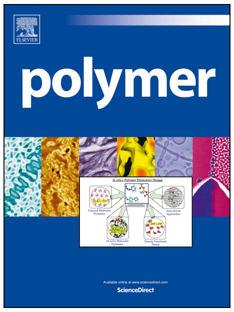

A non-bisphenol-A epoxy resin with high T_g derived from the bio-based protocatechuic Acid:Synthesis and properties

Xingrong Chen, Jiaren Hou, Qun Gu, Qinhong Wang, Junfei Gao, Jing Sun, Qiang Fang

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Dear editor,

We would like to submit our manuscript entitled “A Non-bisphenol-A Epoxy Resin with High Tg Derived from the Bio-based Protocatechuic Acid: Synthesis and Properties” to *Polymer* for publication.

We here give a Credit Author Statement: this manuscript is prepared based on the individual contributions of all authors.

Yours sincerely,

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Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China.

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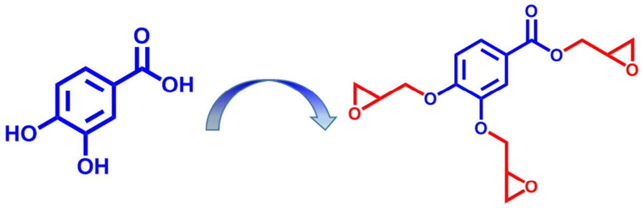

Protocatechuic acid (PA)

PA-EP

A biobased non-bisphenol-A epoxy with high performance

T_g > 250 °C
CTE= 66 ppm/°C
Storage modulus=1.9 GPa

Synopsis：

A new non-bisphenol-A epoxy **(PA-EP**) based on a bio-based protocatechuic acid was reported, which was cured to give a cross-linked network, exhibiting T_g of more than 250 °C and CTE of 66 ppm /°C, which are much outstanding than those of a commercial bisphenol-A epoxy resin (**DGEBA**).

A Non-bisphenol-A Epoxy Resin with High T_g Derived from the Bio-based Protocatechuic Acid：Synthesis and Properties

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Abstract

A new bio-based non-bisphenol-A epoxy (**PA-EP**) resin was synthesized by one-pot reaction between protocatechuic acid (**PA**) and epichlorohydrin. This resin was cured by 4,4'-diaminodiphenyl methane (**DDM**) to give a cross-linked network showing a glass transition temperature (T_g) of more than 250 °C, which was much higher than that of a cured commercial bisphenol-A epoxy resin (**DGEBA**) (189 °C). The cured **PA-EP** resin also displayed the coefficient of thermal expansion (CTE) of 66 ppm /°C, which was lower than 72 ppm /°C of cured **DGEBA** resin. The curing kinetics of **PA-EP/DDM** system was also investigated, indicating that the curing process was a pseudo first order reaction (n = 0.94) and the activation energy was about 54.17 kJ mol^{-1}. Because protocatechuic acid is produced through the bio-transformation of glucose, this contribution may provide a new method for the preparation of non-bisphenol-A high-performance epoxy resins, as well as give a new way for the conversion of the bio-based protocatechuic acid.

Keywords: Protocatechuic acid; Epoxy resins; Thermal stability.

Introduction

Of the high-performance polymers, epoxy resins are one of the most important materials[1] owing to their good adhesion on the substrates, high thermostability, good processability, as well as their low price. Therefore, they have been used in many industrial fields as matrix for the fabrication of the carbon fiber reinforced composites,[1, 2] encapsulation resins for integrated circuit (IC) dies[3, 4] in the microelectronic industry, and the heat-resistant coating and structural adhesives.[5] However, the use of most of epoxy resins is limited due to their production starting from bisphenol-A, a harmful compound to human reproductive system, In order to find the alternative of bisphenol-A, recently much attention has been paid to the development of the non-bisphenol-A epoxy resins.[6-9] Among these new resins, the epoxy resins based on the biomass have become more attractive.[10-15] The reason is that on the one hand the new epoxy resins can replace harmful bisphenol-A and on the other hand they are prepared based on the sustainable biobased feedstock. Over the past few years, many bio-based epoxy resins have been synthesized and characterized, nevertheless, majority of the bio-based epoxy resins exhibit dissatisfactory thermal and mechanical properties than the commercial epoxy resins,[16-18] suggesting that these bio-based epoxy resin can rarely be an alternative to replace bisphenol-A epoxy resins. Thus, it is urgently necessary to develop new bio-based epoxy resins with good performance.

It is noted that protocatechuic acid (3,4-dihydroxybenzoic acid, **PA**) is a bio-based polyphenol compound with a carboxylic group, which exists in many edible plants, such as bran and grain brown rice.[19] In recent years, this compound has been prepared through the fermentation of bio-based glucose. [20]Considering that **PA** has a special chemical structure with multifunctional aryl unit and such a chemical structure is suitable for the preparation of new biobased epoxy resin with high heat-resistance, we have designed and synthesized a **PA**-based epoxy resin by one-pot reaction between **PA** and epichlorohydrin. Pure **PA-EP** was easily obtained as a low melting point (T_m) solid, and easily soluble in common organic solvents, indicating its good processability. After being cured by 4,4'-methylenedianiline (**DDM**) at suitable temperature, the cured **PA-EP** displayed much higher glass transition temperature (T_g) and lower CTE value than a cured commercial epoxy resin (**DGEBA)**. Such results suggest that biobased **PA-EP** is a suitable alternative of the bisphenol-A epoxy resins. Considering that **PA** can be produced in large scale through the fermentation of biobased glucose,[17] this contribution also provides a new way for the conversion of biobased glucose to the high-performance polymers. Here, we report the details.

1. Experimental

1.1 Materials

Protocatechuic acid was provided by Tianjin institute of industrial biotechnology, Chinese Academy of Sciences. Epichlorohydrin, benzyltriethylammonium chloride and 4,4'-methylenedianiline (**DDM**), Sodium hydroxide were purchased from Adamas Company, China. All solvents were utilized as received.

1.2 Instruments

Mass spectrometry (MS) was performed on an Agilent Technologies 5973N. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ecz400 or Agilent 500/54/ASP instrument. FT-IR spectra were detected on a Thermo Scientific Nicolet spectrometer with KBr pellets. DSC was performed using a TA Instrument of DSC Q200 at a heating rate of 10 °C min^{-1} under N_2 flow. Thermo-gravimetric analysis (TGA) was performed on a NETZSCH TG 209 apparatus under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. CTE was measured in N_2 on a NETZSCH DIL 402SE instrument with a heating rate of 3 °C min^{-1}. Dynamic mechanical analysis (DMA) was performed in N_2 on a DMA Q800 V7.5 Build 127 instrument with a heating rate of 3 °C min^{-1}.

1.3 Synthesis of the PA-EP

This monomer was prepared according to a procedure previously reported.[21] The crude **PA-EP** was purified by column chromatography on SiO_2 using a mixture of petroleum and ethyl acetate (1:1, v/v) to give pure product as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6 ppm) δ 7.62 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 4.61 (dd, *J* = 12.4, 2.7 Hz, 1H), 4.49 ~ 4.39 (m, 2H), 4.06 (dd, *J* = 12.4, 6.4 Hz, 1H), 3.92 (dddd, *J* = 21.8, 11.4, 6.6, 1.8 Hz, 2H), 3.38 (dddd, *J* = 8.1, 5.7, 4.2, 2.0 Hz, 2H), 2.91 ~ 2.81 (m, 3H), 2.74 (ddt, *J* = 7.3, 5.0, 2.7 Hz, 3H), 2.54 – 2.47 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$ ppm) δ 165.71, 152.74, 148.00, 124.53, 122.87, 115.26, 112.91, 70.17, 70.10, 69.78, 69.71, 65.36, 50.02, 49.94, 49.49, 44.66, 44.59. HRMS-ESI (m/z): Calcd for $C_{16}H_{18}O_7$ $[M]^+$ 322.11; Found $[M + NH_4]^+$ 340.1389. Anal. Calcd for $C_{16}H_{18}O_7$: C, 59.62; H, 5.63; Found: C, 59.64; H, 5.60.

1.4 Kinetic experiments

The non-isothermal DSC measurement has been used to investigate the kinetic behaviors of current **PA-EP/DDM** system with heating rate of 5, 10, 15, 20, 25 °C min^{-1}, respectively. According to the Kissinger and Carne methods,[19-20] the apparent activation energy (E_α) and reaction order (n) were calculated by using the kinetic data from DSC curves under different heating rate.

1.5 Preparation of the cured **PA-EP** and **DGEBA** samples

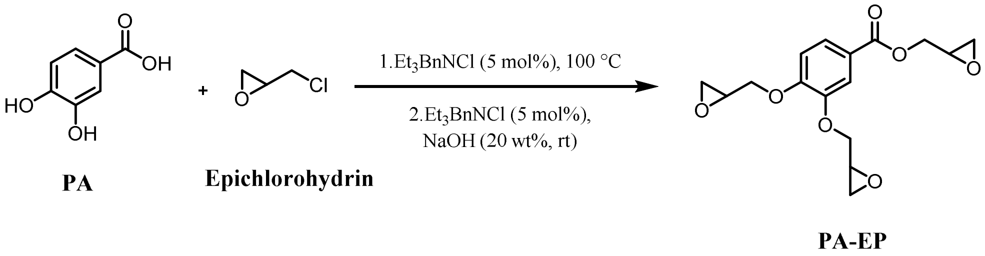
The curing reaction of **PA-EP and DGEBA** was carried out according to the DSC results (see **Fig.** 2). **PA-EP** (2.2 g) and DDM (1.0 g) was mixed in a flask at 60 °C to achieve a homogeneous transparent solution. The obtained hot solution was poured into a rectangle mold made by the alumina foil, and the mold was maintained at 80 °C for 1 h, 100 °C for 1 h, 130 °C for 3 h, and 150 °C for 1 h, respectively. The fully cured sample was thus obtained for DMA and CTE test.

Analogously, the sample of cured **DGEBA** was obtained**.** The mass ratio of **DGEBA** and DDM was 4:1, and the elevating temperature was as bellow: 100 °C for 1 h, 130 °C for 1 h, 160 °C for 3 h, and 190 °C for 1 h.

2. Results and Discussion

2.1 Synthesis and characterization of **PA-EP**

PA-EP was synthesized by one-pot reaction between **PA** and epichlorohydrin in the presence of benzyltriethylammonium chloride (**Scheme 1**). Pure **PA-EP** with a melting point of 63 °C (measured by DSC, see **Fig. S1** of Supporting Information) was obtained by purification of the crude **PA-EP** through column chromatography, and it was easily soluble in common organic solvents.



Scheme 1. Synthesis of **PA-EP**.

The chemical structure of **PA-EP** was confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, HR-MS, and elemental analysis. **Fig. 1** exhibits ^{1}H NMR and ^{13}C NMR spectra of **PA-EP.** For the ^{1}H NMR spectrum, the peaks at 4.5 and 4.0 ppm belong to the protons of the methane ***i***, ***c***, and ***f***, directly connecting with hydroxyl and carboxyl of **PA (**see **Fig. 1a).** The peaks between 2.5-3.5 belong to the protons of epoxy ethyl groups.[21] For the ^{13}C NMR spectrum, the corresponding peaks of methane (***i***, ***c***, and ***f***) are around 65 and 70 ppm, and the peaks of epoxy ethyl groups (***a***, ***d***, ***g***, and ***b***, ***e***, ***h***) are around 45 and 50 ppm (see **Fig. 1b)**. All data are in accord with the proposed chemical structure, suggesting the confirmation of the structure of **PA-EP**.

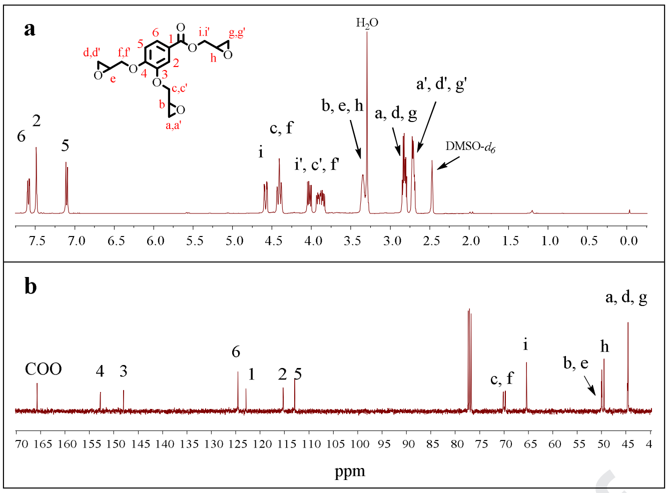
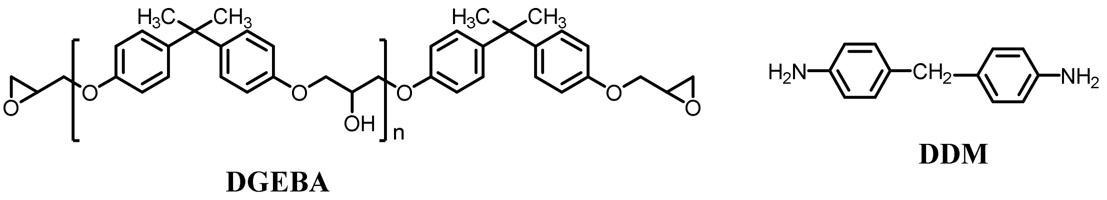


Fig. 1. ^{1}H NMR (a, DMSO-d_6), ^{13}C NMR (b, $CDCl_3$) spectra of **PA-EP**.

2.2 Curing behavior and kinetic evaluation

The curing behavior of **PA-EP** in the presence of stoichiometric **DDM** were investigated by DSC. For comparison, a commercial bisphenol-A based epoxy resin, **DGEBA** (**Scheme 2**), was also cured according to a similar procedure to that of curing **PA-EP. Fig. 2** depicts the curing curves of **PA-EP/DDM** and **DGEBA/DDM** from 40 °C to 250 °C at a heating rate of 10 °C min^{-1}. As can be seen from **Fig.** 2, **PA-EP/DDM** system exhibits a melting peak at 57 °C, and a curing onset temperature of 74 °C. The maximum exothermic peak temperature appears at 132 °C, which is much lower than that of **DGEBA/DDM** (102 °C and 167 °C, respectively). At second scan, both of cured resins do not exhibit obvious exothermic peak, meaning the completion of curing process of two resins. It is noted that cured **DGEBA** resin exhibits an obvious T_g of 164 °C at the second scan, whereas no T_g peak can be observed for cured **PA-EP** resin.



Scheme 2. Chemical structure of a commercial epoxy **(DGEBA)** and a curing agent **(DDM)**.

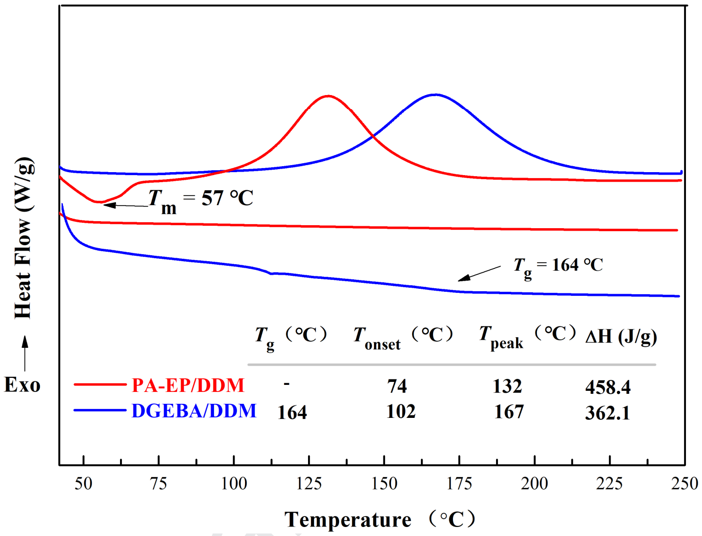


Fig. 2. DSC traces of **PA-EP/DDM** and **DGEBA/DDM** at a heating rate of 10 °C min^{-1} in N_2.

The non-isothermal DSC measurement[22-24] was used to investigate the kinetic behavior of **PA-EP/DDM** system. According to the kinetic data, apparent activation energy (E_α) and reaction order (n) were calculated, respectively. **Fig. 3** depicts the DSC curves of **PA-EP** at different heating rates (β) (5, 10, 15, 20, and 25 °C min^{-1}). As can be seen from **Fig.** 3, as elevating the heating rate, the maximum exothermic peak temperature (T_p) moves to higher temperature. The detailed kinetic data and the calculated results are concluded in **Table 1**. As shown in **Table 1**, T_p raises from 387.52 K to 425.19 K, when β changes from 5°C min^{-1} to 25 °C min^{-1}.

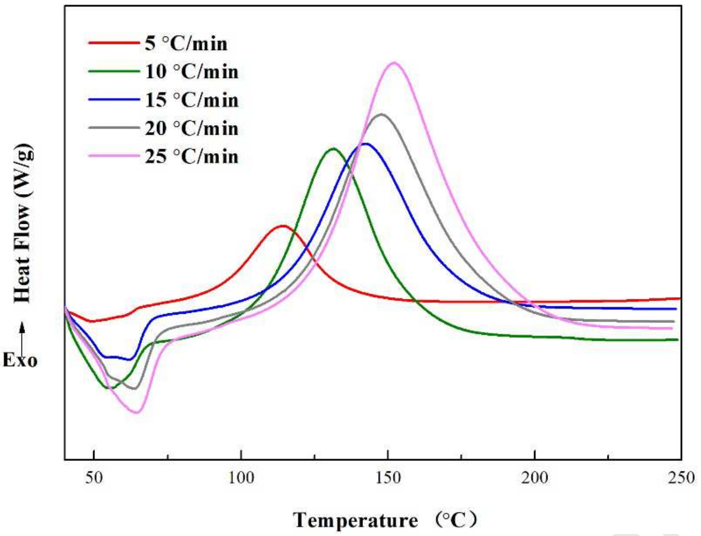


Fig. 3. DSC curves of **PA-EP/DDM** system at different heating rate in N_2.

Table 1. DSC and kinetic data of **PA-EP/DDM** system.

System	β/ (°C/min)	T_p /K	$(1/T_p)\times10^3$ /K^{-1}	$-\ln[(\beta/T_p^2)/$ $((°C\cdot K^2)/min)]$	ln[β/] (°C/min)
PA-EP /DDM	5	387.52	2.58	5.04	1.61
	10	404.63	2.47	4.39	2.30
	15	415.39	2.41	4.01	2.71
	20	420.72	2.38	3.74	3.00
	25	425.19	2.35	3.53	3.22

By using the data listed in Table 1, curing reaction E_α of **PA-EP** can be calculated according to Kissinger equation, as shown in Eq. 1.[19-22]

$$-\ln\left(\frac{\beta}{T_{\mathrm{p}}^2}\right) = \frac{E_{\mathrm{a}}}{RT_{\mathrm{p}}} - \ln\left(\frac{AR}{E_{\mathrm{a}}}\right) \tag{1}$$

Here, R is the gas constant with a value of 8.314 J mol^{-1} K^{-1}, T_p is exothermic peak temperature at a corresponding heating rate (β). **Fig. S2** in supporting information gives the relationship curve between -ln(β/T_p^2) and 1/T_p, as well as a curve of straight ln(β/T_p^2)-1 vs T_p. The curing reaction E_α of **PA-EP/DDM** system is finally calculated as 54.17 kJ/mol according to f **Fig. S2.** In comparison with the E_α of **DGEBA/DDM** that was reported as 58.8 kJ/mol,[23] such a lower E_α of **PA-EP/DDM** system may be attributed to the relatively stronger electron-withdrawing property of ester group in **PA-EP** than that of ether group in **DGEBA**, which could be beneficial for the nucleophilic ring-opening reaction. Furthermore, the curing reaction order of **PA-EP/DDM** is calculated as 0.94 according to Carne equation (Eq 2) based on the relationship between lnβ and 1/T_p, as shown in **Fig. S3** of supporting information. Under the same experimental condition that the DGEBA/DDM system exhibits reaction order of 1.3, which is also near first order reaction. [23]These results indicate that the curing of **PA-EP** resin can carry out under a mild condition, suggesting that this resin is very suitable as the encapsulation resin for the application in microelectronics field, in which the curing of a resin should be avoided at a too high temperature for protecting the devices.

$$\ln\beta = -\left(\frac{\mathrm{Ea}}{\mathrm{nR}} + 2T_p\right)\frac{1}{T_p} \tag{2}$$

2.3 Thermostability

Thermostability of the polymers mainly includes glass transition temperature (T_g), dimensional stability (CTE) and thermal decomposition temperature. In our case, T_g of cured **PA-EP and DGEBA** were detected by DMA, and the results are shown in

Fig. 4. Obviously, cured **DEGBE/DDM** resin exhibits a T_g at 189 °C, similar to those of the previously reported **DEGBE/DDM** resin.[25] For cured **PA-EP/DDM** resin, no obvious T_g peak is observed before 250 °C. These results indicate that the T_g of cured **PA-EP/DDM** resin is higher 60 °C than that of cured **DGEBA/DDM** resin. To the best of our knowledge, this is the highest T_g among the bio-based epoxy resins. It can be also seen from **Fig. 4** that cured **PA-EP/DDM** resin has a higher storage modulus of 1.9 GPa than **DGEBA/DDM** resin (1.6 GPa) at room temperature. The main reason of these results is probably attributed that **PA-EP** has relatively rigid structure in comparison with **DGEBA**.

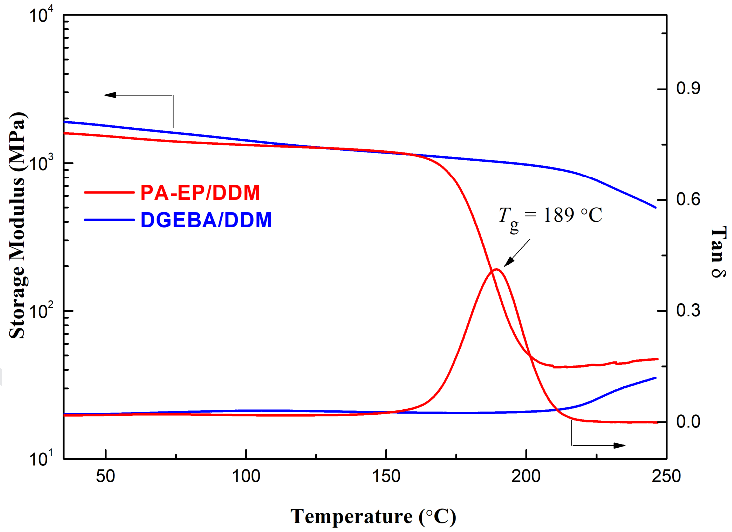


Fig. 4. DMA curves of cured epoxy resins at a heating rate of 3 °C min^{-1}.

Dimensional stability of **PA-EP/DDM** and **DGEBA/DDM** was detected by thermal dilatometer. As shown in **Fig. 5**, cured **PA-EP/DDM** resin exhibits a CTE of 66 ppm /°C before glass transition temperature. Such a CTE is lower than that of 72 ppm /°C of cured **DGEBA/DDM** resin. It can be seen from **Fig. 5** that cured **PA-EP** resin exhibits a T_g of 221 °C, which is also much higher than 176 °C of cured **DGEBA**. These results are identical with the results from DMA data, and both of these indicate that bio-based **PA-EP** has good thermo-mechanical properties, compared to **DGEBA**, a frequently-used commercial bisphenol-A epoxy resin.

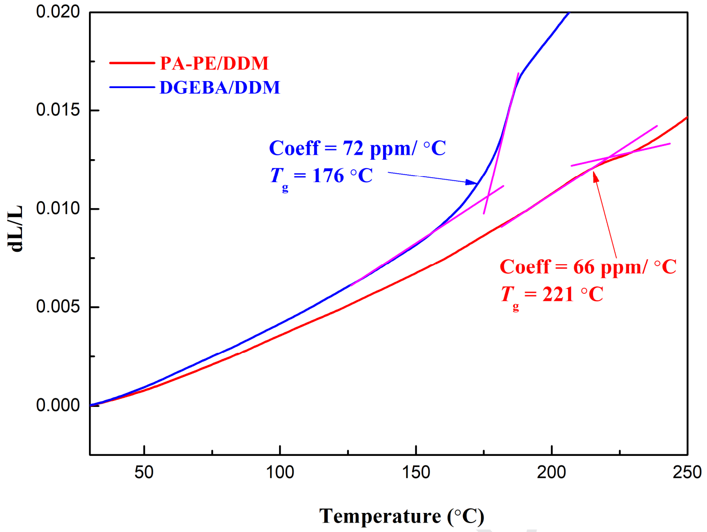


Fig. 5. CTE curves of cured epoxy resins at a heating rate of 3 °C min^{-1}.

Thermal decomposition temperature of cured **PA-EP** and **DGEBA** was investigated by thermo-gravimetric analysis (TGA), and the results are depicted in **Fig. 6**. As shown in **Fig. 6**, cured **DGEBA** resin exhibits a 5 wt% weight loss temperature (T_{5d}) of 364 °C, which is higher than that of cured **PA-EP** resin (321 °C). This result may be due to the existence of an unstable ester group in **PA-EP.** However, cured **PA-EP** displays a residual mass of near 28 % at 1000 °C, which is higher than that of cured **DGEBA** resin (about 16 %). All of the above results indicate that cured **PA-EP** resin display better thermal and thermo-mechanical stability than that of cured **DGEBA** resin.

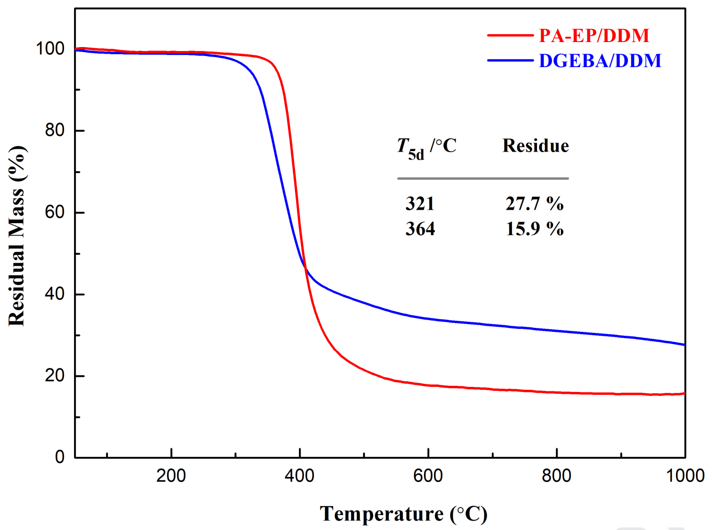


Fig. 6. TGA curves of cured **PA-EP** and **DGEBA** resins with a heating rate of 10 °C min^{-1} in N_2.

3. Conclusions

In summary, we have successfully prepared a new bio-based epoxy resin from protocatechuic acid, and the resin is thermally cured by using a commercial aryl amine (**DDM**) as the curing agent to give a cross-linking network, exhibiting much higher T_g (>250 °C) than a cured commercial bisphenol-A type of epoxy resin (**DGEBA)**. This cured bio-based resin also displays a lower CTE and a higher residual mass at high temperature than cured **DGEBA.** In particular, the **PA-EP/DDM** system exhibits lower curing temperature and lower curing activation energy, which are very desirable for the encapsulation of the microelectronic devices. These results imply that the bio-based epoxy based on protocatechuic acid is a suitable alternative for the commercial bisphenol-A type of epoxy resins. This contribution also expands the application field of protocatechuic acid.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at at http://

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Notes

The authors declare no competing financial interests.

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CRediT authorship contribution statement

Xingrong Chen: Synthesis, Investigation, Data Curation, Writing - original draft.

Jiaren Hou: Writing - review & editing.

Qing Gu: Funding acquisition.

Qinghong Wang: Funding acquisition.

Junfei Gao: Investigation.

Jing Sun: Supervision, Writing - review & editing.

Qiang Fang: Supervision, Conceptualization, Writing - review & editing.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships.

Highlight

A high-performance epoxy resin derived from a bio-based protocatechuic acid;

The cured resin exhibits Tg of more than 250 °C and CTE of 66 ppm /°C;

These properties are better than these of commercial phenolic and epoxy resins.

Dear editor,

We would like to submit our manuscript entitled “A Non-bisphenol-A Epoxy Resin with High Tg Derived from the Bio-based Protocatechuic Acid: Synthesis and Properties” to *Polymer* for publication.

The authors declare no competing financial interest.

Yours sincerely,

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