

Intrinsically Anti-Flammable Apigenin-derived Epoxy Thermosets with High Glass Transition Temperature and Mechanical Strength

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Abstract In this work, apigenin was chosen as a raw material to synthesize a novel epoxy monomer (DGEA), while the bio-based epoxy resin was further obtained after curing with 4,4'-diaminodiphenylmethane (DDM). The control samples were prepared by curing diglycidyl ether of bisphenol A (DGEBA) with DDM. The non-isothermal differential scanning calorimeter (DSC) method was utilized to further investigate the curing behavior and curing kinetics of the DGEA/DDM system. Despite no flame retardant active elements, the DGEA/DDM thermoset still exhibited exceptional anti-flammability. Specifically, the DGEA/DDM thermoset reached a V-0 rating in the UL-94 test and owned a high limiting oxygen index (LOI) value of 37.0%, while DGEBA/DDM resins were consumed completely in the vertical combustion test with a low LOI of 23.0%. Furthermore, the microscale combustion calorimetry (MCC) results manifested that compared with DGEBA/DDM resins, both PHRR and THR values of the DGEA/DDM resins were dropped by 84.0% and 57.6%, respectively. Additionally, the DGEA/DDM resin also presented higher storage modulus and tensile strength compared with DGEBA/DDM one. Particularly, in contrast with that of the cured DGEBA/DDM one (156 °C), the DGEA/DDM thermoset displayed an extremely high glass transition temperature (232 °C). This study breaks new ground on how to produce bio-based monomers with aromatic structures and achieve high-performance thermosetting polymers.

Keywords Bio-based epoxy thermosets; Apigenin; Intrinsic anti-flammability

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INTRODUCTION

As one of the most widely used polymers in today's life and industry fields, epoxy resins (EPs) have been extensively employed in coatings, high-performance composites, adhesives, and electronic encapsulation due to their superior adhesion, mechanical features, processability, and electrical insulation.^[1–3] Despite these advantages, the intrinsic flammability of EP thermosets has limited their use with stringent requirements. In this regard, the development of EP thermosets with proper anti-flammability is highly required. The petroleum-based resource is the main raw material to produce most of the commercially available EPs. Almost 90% of commercial EPs originate from diglycidyl ether of bisphenol A (DGEBA) as raw material, while DGEBA is usually obtained by the reaction between epichlorohydrin (ECH) and bisphenol A (BPA).^[4] However, BPA can only be synthesized by reacting petroleum-based phenol with acetone. Besides, BPA can disturb the endocrine and is classified as a reprotoxic R2 substance, posing a serious threat to human health. The enormous annual output of DGEBA also leads to much more greenhouse gas emissions. Unsustainable petroleum reserves

include "old carbon" sequestered from the atmosphere through natural processes. Under this background, the EPs from renewable resources have gained increasing popularity due to the shortage of fossil resources and environmental concerns.^[5,6] Various bio-based compounds, such as protocatechuic acid,^[7] guaiacol,^[8] isosorbide,^[9] eugenol,^[10] vanillin,^[11–13] furan,^[14] rosin,^[15] and luteolin^[16] have been used as the starting material for EP synthesis. However, like petroleum-based EPs, most bio-based epoxy thermosets also suffer from poor anti-flammability. The improvement of the anti-flammability of bio-based EPs has become an important research topic recently. The incorporation of some flame-retardant elements (phosphorus, bromine, silicon, etc.) into bio-based EPs could improve the anti-flammability but at the cost of glass transition temperature (T_g) and mechanical properties.^[11,12,17] Thus, it is crucial to find renewable feedstock with the great potential charring ability to fabricate self-extinguishing epoxy thermosets without additional incorporation of flame-retardant elements. For instance, Qi *et al.* fabricated a magnolol-based bio-epoxy monomer (DGEM) and cured it with 4,4'-diaminodiphenyl sulfone (DDS) to obtain an intrinsically anti-flammable bio-based epoxy thermoset with UL-94 V-0 grade.^[18] In another study, resveratrol was chosen by Gao and colleagues to synthesize bio-based EP resin (REEP), which owned well-designed chemical structures and trifunctional epoxy groups. In the UL-94 test, the cured REEP/MeHHPA showed a V-0 rating, as well as a high T_g

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value of about 210.8 °C.^[19] However, the use of renewable materials to prepare bio-based EPs with intrinsically anti-flammable properties, high glass transition temperature, and mechanical performance is still required.

Apigenin (API) is a natural product from the group of flavones which can be derived from various fruits and vegetables such as parsley, chamomile, spinach, orange, tea, and wheat sprouts.^[20] The main non-pharmaceutical application of this yellow crystalline solid is its use as wool dye. In comparison with other flavonoids, apigenin could be a health-promoting agent owing to its low toxicity.^[21] In this work, an apigenin-derived epoxy monomer was synthesized and characterized, then cured with 4,4'-diaminodiphenylmethane (DDM). Commercial DGEBA was also cured with DDM to prepare control samples to compare with DGEA/DDM resins. The thermal stability and flame-retardant characteristics, as well as mechanical properties of the epoxy resins, were examined. The objective of this study was to present a novel approach to preparing high-performance bio-based EPs with exceptional anti-flammability and thermo-mechanical behaviors from renewable resources through a facile one-step procedure without additional flame-retardant agents.

EXPERIMENTAL

Materials

Magnesium sulfate anhydrous, apigenin (API), tetrabutylammonium bromide (TBAB), epichlorohydrin (ECH) and 4,4'-diaminodiphenylmethane (DDM) were obtained from Shanghai Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Dichloromethane, ethanol as well as sodium hydroxide were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Bisphenol A diglycidyl ether (DGEBA) was purchased from Hefei Jiangfeng Chemistry Co., Ltd. (Anhui, China).

Synthesis of Apigenin-derived Diglycidyl Ether (DGEA)

Scheme 1 illustrates a pathway of synthesis of apigenin-based epoxy monomer. In detail, 2.65 g of TBAB (3.0 wt% of the mixture) and 19.98 g of API (0.074 mol) were added to 68.46 g of ECH (0.74 mol) in a 250 L four-neck flask under reflux condensation, nitrogen purge, and addition funnel with a constant rate. The suspension temperature was elevated to 100 °C and kept for 4 h; followed by cooling down to room temperature and dropwise addition of aqueous sodium hydroxide solution (6.00 g, 50.0 wt%, 0.15 mol) within 60 min. The reaction continued for 6 h, and then the salt was eliminated after filtering the mixture. The filtrates were extracted with

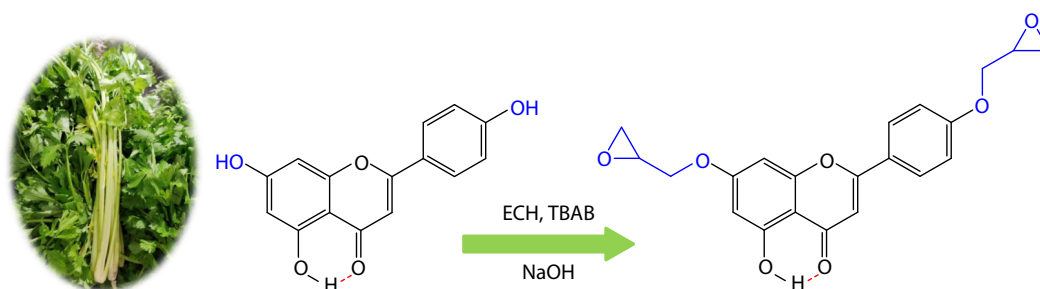
dichloromethane and washed with distilled water for several times. Then the combined organic layer was separated and dried by magnesium sulfate anhydrous overnight. Finally, the dried organic layer was evaporated to remove dichloromethane under vacuum, placed in an oven at 50 °C to dry for 24 h to obtain a yellow liquid (yield: 69%).

Curing Process of the Epoxy Thermosets

DGEA was mixed with DDM to obtain a homogeneous mixture after heating at 110 °C for 15 min, while the stoichiometric ratio (molar ratio of N—H group/epoxy group) was 1/1 after calculation. Then, the mixture was immediately poured into a preheated stainless steel mold at 110 °C for further curing reaction in an air-circulating oven and the curing process was 120, 140, 160 and 180 °C for 2 h, respectively. After cooling down and staying unused for one day, the cured material was obtained. For comparison, the DGEBA/DDM thermoset was also prepared by a similar process.

Characterization

Fourier Transform Infrared spectra (FTIR) were conducted on the NICOLET 6700 (Thermo Electron Scientific Instruments Co., Ltd., USA) spectrometer with a range of 400–4000 cm⁻¹. Morphological assessments were obtained by the Hitachi S-4800 scanning electron microscope (SEM). STA7200 (Germany) was employed to obtain the thermo-gravimetric analysis/differential thermal gravimetric (TGA/DTG) curves in air and N₂ atmosphere from room temperature to 700 °C with a heating rate of 20 °C/min. Bruker AVANCE III 600 spectrometer (Billerica, MA, USA) was utilized to measure the ¹H- and ¹³C-nuclear magnetic resonance (NMR) spectra, operating by chloroform as the solvent. Dynamic mechanical analysis (DMA) was also investigated by the TA instrument (DMA Q800, USA) from 30 °C to 270 °C at a heating rate of 5 °C/min on 50 mm × 10 mm × 3 mm specimens. The non-isothermal curing characteristics were examined at 50–250 °C by a DSC Q25 instrument (TA, USA) under N₂ atmosphere with different heating rates from 5 °C/min to 20 °C/min. Using a cone calorimeter, the ISO 5660 standard protocol was followed to conduct the cone calorimeter test (Fire Testing Technology, UK). Thermal radiations of 50 kW/m² were applied to samples (100 mm × 100 mm × 3 mm) that were arranged horizontally. Applying the TG-FTIR technique, the thermal decomposition products were assessed by combining a TA Q5000 thermal analyzer with a Thermo Nicolet 6700 FTIR spectrophotometer. The flame-retardancy of the samples (FTT, UK) was measured at 100–800 °C with a heating rate of 1 °C/s under the N₂ atmosphere by a microscale combustion calorimeter (MCC) apparatus. Tensile tests were carried out on an Instron-5967 universal electronic testing system (J Lloyd, UK).



Scheme 1 A pathway of synthesis of apigenin-based epoxy monomer (DGEA).

with a rate of 2.0 mm/min according to ASTM D638. The UL-94 vertical burning test was conducted on specimens (100 mm × 13 mm × 3 mm) applying the UL-94 SCZ-3 (Jiangning Instruments, China), based on ASTM D3801-2010. The UL-94 vertical burning test was conducted on specimens (100 mm × 13 mm × 3 mm) applying the UL-94 SCZ-3 (Jiangning Instruments, China), based on ASTM D3801-2010. The limiting oxygen index (LOI) value was measured by an HC-2 oxygen index meter (Jiangning Instruments, China), while the dimension of the samples was 100 mm × 6.5 mm × 3 mm.

RESULTS AND DISCUSSION

Synthesis and Characterization of DGEA

Etherification of hydroxyl groups by ECH is the most common method for phenol-type EP preparation. The mechanism is considered to be an S_N2 reaction, also called the O-glycidylation reaction. In this method, phenolic hydroxyl groups serve as nucleophiles and attack the α carbon of ECH.^[22] FTIR spectra of API and DGEA before and after curing are depicted in Fig. 1(a). In the case of raw material API, the broad band at 3288 cm^{-1} is owing to the stretching vibration of the hydroxyl groups, while those at 2710–2580 cm^{-1} are considered the O—H bonds. Those at 1608–1400 cm^{-1} were assigned to the stretching vibrations of the aromatic rings, whereas the characteristic bands at 908–670 cm^{-1} are attributed to aromatic groups. For DGEA, a moderately intense band appears at around 918 cm^{-1} , corresponding to the epoxy group.^[23] The

disappearance of the band at 3288 cm^{-1} further confirms the successful synthesis of DGEA. After being cured with DDM, the absence of the band at around 918 cm^{-1} manifests the complete reaction between DGEA and DDM. In the ^1H -NMR spectrum, the proton signals at 2.75, 2.92 and 3.35 ppm also verify the formation of the epoxy groups (Fig. 1b). The chemical shifts are greatly consistent with the target product. Additionally, in Fig. 1(c), the ^{13}C -NMR spectrum demonstrates the proper matching of the carbon resonances with the expected structure. Noteworthy, after the glycidylation, the Ar-OH adjacent to the carbonyl group in DGEA remains unchanged, which is mainly due to the strong intramolecular hydrogen bonding between —OH and carbonyl oxygen atom in the structure. Moreover, it drastically decreased the reactivity of phenolic —OH, which has been reported in previous works.^[24] An intense $[\text{M}-\text{H}]^-$ ion peak at $m/z=381.10$ is observed in the high-resolution mass spectrum (Fig. 1d), which is greatly consistent with the molecular weight of DGEA. According to the ASTM D-1652 standard, the epoxy value of the DGEA monomer is approximately 0.51 mol/100g after titration.

Curing Behavior

The non-isothermal DSC approach was utilized to explore the curing behavior and kinetics of the DGEA/DDM. Fig. 2(a) illustrates the non-isothermal DSC thermograms of the DGEA/DDM mixture at a series of heating rates (5, 10, 15, and 20 $^\circ\text{C}/\text{min}$). An endothermic peak at 55–70 $^\circ\text{C}$ appears in all the curing curves and is assigned to the melting of DDM. All the DSC

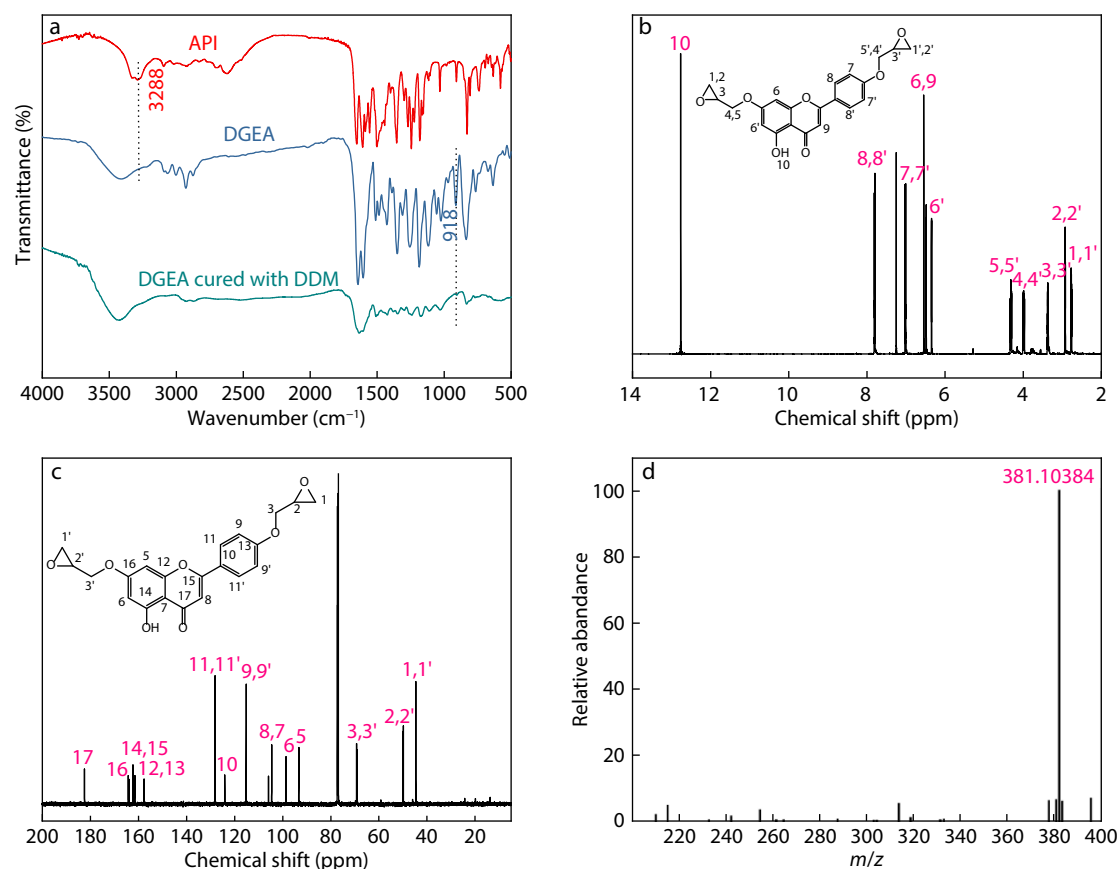


Fig. 1 (a) FTIR spectra of API and DGEA before and after curing; (b) ^1H -NMR and (c) ^{13}C -NMR spectra of DGEA; (d) High-resolution mass spectrum of DGEA.

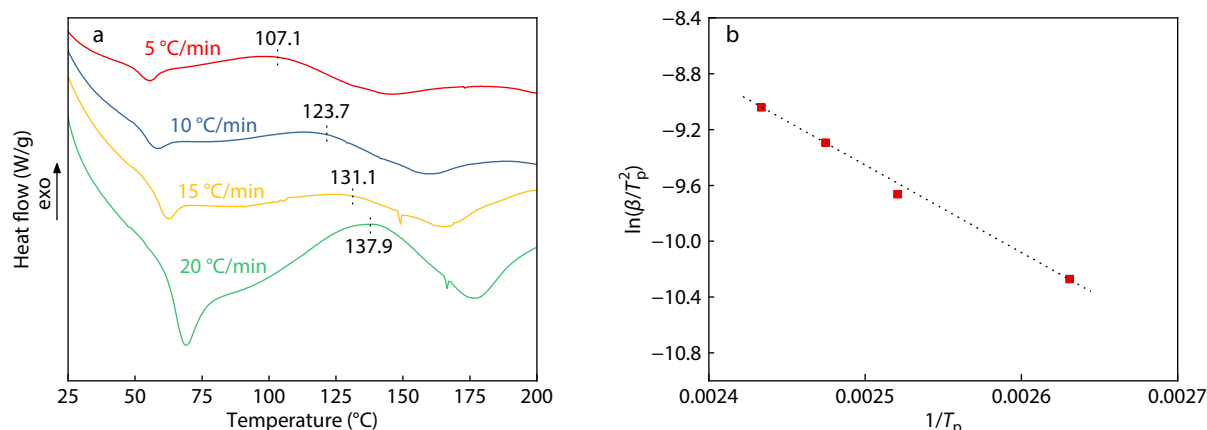


Fig. 2 (a) Non-isothermal DSC thermograms of the DGEA/DDM mixture at a series of heating rates (5, 10, 15, and 20 °C/min); (b) Plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ using Kissinger's method.

thermograms exhibit an exothermic peak, which is ascribed to the occurrence of the curing reaction between DGEA and DDM. Besides, at higher heating rates (15 and 20 °C/min), the heat accumulates more rapidly and cannot dissipate in time, thus resulting in a second exothermic peak appearing after 180 °C. Table 1 provides the starting temperature (T_s), the peak temperature (T_p), the end temperature (T_e), and the enthalpy (ΔH) of the first exothermic peak. The T_s , T_p , and T_e grow gradually as the increase of heating rate, which is ascribed to the lag effect of the curing reaction.^[25,26] In addition, the value of enthalpy increases gradually. Generally, the degree of curing reaction can be reflected by the enthalpy. The higher enthalpy indicates a higher degree of the curing reaction. At a higher heating rate, the molecular chain diffuses faster, thus leading to a higher completion degree of the curing reaction.^[27] In order to explore the curing activity, Kissinger's method is employed to compute the activation energy (E_a) of the DGEA/DDM mixture, as described in Eq. (1):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (1)$$

where A represents the pre-exponential factor, β is the heating rate, and R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{°C}^{-1}$). Fig. 2(b) depicts the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$. The E_a can be calculated from the slope of the plot. E_a of the DGEA/DDM system is calculated to be 51.15 kJ/mol , while that of the DGEBA/DDM resin is 48.81 kJ/mol .^[12] The higher E_a of the DGEA/DDM system implies the lower curing reactivity of the DGEA/DDM system owing to the steric hindrance of rich aromatic structures.

Thermomechanical and Mechanical Properties of DGEA/DDM Resins

The thermomechanical features of the cured DGEA/DDM and DGEBA/DDM systems were assessed by dynamic mechanical analysis (DMA), as depicted in Fig. 3(a) and Table 2. Specifically,

Table 1 DSC data of DGEA/DDM and DGEBA/DDM resins.

Sample	β (°C/min)	T_{onset} (°C)	T_p (°C)	T_e (°C)	ΔH (J/g)	E_a (kJ/mol)
DGEA/DDM	5	67.2	107.1	144.2	22.9	51.15
	10	85.9	123.7	156.8	27.2	
	15	96.7	131.1	163.0	28.7	
	20	101.2	137.9	175.5	36.0	

DGEA/DDM shows a relatively high storage modulus of 2809 MPa at 30 °C (74% higher than that of DGEBA/DDM). The glass transition temperature (T_g), as an indicator of the maximum working temperature of thermosetting resins, is another crucial parameter determined by the DMA test. In high-tech fields such as aerospace, EPs have to operate at high temperatures; thus, T_g values of 220 °C or higher are necessary.^[28] Upon curing with DDM, the DGEA/DDM system achieved a T_g of 232 °C, 76 °C higher than the DGEBA/DDM thermoset (156 °C). Generally, the segmental mobility of polymer chains can be reflected by the T_g value, which is mainly influenced by the cross-linking density (v_e) of resins as well as the monomer architecture. v_e can be computed from the platform of elastic modulus in the rubbery state on the basis of rubber elasticity theory, as shown in Eq. (2):^[29]

$$v_e = E'/3RT \quad (2)$$

which E' denotes the storage modulus of epoxy resins at a rubbery plateau area, T means the absolute temperature, and R indicates the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{°C}^{-1}$). The v_e of the cured DGEA/DDM is about $0.8 \times 10^3 \text{ mol/m}^3$, while the v_e of DGEBA/DDM is $1.1 \times 10^3 \text{ mol/m}^3$. Thus, the high T_g of the cured DGEA/DDM is mostly associated with the molecular rigidity of DGEA with rich aromatic structures. The rigid benzopyrene rings of DGEA restrict the molecular chain motion of the cured DGEA/DDM, which is responsible for the high T_g . Fig. 3(b) presents the tensile stress-strain curves of the cured DGEA/DDM and DGEBA/DDM. The elongation at break and tensile strength of the cured DGEA/DDM are 2.8% and 59.5 MPa, respectively, whereas those of the cured DGEBA/DDM are 2.4% and 55.0 MPa. Fig. 3(c) compares the T_g and tensile strength of the bio-based epoxy thermoset in this work with those values of the previously reported counterparts.^[8,11,30–33] It is obvious that DGEA/DDM system exhibits moderate tensile strength but has a higher T_g compared to the previously reported bio-based epoxy thermosets. Owing to these superior comprehensive characteristics, this bio-based epoxy resin could find potential applications, especially in the field that requires high heat resistance. The DGEA/DDM thermoset also has a flexural strength of 105 MPa, which is comparable to the DGEBA/DDM thermoset (Fig. 3d), confirming the great stiffness of the DGEA/DDM thermoset. The mechanical properties of thermosetting resins are closely related to molecular rigidity and

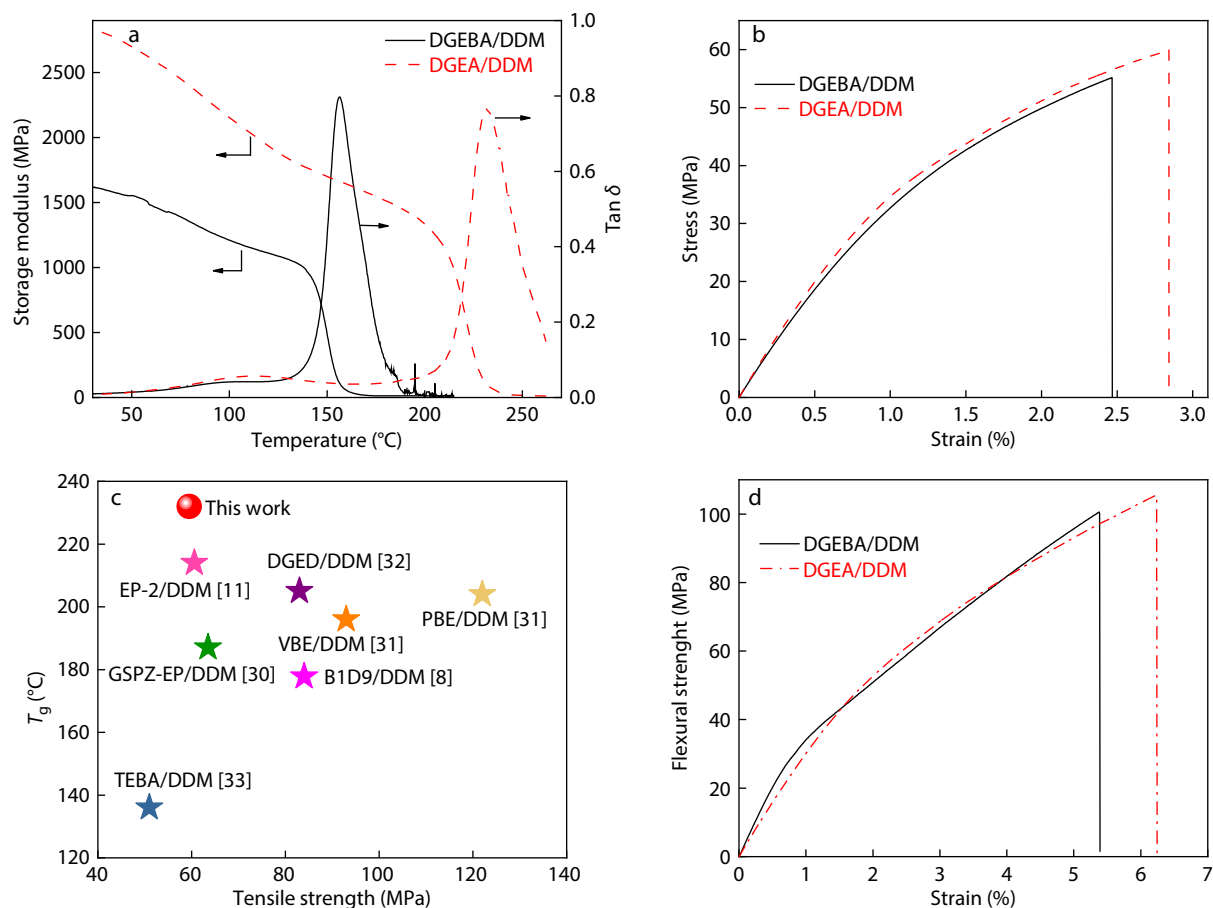


Fig. 3 (a) DMA and (b) Tensile stress-strain curves of the cured DGEA/DDM and DGEBA/DDM; (c) Comparison of T_g and tensile strength of DGEA/DDM with those of the bio-based epoxy thermosets previously reported; (d) Flexural stress-strain curves of the cured DGEA/DDM and DGEBA/DDM.

Table 2 Thermal-mechanical data of the cured DGEA/DDM and DGEBA/DDM.

Sample	T_g (°C)	E' at 30 °C (MPa)	E' at T_{g+30} °C (MPa)	v_e (mol/m ³)	Tensile strength (MPa)	Elongation at break (%)
DGEA/DDM	232	2809	11.0	0.8×10^3	59.5	2.8
DGEBA/DDM	156	1618	13.1	1.1×10^3	55.0	2.4

cross-linking density in their structure. As aforementioned, although the cured DGEA/DDM system owns a slightly lower cross-link density than the cured DGEBA/DDM system, the much higher molecular segmental rigidity is responsible for its higher tensile property.

Thermal Property

Thermogravimetric analysis (TGA) and differential TGA (DTG) curves of the cured DGEA/DDM and DGEBA/DDM under nitrogen are presented in Fig. 4(a). The temperature corresponding to 5% weight loss ($T_{d5\%}$) of DGEA/DDM and DGEBA/DDM resins after curing are 262 and 371 °C, respectively. The $T_{d5\%}$ of DGEA/DDM is lower, indicating that the pyrazone ring of DGEA was degraded earlier during the heating process.^[34] The temperature corresponding to the maximal thermal decomposition rate (T_{max}) of DGEA/DDM and DGEBA/DDM samples are 360 and 396 °C, respectively. Despite the lower $T_{d5\%}$ and T_{max} values, the cured DGEA/DDM thermoset produces much higher char residue (45.1%) than the cured

DGEBA/DDM one (15.1%). The rich aromatic structures in DGEA are responsible for the much higher char residue of DGEA/DDM since rich aromatic structures are generally precursors for charring.^[35] Generally, polymers' anti-flammability is proportional to their char yield under nitrogen.^[36] Such a high char yield without extra flame-retardant fillers or elements suggests the potentially good anti-flammability of the cured DGEA/DDM thermoset. From DTG curves, it can be found that the thermal degradation rate of the DGEA/DDM thermoset is much lower than that of the DGEBA/DDM one, implying a slower weight loss process during the thermal decomposition. The thermal degradation of the cured DGEA/DDM and DGEBA/DDM in the air was assessed as well (Fig. 4b). Different from the results obtained under nitrogen, the $T_{d5\%}$ of the cured DGEA/DDM and DGEBA/DDM systems are 266 and 369 °C, respectively. The cured DGEBA/DDM system exhibits two thermal-degradation stages, while the cured DGEA/DDM behaves in a more complicated thermal-degradation process. The cured DGEA/DDM has a higher carbonization capacity than

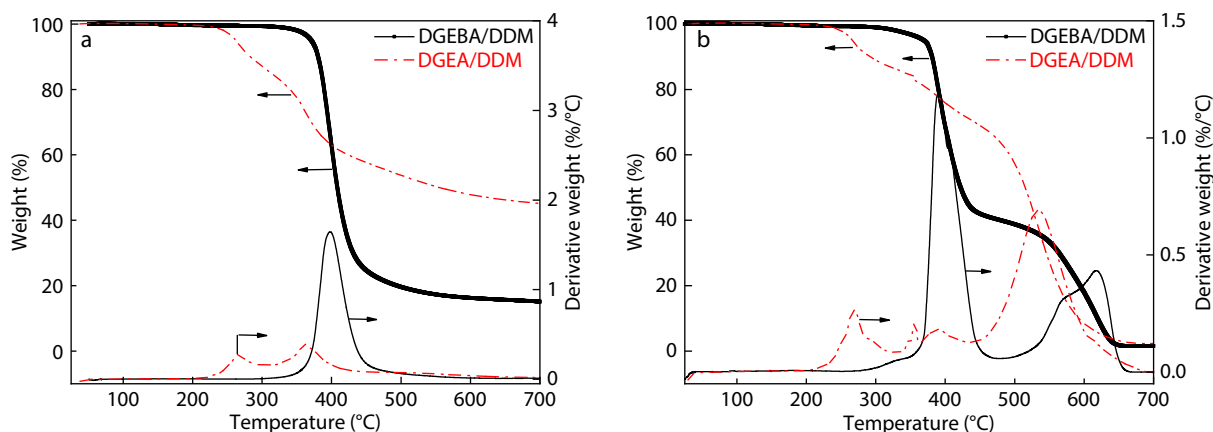


Fig. 4 TGA/DTG curves of APIEP/DDM and DGEBA/DDM at (a) N_2 and (b) air atmospheres.

the cured DGEBA/DDM, as suggested by its higher char yield.

Flame-retardant Performance

As aforementioned, the high char yield of DGEA/DDM resins can reduce the flammability. Microscale combustion calorimetry (MCC) is also a novel method for fast evaluation of the flammability of materials with minimal sample requirements (on milligram quantities). Fig. 5(a) displays the heat release rate (HRR) curves in the MCC test, whereas the specific data are listed in Table 3, including the total heat release (THR), peak heat release rate (PHRR), and the temperature at PHRR (T_{peak}) of the cured DGEA/DDM and DGEBA/DDM. The DGEA/DDM thermoset demonstrates a much lower PHRR value (about 84% reduction) than the cured DGEBA/DDM (81.3 W/g compared with 506.8 W/g). Similarly, there is an obvious decrease (about 58% reduction) in the THR value of DGEA/DDM thermoset compared with DGEBA/DDM (13.9 kJ/g versus 32.8 kJ/g). These results indicate substantially lower flammability of DGEA/DDM than DGEBA/DDM. The reason for the higher anti-flammability of DGEA/DDM is the perfect char-forming ability of DGEA. The higher char residue yield of the DGEA/DDM system is also verified in the pyrolysis experiments (Fig. 5b). The cured DGEA/DDM and DGEBA/DDM were heated in a muffle furnace at 500 °C for 10 min. As can be seen, the cured DGEBA/DDM displays a fractured char residue at the bottom of the crucible, failing in retaining its original contour, while the cured

Table 3 MCC data of the cured DGEA/DDM and DGEBA/DDM resins.

Sample	PHRR (W/g)	THR (kJ/g)	T_{peak} (°C)
DGEA/DDM	81.3	13.9	301
DGEBA/DDM	506.8	32.8	433

DGEA/DDM manages to preserve its integrated char structure. Such a thermally stable char favors decelerating the heat release and propagation of combustible gases during combustion.

Cone calorimetry was used to determine the flammability of the cured thermosets. Fig. 6 illustrates the heat release rate (HRR) and total heat release (THR) curves versus the time of the cured DGEA/DDM and DGEBA/DDM. The peak-HRR value of the cured DGEA/DDM is 541 kW/m², much lower than that of the cured DGEBA/DDM (1293 kW/m²), owing to the formation of an intumescent char of the cured DGEA/DDM that obstructs oxygen and heat exchange during burning. The cured DGEA/DDM shows a THR of 33.8 MJ/m², which is 66.1% lower than the cured DGEBA/DDM (99.7 MJ/m²), suggesting a considerably suppressed flammability.

To further evaluate the flame retardant features, the LOI values of DGEA/DDM and DGEBA/DDM resin were assessed. LOI value of commercial DGEBA/DDM resin is only 23.0%, whereas that of the cured DGEA/DDM reaches 37.0%. Fig. 7 compares the UL-94 test results of DGEA/DDM and

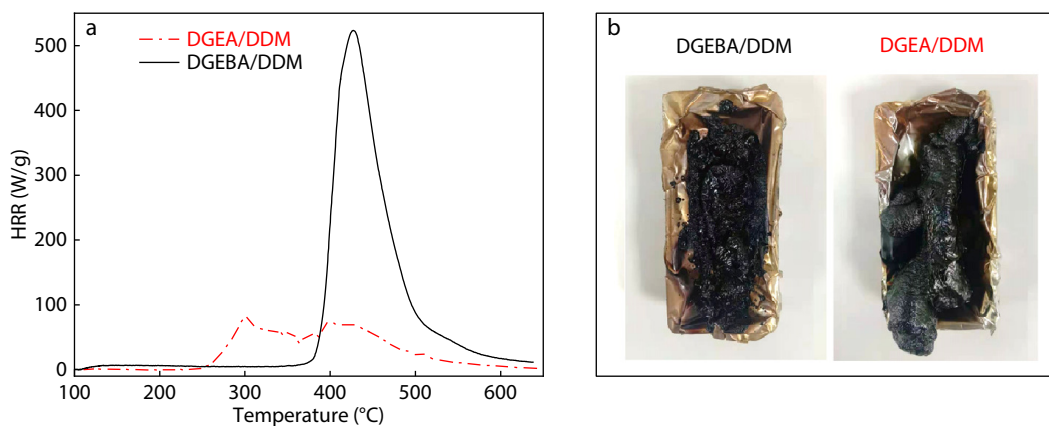


Fig. 5 (a) HRR curves of the cured DGEA/DDM and DGEBA/DDM resins, and (b) their char residue after heating at 500 °C in a muffle furnace.

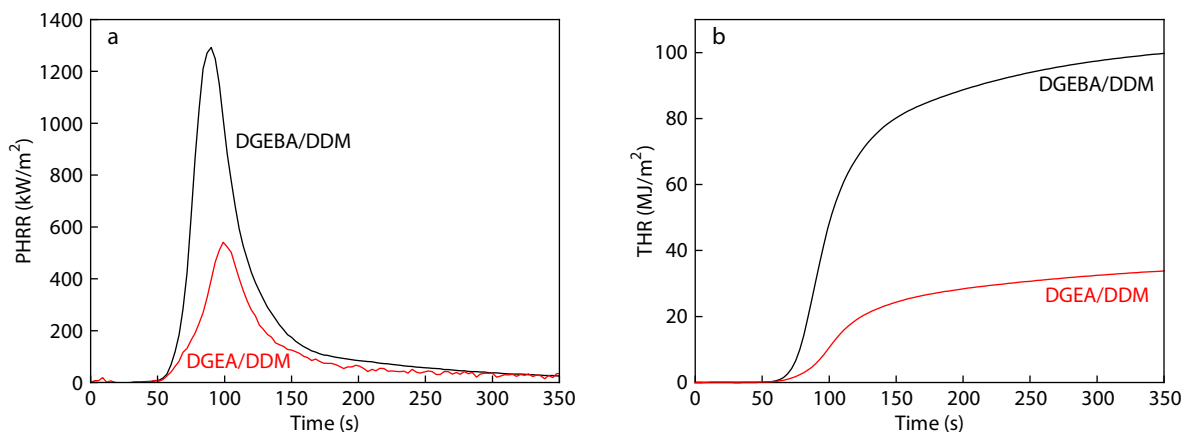


Fig. 6 (a) HRR and (b) THR versus time curves of the cured DGEA/DDM and DGEBA/DDM obtained from cone calorimeter test.

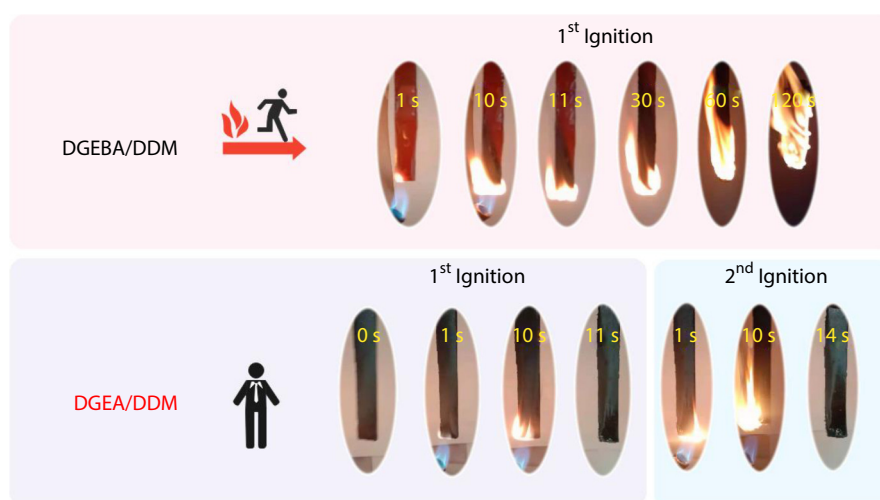


Fig. 7 Digital photographs of DGEBA/DDM and DGEA/DDM resins during UL-94 vertical burning tests.

DGEBA/DDM resins. Upon ignition, the cured DGEBA/DDM progressively burns and does not extinguish even after 120 s. By contrast, the cured DGEA/DDM self-extinguishes within about 4 s after ignition, indicating a significant improvement in fire propagation resistance. Such a self-extinguishing phenomenon is attributed to the rapid carbonization of the cured DGEA/DDM during combustion because of its intrinsically rich aromatic structure. The formation of the char layer retards the fuel diffusion from decomposed epoxy matrix to the combustion zone. Thus, insufficient fuel and heat cannot sustain fire propagation. The MCC and the UL-94 test results manifest the much lower flammability of DGEA/DDM resins compared to DGEBA/DDM resins.

Pyrolysis Volatiles Analysis

TG-IR technique was employed to investigate the anti-flammable mechanism. The gas-phase components can be directly detected by the TG-IR technique during the combustion process. Figs. 8(a) and 8(b) present the three-dimensional FTIR spectra of the pyrolysis products of the cured DGEBA/DDM and DGEA/DDM systems during thermal degradation. FTIR spectra of pyrolysis products of the cured DGEBA/DDM and DGEA/DDM at the maximum decomposition rate are illustrated in Fig. 8(c).

As shown, the majority of pyrolysis products of DGEBA/DDM resins are organic combustible gases, such as various hydrocarbons at 2975 cm^{-1} , carbonyls at 1735 cm^{-1} , aromatic compounds at 1605 and 1510 cm^{-1} , and C—O—C at 1257 and 1176 cm^{-1} . The existence of minor carbon monoxide at 2171 cm^{-1} , carbon dioxide at 2360 cm^{-1} , and water at 3650 cm^{-1} is detected. The pyrolysis products of DGEA/DDM resins mainly include phenol (3016 cm^{-1}) but have fewer other organic combustible gases, such as hydrocarbons, carbonyls, and aromatic compounds. With the use of similar size and weight of the samples, the amount of degradation products is reflected by the intensity of the absorption peak in the three-dimensional spectra reflects. Compared with DGEBA/DDM resins, the absorption intensity of the cured DGEA/DDM is much weaker, suggesting lower emission of the pyrolysis products. The less combustible gases mean that there is less fuel to supply for combustion, and this result is in good accordance with the lower THR and PHRR values in the MCC test.

Char Analysis

The morphology of the char residues of the cured DGEBA/DDM and DGEA/DDM thermosets was assessed by SEM. SEM images of the exterior and interior char residues are depicted in Fig. 9.

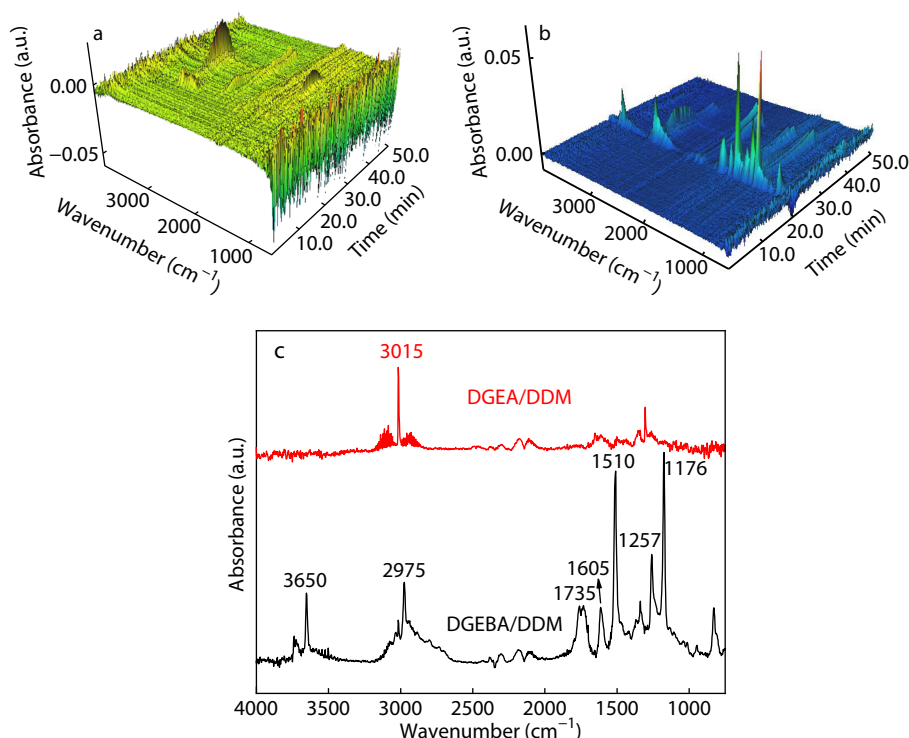


Fig. 8 Three-dimensional FTIR spectra of pyrolysis products of the cured (a) DGEA/DDM and (b) DGEBA/DDM; (c) FTIR spectra of pyrolysis products of the cured DGEA/DDM and DGEBA/DDM at the maximum decomposition rate.

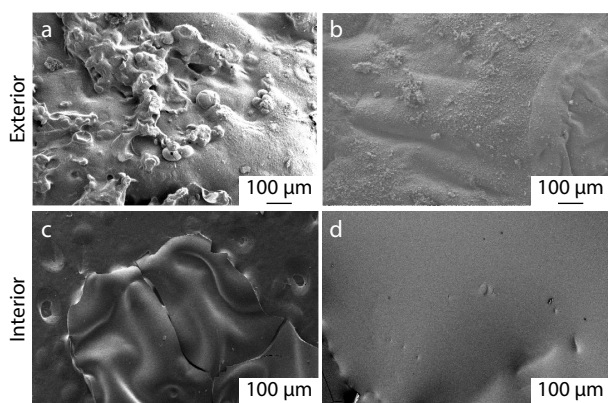


Fig. 9 SEM images of the exterior and interior char residues of the cured (a, c) DGEBA/DDM and (b, d) DGEA/DDM thermosets after the UL-94 test.

The exterior char of DGEBA/DDM is porous, while the interior one is cracked, indicating the occurrence of fierce burning. This structure of the char residue disables it to suppress the heat and combustible volatiles transfer during combustion. By comparison, both the exterior and interior char residues of DGEA/DDM present a dense and intact structure, which could efficiently prevent heat and combustible volatiles transfer, resulting in better flame resistance.^[37]

CONCLUSIONS

In this work, an apigenin-derived epoxy monomer was successfully synthesized, which was subsequently cured with

DDM. The cured DGEA/DDM exhibited an ultrahigh T_g (232 °C), 76 °C higher than that of the cured DGEBA/DDM (156 °C). Moreover, the tensile strength and the elongation at break of the cured DGEA/DDM were comparable to those of the cured DGEBA/DDM. The cured DGEA/DDM showed a much higher char yield compared to the cured DGEBA/DDM (45.1% versus 15.1% at 700 °C under N_2 atmosphere). As a result, the cured DGEA/DDM demonstrated excellent intrinsic anti-flammability. In comparison with the cured DGEBA/DDM, the cured DGEA/DDM showed an 84% and 58% decline in PHRR and THR values. Additionally, DGEA/DDM thermoset reached a V-0 rating in the UL-94 test, whereas DGEBA/DDM thermoset behaved with no rating. In contrast with DGEBA/DDM product, DGEA/DDM resins exhibited a much higher glass transition temperature (232 °C), a superior storage modulus at 30 °C (2808 MPa), and a slightly higher tensile strength (59.5 MPa). Concerning the relatively high cost of the raw material apigenin, this apigenin-derived epoxy monomer is suitable for special structural and/or composite materials.

NOTES

The authors declare no competing financial interest.

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