resulted epoxy resin showed a higher glass transition temperature (T_g,153.4 ^{o}C) than BPA-EP / MHHPA (144.1 ^{o}C) as well as considerably high mechanical properties and better flame retardancy. Wan et al [29]. developed an ultrastiff bio-based epoxy resin derived from an eugenol-based monomer. Compared with conventional epoxy materials, this biobased epoxy resin showed a 33 ^{o}C, 39% and 55% increment in the glass transition temperature (T_g), Young' s modulus and hardness, respectively. Wang et al [30]. reported two kinds of vanillin-based epoxy monomers that were synthesized by one-pot reaction containing Schiff base formation and phosphorus-hydrogen addition between vanillin, diamines, and diethyl phosphite, followed by reacting with epichlorohydrin. After curing the biobased epoxy resins exhibited excellent flame retardancy with UL-94 V0 rating and high limit oxygen index of 31.4%~32.8%.

As expected, there are many similar reports on the design of biobased epoxy resins for the replacement of conventional epoxy materials. However, among these reports, only a few researchers estimated the estrogenic activity of the biomass-derived monomers as the precursor of biobased epoxy resins To the best of our knowledge, some of the natural molecules still possess the estrogenic activity as same as BPA. For example, genistein and apigenin were confirmed to have more potent estrogenic activity than BPA and BPF. Therefore, it is necessary to choose the biomass-derived monomers with low estrogenic activity for ensuring human health as well as sustainable development. In addition, many researchers only focused on the preparation of epoxy resins from biomass-derived monomers. They still used the conventional curing agents that were derived from petroleum resource. However, the curing agent is another important section of epoxy resins besides the epoxy monomer. Thus, the development of biobased hardener is also a crucial task to achieve the renewable epoxy materials.

In this study, we synthesized a eugenol-based bisphenol 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-diallydiphenylmethane (BEF) as the precursor of biobased epoxy resin (BEF-EP) and compared its estrogenic activity with estrogen and commercial bisphenols (BPA and BPF) by a methylthiazolyldiphenyl-tet-razolium bromide (MTT) assay using MCF-7 (human breast adenocarcinoma cell line) as an estrogen receptor (ER). Furthermore, vanillin-based curing agent 3-methoxy-4-hydroxy-phenylbenzimidazole (VBZMI) was prepared as the biobased hardener of renewable epoxy resin. Compared to the epoxy resin based on the commercial hardener benzimidazole (BZMI), the VBZMI cured epoxy resin exhibited higher performance, including thermal stability, mechanical and hydrophobic properties. Therefore, we believed that the novel biobased epoxy resin (BEF-EP) and its biobased hardener (VBZMI) have a wide application prospect as the alternative to conventional epoxy resin and hardener.

2. Experimental

2.1 Materials

Benzimidazole, 1,2-diaminobenzene and ammonium acetate were purchased from Beijing Chemical Company (Beijing, China). ECH was obtained from TCI Shanghai Development Co., Ltd. BFP-EP (NPEF-170) was purchased from Jiadida New Material Co., Ltd. BPF, BPA, eugenol and vanillin were obtained from Energy Chemical. Co. Sodium hydroxide (NaOH) and tetrabutylammonium bromide were purchased from Sinophram Chemical Reagent Co., Ltd. All other reagents and solvents were obtained commercially and used without further purification.

2.2 Synthesis of eugenol-based bisphenol monomer BEF

The synthesis procedure of BEF is described as follows. Eugenol (0.22 mol) and phosphoric acid (7 mL, 85 wt%) were mixed in a three-necked 500 mL flask equipped with a mechanical stirrer. The mixture was heated to 50 ^{o}C and kept at this temperature for 30 minutes. Then the formaldehyde solution (0.1 mol, 38 wt%) was added dropwise within an hour. After that, the mixture was heated to 90 ^{o}C for 6 hour and then washed with deionized water several times until the water was neutralized. The product was recrystallized with a mixed solvent of toluene and ether (1:1 vol / vol). After vacuum filtration and dried at 50 ^{o}C for 12 h, the yellow product was obtained. The chemical structure is shown in Scheme 1.

2.3 Synthesis of biobased epoxy resin (BEF-EP)

A mixture of 3.40 g (0.01 mol) BEF, 16 mL ECH and 0.1 g tetrabutylammonium bromide were stirred in a three-neck flask at 90 ^{o}C for 6 h. After cooling to room temperature, the excess ECH was removed at a reduced pressure. Subsequently, 16 mL toluene and 2.88 g NaOH (50 wt % solution) were added and the mixture was kept at 90^{o}C for 3 h. Then the mixture was washed and distilled under reduced pressure. Finally, the product was washed with obtained by drying in a vacuum oven 12 h at 60 ^{o}C. The chemical structure is also shown in Scheme 1.

2.4 Synthesis of vanillin-based curing agent VBZMI

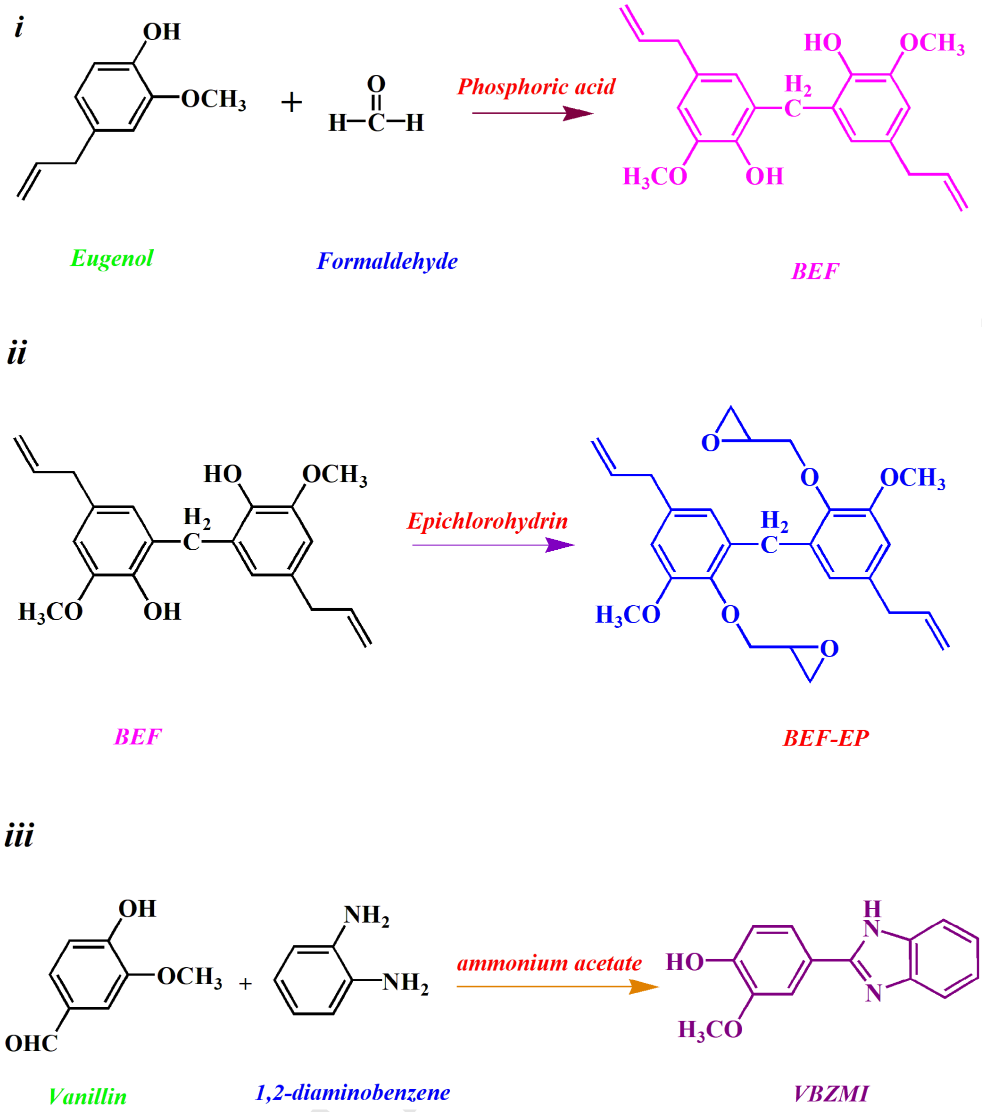
Scheme 1 shows the synthesis route of VBZMI in detail. The monomer of vanillin (15.2 g, 0.1 mol), ammonium acetate (0.4 g, 5.2 mmol) and absolutely ethyl alcohol (40 mL) were added into 250 mL three-neck flask equipped with a mechanical stirrer and a nitrogen protection. After heating to 70 ^{o}C for half an hour, 1,2-diaminobenzene (10.82 g, 0.1 mol) was added into the mixture. After stirring at 70 ^{o}C for 3 h, the solvent was removed from the reaction mixture at a reduced pressure to precipitate the rude product. Finally, the product was washed with the deionized water several times and dried in a vacuum oven 12 h at 60 ^{o}C.

2.5 Preparation of cured epoxy samples

A series of biobased epoxy resins (BEF-EP/BZMI and BEF-EP/VBZMI) were prepared by using VBZMI and commercial benzimidazole (BZMI) as the curing agents, respectively. The procedure is described as follows. The epoxy monomer BEF-EP was placed in the oven at 80 ^{o}C until it was melting. Then, 10 wt% of BZMI or VBZMI were added into BEF-EP to form a clear solution, respectively. The mixture was stirred for 30 min and put into the vacuum oven to remove the entrapped air. Finally, the mixture was poured into a polish mould and cured at 120 ^{o}C for 1 h, 160 ^{o}C for 2 h and 200 ^{o}C for 2 h to obtain those biobased epoxy resins. For comparison, the conventional epoxy resins (BPF-EP/BZMI and BPF-EP/VBZMI) were also prepared according to the similar procedure.

2.6 MTT assay

MCF-7 cells were maintained in RPMI 1640 supplemented with 10 % (V/V) fetal bovine serum (FBS), 100U/mL penicillin and 100 μg/mL streptomycin. MCF-7 cells were seeded into 96-well plates (0.6×10^4 cells/well) for 6 h, and then incubated with BEF / DMSO (dimethyl sulfoxide), estrogen / DMSO, BPA / DMSO and BPF / DMSO at a concentration of 2μM/L, respectively. Next the medicated MCF-7 cells were incubated in a 5 % CO_2 humidified incubator at 37 °C for 24 h. DMSO without any bisphenols was used as the negative control, while BEF, estrogen and commercial bisphenol (BPA and BPF) were used as positive controls. Cell proliferation was then measured by a MTT assay as previously reported [31].



Scheme 1. The synthetic route of BEF, BEF-EP and VBZMI.

2.7 Characterization

^{1}H-NMR spectrum was measured on a 500 MHz Bruker Avance510 spectrometer at 298 K with DMSO-d_6 and chloroform-d as the solvent and tetramethylsilane as the standard.

Dynamic mechanical analysis (DMA) was carried out with a TA instrument DMA Q800 at a heating rate of 3 ^{o}C min^{-1} from 25 ^{o}C to 200 ^{o}C and a load frequency of 1 Hz in single cantilever mode. TGA was conducted on a Pyris 1 TGA analyzer (Perkin-Elmer, USA). The samples were heated from 100 ^{o}C to 800 ^{o}C at a rate of 10 ^{o}C min^{-1} under air atmosphere. Before the heating scan, all the samples were pre-dried under air at 100 ^{o}C for 10 min to remove the residual water and solvent.

Contact angle measurements were performed on a JC2000C2 contact angle goniometer (Shanghai Zhongchen Powereach Company, China) by the sessile drop method with a micro syringe at room temperature.

3. Results and discussion

3.1 Characterization of monomers

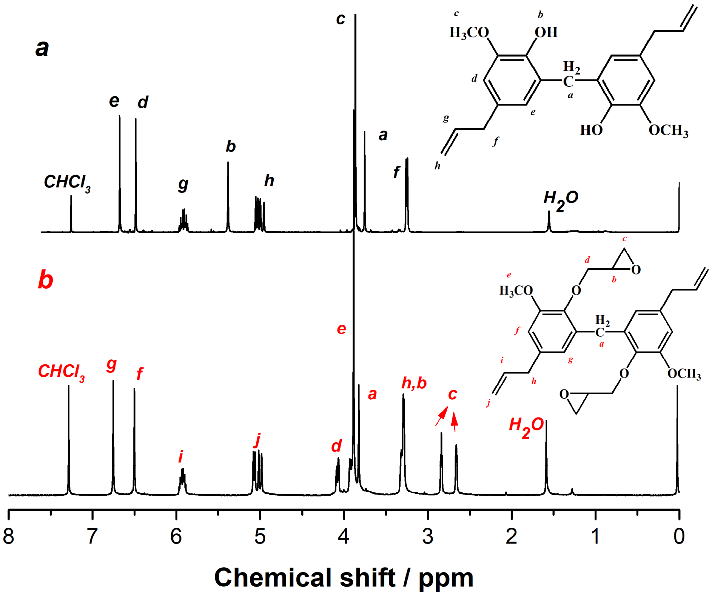


Fig. 1 ^{1}H-NMR spectra of monomers BPF (a) and BPF-EP (b).

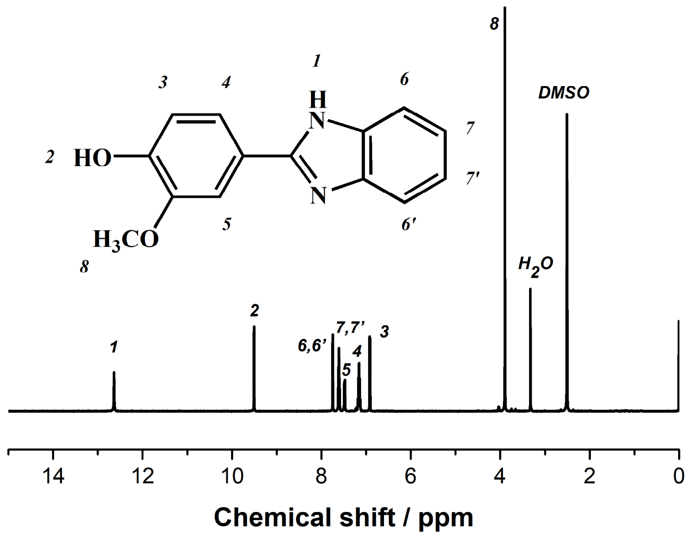


Fig. 2 ^{1}H-NMR spectrum of biobased curing agent VBZMI.

Fig. 1 shows the ^{1}H-NMR spectra of monomers BEF and BEF-EP, respectively. In this spectrum, all the signals could be attributed to the expected protons on the monomers. As seen in Fig. 1 (a), the peaks at 6.69 ppm and 6.46 ppm were attributed to the protons on the aromatic rings of BEF, while the peaks at 5.98 ppm and 5.08 ppm were assigned to the protons on C=C of allyl group. The protons on hydroxyl appeared at 5.40 ppm, and the protons on methoxy could be found at 3.82 ppm. The result indicated that BEF was synthesized successfully via an electrophilic substitution reaction. For the ^{1}HNMR spectrum of BEF-EP in Fig. 1 (b) , it was could clearly observed the signal at 5.40 ppm assigned to the hydroxyl protons disappeared entirely, and new peaks attributed to the graft of ECH appeared at 2.6 ppm to 2.8 ppm. Additional proton peaks assigned to the methylene ($-CH_2-$) groups of glycidol ether were observed in the range from 3.8 ppm to 4.2 ppm. Furthermore, other signals were assigned to the expected protons on the chemical structure of BEF-EP, indicating that the novel epoxy monomer was also prepared successfully.

Fig. 2 displays the ^{1}H-NMR spectrum of the biobased curing agent VBZMI. In the spectrum, the signal of H_1 was attributed to the proton on the imidazole ring. The peak at 9.5 ppm was attributed to the proton on the hydroxyl group (H_2), while the peak at 3.82 ppm was assigned to the protons on the methoxy group (H_8). Additionally, the other peaks were assigned to the protons on the aromatic ring. Thus, the result indicated that the biobased curing agent VBZMI was synthesized successfully.

3.2 Estrogenic activity (BEF, estrogen, BPA and BPF)

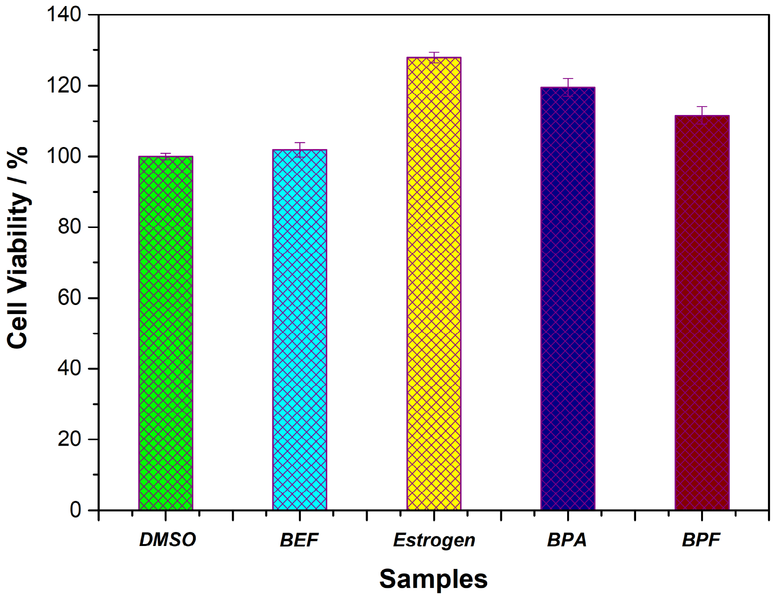


Fig. 3 The cell viability of MCF-7 exposed to different bisphenols and estrogen in 24 h.

The in vitro cell proliferation of BEF was investigated with MCF-7 cells (Fig. 3). The cells were exposed to BEF / DMSO solution at a concentration of 2 μM for 24 h followed by cell proliferation evaluation by MTT assay. DMSO was set as the negative control, while estrogen, BPA and BPF were set as the positive control. Compared to the negative control (DMSO), each positive control group presented the cell proliferation rate of 27 % (Estrogen), 19.5 % (BPA) and 11.6 % (BPF), respectively. Especially, the biobased bisphenol BEF exhibited extremely lower cell proliferation rate (1.87 %) than above positive controls. This result could be explained by the significant difference in the molecular structure between BEF and other monomers (Estrogen, BPA and BPF), which caused the decrease of estrogenic activity. Therefore, the result suggested that BEF can be considered as a genuinely safer alternative to BPA and BPF.

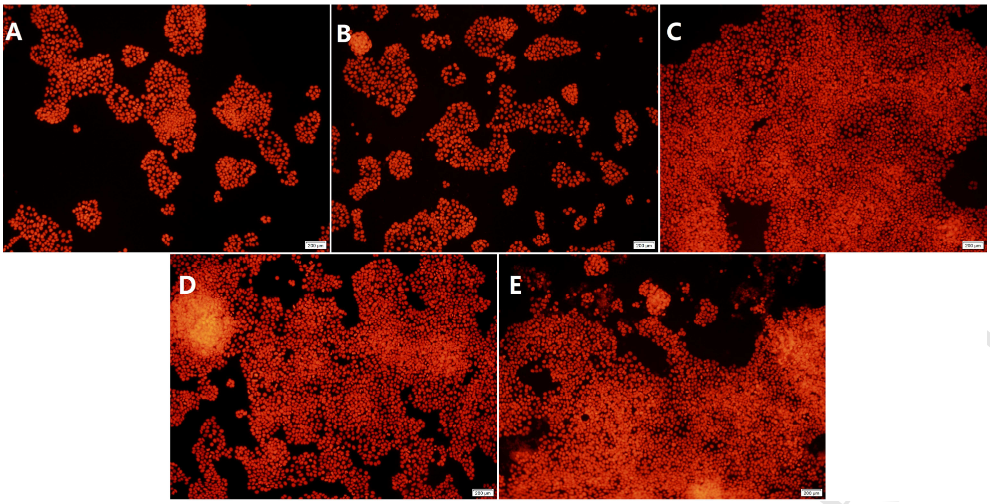


Fig. 4 Fluorescence microscopy of MCF-7 proliferates after exposing to different bisphenols.

The estrogenic activity of different monomer was investigated by fluorescence microscopy. MCF-7 cells treated with BEF (B), estrogen (C), BPA (D) and BPF (E) at a concentration of 2 μM in DMSO for 24 h was visualized by fluorescence microscopy. Compared with DMSO (A) negative control group, estrogen and commercial bisphenols (BPA and BPF) induced higher fluorescence intensity, demonstrating that the commercial bisphenol significantly improved the cellular proliferation. On the contrary, BEF hardly induced the cell proliferation, indicating that the BEF monomer presented lower estrogenic activity than BPA and BPF.

3.3 Mechanical and thermal properties

The mechanical property is essential for epoxy materials to be applied in many fields. Dynamic mechanical analysis (DMA) was performed to investigate the mechanical properties and glass transition temperature (T_g) of the cured epoxy resins. As shown in Fig. 5, it could be clearly observed that BEF-EP materials have lower storage modulus than BPF-EP materials under the identical curing condition. For example, BEF-EP / BZMI possessed the storage modulus of 1080 MPa, 520 MPa lower than BPF-EP / BZMI. Similarly, this phenomenon could be found by comparing the storage modulus between BEF-EP / VBZMI and BPF-EP / VBZMI. The result was mainly caused by two factors. First, the existence of flexible allyl group decreased the stiffness of BEF-EP materials. Second, lots of side groups (allyl and methoxy) in the structure of BEF-EP could reduce the cross-linking density of the epoxy material. Furthermore, the cured epoxy materials using VBZMI as the curing agent possessed better mechanical property than epoxy materials cured with commercial BZMI. For example, BPF-EP / VBZMI had the highest storage modulus of 3250 MPa among all of the epoxy resins within the experimental range. BEF-EP / VBZMI exhibited the storage modulus of 1730 MPa, which was much higher than BPF-EP / BZMI and BEF-EP / BZMI, respectively. This is because that vanillin-based curing agent VBZMI has more than one aromatic ring in the structure, thus leading epoxy/VBZMI to have higher stiff than epoxy / BZMI. Moreover, the existence of hydroxyl in the structure of VBZMI could also improve the cross-linking density of the epoxy materials.

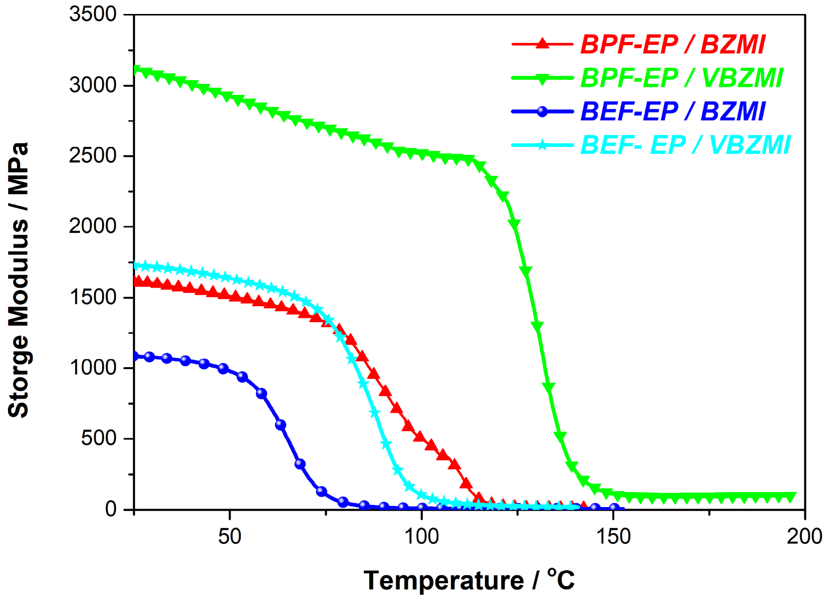


Fig. 5 The storage modulus curves of cured epoxy materials

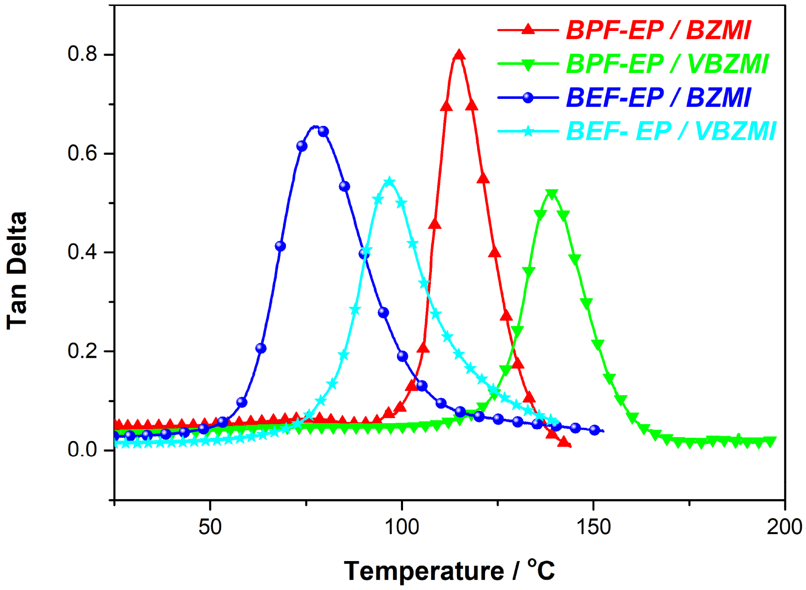


Fig. 6 The tan delta curves of cured epoxy materials

The glass transition temperature (T_g derived from tan δ_{max}) of epoxy materials are shown in Fig 6. The cured BEF-EP materials exhibited lower T_g values than the cured BPF-EP materials. For instance, BPF-EP / VBZMI exhibited the highest T_g (140 ^{o}C) among all the epoxy materials. BPF-EP / BZMI showed a T_g of 115 ^{o}C, which is still 17 ^{o}C and 38 ^{o}C higher than BEF-EP / VBZMI and BEF-EP / BZMI respectively. It could be due to the flexible allyl groups in the BEF-EP structure, which promote the molecular motion at low temperature. Furthermore, it could be easily observed that VBZMI cured materials showed the higher T_g than BZMI cured materials using the same epoxy matrix. For example, BEF-EP / VBZMI exhibited a T_g of 98 ^{o}C, 21 ^{o}C higher than BEF-EP / BZMI. This result indicated the high stiff structure of VBZMI could restrict the molecular motion of the epoxy materials and the existence of hydroxyl in the structure of VBZMI could also improve the cross-linking density of the epoxy materials as we mentioned above.

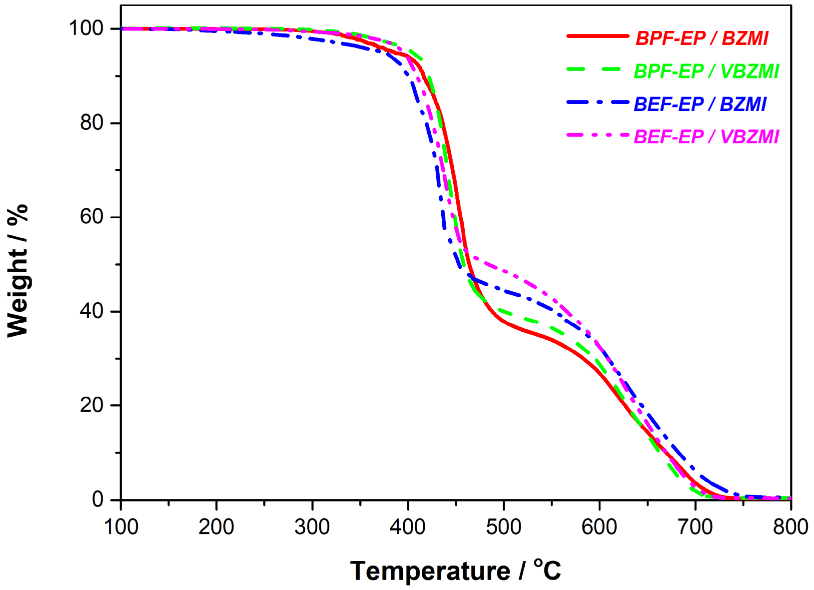


Fig. 7 The TGA curves of cured epoxy resin materials

Table 1. The thermal properties and contact angles of cured epoxy resins.

Samples	TGA [°C]			DMA		Contact Angle
	$T_{d5\%}$	$T_{d10\%}$	T_{dmax}	T_g [°C]	Storage Modulus [MPa]	Degree
BPF-EP / BZMI	385	416	450	115	1600	75.16 ± 0.32
BPF-EP / VBZMI	404	421	438	140	3250	90.04 ± 0.24
BEF-EP / BZMI	372	400	430	77	1080	79.53 ± 0.41
BEF-EP / VBZMI	395	409	439	98	1730	94.07 ± 0.36

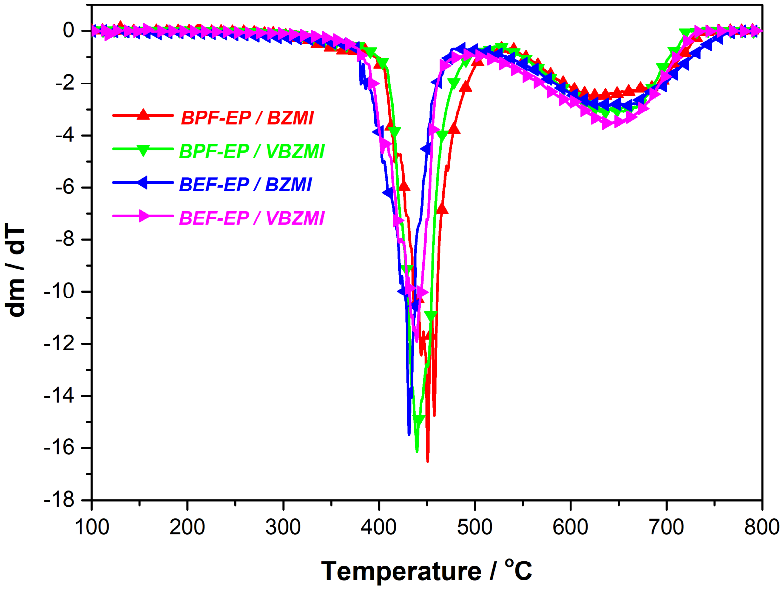


Fig. 8 The DTG curves of cured epoxy materials.

Fig.7 and Fig. 8 show the TGA curves and their differential thermogravimetric (DTG) curves of epoxy resins measured under atmosphere, respectively. The relevant thermal decomposition data, including the decomposition temperature of 5% and 10% weight loss ($T_{d5\%}$ and $T_{d10\%}$), the decomposition temperature for the maximum rate of weight loss (T_{dmax}) are listed in Table 1. As shown in Fig. 7, all the epoxy resins exhibited high initial decomposition temperatures. For example, BEF-EP / BZMI showed the lowest $T_{d5\%}$ of 372 °C among these epoxy resins, while BPF-EP / BZMI, BEF-EP / VBZMI and BPF-EP / VBZMI had the $T_{d5\%}$ of 385 °C, 395 °C and 404 °C, respectively. Therefore, it could be concluded that BEF-EP materials possessed the lower $T_{d5\%}$ than BPF-EP materials with the same curing agent. This could be owing to the dissociation of methoxy and allyl groups from the structure of BEF-EP. Furthermore, it could be obviously observed that epoxy / VBZMI materials exhibited the higher $Td_{5\%}$ than epoxy / BZMI materials. Using the same epoxy matrix, BEF-EP / VBZMI had a $T_{d5\%}$ of 395 °C, 23 °C higher than BEF-EP / BZMI. Similarly, BPF-EP / VBZMI showed a $T_{d5\%}$ almost 20 °C higher than BPF-EP / BZMI. This is because that VBZMI containing more than one aromatic ring in the structure improved the thermal stability of its cured epoxy materials. Meanwhile, the existence of hydroxyl in the structure enhanced the cross-linking density of its cured epoxy materials. Moreover, when the temperature increased to 470 ^{o}C, BEF-EP showed a slower degradation rate than BPF-EP. It might be due to the decomposition of allyl group in the BEF-EP structure, which produced CO_2 and then diluted the concentration of air, thus lowering the degradation rate at high temperature.

3.4 Contact angle test

Wettability, as one of the important property of materials, not only greatly impairs the mechanical and thermal properties of epoxy resins, but also widely limits the usage of epoxy resins in many applications. Therefore, the contact angles of all epoxy resin samples were measured to determine the relative wettability of the surface. As shown in Fig. 9, the contact angle of BPF-EP / BZMI was 75.16^{o}, 3.37^{o} lower than BEF-EP / BZMI. Similarly, BPF-EP / VBZMI showed a contact angle of 90.04^{o}, which is lower than BEF-EP / VBZMI. This indicated the hydrophobic allyl and methoxy in the side chain of BEF-EP could improve the contact angle of materials. For the same epoxy matrix using BZMI and VBZMI as the curing agent, BEF / VBZMI exhibited a contact angle of 94.07^{o}, 14.54^{o} higher than BEF / BZMI. Meanwhile, the contact angle of BPF / VBZMI was also higher than BPF / BZMI. This is because that VBZMI containing more hydrophobic aromatic rings in the structure caused its cured epoxy resins to possess higher hydrophobicity than epoxy / BZMI. Moreover, the existence of hydroxyl groups in VBZMI could also improve the cross-linking density of the epoxy materials and then enhanced the contact angle further.

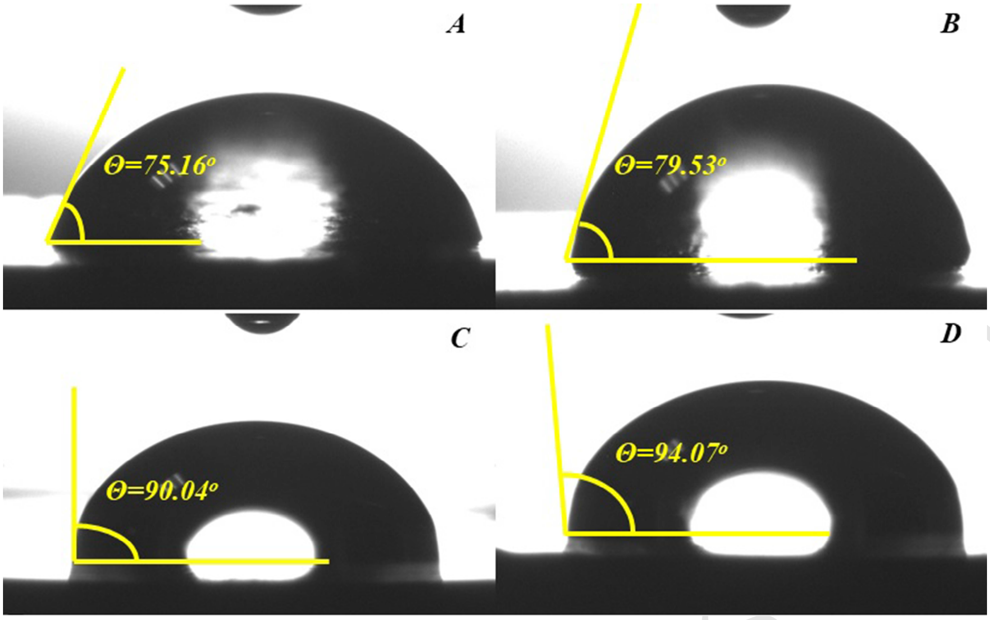


Fig. 9 The contact angles of cured epoxy resin BPF-EP / BZMI (A), BEF-EP / BZMI (B), BPF-EP / VBZMI (C) and BEF-EP / VBZMI (D).

4. Conclusions

A novel biobased bispheonl BEF and its corresponding epoxy resin (BEF-EP) were synthesized via a multi-step procedure derived from eugenol. Meanwhile, we prepared a novel biobased curing agent VBZMI derived from vanillin. Then we cured BEF-EP and commercial epoxy BPF-EP with BZMI and VBZMI, respectively. A series of epoxy materials BEF-EP / BZMI, BEF-EP / VBZMI, BFP-EP / BZMI and BPF-EP / VBZMI were finally prepared for comparison. Comparing the estrogenic activity, BEF exhibited lower estrogenic activity than other commercial bisphenols BPA and BPF. This indicated that BEF can be considered as a genuinely safer alternative to BPA and BPF. Furthermore, the epoxy resins using biobased VBZMI as the curing agent displayed better thermal stability and higher hydrophobic property than the epoxy resins using BZMI as the curing agent. Therefore, we believe that BEF-EP and VBZMI are the promising candidates to replace petroleum-based epoxy resins and curing agents, respectively.

Acknowledgements

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Highlights

1. A novel renewable bisepoxide BEF-EP and its hardener VBZMI were prepared from eugenol and vanillin, respectively.
2. The precursor BEF showed extremely lower estrogenic activity than commercial bisphenols.
3. The biobased epoxy resin cured by VBZMI showed better performance than epoxy resin cured by traditional curing agent.