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**Biomass-Derived Schiff Base Compound Enabled Fire-Safe Epoxy  
Thermoset with Excellent Mechanical Properties and High Glass Transition  
Temperature**

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**Abstract:** Recently, biomass-derived fire-safe epoxy thermosets have been developed for the substitute of petroleum-derived bisphenol A epoxy thermosets due to the shortage of petroleum resources and the negative health impacts of petroleum-derived products. However, the synthesis of bio-based epoxy thermosets combining excellent mechanical properties and fire-safety performance is still a great challenge. In this paper, a novel Schiff base compound 4,4'-((1E,1'E)-((oxybis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene))bis(benzene-1,2-diol) (PH-ODA) was efficiently synthesized from bio-based protocatechualdehyde. PH-ODA was subsequently reacted with epichlorohydrin to obtain the epoxy monomer (1E,1'E)-N,N'-((oxybis(4,1-phenylene))bis(1-(3,4-bis(oxiran-2-ylmethoxy)phenyl)methanimine) (PH-ODA-EP). After curing PH-ODA-EP with 4,4'-diaminodiphenylmethane (DDM), the cured resin PH-ODA-EP/DDM network possessed a high glass transition temperature ( $T_g$ ) of 204.9 °C and showed a 181.8%, 105.8% and 87.0% increase in char yield (in N<sub>2</sub>) (41.7% vs. 14.8%), storage modulus (at 30 °C) (6.01 GPa vs. 2.92 GPa) and tensile modulus (6.21 GPa vs. 3.32 GPa), respectively, compared with the cured bisphenol A epoxy resin (DGEBA)/DDM. Moreover, PH-ODA-EP/DDM possessed excellent fire-safety properties (limited oxygen index (LOI) value = 40.5%) due to the introduction of Schiff base structure, showing a 90.9% and 72.0% reduction (compared with DGEBA/DDM) in peak heat release rate and total heat release value. This work provided a facile and sustainable route for synthesizing Schiff base compounds using biomass-derived resources, exhibiting great potential for the application in high-performance fire-safe epoxy thermosets.

**Keywords:** Biomass; Schiff base; Fire-safe; Epoxy thermosets; Mechanical properties

## 1. Introduction

In recent years, the growing fossil energy crisis and environmental pollution problems have attracted increasing attention from the whole world, and thus promoted the research and development of biomass-derived materials and products to achieve a sustainable future [1-7]. Various important chemicals or materials were successfully developed from biomass resources [8-10], such as cellulose nanocrystals (CNCs) [11-13], bio-oil [14], monoterpenes [15], furfural [16], polylactic acid (PLA) [17], and polycarbonate [18].

Schiff base compounds are very important chemicals and have been widely applied in various areas (i.e., drug release, electrochemical cells, gas separation, and catalysts) because of their diverse properties (i.e., catalytic, magnetic, and biological properties) [19-21]. Recently, Schiff base compounds were applied for fabricating polymers due to their good thermal stability, degradability and mechanical properties [22-24]. Xu et al. [24] reported two Schiff base epoxy resins with the outstanding degradability and antibacterial properties, the Schiff base resins could be degraded in mild acidic medium. Meanwhile, the azomethine (-CH=N-) structure in Schiff base polymers exhibits the good fire-safety performance because it can facilitate the crosslinking of polymers during combustion [25,26]. Obviously, Schiff base compounds have great potential for the application in the fields of high-performance polymers with good fire-safety properties.

Epoxy resins are commonly-used versatile thermosetting materials and have been used for various applications attribute to its high integrated properties [27-32]. Recently, various biomass-derived compounds have been utilized as the feedstocks for preparing the renewable epoxy thermosets [33,34]. However, developing renewable epoxy thermosets that combine

high integrated properties and good fire-safety performance is still a challenge. Interestingly, it was reported that the introduction of Schiff bases into polymers simultaneously enhanced the mechanical properties and fire-safety properties of polymers [35]. Therefore, developing epoxy thermosets from biomass-derived Schiff base compound is a potential way to address the challenge above. However, the preparation of bio-based fire-safe epoxy thermosets derived from Schiff base is still in its infancy. Protocatechualdehyde is a plant-derived phenolic aldehyde compound containing two phenolic hydroxyl groups and an aldehyde group, which has been widely used in medicine because of its biological activities [36,37]. Based on its unique structures and functional groups, protocatechualdehyde might be a promising biomass resource for preparing high-performance Schiff base epoxy thermosets [38]. In addition, the curing process also greatly affects the properties of ultimate epoxy thermosets [39-41]. Therefore, the study on the curing kinetics is of significance to high-performance thermosets. Normally, the curing kinetics study can be carried out with the help of differential scanning calorimetry (DSC) at non-isothermal conditions and many methods (e.g., Kissinger's method and *Cure Index*) have been used to reveal the relationship between the curing process and the properties of epoxy thermosets [42-45].

In this work, for the first time, a bio-based epoxy resin with outstanding mechanical and fire-safety properties is synthesized from a novel biomass-derived aromatic Schiff base compound. The Schiff base compound, 4,4'-((1E,1'E)-((oxybis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene))bis(benzene-1,2-diol) (PH-ODA), is synthesized from renewable protocatechualdehyde and subsequently reacts with epichlorohydrin to obtain the epoxy monomer PH-ODA-EP. The thermal stability,

mechanical properties, and fire-safety performance of the cured resin PH-ODA-EP/DDM, from PH-ODA-EP cured with 4,4'-diaminodiphenylmethane (DDM), are evaluated and compared to commercial bisphenol A epoxy resin (DGEBA)/DDM. The curing kinetics of PH-ODA-EP/DDM and DGEBA/DDM are studied by non-isothermal DSC experiments. It is expected that an epoxy thermoset from a novel biomass-derived aromatic Schiff base compound has the outstanding mechanical and fire-safety properties. This work provides a sustainable and facile route for preparing Schiff base compounds from biomass and a strategy to simultaneously enhance the mechanical properties and fire-safety properties of bio-based epoxy thermosets.

## 2. Materials and methods

### 2.1. Materials

Protocatechualdehyde, 4,4'-diaminodiphenyl ether (ODA), epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB) and 4,4'-diaminodiphenylmethane (DDM) were obtained from Aladdin Reagent Co. Ltd., China. Ethanol, ethyl acetate, sodium hydroxide (NaOH), and anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were purchased from Guangzhou Chemical Reagent Factory, China. DGEBA (epoxy value =  $0.51 \text{ mol} \cdot 100 \text{ g}^{-1}$ ) was purchased from SINOPEC Baling company, China.

### 2.2. Synthesis of Schiff base PH-ODA

Protocatechualdehyde (41.4 g, 0.30 mol) was added in 350 mL of ethanol (in a 500 mL three-necked flask) and dissolved. Then, ODA (19.8 g, 0.10 mol) was slowly added to the above solution. After stirring at 30 °C for 30 min, the reaction system was heated to 80 °C and

kept at this temperature for 5 h ( $N_2$  atmosphere). Afterward, the reaction system was cooled to room temperature and poured into 1000 mL of ice water. The resultant solid was filtered and washed (three times) with ethyl acetate. Then, the resultant solid was vacuum dried at 70 °C for 12 h to obtain the yellow powder PH-ODA (39.0 g, yield 88.7%).

### 2.3. Synthesis of PH-ODA-EP

PH-ODA (22.02 g, 50 mmol), ECH (46.26 g, 0.5 mol), TBAB (1.61 g, 5.0 mmol), 250 mL of ethanol were placed in a 500 mL three-necked flask. The reaction system was stirred at 80 °C for 6 h ( $N_2$  atmosphere). Afterward, the reaction system was cooled down to 60 °C, and NaOH aqueous solution (40 wt %, 35 mL) was dropwise added to the reaction system and then stirred at 60 °C for 6 h. After that, the reaction system was cooled to room temperature and the solvent was removed using a rotary evaporator. Then the resultant product was diluted with ethyl acetate and then washed three times with distilled water. Subsequently, the organic layer was dried using anhydrous  $Na_2SO_4$  and filtered. Finally, rotary evaporation was used to remove the solvent and a brown viscous oil PH-ODA-EP (30.08 g, yield 90.5%) was obtained.

### 2.4. Preparation of the cross-linked thermosets

The cured resin PH-ODA-EP/DDM was prepared via curing reaction of PH-ODA-EP with DDM (molar ratio of epoxy group in PH-ODA-EP to N–H in DDM was 1:1). A stoichiometric mixture of PH-ODA-EP and DDM was mixed homogeneously at 70 °C, and then poured into a mould and degassed at 70 °C for 20 min. Afterward, the mixture was cured at 110 °C for 2 h, 150 °C for 2 h, and 190 °C for 2 h to obtain PH-ODA-EP/DDM. The procedures of DGEBA/DDM fabrication are the same as above.

## 2.5. Characterizations

$^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were collected with a Bruker NMR spectrometer (Billerica, MA, USA) and deuterated dimethylsulfoxide (DMSO- $d_6$ ) was used as the solvent. The infrared spectra (FT-IR) were obtained with a Vertex70 spectrometer (Bruker, Billerica, MA, USA) using KBr pellets.

Differential scanning calorimetry (DSC) tests were carried out with a Netzsch DSC 200F3 in nitrogen for nonisothermal curing behavior. The mixture (about 5 mg) of epoxy monomer and DDM was analyzed at five heating rates of 2.5, 5, 10, 15, and 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$  (from 50 to 250  $^{\circ}\text{C}$ ), respectively. The viscosity of curing system (epoxy monomer and DDM) was measured (heating rate = 3  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , angular frequency = 1 Hz) using a Rheo Stress (RS150) rheometer (Haake, Germany). Thermogravimetric analyses (TGA) were conducted using a TG-209F1 TGA (Netzsch, Selb, Germany) at a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  ( $\text{N}_2$  atmosphere), and the temperature range was from 50 to 700  $^{\circ}\text{C}$ . Dynamic mechanical analysis (DMA) was conducted using a TA instrument (DMA Q800, America) at a heating rate of 3  $^{\circ}\text{C}\cdot\text{min}^{-1}$  (from 25 to 230  $^{\circ}\text{C}$ ). The dimensions of cured samples for measurement were 40  $\times$  10  $\times$  3.0 mm.

Tensile and flexural properties were analyzed based on ASTM D638-08 and ASTM D790-07, respectively, on an Instron-5967 universal electronic testing machine.

UL-94 vertical burning tests were conducted with a UL 94 flame chamber (Fire Testing Technology, UK) according to ASTM D3801-10 (sample dimension of 125 $\times$ 13 $\times$ 3 mm). Limiting oxygen index (LOI) tests were conducted using an oxygen index instrument (Fire Testing Technology, UK) according to ASTM D2863-97 (sample dimension of 150 $\times$ 6.5 $\times$ 3.2



mm). Cone calorimeter tests (CCT) were conducted using a FTT cone calorimeter according to ISO5660 (sample dimension of 100×100×5 mm).

Scanning electron microscopy (SEM) experiments were conducted with a NOVA NANOSEM 430 machine. The sample was sputter-coated with gold before testing. X-ray photoelectron spectrum (XPS) was conducted using a Axis Ultra spectrometer (Kratos, England). Thermogravimetry-Fourier transform infrared spectrometer (TGA-FTIR) tests were conducted with a STA449C/3MFC/G instrument (Bruker, USA) (N<sub>2</sub> atmosphere, heating rate = 20 °C/min).

### 3. Results and discussion

#### 3.1. Synthesis strategy

The renewable aromatic Schiff base epoxy monomer PH-ODA-EP is prepared from protocatechualdehyde, ODA and ECH in two steps illustrated in Fig. 1: (i) protocatechualdehyde reacts with ODA to obtain a Schiff base intermediate PH-ODA; (ii) PH-ODA reacts with ECH (obtained from the chlorination of biomass-derived glycerol [46]) to get a renewable epoxy monomer PH-ODA-EP. The above synthesis steps are simple and high-yield, which provides a feasible way for the scalable and sustainable production of bio-based epoxy thermosets.

The structures of the Schiff base compounds PH-ODA and PH-ODA-EP are verified using FT-IR (Fig. 2), <sup>1</sup>H and <sup>13</sup>C-NMR techniques (Fig. 3). As shown in the FTIR spectra of protocatechualdehyde, ODA, PH-ODA and PH-ODA-EP (Fig. 2), the absorption peaks at 3442 cm<sup>-1</sup> (N-H stretching) and 1672 cm<sup>-1</sup> (C=O stretching), which are respectively observed

in the spectra of ODA and protocatechualdehyde, disappear in PH-ODA and PH-ODA-EP spectra. Meanwhile, the absorption peak at  $1605\text{ cm}^{-1}$  (-OH stretching) appears in both spectra of protocatechualdehyde and PH-ODA. The above results demonstrate the successful synthesis of PH-ODA from protocatechualdehyde and ODA. Besides, the disappearance of the absorption peak at  $1605\text{ cm}^{-1}$  (-OH stretching) in PH-ODA spectrum and the appearance of the peak at  $974\text{ cm}^{-1}$  (C-O-C stretching of epoxy group) in PH-ODA-EP spectrum suggest that PH-ODA is successfully converted to PH-ODA-EP. The  $^1\text{H-NMR}$  spectra of the obtained PH-ODA and PH-ODA-EP are illustrated in Fig. 3. It is depicted that the actual chemical shifts of H atoms in the  $^1\text{H-NMR}$  spectra are in good agreement with the theoretical values from the PH-ODA and PH-ODA-EP structures. It is noted that PH-ODA-EP shows to be the mixture of oligomers and monomers according to the PH-ODA-EP spectrum, which is in accordance with the results of literature [47]. Therefore, PH-ODA and PH-ODA-EP are successfully synthesized by a facile and sustainable route.

### 3.2. Curing kinetics, viscosity and processability

The nonisothermal curing kinetics of the PH-ODA-EP/DDM and DGEBA/DDM curing systems are studied using DSC at various heating rates [48] and depicted in Fig. 4. It is visible that both PH-ODA-EP/DDM and DGEBA/DDM curing systems show one curing stage with an exothermic peak. The onset, peak, and endset cure temperatures ( $T_{\text{onset}}$ ,  $T_p$  and  $T_{\text{endset}}$ ), the complete cure temperature interval ( $\Delta T$ ), and total heat release during the complete cure process ( $\Delta H_{\infty}$ , determined by calculating the surface area under the DSC curves [49]) for PH-ODA-EP/DDM and DGEBA/DDM curing systems at five heating rates (2.5, 5, 10, 15 and

20 °C/min) are listed in Table 1. According to the investigated protocol for the cure analysis of thermosets [49], the curing process of PH-ODA-EP/DDM and DGEBA/DDM at five heating rates (2.5, 5, 10, 15 and 20 °C/min) was studied qualitatively by the use of *Cure Index (CI)* [43,44], which can be calculated according to the literature [42,45]. The *CI* values show that the cure behavior of PH-ODA-EP/DDM at different heating rates (2.5, 5, 10, 15 and 20 °C/min) belongs to the case of *Poor* cure compared with that of DGEBA/DDM (Table 1). According to the protocol from literature [42,43], diffusion is the main mechanism during the curing process of PH-ODA-EP/DDM. The early stage of curing reaction leads to the prematuration gelation of curing systems, which restricts the interaction between the polymer chains and curing agent. In this case, the curing reaction is mainly controlled by the diffusion ability of polymer chains and curing agent.

Kissinger's method is utilized for the calculation of the curing apparent activation energy [50]:

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

where  $\beta$  and  $R$  respectively represent the heating rate and the ideal gas constant.  $E_a$  and  $A$  represent the apparent activation energy and the pre-exponential factor, respectively.

The related results are calculated and showed in Fig. 5 and Table 1, which can be found that PH-ODA-EP/DDM curing systems possesses higher  $E_a$  (73.4 kJ·mol<sup>-1</sup>) than DGEBA/DDM curing systems (50.4 kJ·mol<sup>-1</sup>), indicating the lower reactivity of PH-ODA-EP/DDM curing systems compared with DGEBA/DDM [51]. This result is mainly caused by the larger molecular weight of PH-ODA-EP than that of DGEBA and the steric hindrance of PH-ODA-EP molecule [52]. In addition, the curing reaction is mainly controlled

by the diffusion ability of reagents according to the  $CI$  value of PH-ODA-EP/DDM curing systems [42,43].

The viscosity of epoxy curing systems is one of the major parameters that determines its end use due to the close relationship between viscosity and processing [53]. Fig. 6 illustrates the effect of temperature on the viscosity of PH-ODA-EP/DDM and DGEBA/DDM curing systems. As seen, the viscosity of PH-ODA-EP/DDM curing system is lower than that of DGEBA/DDM curing system in nearly the whole curing process, which indicates that PH-ODA-EP/DDM curing system is acceptable for processing.

### 3.3. Thermal stability

Fig. 7 depicts the TGA profiles of the cured resins PH-ODA-EP/DDM and DGEBA/DDM ( $N_2$  atmosphere), and corresponding results are collected (Table 2). As seen from Fig. 7 (a), the 5 wt% mass loss temperature ( $T_{5\%}$ ) of PH-ODA-EP/DDM is lower than DGEBA/DDM, which is probably due to the low bonding energy of imine bond (C=N) from PH-ODA-EP moieties [54]. In spite of that, the  $T_{5\%}$  of PH-ODA-EP/DDM is much higher than its glass transition temperature ( $T_g$ ) (see below). Different from DGEBA/DDM with one single degradation stage, PH-ODA-EP/DDM has two degradation stages according to the differential thermogravimetry (DTG) curve. The first degradation stage (280-350 °C) is mainly related to the early degradation of the Schiff base structure, which forms stable cross-linking networks and promotes the char forming [25]. The second degradation process (350-700 °C) is mainly attributed to the degradation of the epoxy matrix. Besides, the 50 wt% loss temperature ( $T_{max}$ ) of PH-ODA-EP/DDM is 89 °C higher than that of DGEBA/DDM (503

°C vs. 414 °C), showing that the early decomposition of Schiff base structure can inhibit the further thermal degradation of epoxy matrix. As depicted in Fig. 7 (b), the maximum degradation rate ( $R_{max}$ ) of PH-ODA-EP/DDM ( $5.1\% \cdot \text{min}^{-1}$ ) is far lower than DGEBA/DDM ( $31.3\% \cdot \text{min}^{-1}$ ) and the reduction is 83.7%, indicating that the PH-ODA-EP/DDM possesses an excellent inhibition effect over thermal degradation. More impressively, the char yield ( $Y_c$ ) of PH-ODA-EP/DDM reaches 41.7% at 700 °C, showing 182% higher than DGEBA/DDM (14.8%). The extremely low decomposition rate and high char yield of PH-ODA-EP/DDM mainly attribute to the introduction of Schiff base structure in PH-ODA-EP, which promotes the char forming during the degradation of epoxy matrix [26,55]. Besides, the compact aromatic structure in PH-ODA-EP molecule also contribute to the formation of char layer [56]. PH-ODA-EP/DDM possesses great potential for the application in fire-safe epoxy epoxy thermosets originated from its superior charring ability.

### 3.4. Fire-safety properties

Fire-safety properties are important properties for high performance epoxy thermosets used in many fields (i.e., aerospace and electronic industry) [57-59]. The limiting oxygen index (LOI) and vertical burning test (UL-94) are effective techniques for assessing the fire-safety properties of epoxy thermosets [60,61]. The results from the two measurements are collected in Table 3. It is seen that a UL-94 rating of V-0 (highest rating of fire-safety performance) is achieved for cured PH-ODA-EP/DDM using the vertical burning test. Conversely, the DGEBA/DDM system is unrated with melt-dripping. Moreover, the LOI analysis shows that the LOI value of PH-ODA-EP/DDM reaches 40.5%, which is far higher than DGEBA/DDM (23.5%). The above data proves that PH-ODA-EP/DDM displays

superior fire-safety properties, which is mainly from the excellent char formation ability from the Schiff base and aromatic structure in PH-ODA-EP molecule in the combustion process [25,26].

Cone calorimeter test (CCT) is utilized to further examine the fire-safety performance of PH-ODA-EP/DDM [62]. Fig. 8 depicts the heat release rate (*HRR*) and total heat release (*THR*) curves of cured epoxy thermosets, and the corresponding data (*THR*, time to ignition (*TTI*), and peak of *HRR* (*pHRR*)) are displayed in Table 4. It is generally known that *HRR* value (especially *pHRR*) is an important parameter that can be served as the main indicator of the fire-safety properties of materials [34]. It is found that the *pHRR* of DGEBA/DDM is up to  $1045.4 \text{ kW}\cdot\text{m}^{-2}$ , whereas PH-ODA-EP/DDM exhibits the *pHRR* value of  $95.3 \text{ kW}\cdot\text{m}^{-2}$ , the reduction is about 90.9%. Similarly, the reduction in *THR* for PH-ODA-EP/DDM is up to 72.0% compared with that of DGEBA/DDM ( $42.9 \text{ MJ}\cdot\text{m}^{-2}$  vs.  $153.2 \text{ MJ}\cdot\text{m}^{-2}$ ). These results clearly verify that the introduction of Schiff base structure can significantly enhance the fire-safety properties of epoxy matrix. According to the literature [25,26], Schiff base structure is cross-linkable at high temperature and forms stable cross-linking networks and char layer, which act as a protective layer to reduce the flammability. Besides, the *TTI* (18 s) of PH-ODA-EP/DDM is lower than DGEBA/DDM (50 s), which is ascribed to the early decomposition of Schiff base structure. The *TTI* results are in agreement with the TGA results. According to the literature [63], the performance of fire-safety properties (*Poor*, *Good*, or *Excellent*) for polymers can be qualitatively studied by the use of the universal *Flame Retardancy Index (FRI)*. The *FRI* is obtained from the results (*pHRR*, *THR*, and *TTI*) of CCT and is defined by the literature (listed in Table 4) [64]. As seen from Table 4, the *FRI* value

(14.1) of PH-ODA-EP/DDM is between 10 and  $10^2$ , which is the characteristic of *Excellent* performance [65]. The *Excellent FRI* value further proved the superior fire-safety properties of PH-ODA-EP/DDM with Schiff base structure.

### 3.5. TG-FTIR analysis of gas products

TG-FTIR is utilized to explore the gas-phase flame-retardant mechanism by detecting the gas products from the degradation process of PH-ODA-EP/DDM and DGEBA/DDM. Fig. 9 (a) and (b) show the FTIR spectra of gas products at initial degradation temperature (285 °C for PH-ODA-EP/DDM and 390 °C for DGEBA/DDM) and maximum degradation temperature (300 °C and 425 °C respectively for the first and second degradation stage of PH-ODA-EP/DDM and 405 °C for DGEBA/DDM), respectively. The gas products of DGEBA/DDM and PH-ODA-EP/DDM are analyzed as below: 1170  $\text{cm}^{-1}$  (ether compounds), 1503 and 1332  $\text{cm}^{-1}$  (aromatic compounds), 3658  $\text{cm}^{-1}$  (phenolic compounds), 2343 and 2302  $\text{cm}^{-1}$  ( $\text{CO}_2$ ), 3037 and 2960  $\text{cm}^{-1}$  (aliphatic hydrocarbon) [66]. Compared with the spectrum of DGEBA/DDM, there is a new peak (1031  $\text{cm}^{-1}$ ) belonging to nitrogen-containing compounds (C-N) in the spectrum of PH-ODA-EP/DDM [67], which plays an important role of gas-phase flame retardancy.

### 3.6. Char analysis

Fig. 10 depicts the photos of the char residues of cured epoxy thermosets (after CCT). As seen, the DGEBA/DDM char residue is fragile and only a little char is left due to its high flammability and poor charring property, which agrees with the TGA result of DGEBA/DDM. Conversely, the PH-ODA-EP/DDM char residue exhibits dense, strong and bulky intumescent structure, which acts as protective layer to well isolate heat and oxygen in combustion process.

The above phenomenon is mainly caused by the cross-linking of the Schiff base group in PH-ODA-EP in combustion, which promotes the formation of intumescent char and provides the superior fire-safety properties of PH-ODA-EP/DDM networks [25].

Fig. 11 depicts the morphology of char residues (PH-ODA-EP/DDM and DGEBA/DDM) obtained from SEM. It is clearly observed that there are many open holes in the char residue of DGEBA/DDM, and the char residue exhibits the cracks and fissures, which is unable to isolate heat and gaseous compounds during combustion. Conversely, the char residue of PH-ODA-EP/DDM shows the compact and continuous structure with some intumescent bubbles on the char surface. This specific compact structure is of great importance to the gas and heat insulation during combustion. The results are aroused by the cross-linkable Schiff base structure under high temperature [26], which forms dense char layer during combustion, providing the superior fire-safety properties of PH-ODA-EP/DDM.

Chemical components of the char residues of PH-ODA-EP/DDM and DGEBA/DDM are analyzed by XPS (Table 5). As seen, for PH-ODA-EP/DDM, the contents of C and N are respectively 85.67% and 4.23% in the char residues, which are higher than those (80.87% and 4.21%, respectively) of DGEBA/DDM. The results imply that the Schiff base structure in the PH-ODA-EP increase the proportion of C in char residue, which is because the Schiff base structure promotes the carbonization process via cross-linking reaction in combustion process [25,26]. The results are also in agreement with those of the above tests.

### 3.7. Thermomechanical and mechanical properties

In general, the introduction of flame retardant components into epoxy resins decreases other properties (thermomechanical and mechanical properties) [68,69]. Nevertheless,



PH-ODA-EP/DDM possesses superior fire-safety performance due to the intrinsic Schiff base structure, which is also beneficial to enhance the mechanical properties of epoxy networks [57,70]. DMA is conducted to investigate the thermomechanical performance of cured epoxy thermosets. Fig. 12 shows the temperature effect on the storage modulus and  $\tan\delta$  of the cured epoxy thermosets, and the corresponding parameters (storage modulus at room temperature ( $E'$  at 30 °C), cross-linking density ( $\nu_e$ ), and glass transition temperature ( $T_g$ )) are collected in Table 6. In Fig. 12 (a), PH-ODA-EP/DDM shows far higher  $E'$  compared with DGEBA/DDM in nearly the whole temperature range. Particularly at 30 °C, the  $E'$  of PH-ODA-EP/DDM reaches 6.01 GPa, which is 105.8% higher than DGEBA/DDM (2.92 GPa). The presence of the rigid Schiff base and aromatic structure in PH-ODA-EP molecule contributes to the high stiffness of PH-ODA-EP/DDM [71,72].

In Fig. 12 (b), the  $T_g$  (the temperature corresponding to the peak value in  $\tan\delta$  curve) of PH-ODA-EP/DDM is as high as 204.9 °C, which shows 42.8 °C higher than DGEBA/DDM (162.1 °C). In general,  $T_g$  is determined primarily by the cross-link density and the structure rigidity of polymer [73,74]. The rigid Schiff base and aromatic structure help to reduce molecular chain movements, and thus increase the  $T_g$  of epoxy networks. Although PH-ODA-EP/DDM possesses a lower cross-link density ( $3.82 \times 10^3 \text{ mol}\cdot\text{m}^{-3}$ , calculated based on the rubbery elasticity theory [50]) compared with DGEBA/DDM ( $5.04 \times 10^3 \text{ mol}\cdot\text{m}^{-3}$ ), the higher  $T_g$  of PH-ODA-EP/DDM is due to that rigidity effect is the primary factor affecting  $T_g$  in this work. In addition, the broader  $\tan\delta$  peak of PH-ODA-EP/DDM (compared with DGEBA/DDM) is mainly caused by the stronger intermolecular interactions in PH-ODA-EP/DDM, which restrict the movements of chain segments and thus require a

wider temperature range to trigger the chain mobility [75,76]. Moreover, the secondary relaxation is obviously observed (between 60 °C and 80 °C) in the  $\tan\delta$  curve of DGEBA/DDM (Fig. 12 (b)), which is attributed to the local motion of the polymer chains (i.e., the motion of hydroxyl and ether groups) [77,78].

The tensile and flexural properties of cured epoxy thermosets are displayed in Fig. 13. The tensile modulus and flexural modulus of PH-ODA-EP/DDM are 6.21 GPa and 5.04 GPa, which are respectively 87.0% and 84.6% higher than DGEBA/DDM. The results further prove the high stiffness of PH-ODA-EP/DDM. Moreover, compared with DGEBA/DDM, the tensile and flexural strength of PH-ODA-EP/DDM are respectively increased by 42.3% and 45.9%. The excellent mechanical properties of PH-ODA-EP/DDM are attributed to the introduction of rigid Schiff base and aromatic structure in PH-ODA-EP molecule [57,70]. In general, the synthesis of bio-based epoxy resins combining high mechanical properties and high  $T_g$  is the goal for high-performance epoxy resins [79,80]. In Fig. 13 (b), the  $T_g$  and flexural modulus of PH-ODA-EP/DDM and other biobased epoxy resins reported in the literature are collected [72,81-87]. In the present research, PH-ODA-EP/DDM network possesses the  $T_g$  of 204.9 °C, and its flexural modulus is as high as 5.04 GPa. As seen from Fig. 13 (b), PH-ODA-EP/DDM is located at the upper right region, which clearly proves the outstanding integrated performance of PH-ODA-EP/DDM.

Fig. 14 shows the morphology of the fracture surface of PH-ODA-EP/DDM and DGEBA/DDM obtained from SEM. For DGEBA/DDM, the fracture surface is homogeneous and smooth except for some cracks, indicating the typical brittle property of DGEBA/DDM [88]. The fracture surface of PH-ODA-EP/DDM is relatively rough and jagged. The jagged

surface could absorb more energy, which leads to an increase in the amount of energy and force for crack propagation and the formation of new surface [89-91].

#### 4. Conclusions

In this paper, we investigated a facile and sustainable route for preparing renewable Schiff base compounds PH-ODA and PH-ODA-EP. After cured with DDM, the Schiff base structure of PH-ODA-EP showed both excellent mechanical properties and fire-safety performance compared with DGEBA. The PH-ODA-EP/DDM possessed a char yield of 41.7% ( $N_2$  atmosphere), which was 182% than that of DGEBA/DDM (14.8%). PH-ODA-EP/DDM passed V-0 rating of UL94 test (LOI value = 40.5%), and showed a 90.9% and 72.0% decrease in pHRR and THR compared to DGEBA/DDM. Moreover, PH-ODA-EP/DDM showed excellent integrated properties with a storage modulus of 6.01 GPa (30 °C), a tensile modulus of 6.21 GPa, and a high  $T_g$  of 204.9 °C. All these results suggested that PH-ODA-EP possessed great potential to replace petroleum-derived DGEBA in various applications. By introducing Schiff base structure, a facile and effective strategy was proposed in this paper for simultaneously enhancing the mechanical properties and fire-safety properties of bio-based polymers.

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## Figure Captions

**Fig. 1** A sustainable route of renewable Schiff based compounds (PH-ODA and PH-ODA-EP).

**Fig. 2** FT-IR spectra of protocatechualdehyde, ODA, PH-ODA and PH-ODA-EP.

**Fig. 3** <sup>1</sup>H-NMR spectrum of (a) PH-ODA and (b) PH-ODA-EP.

**Fig. 4** Exothermic curves from DSC of (a) PH-ODA-EP/DDM and (b) DGEBA/DDM curing systems.

**Fig. 5** Linear plots of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  of PH-ODA-EP/DDM and DGEBA/DDM curing systems based on Kissinger's method.

**Fig. 6** Viscosity of PH-ODA-EP/DDM and DGEBA/DDM as a function of temperature.

**Fig. 7** (a) TGA and (b) DTG curves of cured epoxy thermosets in N<sub>2</sub>.

**Fig. 8** (a) HRR and (b) THR curves of cured epoxy thermosets.

**Fig. 9** The FTIR spectra of gas products of PH-ODA-EP/DDM and DGEBA/DDM at (a) the initial and (b) maximum degradation temperatures.

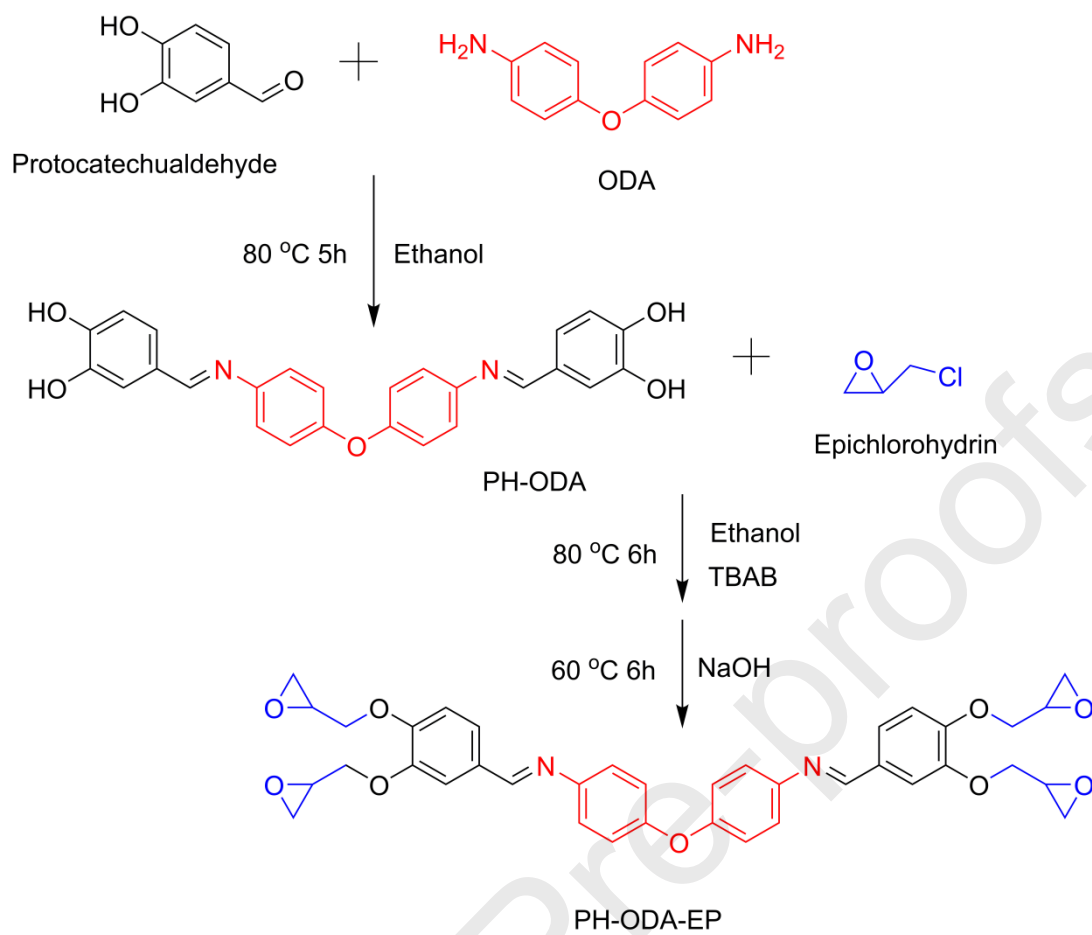
**Fig. 10** Digital photos of char residue of (a) PH-ODA-EP/DDM and (b) DGEBA/DDM after CCT.

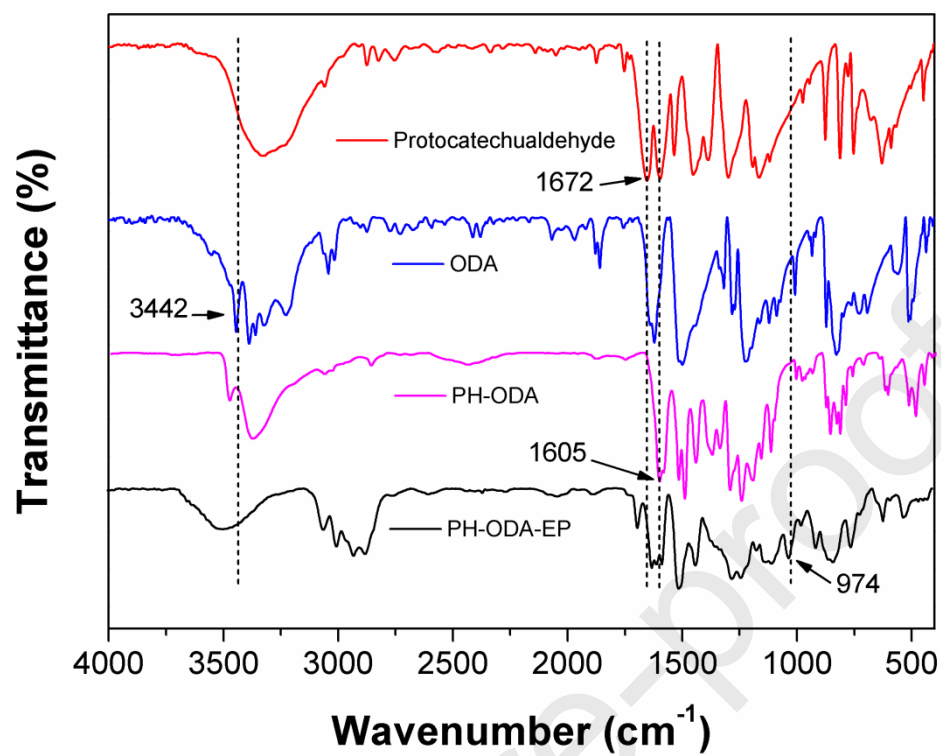
**Fig. 11** SEM photographs of (a) PH-ODA-EP/DDM and (b) DGEBA/DDM after CCT.

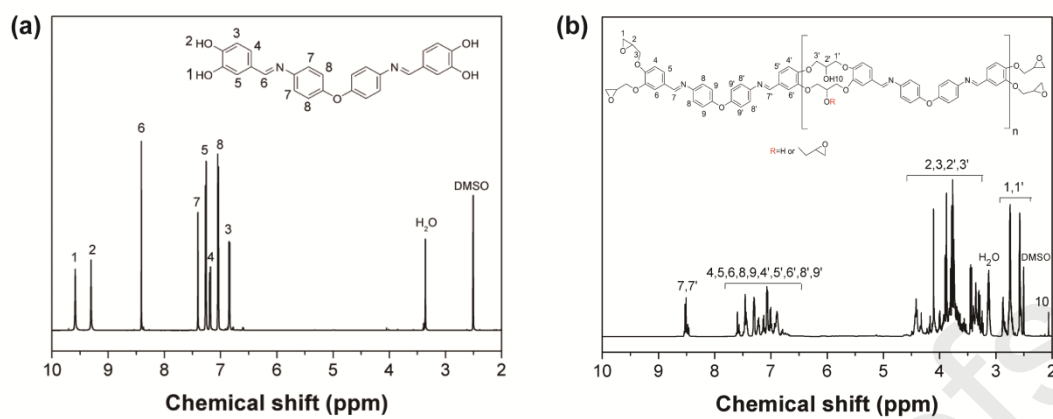
**Fig. 12** (a) Storage modulus (E') and (b) tan  $\delta$  curves for cured epoxy thermosets.

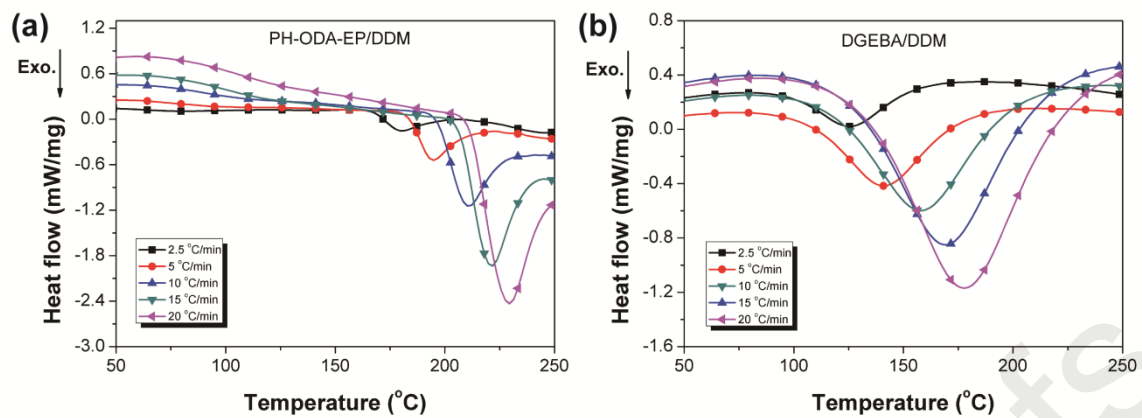
**Fig. 13** (a) Tensile and flexural properties of cured epoxy thermosets and (b) T<sub>g</sub> and flexural modulus of PH-ODA-EP/DDM and literature results.

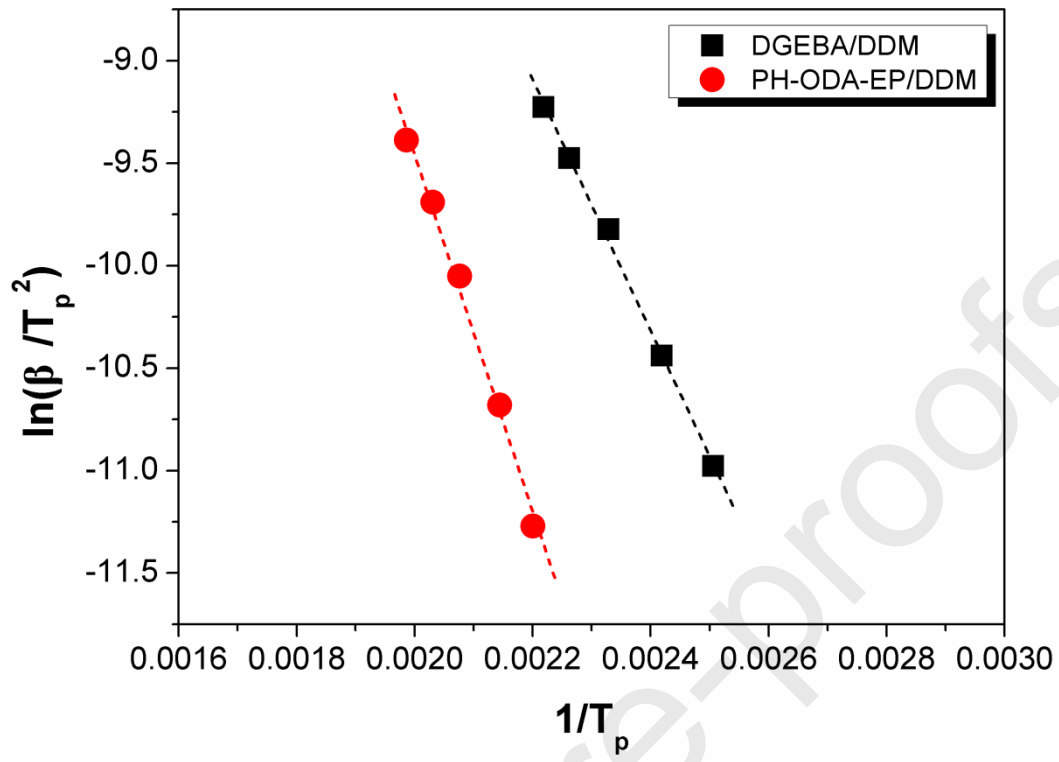
**Fig. 14** SEM photos of the fracture surfaces of (a) PH-ODA-EP/DDM and (b) DGEBA/DDM.

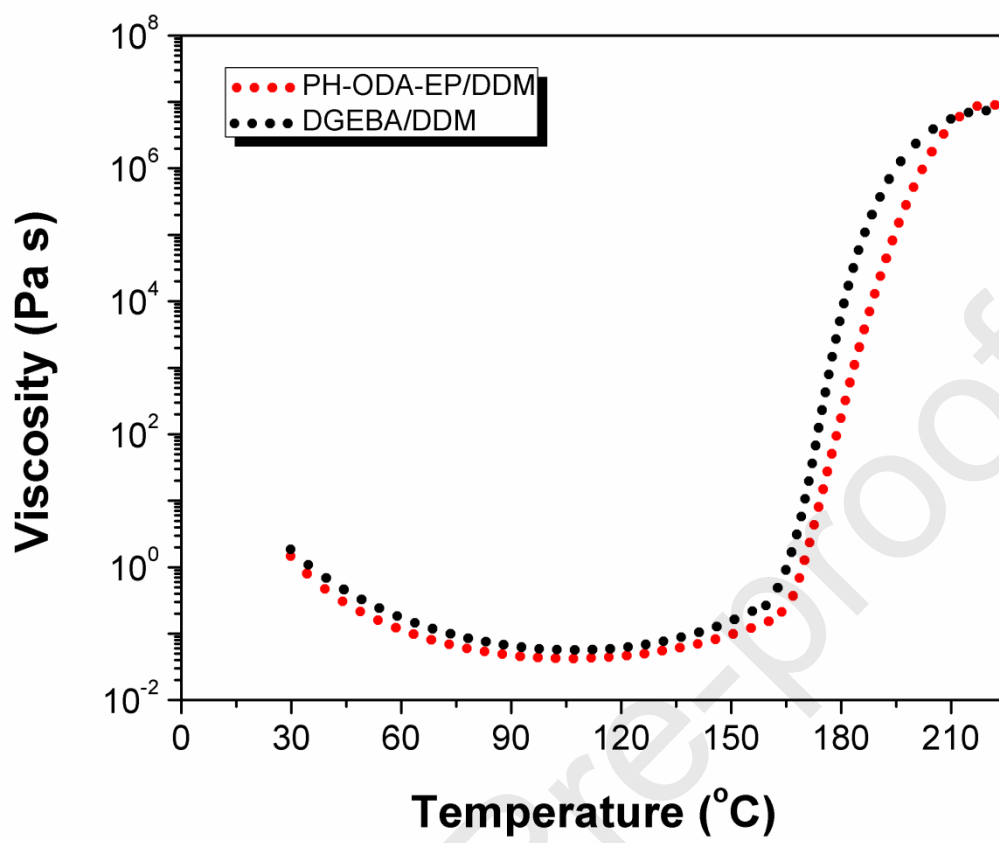


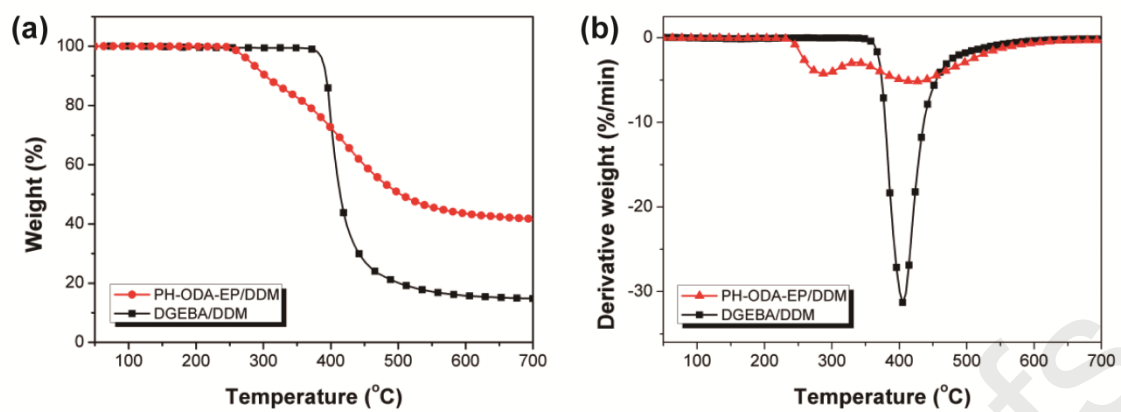




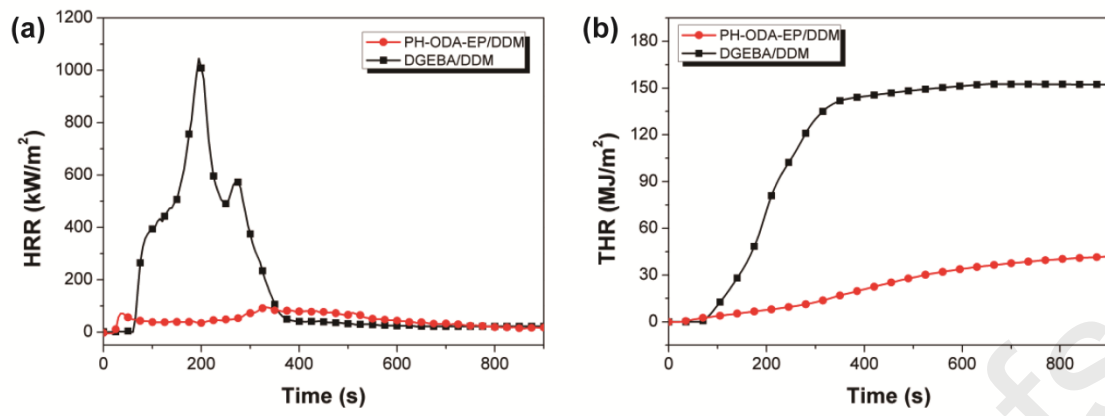


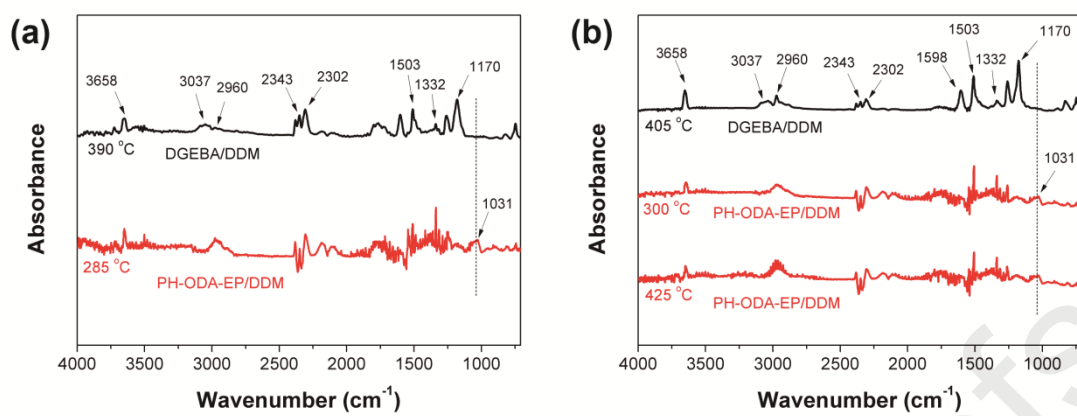


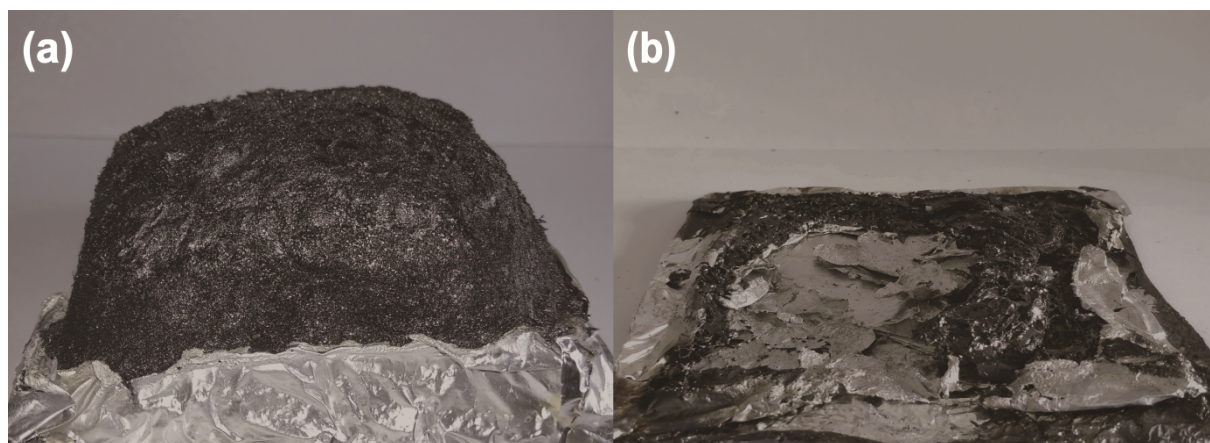




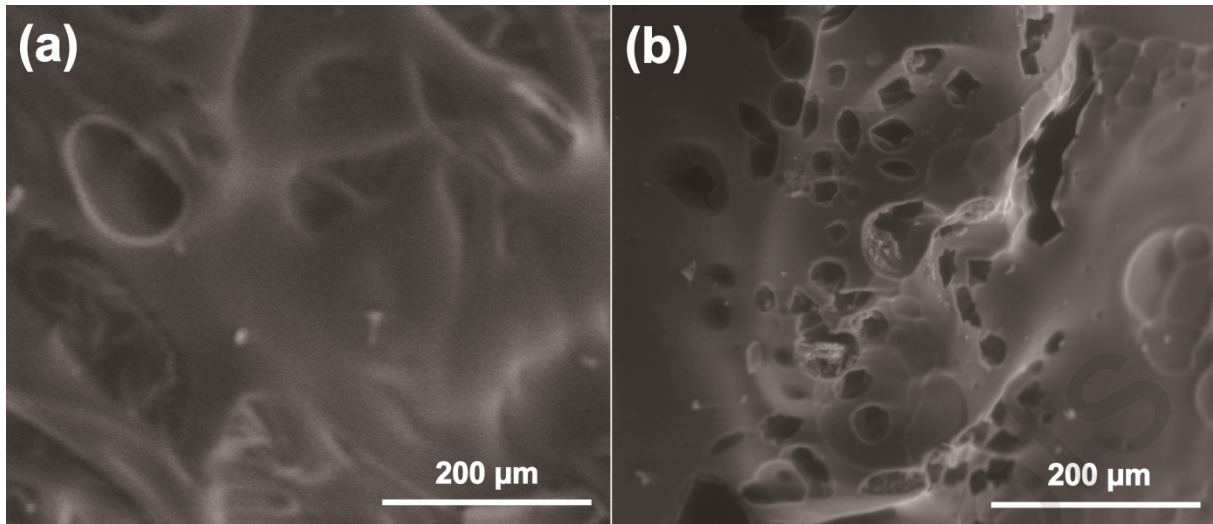


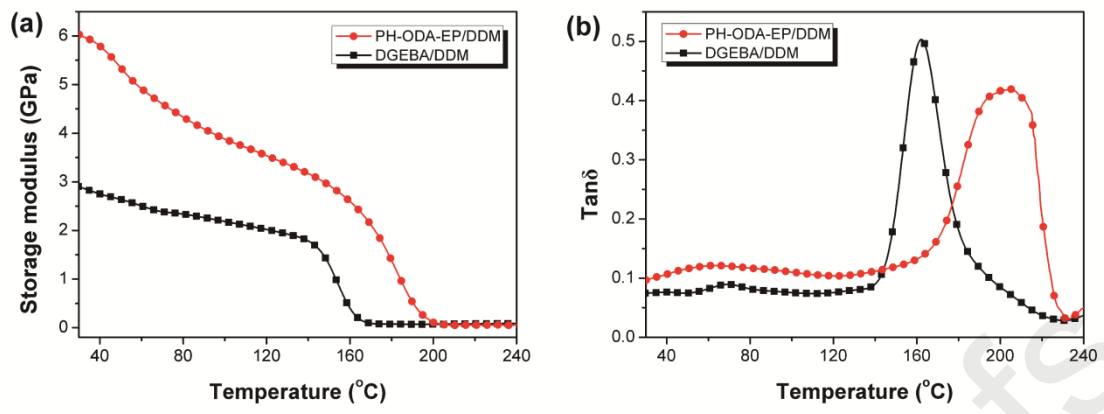


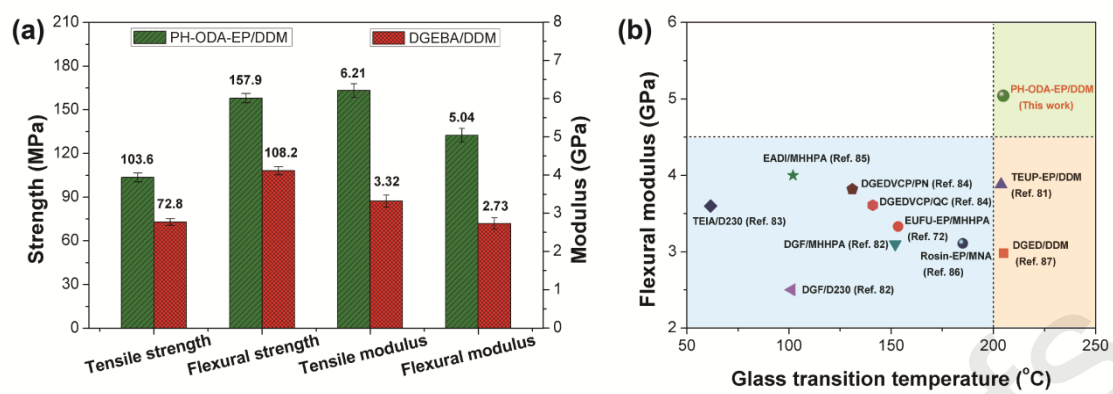


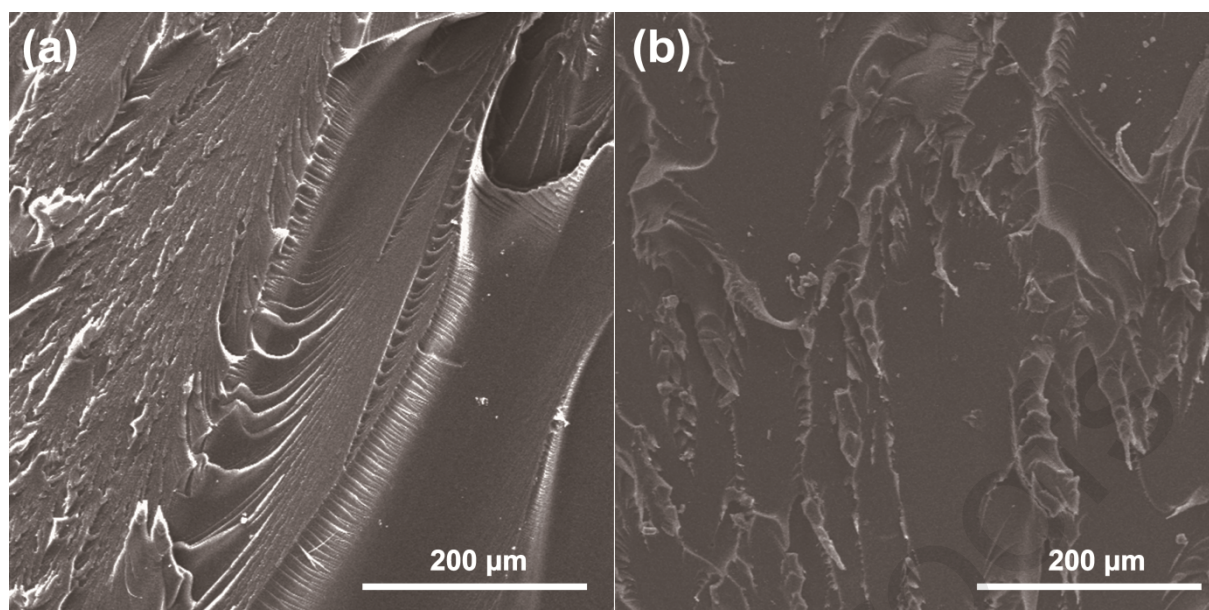


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## Tables

**Table 1** Cure characteristics of the PH-ODA-EP/DDM and DGEBA/DDM curing systems

Samples	Heating rate (°C/min)	$T_{onset}$ (°C)	$T_p$ (°C)	$T_{endset}$ (°C)	$\Delta T$ (°C)	$\Delta H_{\infty}$ (J·g <sup>-1</sup> )	$CI$	$E_a$ (kJ·mol <sup>-1</sup> )	$R^2$
DGEBA/ DDM	2.5	80.7	129.1	187.2	106.5	235.3	1.00	50.4	0.998
	5	84.1	140.3	206.5	122.4	258.2	1.00		
	10	92.5	156.3	234.7	142.2	295.7	1.00		
	15	94.2	168.9	256.6	162.4	301.5	1.00		
	20	98.3	177.6	273.2	174.9	292.5	1.00		
PH-ODA- EP/DDM	2.5	164.9	177.3	206.3	41.4	247.3	0.41	73.4	0.994
	5	177.6	194.2	219.5	41.9	237.4	0.35		
	10	191.3	210.4	233.5	42.2	241.2	0.24		
	15	199.3	221.3	246.1	46.8	277.1	0.27		
	20	204.8	229.3	253.2	48.4	265.1	0.25		

**Table 2** TGA and DTG data of the cured thermosets

Samples	$T_{d5\%}$ (°C)	$T_{d50\%}$ (°C)	$Y_c$ (%)	$R_{max}$ (%·min <sup>-1</sup> )
PH-ODA-EP/DDM	280.1	504.1	41.7	5.1
DGEBA/DDM	388.2	414.3	14.8	31.3

**Table 3** Results of UL-94 and LOI tests for cured epoxy thermosets

Samples	LOI (%)	$t_1+t_2$ (s)	Dripping	UL-94 rating
PH-ODA-EP/DDM	40.5	0.5±0.1	No	V-0
DGEBA/DDM	23.5	Last burning	Yes	No rating

**Table 4** CCT data for cured epoxy thermosets

Samples	TTI (s)	$pHRR$ (kW·m <sup>-2</sup> )	THR (MJ·m <sup>-2</sup> )	FRI
PH-ODA-EP/DDM	18	95.3	42.9	14.1
DGEBA/DDM	50	1045.4	153.2	1.0

**Table 5** XPS analysis of char residues after CCT

Samples	C (wt %)	O (wt %)	N (wt %)
PH-ODA-EP/DDM	85.67	10.19	4.23
DGEBA/DDM	80.87	14.92	4.21

**Table 6** Key parameters collected from DMA for cured epoxy thermosets

Samples	$E'$ at 30 °C (GPa)	$T_g$ (°C)	$\nu_e$ (10 <sup>3</sup> mol·m <sup>-3</sup> )
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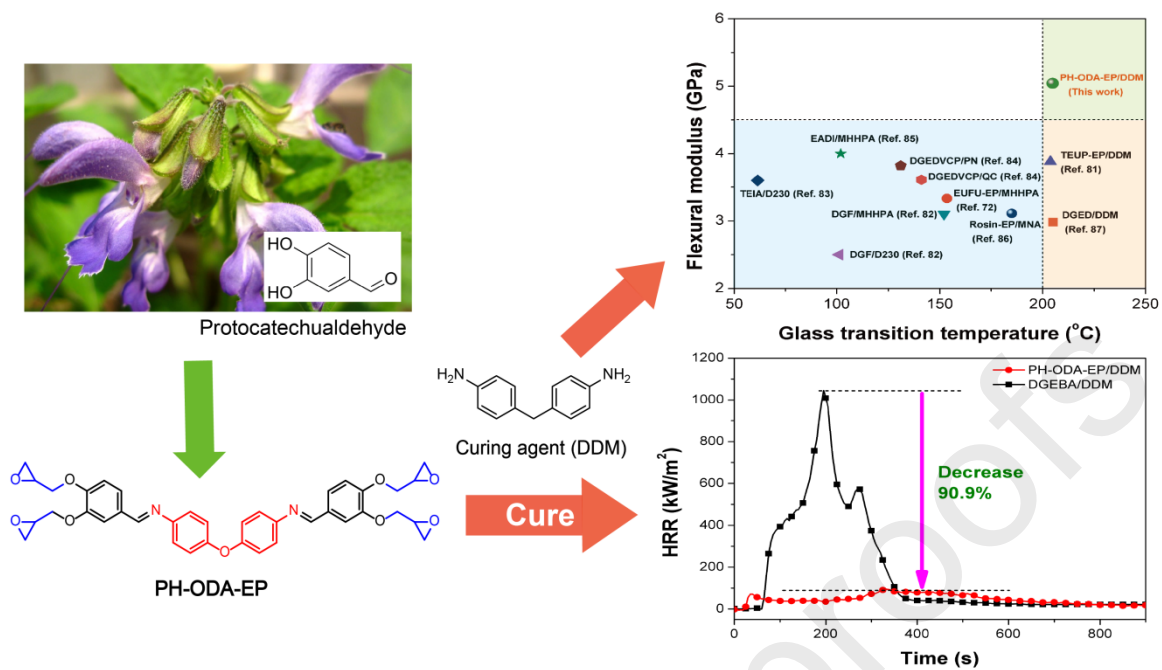
DGEBA/DDM	2.92	162.1	5.04
PH-ODA-EP/DDM	6.01	204.9	3.82

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**Declaration of interests**

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



## Highlights

- A novel biomass-derived epoxy thermoset was synthesized from Schiff base compound.
- Schiff base structure promotes char formation and reduces the fire hazards of epoxy thermoset.
- The new epoxy thermoset exhibits superior mechanical properties and high glass transition temperature.
- This paper provides a new strategy for simultaneously enhancing the mechanical properties and fire-safety performance.