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A renewable resveratrol-based epoxy resin with high T_g , excellent mechanical properties and low flammability

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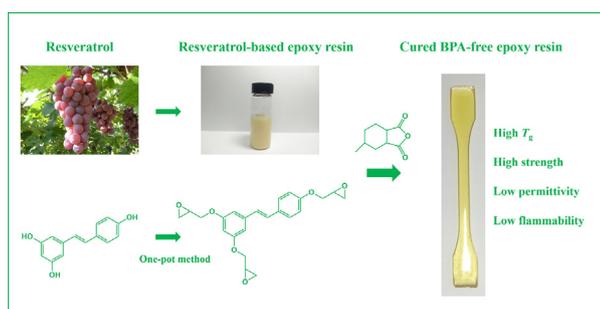
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HIGHLIGHTS

- A renewable resveratrol-based epoxy resin was prepared.
- REEP/MeHHPA exhibits high T_g , high strength and high modulus.
- REEP/MeHHPA possesses exceptional low permittivity.
- REEP/MeHHPA shows low flammability and corresponding mechanisms are investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Preparing low-flammable biobased epoxy resins with a high glass transition temperature (T_g) and excellent mechanical properties is significant for the rapid growing electronics and microelectronics industry. In this research, a resveratrol-based epoxy resin (REEP) with well-designed chemical structures possessing trifunctional epoxy groups and rigid conjugate structures was prepared through the one-pot method and was then cured by methyl hexahydrophthalic anhydride (MeHHPA). The conventional petroleum-based epoxy resin (DGEBA) was cured by the same kind of curing agent. Results showed that T_g of REEP/MeHHPA was up to 210.8 °C, much higher than that of DGEBA/MeHHPA (only 146.5 °C). The tensile strength and modulus of REEP/MeHHPA were 73.5 MPa and 3.0 GPa, respectively. More importantly, REEP/MeHHPA exhibited exceptional low permittivity (about 3.5) and low flammability with high char yield of 19.0% (800 °C). Therefore, the resveratrol-based epoxy resin could be a promising candidate for DGEBA and has great potential application in electronics and microelectronics industry.

1. Introduction

Epoxy resins, with the superior and comprehensive performance of tunable T_g and sound mechanical properties, are widely used in coatings, adhesives, microelectronic packaging and matrix composites. It

was reported that the annual global production of epoxy resins was up to 3 million tons [1], in which bisphenol A-based epoxy resin (DGEBA), bisphenol F-based epoxy resin and N, N-diglycidyl-4-glycidyl-oxyaniline [2] are mostly prepared from petroleum-based resources [3–5]. For example, DGEBA, accounting for approximately 85% of commercial

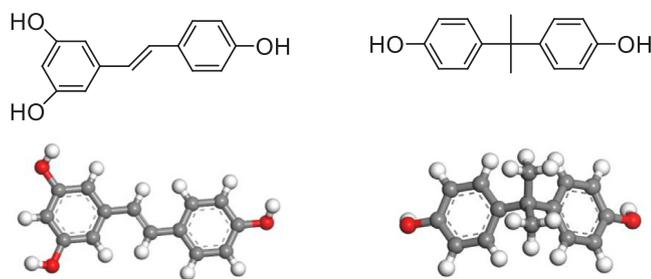
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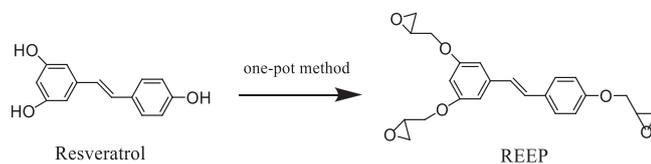
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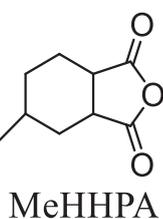
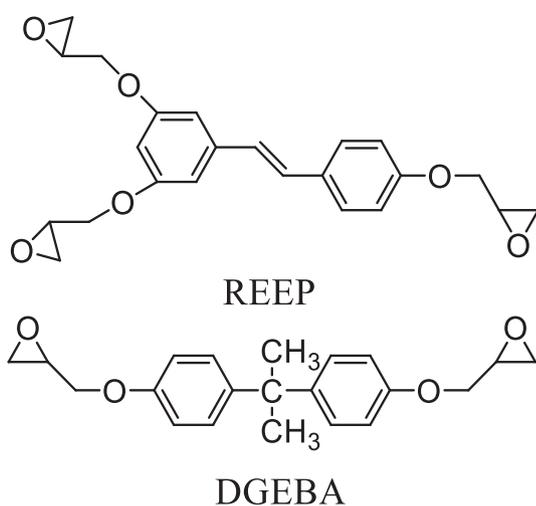
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Scheme 1. Chemical structures and ball-and-stick models of resveratrol and bisphenol A.



Scheme 2. Synthesis route of REEP.



Scheme 3. Main chemical structures in this work.

epoxy, was synthesized from epichlorohydrin (ECH) and bisphenol A (BPA) [6]. ECH, synthesized from glycerine via glycerol chlorination, is considered environment-friendly [7], but BPA is heavily unrenewable due to its fossil resources from phenol and acetone [8–10]. The commercial products of BPA were highly restricted in the fields such as baby bottles and medical supplies because of its potential cause for health problems [9,11–13]. Thus, much attention has been paid to

Table 1

Formulations and C, H, and O contents (%) of REEP/MeHHPA and DGEBA/MeHHPA.

Samples	REEP (g)	DGEBA (g)	MeHHPA (g)	DMP-30 (g)	C, H, and O contents (%)
REEP/MeHHPA	10.00	—	11.68	0.10	99.99
DGEBA/MeHHPA	—	10.00	8.41	0.10	99.99

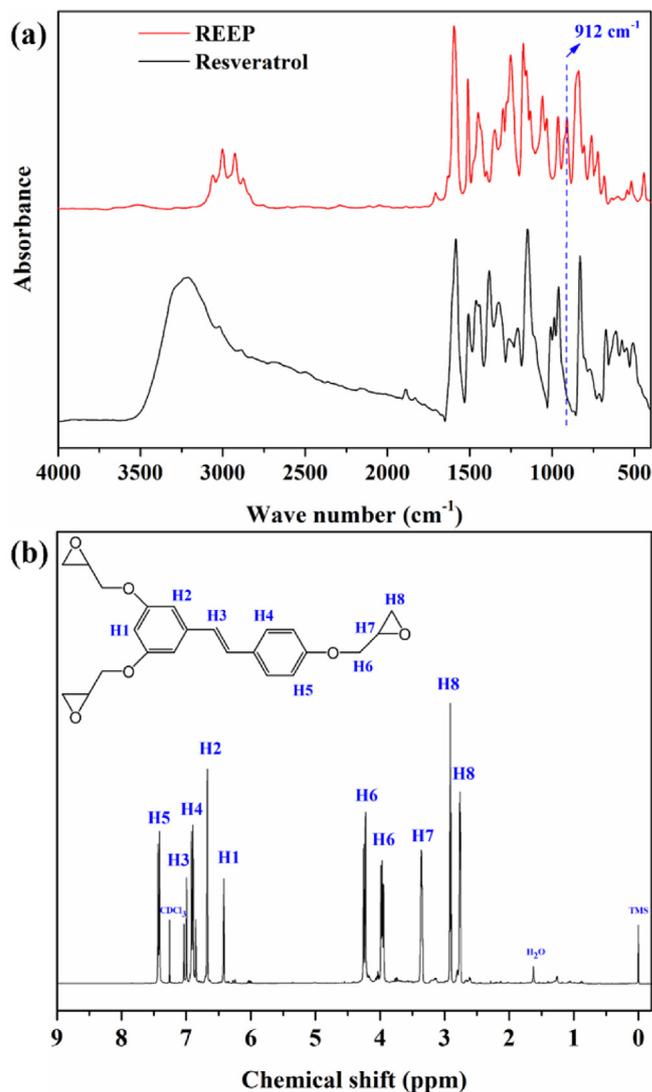


Fig. 1. (a) FTIR spectra of resveratrol and REEP; (b) ^1H NMR of REEP.

develop a kind of sustainable starting materials to replace BPA [14–20].

Over the past decades, biobased starting materials, including plant oils, lignin, eugenol, vanillin, tannins, cardanol, cellulose, and hemicellulose, were applied for the preparation of epoxy resins [21–24]. Moreover, through the selection and design of chemical structures, remarkable progress has been made to enhance the T_g and mechanical performance of biobased epoxy resins. For instance, Qin et al. [25] reported a low-toxicity method to prepare a biobased epoxy resin with a high epoxide equivalent of 129 g mol^{-1} . Also, its hexahydrophthalic anhydride (HHPA) cured epoxy showed a relatively high T_g of $114.2 \text{ }^\circ\text{C}$. Kristufek et al. [26] prepared a quercetin-based epoxy resin, which was nadic methyl anhydride (NMA)-cured with T_g of $134 \text{ }^\circ\text{C}$ and tensile strength of 37 MPa .

However, biobased epoxy/anhydride systems are usually considered highly flammable, because the formulation of such systems consists of C, H, and O elements [27]. The high flammability constrains its further application because of the induction of fire situations that lead to heavy

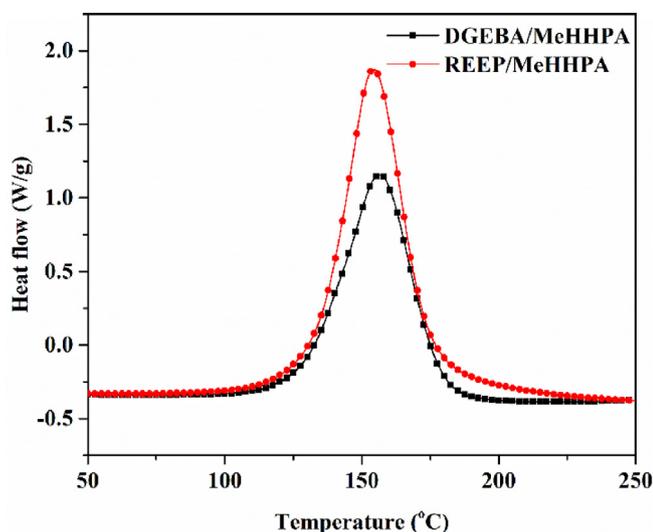


Fig. 2. Non-isothermal curing behaviors of REEP/MeHHPA and DGEBA/MeHHPA ($10\text{ }^{\circ}\text{C min}^{-1}$).

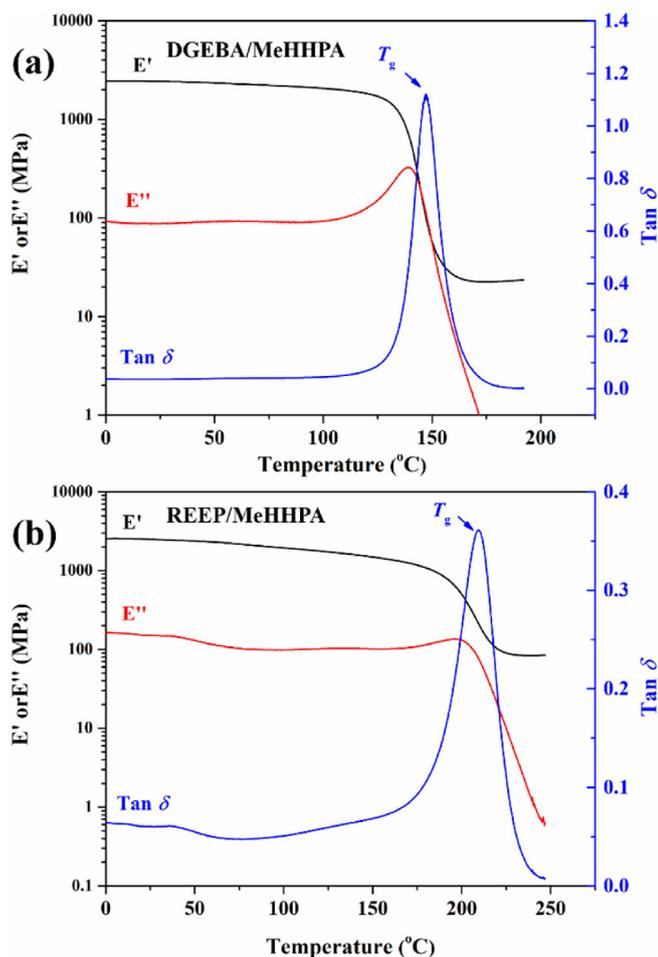


Fig. 3. Thermal-mechanical properties of (a) DGEBA/MeHHPA and (b) REEP/MeHHPA.

casualties and severe financial losses. Some effective strategies have been studied and carried out to reduce flammability. One method is the introduction of halogenated elements into the biobased epoxy resins systems. It is useful yet harmful to the human body and is highly restricted when applying to the electronics and microelectronics industry [28]. The other method is the corporation of phosphorus [29] or silicon

elements [30] into the epoxy resins systems, which can effectively reduce its flammability but significantly decrease the T_g and mechanical properties [31]. Recently, designing biobased epoxy resin with rigid structures to generate high residual char yields has emerged as a powerful strategy [32]. Miao et al. [33] prepared a BPA-free epoxy resin (EUFU-EP) possessing rigid aromatic and furan groups cured by methyl hexahydrophthalic anhydride (MeHHPA). The char yield of EUFU-EP/MeHHPA was 10.9% higher than that of DGEBA/MeHHPA. Also, employing TG-FTIR analysis, fewer organic combustible gases but more CO_2 production were observed in EUFU-EP/MeHHPA during the thermal degradation process, indicating low flammability of such material. It was noted that the flexural strength of EUFU-EP/MeHHPA was still lower than that of DGEBA/MeHHPA. Therefore, the design and preparation of a type of biobased epoxy resin with low flammability without sacrificing other properties such as T_g and mechanical properties is a significant issue for meeting the demand in today's rapid growing electronics and microelectronics industry. Besides, the cured biobased epoxy resins with low dielectric permittivity will gain many advantages in industrial applications.

Resveratrol, known as 'French paradox', serves as one of the most widely used sustainable resources with attractive properties causing by its antioxidative and anticancer properties [34]. It is commonly derived from natural plants such as grape skin, peanut, Japanese knotweed and pines [35,36]. Several synthetic routes were also available for providing high-quality and high-yield resveratrol [37,38]. Recently, a more sustainable and environment-friendly method was reported to collect resveratrol from cell culture [39,40]. Scheme 1 displays the well-defined chemical structures and ball-and-stick models of resveratrol, which possesses more functional phenolic hydroxyl groups and rigid conjugate structures than those of BPA. Harvey et al. [41,42] prepared a resveratrol-based tricyanate ester with higher T_g than $340\text{ }^{\circ}\text{C}$ and char yield of 71% at $600\text{ }^{\circ}\text{C}$. Zhang et al. [43] synthesized a trioxazine benzoxazine resin (RES-fa) from resveratrol. The char yield ($800\text{ }^{\circ}\text{C}$) of poly (RES-fa) was 64%. Recently, a biobased epoxy oligomer was prepared from resveratrol after curing with diamine [44]. The char yield ($900\text{ }^{\circ}\text{C}$) of cured epoxy oligomer was 38.5%. Therefore, preparation of resveratrol-based epoxy resin as a BPA-free substitute for DGEBA, due to its inherent rigid chemical structures, may effectively increase the char yield of the cured epoxy resins and thus achieve the purpose of low flammability.

In this work, a resveratrol-based epoxy resin (REEP) with simultaneous high T_g , excellent mechanical properties, and attractive low flammability was prepared by the one-pot method after cured with MeHHPA. The curing behaviors, thermo-mechanical, mechanical performance, dielectric properties, thermal stability and flammability of REEP/MeHHPA and DGEBA/MeHHPA were then investigated and tested. Results showed that REEP/MeHHPA exhibited exceptional low dielectric permittivity and low flammability, which explicitly illustrated the fact that biobased REEP may serve as an attractive candidate for DGEBA and embed with high potential values in electronics and microelectronics industry.

2. Materials and methods

2.1. Materials

Resveratrol (98%), methyl hexahydrophthalic anhydride (MeHHPA, 98%) and tris (dimethylaminomethyl) phenol (DMP-30, 95%) were supplied by Energy Chemical. Epichlorohydrin (ECH), tetramethyl ammonium bromide (97%) (TMAB), sodium hydroxide (NaOH) and methyl ethyl ketone (MEK) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. DGEBA (epoxy equivalent was $200\text{ g}\cdot\text{mol}^{-1}$) was supplied by China Petrochemical Group Baling Petrochemical Co., Ltd.

Table 2
Thermal-mechanical properties of REEP/MeHHPA and DGEBA/MeHHPA.

Sample	T_g (°C)	E' (25°) (MPa)	Maximum value of $\tan \delta$	E' at $T_g + 30$ °C (MPa)	ν_e (mol/m ³)
REEP/MeHHPA	210.8 ± 0.7	2530 ± 43	0.38 ± 0.02	83.3 ± 1.7	6900.6 ± 140.9
DGEBA/MeHHPA	146.5 ± 0.9	2417 ± 39	1.03 ± 0.07	21.8 ± 1.1	2087.4 ± 101.6

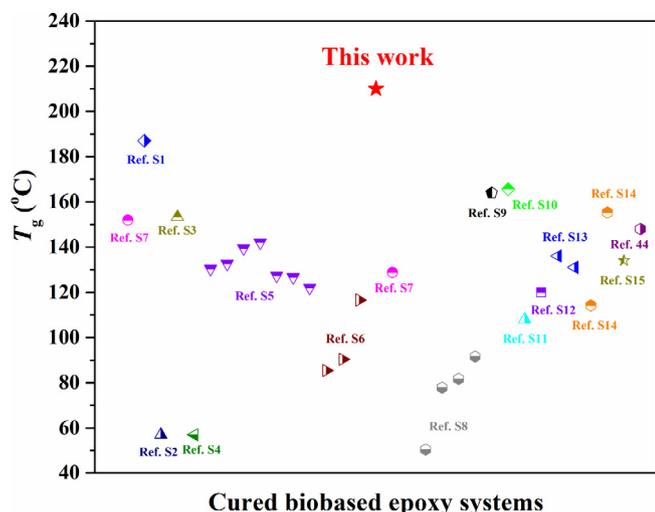


Fig. 4. T_g s of cured biobased epoxy systems.

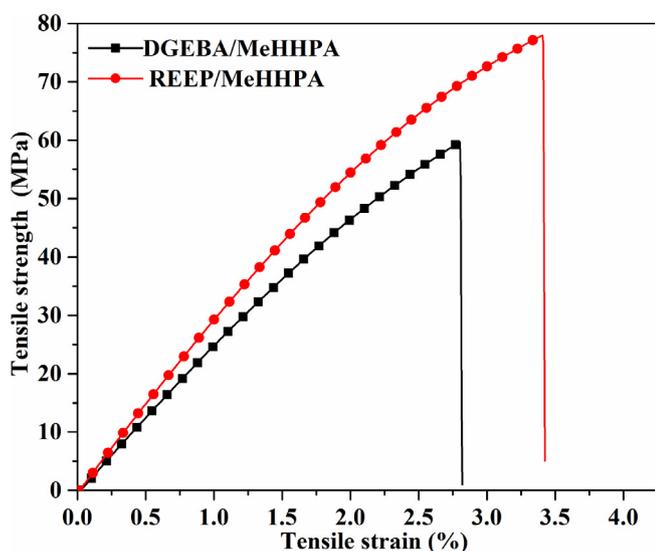


Fig. 5. Mechanical behaviors of REEP/MeHHPA and DGEBA/MeHHPA.

Table 3
Mechanical behaviors of REEP/MeHHPA and DGEBA/MeHHPA at room temperature.

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile strain (%)
REEP/MeHHPA	73.5 ± 3.9	3.0 ± 0.1	3.4 ± 0.3
DGEBA/MeHHPA	59.1 ± 0.7	2.8 ± 0.3	3.3 ± 0.8

2.2. Synthesis of resveratrol-based epoxy resin

The resveratrol (20 g), ECH (97 g) and MEK (hydrotropic agent, 10 g) were mixed by mechanical agitation in a 250 ml round-bottom flask. The mixture solution was heated to 65–70 °C. Then, NaOH and TMAB, the catalyst, were added. After refluxing for 4 h, the mixture was

cooled down to room temperature and washed with deionized water three times. Finally, the epoxy equivalent of resulting epoxy was determined by hydride chloride/acetone method (144 g·mol⁻¹) after getting rid of the solvent with a rotary evaporator. Synthesis route of REEP is displayed in Scheme 2.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, 2H), 7.01 (d, 1H), 6.96–6.83 (m, 3H), 6.68 (d, 2H), 6.42 (d, 1H), 4.24 (dd, 3H), 3.97 (ddd, 3H), 3.36 (dq, 3H), 2.91 (t, 2H), 2.76 (dd, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.83, 158.34, 139.82, 130.34, 128.91, 127.88, 126.55, 114.88, 105.58, 100.92, 68.90, 50.12, 44.74.

2.3. Preparation of the epoxy resin network

Scheme 3 displays that epoxy resin (DGEBA or REEP), curing agent (MeHHPA, the molar ratio of epoxy groups to anhydrides groups was 1:1) and DMP-30 (1% mass content of epoxy resin) were loaded into a glass beaker. The solution was mixed homogeneously and then poured into a copper mould. The sample was cured in temperature per number of hours as follows: 100 °C for 2 h, 150 °C for 2 h and 180 °C for 1 h. The formulations and C, H, and O contents (%) of REEP/MeHHPA and DGEBA/MeHHPA are displayed in Table 1.

2.4. Characterization

2.4.1. FTIR

Fourier Transform Infrared Spectroscopy was supplied by a Bruker Alpha FTIR in a wave-number ranging from 4000 to 400 cm⁻¹ using KBr pellet.

2.4.2. NMR

¹H NMR and ¹³C NMR of REEP were recorded on a Bruker Advance spectrometer (400 M) using CDCl₃ as a solvent.

2.4.3. DSC

The curing process of epoxy resins was evaluated with a TA Instruments Q20. The curing behavior of epoxy resin (6 ± 1 mg) was heated from 50 °C to 250 °C at a heating rate of 10 °C·min⁻¹. Five specimens of each epoxy resin were tested for the DSC results.

2.4.4. DMA

The dynamic mechanical analysis was conducted using a TA Instrument Q800. The sample (25 × 3 × 0.2 mm³) was heated from 0 °C to 250 °C by multi-frequency strain module at the heating rate of 3 °C·min⁻¹. To increase the accuracy of DMA results, five specimens of each cured epoxy resin were tested.

2.4.5. Tensile test

The mechanical properties of REEP/MeHHPA and DGEBA/MeHHPA at room temperature were measured by a SANS UTM5205XHD (10 mm·min⁻¹). The dimensions of dumbbell cured epoxy resin were 80 mm × 4 mm × 2 mm. The mechanical results of each cured epoxy resin were obtained from five specimens.

2.4.6. TGA

The cured epoxy resin was analyzed by a TG 209 F1 Libra®. The sample was heated to 800 °C at a heating rate of 10 °C·min⁻¹ in Ar atmosphere. And five specimens of each cured epoxy resin were tested. Gases produced during the heating process were directly injected into

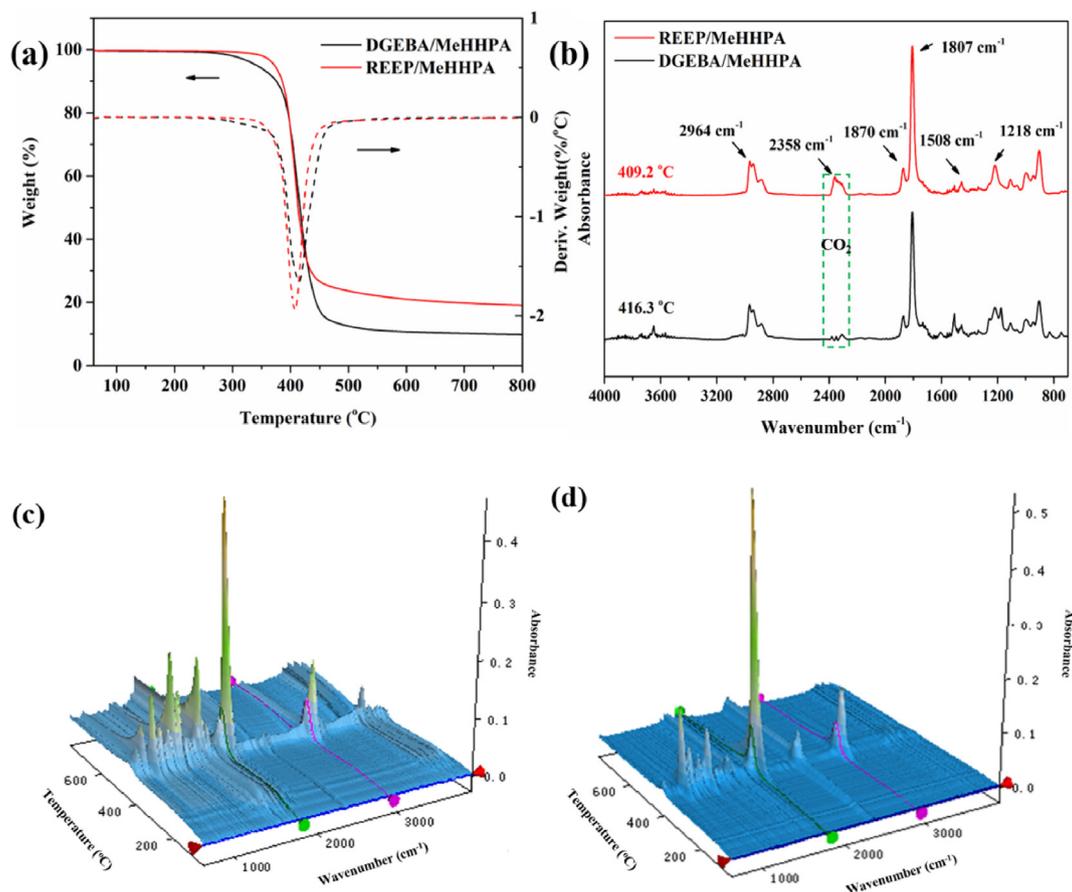


Fig. 6. (a) TGA curves, (b) FTIR curves of T_{max} and 3D FTIR spectra of the gases produced during heating process for (c) DGEBA/MeHHPA and (d) REEP/MeHHPA.

Table 4

Thermal stability of REEP/MeHHPA and DGEBA/MeHHPA.

Sample	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	T_{max} (°C)	Char yield (%)
REEP/MeHHPA	365.6 ± 6.1	380.1 ± 4.7	404.8 ± 3.8	19.0 ± 0.1
DGEBA/MeHHPA	346.9 ± 5.0	376.1 ± 0.6	411.1 ± 4.5	9.5 ± 0.3

the FTIR spectrometer via PERSEUS coupling.

2.4.7. Horizontal burning test

Low flammability of cured epoxy resins was confirmed by the horizontal burning test. Carbon layer was tested by S7800 (Japan) under an accelerating voltage of 10 kV.

2.4.8. Dielectric properties

An Agilent 4294A (40 Hz to 30 MHz) was applied to test the dielectric properties of cured epoxy resins at 25 °C.

3. Results and discussion

3.1. Synthesis and characterization of REEP

Scheme 2 illustrates the synthetic process of REEP. Fig. 1 displays the FTIR spectra of resveratrol and REEP. In Fig. 1a, the absorption peaks at 1510 cm^{-1} and 1450 cm^{-1} are ascribed to the stretching vibration of the benzene ring [45]. The absorption peak at 912 cm^{-1} of the characteristic peak of epoxy groups in REEP was then found [46]. In contrast, the absorption peaks at $3400\text{--}3500\text{ cm}^{-1}$ in correspondence to -OH groups in resveratrol almost disappeared, indicating successful synthesis of REEP. The chemical structures of REEP were further characterized by the ^1H NMR (Fig. 1b) and ^{13}C NMR (Fig. S1). In

Fig. 1b, the characteristic peaks at 7.42, 7.01, 6.96–6.83, 6.68, and 6.42 ppm are attributed to protons on H_5 , H_3 , H_4 , H_2 , and H_1 of the stilbene structure, respectively. Meanwhile, the characteristic peaks at 4.24, 3.97, 3.36, 2.91, and 2.76 ppm correspond to protons on epoxy groups of REEP. Additionally, from the ^{13}C NMR spectra (Fig. S1) of REEP, the characteristic peaks at 68.90, 50.12, and 44.74 ppm were observed, demonstrating the presence of $\text{C}_{15,18,21}$, $\text{C}_{16,19,22}$, and $\text{C}_{17,20,23}$ on epoxy groups in REEP. However, such peaks were not observed in the ^{13}C NMR of resveratrol [47], suggesting that the -OH groups of resveratrol are successfully epoxidated.

3.2. Non-isothermal curing behaviors of epoxy resins systems

The non-isothermal curing behaviors of REEP/MeHHPA and DGEBA/MeHHPA are presented in Fig. 2. It can be found that the overall reaction heat of REEP/MeHHPA ($403.9 \pm 1.4\text{ J}\cdot\text{g}^{-1}$) is significantly higher than that of DGEBA/MeHHPA ($289.3 \pm 9.5\text{ J}\cdot\text{g}^{-1}$), which can be regarded as a higher concentration of epoxy groups in REEP/MeHHPA. Besides, the exothermic peak temperature of REEP/MeHHPA ($154.1 \pm 0.3\text{ }^\circ\text{C}$) and DGEBA/MeHHPA ($156.0 \pm 1.4\text{ }^\circ\text{C}$) present similar values, suggesting similar reaction mechanisms between epoxy groups and acid anhydride groups in REEP/MeHHPA and DGEBA/MeHHPA [48].

3.3. Thermal-mechanical properties of cured epoxy resins

Thermal-mechanical properties of REEP/MeHHPA and DGEBA/MeHHPA are displayed in Fig. 3. And when the temperature is around 25 °C, the E' of REEP/MeHHPA and DGEBA/MeHHPA is $2530 \pm 43\text{ MPa}$ and $2417 \pm 39\text{ MPa}$, respectively, which remains the same without significant difference. Moreover, REEP/MeHHPA

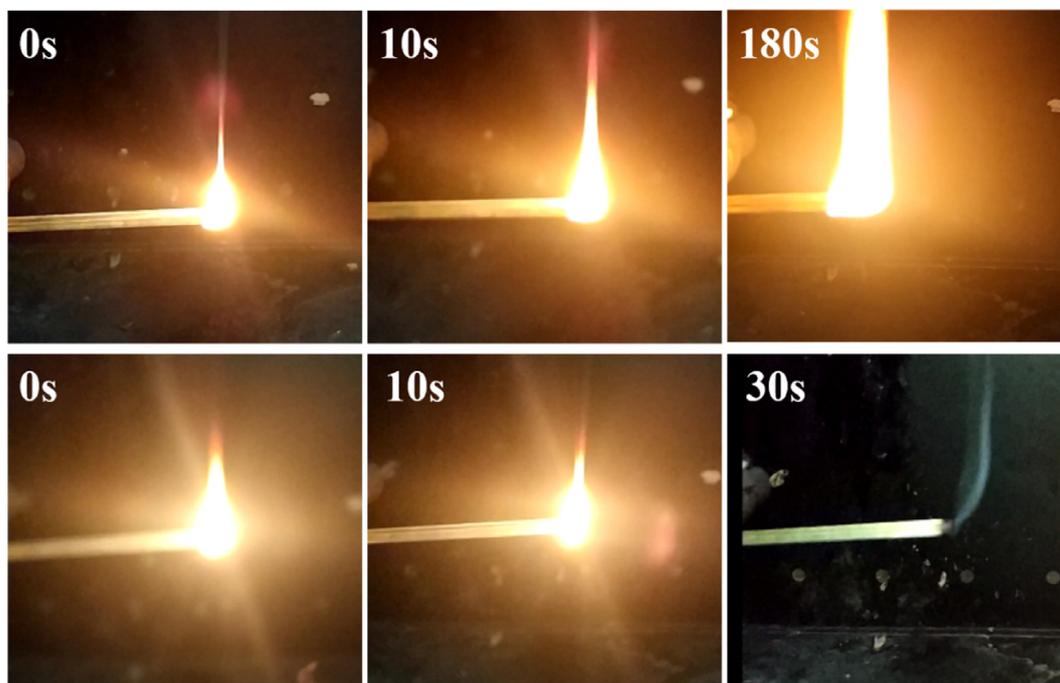


Fig. 7. The horizontal burning test of DGEBA/MeHHPA (top three pictures) and REEP/MeHHPA (bottom three pictures).

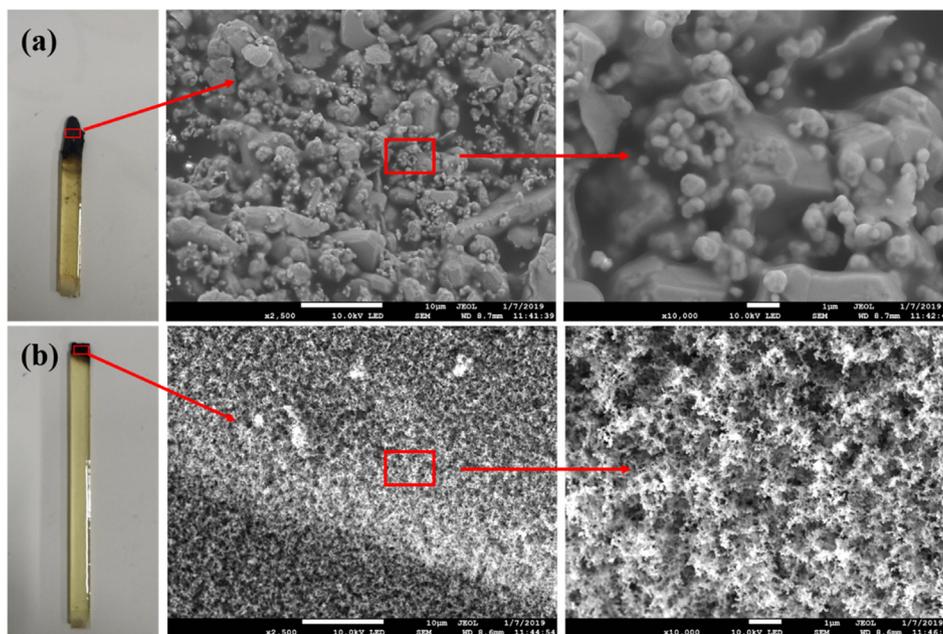


Fig. 8. Digital photographs and SEM images for (a) DGEBA/MeHHPA (top three pictures) and (b) REEP/MeHHPA (bottom three pictures) after horizontal burning test.

possesses a significantly higher T_g (210.8 ± 0.7 °C) than that of DGEBA/MeHHPA (146.5 ± 0.9 °C). Besides, the crosslinking density (ν_e) is measurable by applying a rubber elasticity model [45]. The ν_e can be calculated from the following Eq. (1):

$$E' = 3\nu_e RT \quad (1)$$

where E' , R and T respectively represent the E' at $T = (T_g + 30)$ °C, gas constant and absolute temperature. Calculated ν_e of the cured epoxy networks are listed in Table 2. The ν_e of REEP/MeHHPA is approximately 3.3 times higher than that of DGEBA/MeHHPA.

Due to more reaction groups and higher stiffness segments of aromatic amine curing agents, the T_g s of cured biobased epoxy/aromatic

amine systems (in the range of 110–207 °C) [32,44,49] are usually higher than those of biobased epoxy/anhydride systems (50–187 °C, shown in Table S1 and Fig. 4). However, the T_g of REEP/MeHHPA here is superior to the highest T_g of biobased epoxy/aromatic amine systems, demonstrating ground-breaking discovery in the field of biobased epoxy/anhydride systems.

The typical mechanical properties of REEP/MeHHPA and DGEBA/MeHHPA are presented in Fig. 5 and Table 3. From Fig. 5, the tensile strength of REEP/MeHHPA and DGEBA/MeHHPA are 73.5 ± 3.9 MPa and 59.1 ± 0.7 MPa, respectively. The tensile modulus of REEP/MeHHPA and DGEBA/MeHHPA are 3.0 ± 0.1 GPa and 2.8 ± 0.3 GPa, respectively. And the tensile strain of REEP/MeHHPA and DGEBA/

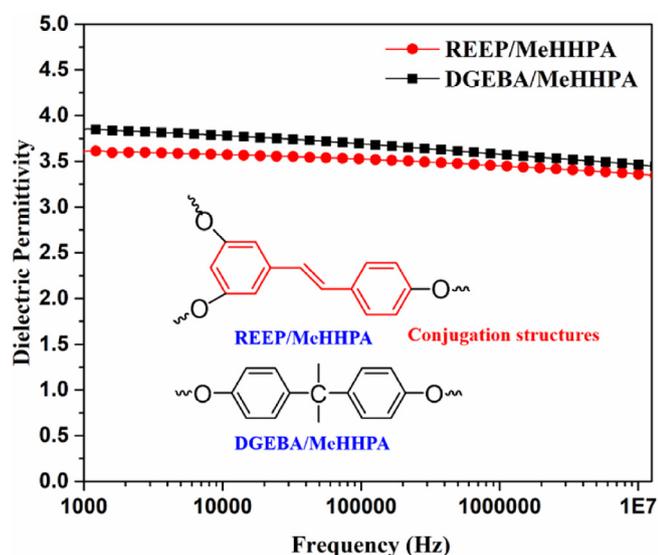


Fig. 9. Broadband dielectric properties of REEP/MeHHPA and DGEBA/MeHHPA.

MeHHPA are $3.4 \pm 0.3\%$ and $3.3 \pm 0.8\%$, respectively. From the results above, we can find that REEP/MeHHPA possesses higher mechanical performance than that of DGEBA/MeHHPA.

3.4. Thermal stability and low flammability of cured epoxy resins

The thermal stability of REEP/MeHHPA and DGEBA/MeHHPA are indicated in Fig. 6 and Table 4. In Fig. 6a, initial degradation temperature ($T_{d5\%}$) of REEP/MeHHPA (365.6 ± 6.1 °C) depicts a higher value than that of DGEBA/MeHHPA (346.9 ± 5.0 °C), demonstrating higher chemical stability of REEP/MeHHPA. From DTG curves, the maximum mass loss temperature (T_{max}) of REEP/MeHHPA and DGEBA/MeHHPA are 404.8 ± 3.8 °C and 411.1 ± 4.5 °C, respectively. The char yield (800 °C) of REEP/MeHHPA is around $19.0 \pm 0.1\%$, much higher than that of DGEBA/MeHHPA ($9.5 \pm 0.3\%$), caused by the higher crosslinking networks and more rigid chemical structures of REEP/MeHHPA [50].

In previous investigations, high char yield of cured epoxy resins indicated the reduced flammability. In this research, the horizontal burning test was adopted to investigate the burning behaviors of DGEBA/MeHHPA and REEP/MeHHPA [51]. As shown in Fig. 7, DGEBA/MeHHPA burned for 180 s, showing easy-flammable properties, and with the growth of flames, a large volume of black smoke was produced during the combustion. In comparison, flames of REEP/MeHHPA gradually turned small and self-extinguished within the 30 s.

Fig. 8 visualized REEP/MeHHPA and DGEBA/MeHHPA after the horizontal burning test through digital photographs and SEM images. After 180 s, the burning flames of DGEBA/MeHHPA were blown out, and its length became short due to the continuous generation of black smoke. The past study suggests that the morphology structures of the carbon residue can reflect the combustion characteristics of cured epoxy resins [52–54]. According to Fig. 8, the dense residual carbon layers were covered on the surface of REEP/MeHHPA, preventing the cured epoxy resins from being exposed to oxygen and heat in horizontal burning test [55]. For DGEBA/MeHHPA, almost no carbon layer structures were covered on the carbon residue. The oxygen and heat can directly reach the epoxy matrix to accelerate the combustion of DGEBA/MeHHPA. Therefore, the dense carbon layer structures have an outstanding effect on blocking oxygen and heat during the combustion process, suggesting low flammability of REEP/MeHHPA.

To further investigate the mechanisms of reduced flammability of the cured epoxy resins, TGA-FTIR measurement was carried out to

determine the content of gases produced during the heating operation. The FTIR curves at T_{max} for DGEBA/MeHHPA and REEP/MeHHPA are shown in Fig. 6b–d. It can be observed that the substances produced are associated with hydrocarbons compounds (2964 cm^{-1} , 2940 cm^{-1} , and 2884 cm^{-1}), benzene compounds (1508 cm^{-1}) and carbonyl compounds (1807 cm^{-1}), while CO_2 (at the vicinity of 2358 cm^{-1} [56]) peaks for REEP/MeHHPA are much stronger than those of DGEBA/MeHHPA, replying to the reduced flammability of REEP/MeHHPA.

3.5. Broadband dielectric spectroscopy and potential application of cured epoxy resins

The broadband dielectric properties of REEP/MeHHPA and DGEBA/MeHHPA are displayed in Fig. 9. The dielectric permittivity of REEP/MeHHPA (about 3.5) is slightly lower than that of DGEBA/MeHHPA, which indicates low current loss and low leakage current of REEP/MeHHPA in the electronics field [57].

It is known that the epoxy/anhydride systems played an indispensable role in electronics and microelectronics industry, due to low initial viscosity, a long storage life, and low dielectric permittivity [58], while relatively low T_g and high flammability have largely constrained further development and advanced application. Therefore, REEP/MeHHPA, the novel biobased epoxy resin with high T_g and mechanical performance as well as attractive dielectric properties and low flammability, stands out among commercial epoxy resins and shows a great potential application in the field of electronics and electronics [59,60].

4. Conclusions

In this research, resveratrol-based epoxy resin (REEP) was synthesized via the one-pot reaction and then cured with MeHHPA. The T_g of REEP/MeHHPA was 210.8 ± 0.7 °C. The tensile strength, tensile modulus and tensile strain of REEP/MeHHPA at room temperature were 73.5 ± 3.9 MPa, 3.0 ± 0.1 GPa and $3.4 \pm 0.3\%$, respectively, much higher than those of DGEBA/MeHHPA. The $T_{d5\%}$ of REEP/MeHHPA (365.6 ± 6.1 °C) was higher than that of DGEBA/MeHHPA (346.9 ± 5.0 °C), and the char yield (800 °C) of REEP/MeHHPA was $19.0 \pm 0.1\%$, much higher than that of DGEBA/MeHHPA ($9.5 \pm 0.3\%$). Additionally, REEP/MeHHPA possessed attractive dielectric properties and low flammability. In summary, REEP is a sustainable biobased epoxy resin which could be used as electronics and electronics materials to replace petroleum-based epoxy resin (DGEBA).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.123124>.

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