

Synthesis of Bio-based Epoxy Containing Phosphine Oxide as a Reactive Additive Toward Highly Toughened and Fire-retarded Epoxy Resins

Chunxiang Wei^{a,b,†}, Tianyu Gao^{a,†}, Yu Xu^a, Wenjie Yang^c, Guangjian Dai^a, Ruiting Li^b, SanE Zhu^a, Richard K. K. Yuen^c, Wei Yang^{a*}, and Hongdian Lu^{a*}

^a School of Energy, Materials and Chemical Engineering, Hefei University, Hefei 230601, China

^b Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, U. K.

^c Department of Architecture and Civil Engineering, City University of Hong Kong, Hong Kong 999077, China

Electronic Supplementary Information

Abstract The integration of high mechanical toughness, impact strength as well as excellent flame-retardant properties toward epoxy resins (EPs) have always been a dilemma. The inadequate overall performance of EPs severely restricts their sustainable utilization in engineering aspects over long-term. Herein, a new bio-based agent (diglycidyl ether of magnolol phosphine oxide, referred as DGEMP) derived from magnolol (classified as lignan), extracted from natural plants *Magnolia officinalis*, was successfully synthesized and further employed as a flame-retardant reactive additive to diglycidyl ether of bisphenol A (DGEBA). As demonstration, the composite resin, DGEBA/15DGEMP (15 wt% DGEMP), achieved an Underwriters Laboratories-94 V-0 rating with a high limiting oxygen index (LOI) value (41.5%). In cone calorimeter tests, it showed that heat release and smoke production were effectively inhibited during combustion, wherein the peak heat release rate (PHRR) value of DGEBA/15DGEMP was reduced by 50% compared to neat DGEBA. Additionally, it exhibited a superior tensile strength (82.8 MPa), toughness (5.11 MJ/m³) and impact strength (36.5 kJ/m²), much higher than that of neat DGEBA (49.7 MPa, 2.05 MJ/m³ and 20.9 kJ/m²). Thus, it is highly anticipated that DGEMP imparts significantly improved mechanical and fire-retarded properties to conventional EPs, which holds a great potential to address the pressing challenges in EP thermosets industry.

Keywords Epoxy resin; Magnolol; Phosphine oxide; Toughness; Flame retardant

Citation: Wei, C.; Gao, T.; Xu, Y.; Yang, W.; Dai, G.; Li, R.; Zhu, S.; Yuen, R. K. K.; Yang, W.; Lu, H. Synthesis of bio-based epoxy containing phosphine oxide as a reactive additive toward highly toughened and fire-retarded epoxy resins. *Chinese J. Polym. Sci.* 2023, 41, 1733–1746.

INTRODUCTION

Among the widely applied thermosetting polymers, epoxy resins (EPs), endowed with excellent chemical resistance, electrical insulation and adhesive properties, are extensively utilized in the fields of electronics, coatings, automotive and aerospace.^[1–4] Nowadays, the most commonly used EP monomer is petroleum-based commercial diglycidyl ether of bisphenol A (DGEBA).^[5] Unfortunately, DGEBA-type EPs exhibits brittleness with relatively poor resistance to crack growth and initiation.^[6] Moreover, their impact resistance is also inadequate due to their highly crosslinked density of backbone structure.^[7,8] Herein, their applications are severely restricted to high-performance engineering materials, which demands high

toughness and impact strength to prevent easy fractures and damages during long-term use.

In addition to the intrinsic brittleness, DGEBA-type EPs are inherently highly flammable, which can release large amount of hazardous smokes during combustion, leading to tremendous damage to the ecological environment. As part of the process to reduce the flammability of thermosetting epoxy resins, flame retardants are usually introduced to improve their flame-retardant performance. They can be categorized as reactive or additive flame retardants based on their participation in the curing process.^[9] Usually, additive flame retardants are incorporated into epoxy resin systems by a straightforward physical mixing/blending procedure. It is possible to significantly reduce the flammability of epoxy resins by adding halogen elements, while these systems emit highly toxic gases during combustion, violating the regulations of sustainable and green chemistry.^[10] Other additive flame retardants such as phosphorus,^[11] boron,^[12] layered double hydroxides,^[13] etc., are more environmentally friendly and show satisfactory flame retardant effects, but exhibit poor affinity

* Corresponding authors, E-mail: yangwei@hfu.edu.cn (W.Y.)
E-mail: luhdo@hfu.edu.cn (H.L.)

[†] These authors contributed equally to this work.

Received October 10, 2022; Accepted December 19, 2022; Published online February 21, 2023

with polymer matrix, deteriorating the mechanical properties of the composite material.^[14] Contrary to this, reactive flame retardants combining chemically with the matrix resins, are compatible, and do not adversely affect the mechanical properties of the substrate.^[15] The investigation of bio-based epoxy monomer as a reactive flame retardant is one of the key research directions at present to reduce petroleum resource consumption. However, due to lack of cost-competitive prices as petrochemical one, the full bio-based EP with excellent flame retardancy still cannot replace conventional EPs completely.

To address these challenges, a new agent that simultaneously possesses toughening and flame-retardant effects for EPs is proposed. In this work, we envisage to take full advantages of reactive- and additive-type flame retardants, designing and synthesizing a biomass-derived agent which simultaneously improves the flame retardancy and toughness of DGEBA-based thermosets. Among the various bio-based materials, magnolol is a lignan that can be extracted from natural plants *Magnolia officinalis*.^[16] Its unique structure contains symmetrical phenolic hydroxyl groups and two reactive allyl groups, enabling its modification and utilization in a wide range of bio-based polymers and additives.^[17] Previous studies have demonstrated that magnolol-based epoxy monomers exhibited enhanced flame retardant properties than DGEBA-based ones, on account of the introduction of biphenyl structure in magnolol.^[18,19] Additionally, it is well known that phosphine oxide-based flame retardants containing low oxidation state phosphorus possess high fire-retarded efficiency. These flame retardants can rapidly generate and release PO· free radicals and PH₃ during pyrolysis, which can capture free radicals more effectively and further catalyze the polymer matrix into chars.^[20,21] Herein, there is a promising prospect to prepare an efficient flame retardant based on lowly oxidized phosphorus and magnolol.

To this end, a magnolol-based epoxy monomer (diglycidyl ether of magnolol phosphine oxide, referred as DGEMP) was synthesized via two-step method by utilizing magnolol and diphenylphosphinic chloride as reactant (Scheme 1). DGEMP was introduced to DGEBA in proportion as additive, and 4,4'-diaminodiphenylmethane (DDM) was used as the curing agent for the curing reaction to obtain DGEBA/DGEMP thermosetting epoxy resin. The mechanical properties, thermal stability, flame retardant properties and related mechanism of DGEBA/DGEMP were comprehensively studied.

EXPERIMENTAL

Materials

Magnolol (98%) was purchased from YuNing Biotechnology Co., Ltd., China. diphenylphosphonyl chloride (98%), *m*-

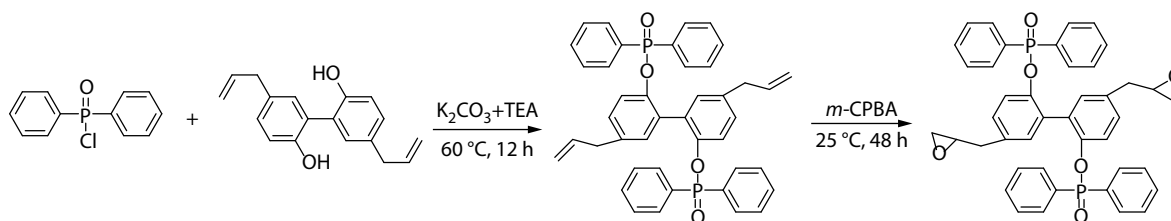
chloroperoxybenzoic acid (*m*-CPBA, ≥85%), tetraethylammonium bromide (99%) and 4,4'-diaminodiphenylmethane (DDM, 97%) were purchased from Aladdin reagent Co., Ltd., (Shanghai, China). Ethyl acetate (≥99.5%), anhydrous magnesium sulfate (≥98%) were provided by Sinopharm Chemical Reagents Co., Ltd., (Shanghai, China). Triethylamine (TEA), anhydrous potassium carbonate, sodium bicarbonate and sodium thiosulfate were supplied by Zhanyun Chemical Co., Ltd., (Shanghai, China). Dichloromethane was purchased from Zhiyuan Chemical Reagent Co., Ltd., (Tianjin, China). Epoxy monomer, DGEBA (epoxy equivalent=210–230 g/mol) was obtained from Nantong Xingchen Synthetic Materials Co., Ltd. All chemicals were used as received without further purification.

Synthesis of Magnolol Phosphine Oxide (MP) and Diglycidyl Ether of Magnolol Phosphine Oxide (DGEMP)

Magnolol (10.7 g, 40.4 mmol), TEA (5 mL), potassium carbonate (6.3 g, 44.4 mmol) and tetrahydrofuran (100 mL) were added to a 500 mL flask equipped with a magnetic stirrer and reflux condenser. Diphenylphosphinic chloride (20.8 g, 84.1 mmol) was added dropwise with a dropping funnel for 30 min, then heated to 60 °C and kept for 12 h under nitrogen. The organic phase was extracted with dichloromethane and deionized water and dried for 12 h with anhydrous magnesium sulfate. The solvent dichloromethane was removed by distillation under reduced pressure to obtain the oily product MP, which was dried under vacuum at 80 °C for 24 h (yield 79.0%). In a 1000 mL three-neck flask equipped with a magnetic stirrer, MP (20.4 g, 30.6 mmol) and 100 mL of dichloromethane were added. Then, *m*-CPBA (18.7 g, 92.1 mmol) dissolved in 500 mL of dichloromethane was added to the three-neck flask in batches and the reaction was stirred at 25 °C for 48 h. After the reaction, the mixture was filtered to remove *m*-CPBA, then washed with 10% sodium thiosulfate solution, saturated sodium bicarbonate solution and finally deionized water to neutralize it. This was followed by the drying of the organic phase with anhydrous magnesium sulfate for 12 h, filtration and distillation under reduced pressure of the solvent to obtain the oily product DGEMP, which was then dried under vacuum at 60 °C for 24 hours (yield 90.1%).

Measurement of Epoxy Equivalent Weight (EEW)

The EEW of DGEMP was determined using the direct titration method of quaternary ammonium bromide. DGEMP (0.5–1.0 g) dissolved in 20–30 mL of chloroform was filled with a 150 mL flask, followed by addition of 10 mL of tetraethylammonium bromide reagent and three drops of crystal violet indicator, and finally titrated to reach green using 0.1 mol/L perchloric acid-glacial acetic acid standard solution. EEW can be calculated as following formula:



Scheme 1 Synthesis route to DGEMP.

$$EEW = \frac{1000W}{N(V - V_0)} \quad (1)$$

where W is the mass of epoxy resin, N is the concentration of perchloric acid/glacial acetic acid standard solution (mol/L), V is the volume of perchloric acid/glacial acetic acid standard solution used (mL), and V_0 is the volume of perchloric acid/glacial acetic acid standard solution used for the blank titration. The EEW of DGEMP determined by direct titration with quaternary ammonium bromide was 356 g/mol.

Preparation of DGEBA and DGEBA/DGEMP EPs

DDM was used as a curing agent in this work. The DGEBA/DGEMP mixture and DDM were heated and melted at 80 and 120 °C, respectively. Afterwards, the DGEBA/DGEMP mixture was mixed with DDM to form a homogeneous mixture. This resin was poured into preheated PTFE molds and cured at 70 °C for 2 h, 110 °C for 2 h, 140 °C for 2 h and 180 °C for 2 h, respectively. After curing, the thermosetting EP was cooled to room temperature. The formulation of DGEBA/DGEMP is listed in Table 1.

Table 1 Formulation of DGEBA/DGEMP.

Sample	DGEBA (wt%)	DDM (wt%)	DGEMP (wt%)	P content (wt%)
DGEBA	80.9	19.1	0	0
DGEBA/5DGEMP	76.3	18.7	5	0.44
DGEBA/10DGEMP	71.7	18.3	10	0.89
DGEBA/15DGEMP	67.0	18.0	15	1.33

Characterizations

The chemical structure of epoxy monomers was characterized by ^1H -, ^{31}P - and ^{13}C -NMR spectra recorded on a 400 MHz AVANCE III Bruker NMR spectrometer, using deuterated chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as an internal standard. The chemical structure of epoxy monomers was also measured by using FTIR spectrometer (Nicolet iS 50+, Thermo Fisher Scientific Inc., USA).

The curing behaviors were analyzed *via* differential scanning calorimetry (DSC) of TA Instruments (TA Q2000) in a high-purity nitrogen atmosphere. The mixture (the range of 5–10 mg) was placed in an aluminum crucible and heated from 30 °C to 220 °C at a heating rate of 10 °C/min.

Thermogravimetric analysis (TGA) was carried out on a TA Instruments (TA Q500) under nitrogen/air condition. The samples were heated from 50 °C to 700 °C with a heating rate of 20 °C/min.

Dynamic mechanical analysis (DMA) was performed on TA Instruments Q800 in air. The sample (10 mm × 6 mm × 2 mm) was tested at a heating rate of 3 °C/min and constant frequency of 1 Hz.

The tensile and flexural properties of cured resins were assessed using a Universal Mechanical Testing Machine (TH-8201S, Suzhou Tophung Machine Equipment Co., Ltd., China). The cross-head speed is 2 mm/min for tensile and flexural properties. The unnotched impact properties were measured using an impact testing machine (XJZ-5.5, JiNan TIME SNKO Test Instrument Co., Ltd., China). An average of five individual determinations was obtained for all mechanical performance tests.

Limiting oxygen index (LOI) was determined by an HC-2 Oxygen Index instrument (Jiangning Analytical Instrument

Co., Ltd., China) according to ASTM D2863-2008. The samples size in the test was 100 mm × 6.5 mm × 3 mm.

UL-94 vertical burning tests were performed on a following the procedure described in ANSI/UL 94-2010 *via* a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China). The samples size was 130 mm × 13 mm × 3 mm.

Cone calorimeter (Fire Testing Technology, UK) was employed to evaluate the burning behavior and toxicity hazards of epoxy resins at an incident flux of 50 kW/m². Prior to tests, all the samples with the dimensions of 100 mm × 100 mm × 3 mm were wrapped with aluminum foil.

The morphology of char residues after LOI tests was observed using Hitachi SU8010 SEM (Japan) under high vacuum with a voltage of 10 kV. Prior to SEM observations, a conductive gold layer was coated on the char residues.

Laser Raman spectroscopy was carried out by Laser Confocal Micro Raman Spectrometer of Thermo Fisher (DXR, USA) in the wavenumber range of 500–2000 cm^{−1}.

TGA-FTIR spectra were recorded on a TA Instruments (TA Q50) under nitrogen with a Thermo Fisher FTIR. The temperature of transferring line between TGA and FTIR was determined to be 200 °C. 5–10 mg of specimen was heated from 50 °C to 700 °C under a nitrogen atmosphere at the heating rate of 20 °C/min. FTIR spectra were collected every 40 s during the whole testing process.

RESULTS AND DISCUSSION

Characterizations of MP and DGEMP

The chemical structure of Magnolol-based epoxy resin DGEMP was verified by ^1H -NMR, ^{31}P -NMR and FTIR, respectively. Fig. 1 illustrates the ^1H -NMR and ^{31}P -NMR for the chemicals. Protons from the benzene ring (1–6) are responsible for the chemical shifts between 6.85–7.59 ppm (Figs. 1b and 1c). The chemical shifts at 5.82–5.89, 5.00–5.05 and 3.27–3.29 correspond to protons 8, 9 from the allyl group, and protons 7 in methylene group. Compared with magnolol (Fig. 1a), the disappearance of the hydroxyl group in the ^1H -NMR spectrum of MP suggests that the hydroxyl group of magnolol reacted with diphenylphosphinic chloride completely. The characteristic peaks with chemical shifts between 3.02–3.03 and 2.46–2.75 in ^1H -NMR spectrum (Fig. 1e) confirm the introduction of the epoxy group to DGEMP structure. Chemical shifts and integral areas of the peaks are in agreement with the target structure. From the ^{31}P -NMR (Figs. 1b–1f), phosphorus has been successfully introduced into the MP and DGEMP, supporting their successful synthesis as well.

Furthermore, Fig. 2 summarizes the FTIR spectra of diphenylphosphinic chloride, magnolol, MP and DGEMP. For Magnolol, the broad bands around 3082 cm^{−1} are attributed to the stretching vibration of —OH. The bands at 1638 and 996 cm^{−1} are originated from of stretching vibration of —C=CH₂ and out of plane bending vibration of olefin.^[18,22] Compared with magnolol, the characteristic band of —OH disappeared completely in the infrared spectrum of MP, indicating that the —OH groups were completely reacted with diphenylphosphinic chloride. The infrared characteristic absorption band at 1128, 1204 and 1438 cm^{−1} corresponding to P—O—C_{AR}, P=O and P—C_{AR}, respectively, which clearly proved that the magnolol-based MP containing phosphorus was successfully prepared.^[23–25] In the infrared spectrum of DGEMP, the bands

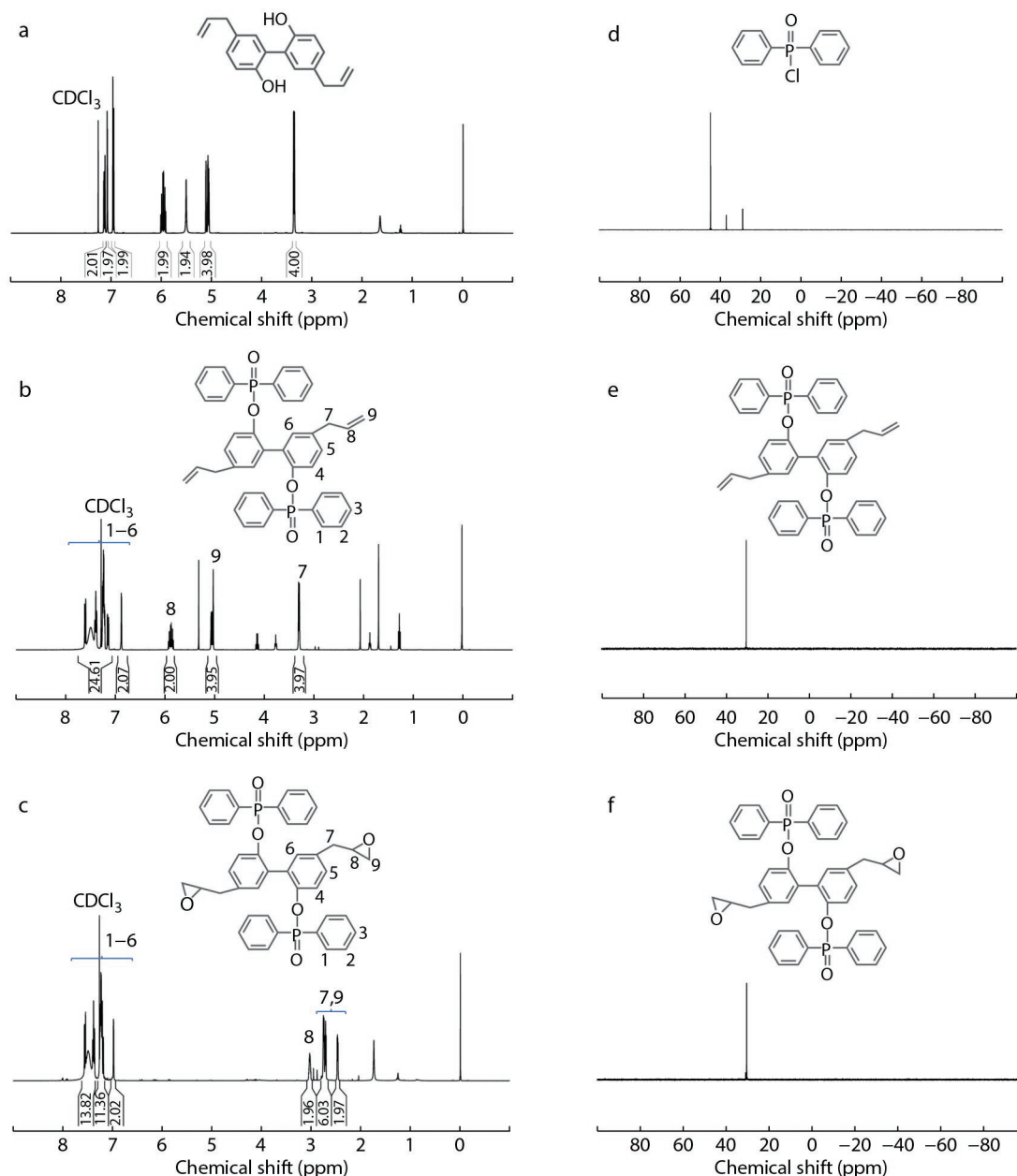


Fig. 1 ^1H -NMR spectra (CDCl_3) of (a) magnolol, (b) MP and (c) DGEMP; ^{31}P -NMR spectra (CDCl_3) of (d) diphenylphosphoryl chloride, (e) MP and (f) DGEMP.

of —C=CH_2 (1638 cm^{-1}) disappears, while the characteristic absorption bands of epoxy group appear at 915 cm^{-1} overlapping with olefin band.^[26] These results confirm that the allyl group in MP was successfully converted into epoxy group through the oxidation of *m*-CPBA, and the new bio-mass-derived epoxy monomer DEGMP was successfully prepared.

Curing Behaviors of DGEBA and DGEBA/DGEMP

In this study, differential scanning calorimetry (DSC) was used to investigate the curing behaviors of different curing systems (DGEBA, DGEBA/15DGEMP) at different heating rates. Ring-opening reaction occurs between epoxy resin and amino groups, resulting in an exothermic peak on DSC heating curves, where lower peak temperatures indicate a higher curing

reactivity.^[27] As shown in Figs. 3(a) and 3(b), at the same heating rate, the peak exothermic temperature of the DGEBA/15DGEMP curing system was lower than that of DGEBA, suggesting that DGEMP has a higher ring-opening activity than DGEBA. As a result of the introduction of DGEMP, the curing reaction of the mixed epoxy resin system can be accelerated.^[28]

According to the Kissinger and Flynn-wall-Ozawa equations, the activation energies (E_a) of DGEBA and DGEBA/15DGEMP mixtures can be calculated using the following equations (Figs. 3c and 3d):

Kissinger equation:

$$-\ln\left(\frac{q}{T_p^2}\right) = -\ln\left(\frac{AR}{E_a}\right) + \frac{E_a}{RT_p} \quad (2)$$

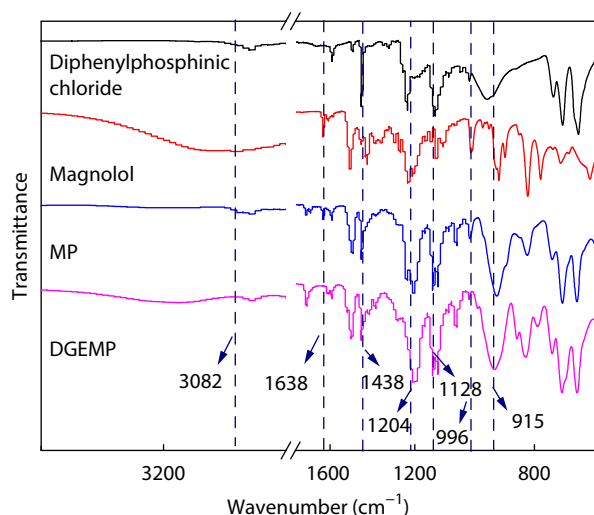


Fig. 2 FTIR spectra of diphenylphosphinic chloride, magnolol, MP and DGEMP.

Ozawa equation:

$$\ln(q) = -1.052 \times \frac{E_a}{RT_p} + \ln\left(\frac{AE_a}{R}\right) - \ln(x) - 5.331 \quad (3)$$

where q is the heating rate, T_p is the peak exothermic temperature, E_a is the activation energy, R is the gas constant, A

is the pre-exponential factor and $g(x)$ is a conversion dependent term. The E_a values can be calculated from the slope of the linear fitting graph recorded in Table 2. As the E_a values of DGEBA and DGEBA/15DGEMP are relatively close, it can be concluded that both DGEBA and DGEMP can be cured effectively under the same curing conditions, which facilitates the formation of a homogeneous and compatible system.^[29]

Thermal Stability of DGEBA and DGEBA/DGEMP

Thermogravimetric analysis (TGA) was performed to study the thermal stability of DGEBA and DGEBA/DGEMP, under both nitrogen and air conditions (Fig. 4, Tables S1 and S2 in the electronic supplementary information, ESI). $T_{d5\%}$ and T_{max} denote the decomposition temperature for thermal weight loss 5% and the temperature at the maximum degradation rate. V_{max} and CY700 corresponding to the maximum mass loss rate, and the carbon formation rate at 700 °C, respectively.

As shown in Figs. 4(a) and 4(b) and Table S1 (in ESI), $T_{d5\%}$ and T_{max} of DGEBA are 402.5 and 424.3 °C under nitrogen atmosphere, respectively. Notably, A higher DGEMP content led to a lower $T_{d5\%}$ and T_{max} for DGEBA/DGEMP. Among the reasons for this are the P—O—C and P—C bonds in DGEBA/DGEMP less stable than the C—C bonds in epoxy resin, and are more likely to degrade at relatively high temperature, generating phosphoric acid and similar species.^[11] By catalyzing the carbonization of epoxy resin, phosphoric acid compounds can reduce the initial degradation temperature of

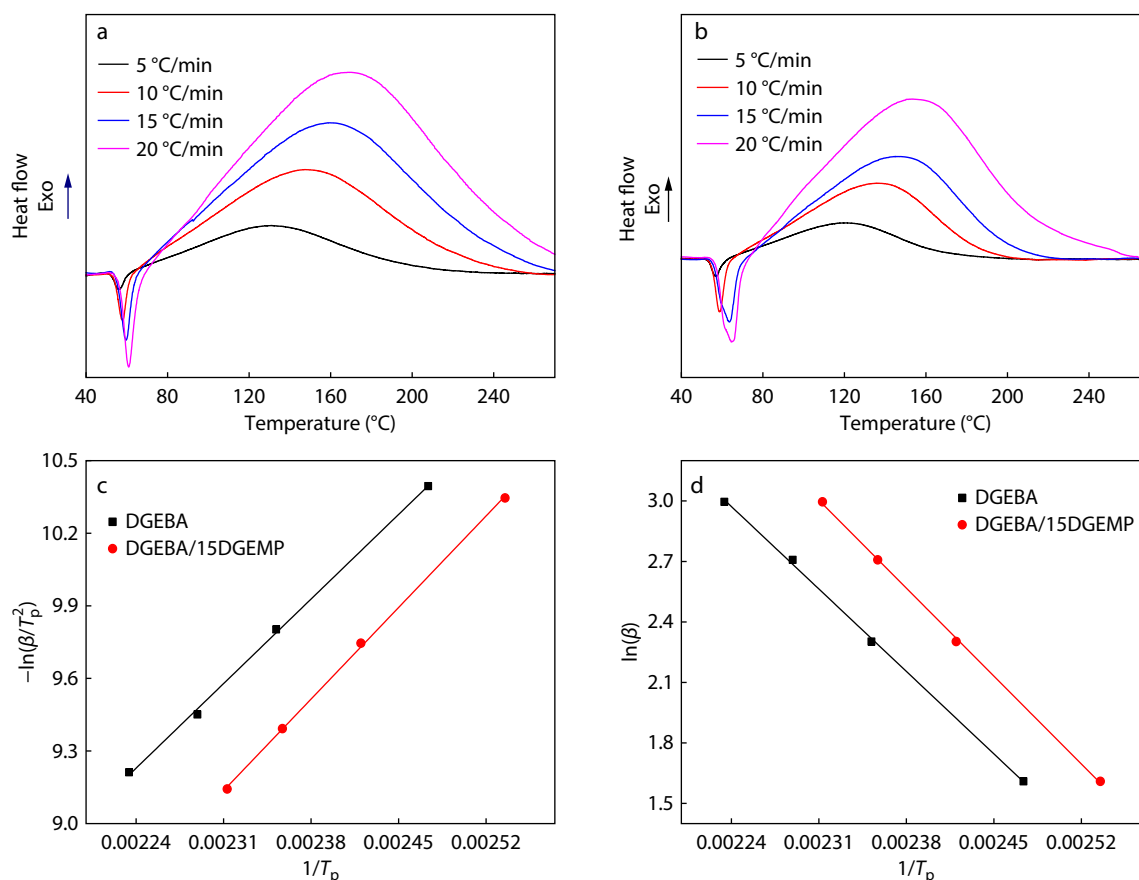


Fig. 3 Curing heat release curves of (a) DGEBA and (b) DGEBA/15DGEMP; (c) Kissinger fitting curves and (d) Ozawa fitting curves of DGEBA and DGEBA/15DGEMP curing systems.

Table 2 Curing kinetics data of DGEBA and DGEBA/15DGEMP.

Samples	Heating rate (°C/min)	T_p (°C)	E_a (kJ/mol)	
			Kissinger	Ozawa
DGEBA	5	131.1	41.5	46.2
	10	152.0		
	15	163.7		
	20	174.4		
DGEBA/15DGEMP	5	121.3	44.9	49.2
	10	140.1		
	15	151.1		
	20	159.2		

DGEBA/DGEMP resins. The carbon residue of DGEBA/DGEMP at 700 °C enhances continuously with increasing DGEMP content. The carbon residue of DGEBA/DGEMP reach 21.6 wt% with 15 wt% of DGEMP, which is much higher than the carbon residue of DGEBA (15.5 wt%). This can be ascribed to the enhanced carbon formation ability of the epoxy resin by the phosphoric acid compounds, which was generated by the cleavage of the phosphorus-containing groups.^[30] Moreover, the introduction of DGEMP causes a sharp decrease in V_{max} from 1.42 %/°C for DGEBA to 0.71 %/°C (DGEBA/15DGEMP). These indicate that DGEMP forms a denser carbon layer during the thermal degradation of the epoxy resin, which provides good thermal insulation to the internal matrix, resulting in a significant reduction in V_{max} .

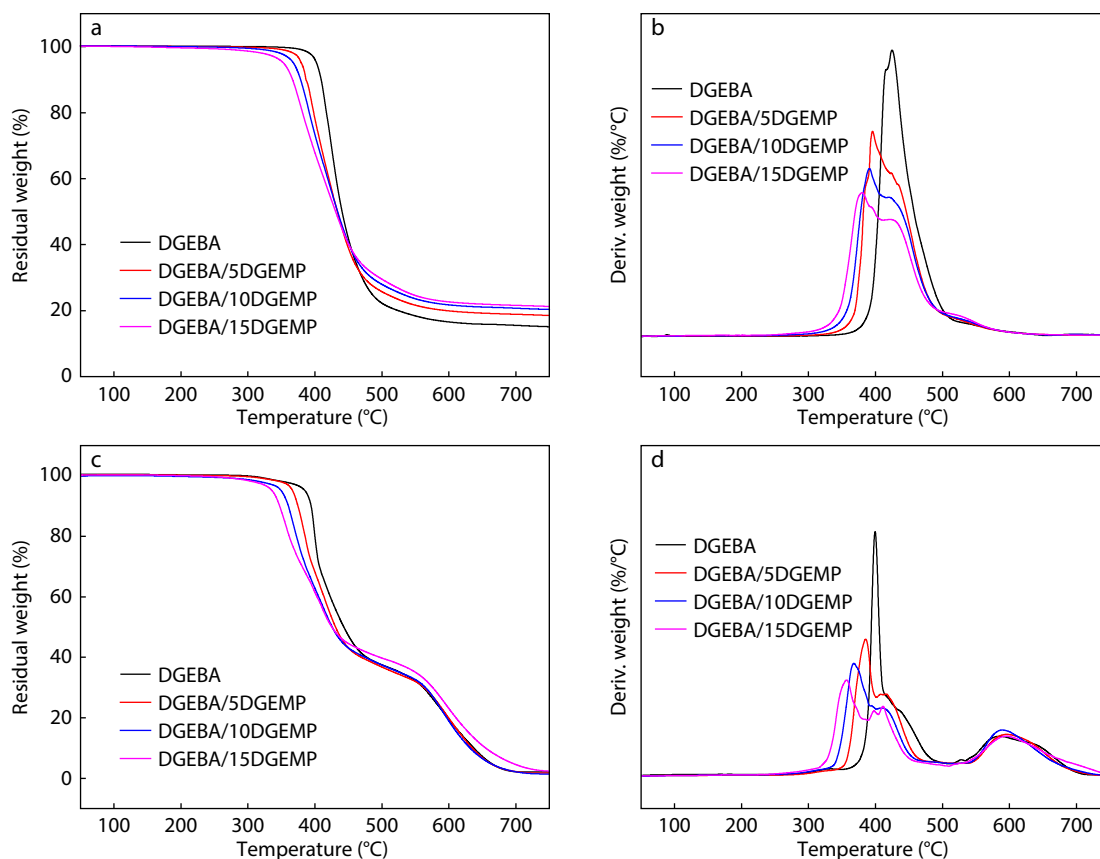
Under air condition (Figs. 4c and 4d and Table S2 in ESI), DGEBA and DGEBA/DGEMP decompose in two stages. The

epoxy resin matrix underwent thermal oxidative degradation at 330–500 °C at first stage. The $T_{d5\%}$ of DGEBA/5DGEMP, DGEBA/10DGEMP and DGEBA/15DGEMP are 366.9, 350.0, 336.4 °C, and the corresponding T_{max} are 385.1, 367.6 and 357.0 °C, which are all lower than those of DGEBA ($T_{d5\%}$ =383.6 °C, T_{max1} =399.4 °C). Furthermore, the V_{max} decreased from 1.84 %/°C for DGEBA to 0.72 %/°C for DGEBA/15DGEMP, which is consistent with the decomposition behavior under nitrogen atmosphere. The second step involves further degradation of residual carbon at 520–700 °C. The temperatures of DGEBA/5DGEMP, DGEBA/10DGEMP and DGEBA/15DGEMP at the maximum degradation rate were 595.5, 589.8 and 595.4 °C, respectively, all of which were higher than that of DGEBA (T_{max2} =585.8 °C). As a result of the inclusion of DGEMP of the mixed epoxy resin, an additional, stable carbon layer is formed during thermal oxidation, thus preventing further decomposition of the resin's internal matrix.

The study conducted above clearly shows that DGEMP can promote the formation of carbon layer during thermal decomposition of epoxy resin, which prevents the diffusion of heat and combustible volatile organic compounds (VOCs) to the interior of the material matrix, thus inhibiting the further decomposition within the epoxy matrix and reducing the combustibility of epoxy resin.

Mechanical Properties

EPs are commonly evaluated based on their mechanical properties. Dynamic mechanical behaviors of cured EP thermosets were investigated via DMA testing. Fig. 5 and Table

**Fig. 4** TGA and DTG curves of DGEBA and DGEBA/DGEMP in (a, b) N_2 and (c, d) air.

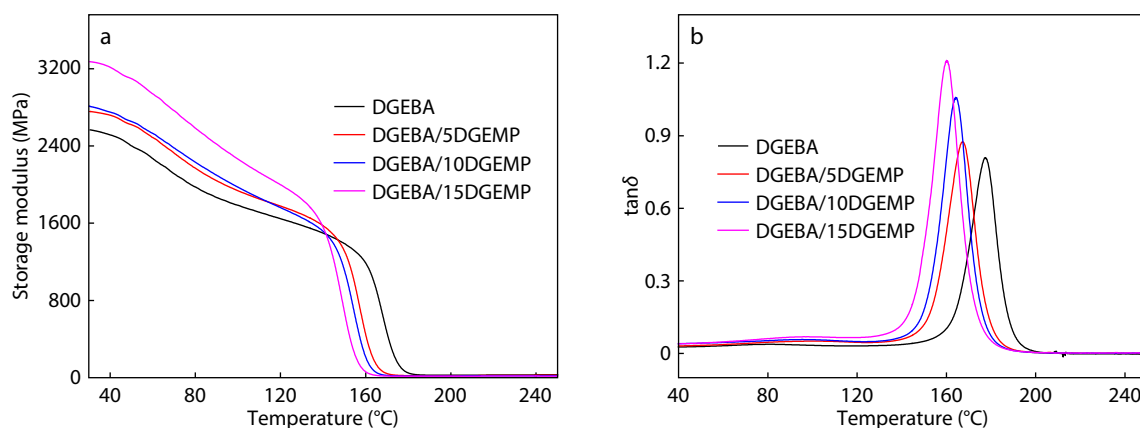


Fig. 5 (a) Storage modulus and (b) $\tan\delta$ determined by DMA for DGEBA and DGEBA/DGEMP.

Table 3 E , T_g and ν_e of DGEBA and DGEBA/DGEMP.

Sample	T_g based on DSC ($^{\circ}\text{C}$)	T_g based on DMA ($^{\circ}\text{C}$)	E (MPa) at 30 $^{\circ}\text{C}$	E (MPa) at $T_g + 30$ $^{\circ}\text{C}$	$\nu_e / 10^3$ (mol/m ^{3})
DGEBA	160.4	177.6	2566	26.0	2.2
DGEBA/5DGEMP	152.5	167.4	2757	21.8	1.9
DGEBA/10DGEMP	137.3	164.0	2810	17.8	1.5
DGEBA/15DGEMP	132.8	160.4	3272	15.3	1.3

3 illustrate the relations of the storage modulus (E') and $\tan\delta$ of DGEBA and DGEBA/DGEMP with temperature. EP is shown to have a higher E' when treated with DGEMP. On account of the high rigidity of DEGMP, the E' of DGEBA/15DGEMP increases to 3272 MPa, which is 28% higher than that of neat DGEBA (Fig. 5a, Table 3). The glass transition temperature (T_g) is an important parameter verifying the mobility of polymer chains, which can be determined by the peak value of $\tan\delta$ (Fig. 5b) and DSC (Fig. S1 in ESI). Generally, the incorporation of rigid groups inhibits the mobility of macromolecular chains, leading to a higher T_g .^[31,32] However, in this work, the T_g values of cured composite DGEBA/DGEMP decrease gradually with the increasing content of DGEMP. To better understand this behavior, the crosslink density (ν_e) of EP was calculated according to rubber elasticity theory^[33] as below:

$$\nu_e = \frac{E'}{3RT} \quad (4)$$

where E' is the energy storage modulus of EP at $T = (T_g + 30)$ $^{\circ}\text{C}$, R is the ideal gas constant, and T denotes the absolute temperature. As illustrated in Table 3, there is a gradual reduction of ν_e for cured DGEBA/DGEMP thermosets as the DGEMP content increases, which reaches to 1.3×10^3 mol/m ^{3} (DGEBA/15DGEMP), indicating that more uncrosslinked segments exist in the EP system. Therefore, the mobility of EP chains may be enhanced leading to the reduction of T_g .^[34,35]

Further investigation of the influence of DGEMP on the mechanical properties (tensile, bending and impact property tests) of DGEBA/DGEMP were performed (Fig. 6 and Table 4). The tensile strength, elongation at break and toughness of DGEBA are 49.7 MPa, 8.2% and 2.05 MJ/m ^{3} , respectively (Figs. 6a–6c). The tensile properties of DGEBA/DGEMP enhanced gradually with the increase of DGEMP content. The tensile strength, elongation at break and toughness of DGEBA/15DGEMP are 82.8 MPa, 12.1% and 5.11 MJ/m ^{3} , which increased 33.1 MPa, 3.9% and 3.06 MJ/m ^{3} , respectively, compared with neat DGEBA. These results confirm that DGEMP as

additive significantly increase the strength and toughness of neat EP. Moreover, DGEBA/DGEMP composite EPs exhibit a steady enhancement in bending modulus, bending strength, and unnotched impact strength (Figs. 6d and 6e) with increased loading of DGEMP as well. Which is in line with the fracture morphology in Fig. S2 (in ESI), DGEBA/DGEMP15 presents apparent wrinkled structures and more short fibres compared with DGEBA, suggesting energy dissipation and improved toughness. Moreover, there are no cavities existing between DGEMP and the skeleton chains, indicating excellent compatibility that may be helpful for the enhancement of mechanical performance. Fig. 6(f) illustrates the comparison of mechanical properties between DGEMP and the other bio-based epoxy resins. The detailed data are summarized in Table S3 (in ESI). It is clearly observed that DGEBA/DGEMP shows more prominent comprehensive mechanical properties than the others, such as DOPO-M,^[36] DPPA-HPM,^[37] DOP-ABZ,^[38] LMA,^[39] CLEP-DOPO-POSS^[40] and EDPDO.^[41] The improved overall mechanical performance (tensile strength, elongation at break, toughness, bending strength, and impact strength properties) of the composite DGEBA/DGEMP resins could be ascribed to two effects: (i) the compatibility and newly formed network between DGEMP and DGEBA during curing process; (ii) the presence of abundant aromatic rings from DGEMP can enhance the rigidity of EP, meanwhile, the intermolecular forces of DGEMP and DGEBA can be strengthened by the π - π interaction between the aromatic rings.^[30]

Flame Retardancy

The flame-retardant properties of DGEBA and DGEBA/DGEMP were investigated and compared using LOI and UL-94 vertical flammability tests, the results are summarized in Table 5. The LOI value of DGEBA/DGEMP gradually increased when DGEMP was increased from 5 wt% to 15 wt%, reaching to 41.5%, much higher than DGEBA (28.5%). DGEBA was extremely flammable during UL-94 test, the specimen ignited rapidly and failed to

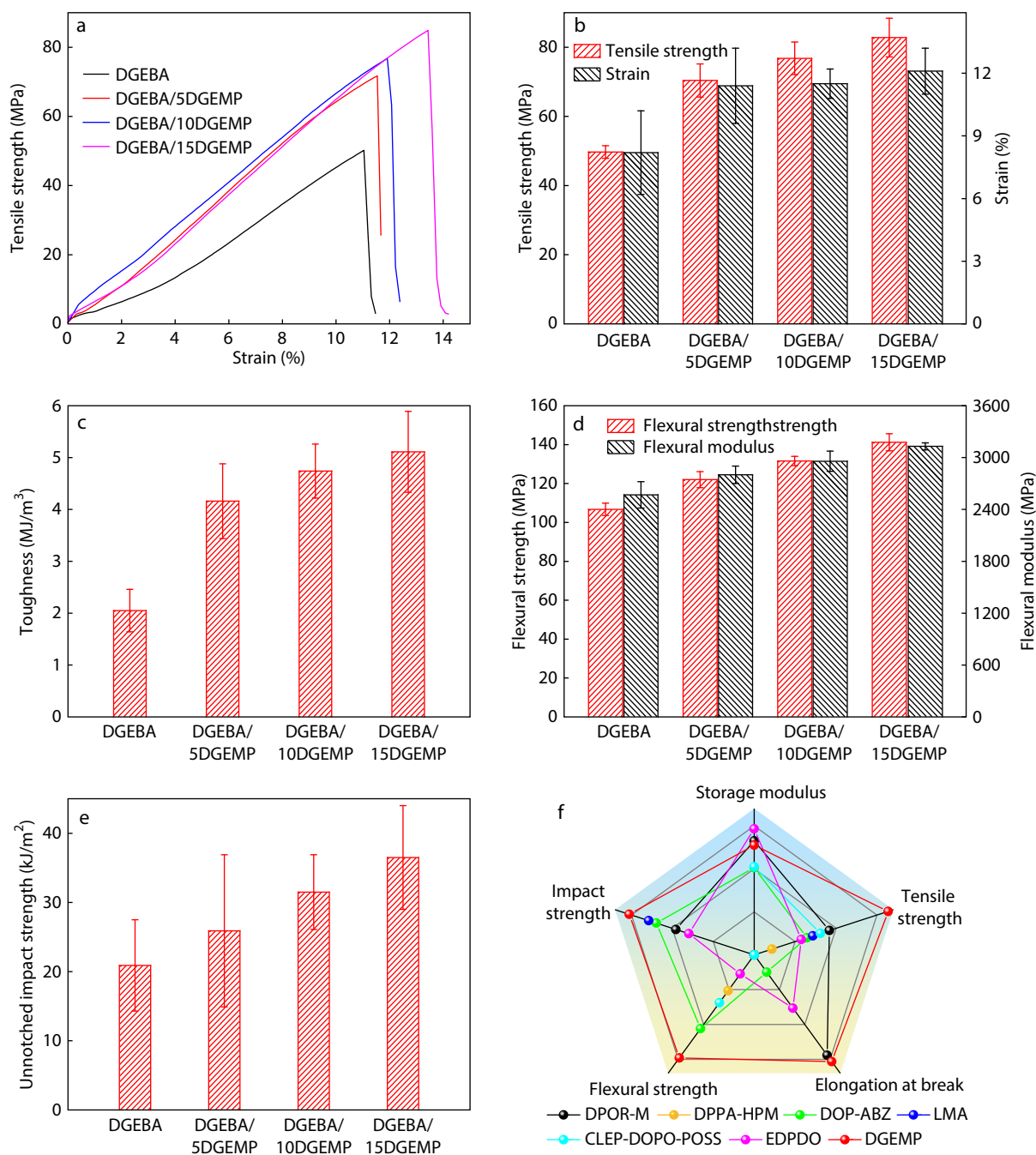


Fig. 6 Mechanical properties of DGEBA and DGEBA/DGEMP: (a) tensile stress–strain curves; (b) tensile strength and strain; (c) toughness; (d) flexural strength and flexural modulus; (e) unnotched impact strength; (f) vector diagram for comparison of mechanical properties between this work and the reported results.

Table 4 Mechanical properties for DGEBA and DGEBA/DGEMP.

Sample	Tensile strength (MPa)	Elongation at break (%)	Toughness (MJ/m ³)	Flexural strength (MPa)	Flexural modulus (MPa)	Unnotched impact strength (kJ/m ²)
DGEBA	49.7±1.8	8.2±2.0	2.05±0.41	106.7±3.2	2569±152	20.9±6.6
DGEBA/5DGEMP	70.4±4.8	11.4±1.8	4.16±0.72	122.0±4.1	2801±101	25.9±11.0
DGEBA/10DGEMP	76.8±4.7	11.5±0.7	4.74±0.52	131.6±2.4	2957±117	31.5±5.4
DGEBA/15DGEMP	82.8±5.6	12.1±1.1	5.11±0.78	141.2±4.4	3130±41	36.5±7.5

self-extinguish until they were completely burned out, along with numerous molten drops. In contrast, DGEBA/DGEMP hybrid EP system passed UL-94 V-1 rating when the DGEMP

content was 5 wt%, no molten droplets were produced during combustion, and the blowout phenomenon was observed during combustion.^[42] DGEBA/DGEMP passed the UL-94 V-0

Table 5 The LOI and UL-94 data of DGEBA and DGEBA/DGEMP.

Sample	LOI (%)	UL-94 (3.0 mm)			
		t_1 (s)	t_2 (s)	Flaming drips	Rating
DGEBA	28.5±0.5	>120	\	Yes	NR
DGEBA/5DGEMP	35.5±0.5	4	14	No	V-1
DGEBA/10DGEMP	37.0±0.5	4	5	No	V-0
DGEBA/15DGEMP	41.5±0.5	4	3	No	V-0

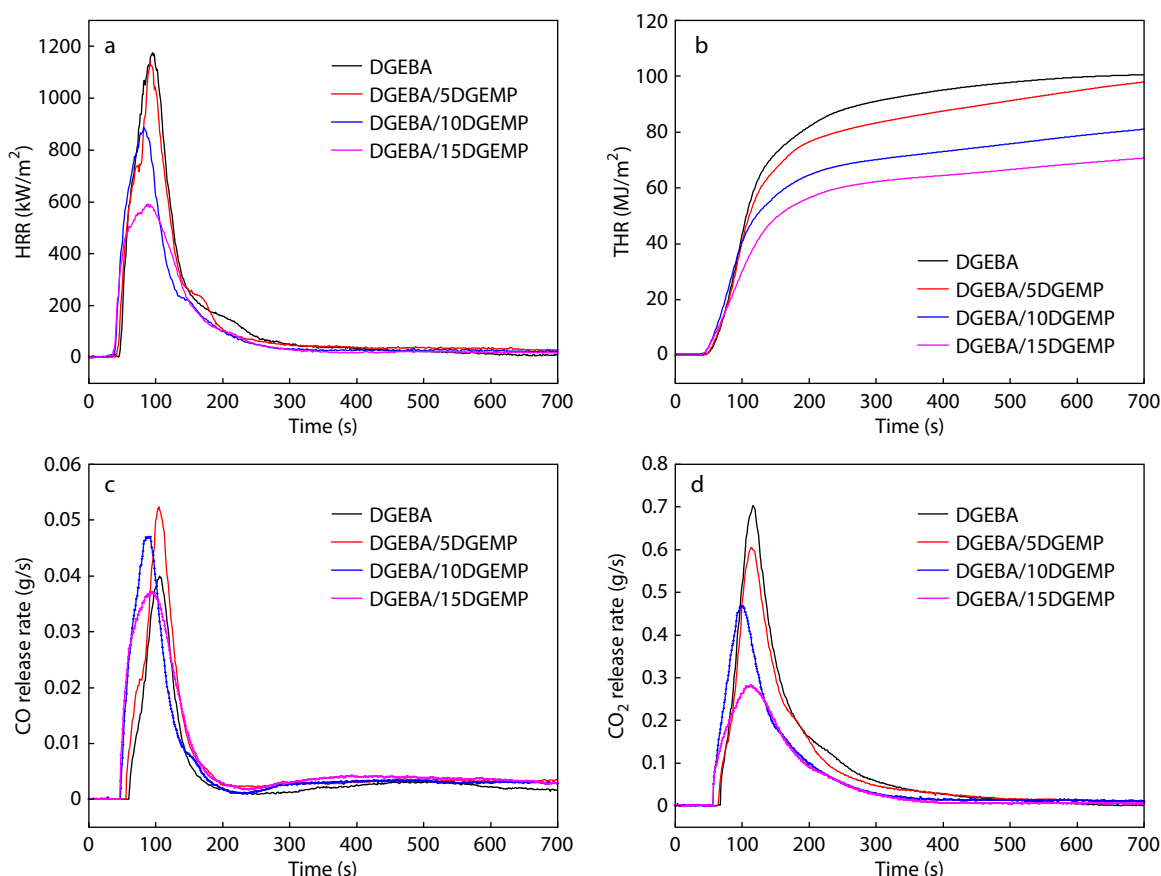
rating, when the DGEMP content reached 10 wt% and 15 wt%. The results of this study suggest that the introduction of DGEMP clearly improves the flame-retardant properties of EP.

Material flammability and fire safety properties were assessed by using cone calorimetry test (CCT), which can simulate real fire conditions. Flammability parameters such as time to ignition (TTI), peak heat release rate (PHRR), time to peak heat release rate (t_{PHRR}), total heat release (THR), effective heat of combustion (EHC), peak CO production (PCOP), peak CO₂ production (PCO₂P), char yield at 600 s (CY₆₀₀) and total

smoke production (TSP) could be extracted from CCT results.

From Fig. 7(a) and Table 6, the TTI of the DGEBA/DGEMP system decreases with the loading of DGEMP, reaching to 34 s when DGEMP content is 15 wt%. This can be explained as phosphorus-containing groups in DGEMP decomposed at high temperatures, phosphoric acid and similar species were released, which can accelerate the dehydration and degradation of EPs to aid the char formation,^[43,44] resulting in a lower TTI. Compared to DGEBA, DGEBA/10DGEMP and DGEBA/15DGEMP have PHRRs of 886 and 591 kW/m², which are 25% and 50% lower than DGEBA, respectively, indicating that DGEMP can significantly reduce the combustion intensity of EP. Moreover, the THR of DGEBA/DGEMP also decreased continuously with the increase content of DGEMP (Fig. 7b).

Fig. S3 (in ESI) shows the mass loss curves of DGEBA and DGEBA/DGEMP. As the content of DGEMP increases, the carbon residues during the combustion of DGEBA/DGEMP also rise. As summarized in Table 6, DGEBA/5DGEMP, DGEBA/

**Fig. 7** Relationships between (a) HRR, (b) THR, (c) CO release rate, (d) CO₂ release rate and time of DGEBA and DGEMP/DGEBA.**Table 6** Data of DGEBA and DGEBA/DGEMP tested by CCT.

Sample	TTI (s)	PHRR (kW/m ²)	t_{PHRR} (s)	THR (MJ/m ²)	EHC (MJ/kg)	PRR (g/s)		CY ₆₀₀ (wt%)	TSP (m ²)
						CO	CO ₂		
DGEBA	43	1175	95	101	34.3	0.040	0.70	3.4	18.9
DGEBA/5DGEMP	39	1143	91	103	35.6	0.052	0.61	6.2	23.5
DGEBA/10DGEMP	35	886	82	85	34.1	0.047	0.47	7.9	21.8
DGEBA/15DGEMP	34	591	88	74	26.0	0.037	0.28	10.7	21.4

10DGEMP, and DGEBA/15DGEMP have higher CY_{600} than DGEBA. This proves that DGEMP inhibits the transfer of heat and combustible volatiles, *via* producing a stable and dense carbon layer during combustion of EP. In addition, EHC, refers to the ratio of exothermic heat to mass loss at a given point during combustion, can accurately reflect the heat released by gas volatile burning.^[45] The EHC of DGEBA/DGEMP decreases with the enhancing DGEMP content, where the EHC of DGEBA/15DGEMP (26.0 MJ/kg) is almost 24.2% lower than that of DGEBA (34.3 MJ/kg). These show that DGEMP exerted gas-phase flame-retardant effect, reducing the flammability of volatiles generated by the burning of EP.

The release of CO_2 and CO is also an important parameter to reflect the degree of material combustion. With regards to the CO release rate, DGEBA/10DGEMP and DGEBA/15DGEMP are higher than that of DGEBA, while the CO release rate of DGEBA/5DGEMP is lower than that of DGEBA (Fig. 7c). From Fig. 7(d), it can be seen that the CO_2 release rate decreases gradually with the increase of DGEMP content, indicating that DGEMP can reduce the burning intensity of epoxy resin. This indicates that when the content of DGEMP is 10 wt% and 15 wt%, it can scavenge $OH\cdot$ radicals in the gas phase and inhibit the conversion of CO to CO_2 , leading to incomplete combustion. This proves that the addition of DGEMP can cause a gaseous phase flame-retardant effect, which is consistent with the results from EHC. In addition, the increase loading of DGEMP did not improve the smoke production of DGEBA (Fig. S4 in ESI). Combining these results above, it can be concluded that DGEMP exhibits a synergic condensed- and gaseous-phase flame inhibition effect.

Flame-retardant Mechanism

The flame-retardant mechanism of DGEBA/DGEMP were analyzed by comparing the digital photographs of DGEBA and DGEBA/15DGEMP after CCT, before and after calcination in air at 500 °C, as well as the morphology (SEM images) of char residues.

Figs. 8(a) and 8(c) demonstrate that DGEBA is almost completely burned out following CCT and only very small amounts of residual char remain. In contrast to DGEBA,

DGEBA/15DGEMP produces more char residue after combustion, exhibiting a relatively continuous and expanded carbon layer structure (Figs. 8b and 8d). Consequently, the release and diffusion of inflammable gas and diffusion are reduced, ensuring that the matrix inside the carbon layer is protected.

The residual carbon images of DGEBA and DGEBA/15DGEMP before and after calcination at 500 °C in air are shown in Fig. 9. As a result of combustion, DGEBA/15DGEMP formed a continuous carbon layer structure after combustion (Fig. 9f). As opposed to DGEBA, whose carbon collapsed and fragmented discontinuously (Fig. 9b). SEM was used to analyze the microstructure of the carbon layer. The carbon layer of DGEBA had many large-sized cracks on the surface (Figs. 9c and 9d), which could not block the diffusion of heat and combustible volatiles that degraded the internal resin matrix, leading to continuous combustion. Meanwhile, the continuous dense and smooth surface of the DGEBA/15DGEMP carbon layer can effectively block the heat transfer and the diffusion of combustible volatiles, effectively preventing the further degradation of the internal matrix (Figs. 9g and 9h).

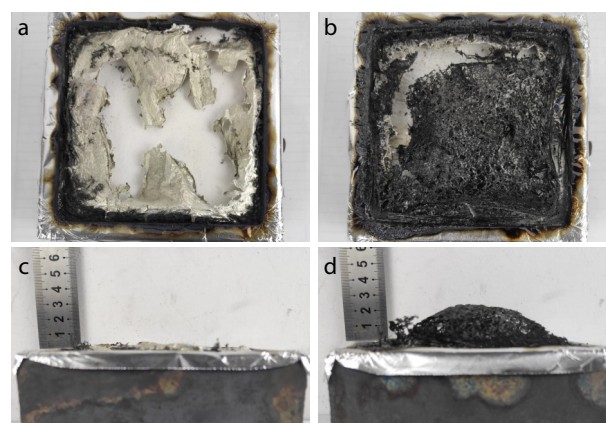


Fig. 8 Digital photos of residues (a, c) DGEBA and (b, d) DGEBA/15DGEMP after CCT.

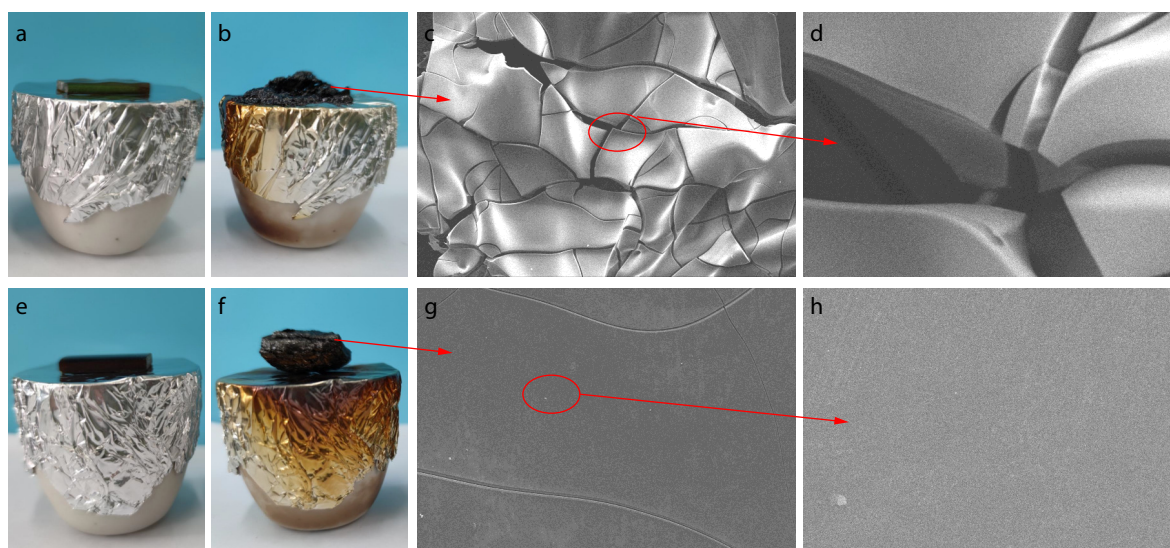


Fig. 9 Digital photos of (a, b) DGEBA and (e, f) DGEBA/15DGEMP before and after calcination at 500 °C in air; SEM images of char residues for (c, d) DGEBA and (g, h) DGEBA/15DGEMP.

Based on the results above, DGEMP is responsible for catalyzing the carbonization of DGEBA. By inducing high-quality stable carbon layers during combustion, DGEMP prevents the transfer of combustible volatiles, heat, and oxygen, thereby improving the flame retardancy of EPs.

The char residue of DGEBA and DGEBA/15DGEMP after calcination in air at 500 °C were also characterized by Raman spectroscopy (Fig. 10). The Raman spectra exhibit two distinct bands around 1343 cm^{-1} (D band) and 1581 cm^{-1} (G band), arising from disordered amorphous carbon and graphitic carbon, respectively. The integral intensity ratio of D and G bands (I_D/I_G) helps to evaluate the degree of graphitization where a lower ratio ensures a high carbon order (low defect).^[46–48] A higher graphitization of residual carbon generally results in improved thermal insulation, thereby inhibiting the heat and mass transfer during combustion and improving the flame-retardant properties of materials.^[49] Com-

pared to DGEBA (2.75), DGEBA/15DGEMP has a lower I_D/I_G value (2.70), which indicates that the residual carbon generated during combustion has a higher degree of graphitization and a more compact carbon layer, in line with SEM analysis results.

TGA-FTIR analysis of gaseous products released during thermal decomposition of DGEBA and DGEBA/15DGEMP were conducted to further explore the flame-retardant mechanism. As illustrated in Fig. S5 (in ESI), DGEBA/15DGEMP generated much less gas products than DGEBA during their degradation process. FTIR spectra of the pyrolysis products at the maximum decomposition rate are exhibited in Fig. 11(a), similar volatiles can be detected from thermal degradation of DGEBA and DGEBA/15DGEMP, including hydrocarbons (2975 cm^{-1}), carbonyl compounds (1730 cm^{-1}), aromatic compounds (1510 cm^{-1}), Ar–O (1258 cm^{-1}) and aliphatic ethers (1175 cm^{-1}). As shown in Figs. 11(b)–11(f), the thermal de-

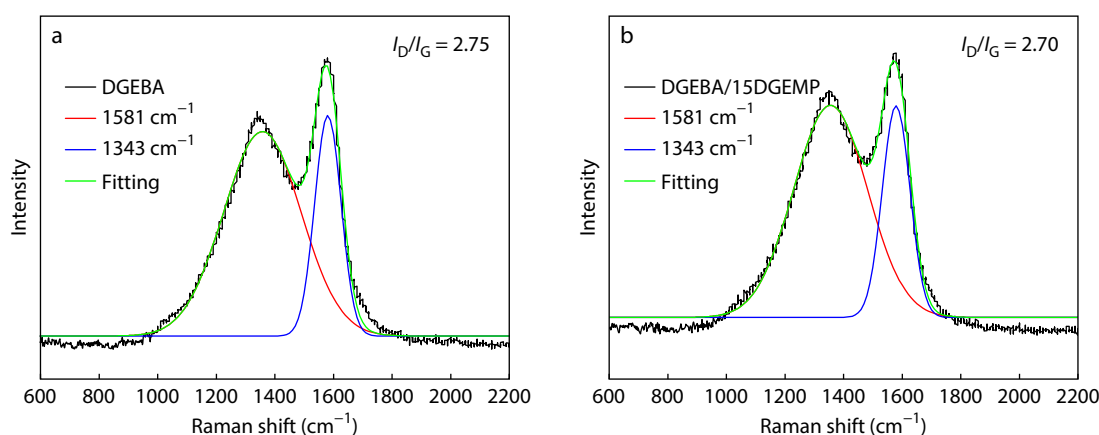


Fig. 10 Raman spectra of char residues for (a) DGEBA and (b) DGEBA/15DGEMP.

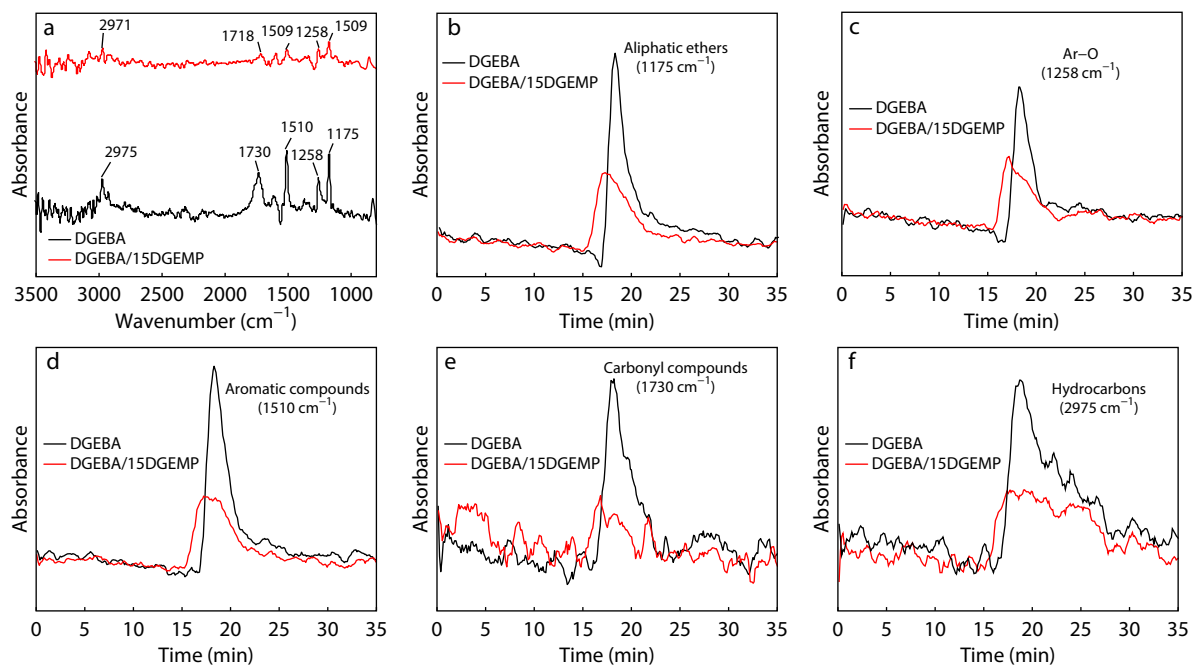
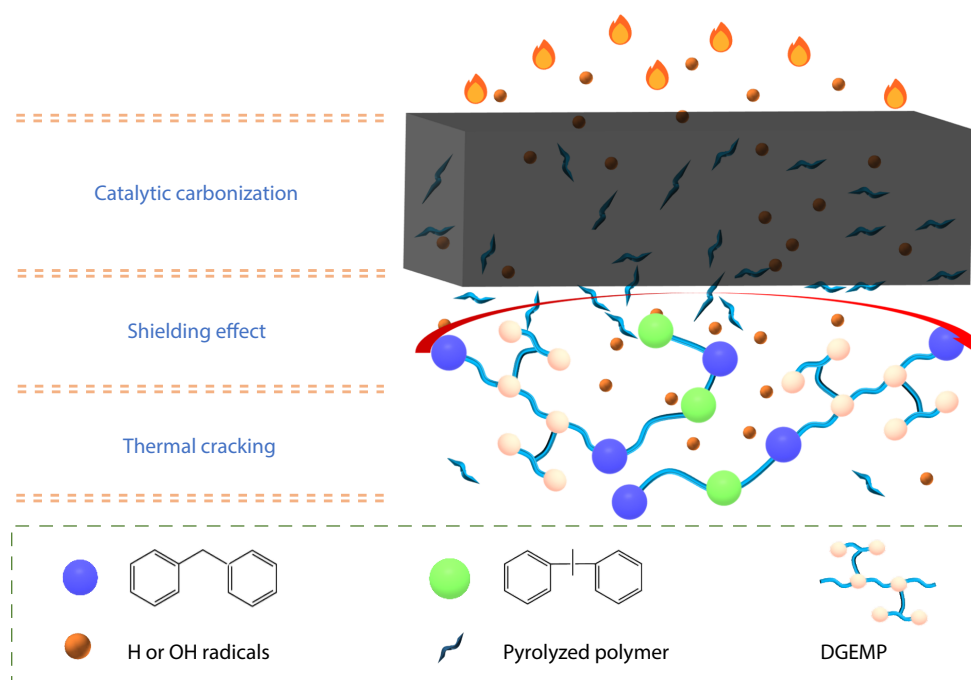


Fig. 11 FTIR spectra of the pyrolysis products of (a) the cured resins DGEBA and DGEBA/15DGEMP at the maximum decomposition rate, (b) aliphatic ethers, (c) Ar–O, (d) aromatic compounds, (e) carbonyl compounds, (f) hydrocarbons.



Scheme 2 Schematic flame retardant mechanism of DGEBA/DGEMP.

composition of DGEBA/15DGEMP releases a much lower content of hydrocarbons, carbonyl compounds, aromatic compounds, Ar—O, and aliphatic ethers than DGEBA. This indicates that most of the gaseous products are immobilized in condensed phase during the thermal decomposition of DGEBA/15DGEMP. The reduction of such flammable VOCs caused by the free radicals annihilation reduces the flammability of the material and prevents further combustion. Among these, there is an abundance of residual aromatic compounds remaining in DGEBA/15DGEMP following its decomposition. It contributes to the formation of a mechanically stable char layer which serves as a shielding barrier to inhibit the release of flammable volatiles and further degradation of the EP matrix (Scheme 2).

CONCLUSIONS

A novel bio-based reactive additive, DGEMP, was synthesized and structurally identified. The combination of rigid biphenyl moiety and epoxide group from magnolol-based epoxy, along with lowly oxidized phosphorus, significantly enhanced toughness and impact strength of composite EP. This is attributed to the newly formed network and intermolecular π - π interaction of DGEMP with DGEBA matrix. In addition to providing EP thermosets with remarkable mechanical performance, the DGEMP also enabled thermosets to achieve significant improved flame retardancy with char promotion and a synergic condensed- and gaseous-phase flame inhibition effect. The composite EPs exhibited outstanding anti-ignition (high LOI value, 41.5%) and self-extinguishing (high UL-94 level, V-0) performance, lower combustion intensity (lower PHRR, 591 kW/m²), and lower heat release (lower THR, 74 MJ/m²). These results demonstrated that bio-based DGEMP agent can be a valuable reactive additive to develop high-performance materials based on conventional EPs, thus paving a new path to

address the most concerned challenges in the EP thermosets industry.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2932-4>.

ACKNOWLEDGMENTS

This work was financially supported by Anhui Provincial Natural Science Foundation for Distinguished Young Scholar (No. 2008085J26), Natural Science Foundation in University of Anhui Province (Nos. KJ2021ZD0119 and 2022AH040251), China Scholarship Council (No. 202008340021), Start-up Fund for Distinguished Scholars in Hefei University (No. 20RC37), Anhui Provincial Natural Science Foundation (No. 2108085QB47) and Research Grants Council of the Hong Kong Special Administrative Region (No. CityU 11208617).

REFERENCES

- Jin, F. L.; Li, X.; Park, S. J. Synthesis and application of epoxy resins: A review. *J. Ind. Eng. Chem.* **2015**, 29, 1–11.
- May, C. *Epoxy resins: chemistry and technology*. Routledge: **2018**.
- Gao, T. Y.; Wang, F. D.; Xu, Y.; Wei, C. X.; Zhu, S. E.; Yang, W.; Lu, H. D. Luteolin-based epoxy resin with exceptional heat resistance, mechanical and flame retardant properties. *Chem. Eng. J.* **2022**,

- 428, 131173.
- 4 Kong, Q.; Zhu, H.; Huang, S.; Wu, T.; Zhu, F.; Zhang, Y.; Wang, Y.; Zhang, J. Influence of multiply modified FeCu-montmorillonite on fire safety and mechanical performances of epoxy resin nanocomposites. *Thermochim. Acta* **2022**, 707, 179112.
- 5 Auvergne, R.; Caillol, S.; David, G.; Boutevin, B.; Pascault, J. P. Biobased thermosetting epoxy: present and future. *Chem. Rev.* **2014**, 114, 1082–1115.
- 6 Mi, X.; Liang, N.; Xu, H.; Wu, J.; Jiang, Y.; Nie, B.; Zhang, D. Toughness and its mechanisms in epoxy resins. *Prog. Mater. Sci.* **2022**, 130, 100977.
- 7 Ye, G.; Huo, S.; Wang, C.; Shi, Q.; Yu, L.; Liu, Z.; Fang, Z.; Wang, H. A novel hyperbranched phosphorus-boron polymer for transparent, flame-retardant, smoke-suppressive, robust yet tough epoxy resins. *Compos. Part B: Eng.* **2021**, 227, 109395.
- 8 Wang, X.; Zhou, S.; Guo, W. W.; Wang, P. L.; Xing, W.; Song, L.; Hu, Y. Renewable cardanol-based phosphate as a flame retardant toughening agent for epoxy resins. *ACS Sustainable Chem. Eng.* **2017**, 5, 3409–3416.
- 9 Huo, S.; Song, P.; Yu, B.; Ran, S.; Chevali, V. S.; Liu, L.; Fang, Z.; Wang, H. Phosphorus-containing flame retardant epoxy thermosets: recent advances and future perspectives. *Prog. Polym. Sci.* **2021**, 114, 101366.
- 10 Mendis, G. P.; Weiss, S. G.; Korey, M.; Boardman, C. R.; Diertenberger, M.; Youngblood, J. P.; Howarter, J. A. Phosphorylated lignin as a halogen-free flame retardant additive for epoxy composites. *Green Mater.* **2016**, 4, 150–159.
- 11 Velencoso, M. M.; Battig, A.; Markwart, J. C.; Scharrel, B.; Wurm, F. R. Molecular firefighting—how modern phosphorus chemistry can help solve the challenge of flame retardancy. *Angew. Chem. Int. Ed.* **2018**, 57, 10450–10467.
- 12 Huo, S.; Zhou, Z.; Jiang, J.; Sai, T.; Ran, S.; Fang, Z.; Song, P.; Wang, H. Flame-retardant, transparent, mechanically-strong and tough epoxy resin enabled by high-efficiency multifunctional boron-based polyphosphonamide. *Chem. Eng. J.* **2022**, 427, 131578.
- 13 Xue, T.; Fan, W.; Zhang, X.; Zhao, X.; Yang, F.; Liu, T. Layered double hydroxide/graphene oxide synergistically enhanced polyimide aerogels for thermal insulation and fire-retardancy. *Compos. Part B: Eng.* **2021**, 219, 108963.
- 14 Chu, F.; Qiu, S.; Zhou, Y.; Zhou, X.; Cai, W.; Zhu, Y.; He, L.; Song, L.; Hu, W. Novel glycerol-based polymerized flame retardants with combined phosphorus structures for preparation of high performance unsaturated polyester resin composites. *Compos. Part B: Eng.* **2022**, 233, 109647.
- 15 Liu, M.; Peng, B.; Su, G.; Fang, M. Reactive flame retardants: are they safer replacements. *Environ. Sci. Technol.* **2021**, 55, 14477–14479.
- 16 Guo, W.; Liang, F.; Chen, S.; Yu, K.; Sun, J.; Pang, Z.; Fei, B. Magnolol-derived thiol-ene photo-polymerized membranes with intrinsic anti-flammability and high transparency. *Compos. Part B: Eng.* **2022**, 242, 110074.
- 17 Teng, N.; Yang, S.; Dai, J.; Wang, S.; Zhao, J.; Zhu, J.; Liu, X. Making benzoxazine greener and stronger: renewable resource, microwave irradiation, green solvent, and excellent thermal properties. *ACS Sustainable Chem. Eng.* **2019**, 7, 8715–8723.
- 18 Qi, Y.; Weng, Z.; Zhang, K.; Wang, J.; Zhang, S.; Liu, C.; Jian, X. Magnolol-based bio-epoxy resin with acceptable glass transition temperature, processability and flame retardancy. *Chem. Eng. J.* **2020**, 387, 124115.
- 19 Cao, Q.; Weng, Z.; Qi, Y.; Li, J.; Liu, W.; Liu, C.; Zhang, S.; Wei, Z.; Chen, Y.; Jian, X. Achieving higher performances without an external curing agent in natural magnolol-based epoxy resin. *Chin. Chem. Lett.* **2022**, 33, 2195–2199.
- 20 Yang, H.; Song, L.; Tai, Q.; Wang, X.; Yu, B.; Yuan, Y.; Hu, Y.; Yuen, R. K. Comparative study on the flame retarded efficiency of melamine phosphate, melamine phosphite and melamine hypophosphite on poly(butylene succinate) composites. *Polym. Degrad. Stabil.* **2014**, 105, 248–256.
- 21 Braun, U.; Balabanovich, A. I.; Scharrel, B.; Knoll, U.; Artner, J.; Ciesielski, M.; Döring, M.; Perez, R.; Sandler, J. K.; Altstädt, V. Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites. *Polymer* **2006**, 47, 8495–8508.
- 22 Luo, Q.; Liu, M.; Xu, Y.; Ionescu, M.; Petrović, Z. S. Thermosetting allyl resins derived from soybean oil. *Macromolecules* **2011**, 44, 7149–7157.
- 23 Jian, R. K.; Ai, Y. F.; Xia, L.; Zhang, Z. P.; Wang, D. Y. Organophosphorus heteroaromatic compound towards mechanically reinforced and low-flammability epoxy resin. *Compos. Part B: Eng.* **2019**, 168, 458–466.
- 24 Ma, C.; Li, J. Synthesis of an organophosphorus flame retardant derived from daidzein and its application in epoxy resin. *Compos. Part B: Eng.* **2019**, 178, 107471.
- 25 Yu, M.; Zhang, T.; Li, J.; Tan, J.; Zhang, M.; Zhou, Y.; Zhu, X. Facile synthesis of eugenol-based phosphorus/silicon-containing flame retardant and its performance on fire retardancy of epoxy resin. *ACS Appl. Polym. Mater.* **2022**, 4, 1794–1804.
- 26 Qi, Y.; Weng, Z.; Kou, Y.; Li, J.; Cao, Q.; Wang, J.; Zhang, S.; Jian, X. Facile synthesis of bio-based tetra-functional epoxy resin and its potential application as high-performance composite resin matrix. *Compos. Part B: Eng.* **2021**, 214, 108749.
- 27 Dai, J.; Teng, N.; Liu, J.; Feng, J.; Zhu, J.; Liu, X. Synthesis of bio-based fire-resistant epoxy without addition of flame retardant elements. *Compos. Part B: Eng.* **2019**, 179, 107523.
- 28 Liu, X. F.; Xiao, Y. F.; Luo, X.; Liu, B. W.; Guo, D. M.; Chen, L.; Wang, Y. Z. Flame-retardant multifunctional epoxy resin with high performances. *Chem. Eng. J.* **2022**, 427, 132031.
- 29 Liu, J.; Dai, J.; Wang, S.; Peng, Y.; Cao, L.; Liu, X. Facile synthesis of bio-based reactive flame retardant from vanillin and guaiacol for epoxy resin. *Compos. Part B: Eng.* **2020**, 190, 107926.
- 30 Xu, Y.; Yang, W. J.; Zhou, Q. K.; Gao, T. Y.; Xu, G. M.; Tai, Q. L.; Zhu, S. E.; Lu, H. D.; Yuen, R. K. K.; Wang, W.; Wei, C. X. Highly thermostable resveratrol-based flame retardant for enhancing mechanical and fire safety properties of epoxy resins. *Chem. Eng. J.* **2022**, 450, 138475.
- 31 Zhao, D.; Wang, J.; Wang, X. L.; Wang, Y. Z. Highly thermostable and durably flame-retardant unsaturated polyester modified by a novel polymeric flame retardant containing Schiff base and spirocyclic structures. *Chem. Eng. J.* **2018**, 344, 419–430.
- 32 Wei, C.; Esposito, D.; Tauer, K. Thermal properties of thermoplastic polymers: influence of polymer structure and procedure of radical polymerization. *Polym. Degrad. Stabil.* **2016**, 131, 157–168.
- 33 Ma, X.; Guo, W.; Xu, Z.; Chen, S.; Cheng, J.; Zhang, J.; Miao, M.; Zhang, D. Synthesis of degradable hyperbranched epoxy resins with high tensile, elongation, modulus and low-temperature resistance. *Compos. Part B: Eng.* **2020**, 192, 108005.
- 34 Huo, S.; Sai, T.; Ran, S.; Guo, Z.; Fang, Z.; Song, P.; Wang, H. A hyperbranched P/N/B-containing oligomer as multifunctional flame retardant for epoxy resins. *Compos. Part B: Eng.* **2022**, 234, 109701.
- 35 Fei, X.; Wei, W.; Tang, Y.; Zhu, Y.; Luo, J.; Chen, M.; Liu, X. Simultaneous enhancements in toughness, tensile strength, and thermal properties of epoxy-anhydride thermosets with a carboxyl-terminated hyperbranched polyester. *Eur. Polym. J.* **2017**, 90, 431–441.
- 36 Hu, G.; Zhang, X.; Bu, M.; Lei, C. Toughening and strengthening epoxy resins with a new bi-DOPO biphenyl reactive flame retardant. *Eur. Polym. J.* **2022**, 178, 111488.
- 37 Luo, Q.; Sun, Y.; Yu, B.; Li, C.; Song, J.; Tan, D.; Zhao, J. Synthesis of a novel reactive type flame retardant composed of

- phenophosphazine ring and maleimide for epoxy resin. *Polym. Degrad. Stabil.* **2019**, *165*, 137–144.
- 38 Jian, R. K.; Ai, Y. F.; Xia, L.; Zhao, L. J.; Zhao, H. B. Single component phosphamide-based intumescent flame retardant with potential reactivity towards low flammability and smoke epoxy resins. *J. Hazard. Mater.* **2019**, *371*, 529–539.
 - 39 Liu, Y.; Liu, B.; Sun, Z.; Zhang, H.; Men, Y.; Hu, W.; Shao, Z. Bioinspired mono-component lignin endowing epoxy resin with simultaneously improving flame retardancy and mechanical properties. *Compos. Commun.* **2022**, *35*, 101306.
 - 40 Li, S.; Zhao, X.; Liu, X.; Yang, X.; Yu, R.; Zhang, Y.; Huang, W.; Deng, K. Cage-ladder-structure, phosphorus-containing polyhedral oligomeric silsesquinoxanes as promising reactive-type flame retardants for epoxy resin. *J. Appl. Polym. Sci.* **2019**, *136*, 47607.
 - 41 Ma, C.; Qian, L.; Li, J. Effect of functional groups of magnolol-based cyclic phosphonate on structure and properties of flame retardant epoxy resin. *Polym. Degrad. Stabil.* **2021**, *190*, 109630.
 - 42 Wang, P.; Yang, F.; Li, L.; Cai, Z. Flame retardancy and mechanical properties of epoxy thermosets modified with a novel DOPO-based oligomer. *Polym. Degrad. Stabil.* **2016**, *129*, 156–167.
 - 43 Yan, H.; Li, N.; Fang, Z.; Wang, H. Application of poly(diphenolic acid-phenyl phosphate)-based layer by layer nanocoating in flame retardant ramie fabrics. *J. Appl. Polym. Sci.* **2017**, *134*, 44795.
 - 44 Li, Y. C.; Mannen, S.; Morgan, A. B.; Chang, S.; Yang, Y. H.; Condon, B.; Grunlan, J. C. Intumescent all-polymer multilayer nanocoating capable of extinguishing flame on fabric. *Adv. Mater.* **2011**, *23*, 3926–3931.
 - 45 Jiang, G.; Xiao, Y.; Qian, Z.; Yang, Y.; Jia, P.; Song, L.; Hu, Y.; Ma, C.; Gui, Z. A novel phosphorus-, nitrogen- and sulfur-containing macromolecule flame retardant for constructing high-performance epoxy resin composites. *Chem. Eng. J.* **2023**, *451*, 137823.
 - 46 Pol, V. G.; Motiei, M.; Gedanken, A.; Calderon-Moreno, J.; Yoshimura, M. Carbon spherules: synthesis, properties and mechanistic elucidation. *Carbon* **2004**, *42*, 111–116.
 - 47 Wu, J. N.; Chen, L.; Fu, T.; Zhao, H. B.; Guo, D. M.; Wang, X. L.; Wang, Y. Z. New application for aromatic Schiff base: high efficient flame-retardant and anti-dripping action for polyesters. *Chem. Eng. J.* **2018**, *336*, 622–632.
 - 48 Chen, H. R.; Meng, W. M.; Wang, R. Y.; Chen, F. L.; Li, T.; Wang, D. D.; Wang, F.; Zhu, S. E.; Wei, C. X.; Lu, H. D.; Yang, W. Engineering highly graphitic carbon quantum dots by catalytic dehydrogenation and carbonization of $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene wrapped polystyrene spheres. *Carbon* **2022**, *190*, 319–328.
 - 49 Wang, X.; Xing, W.; Feng, X.; Yu, B.; Song, L.; Hu, Y. Functionalization of graphene with grafted polyphosphamide for flame retardant epoxy composites: synthesis, flammability and mechanism. *Polym. Chem.* **2014**, *5*, 1145–1154.