



# A resveratrol-based epoxy resin with ultrahigh $T_g$ and good processability

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## ABSTRACT

Preparing and designing an epoxy system with ultrahigh glass transition temperature ( $T_g > 300$  °C) is always a big challenge, which restrict its applications in some cutting-edge areas such as aerospace engineering and electrical electronics. Herein, a biomass-based epoxy resin (REEP) was prepared from resveratrol, and then curing behavior, thermal-mechanical properties, mechanical performance, thermal stability, dielectric properties and optical properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were respectively studied systematically. Results suggested that the  $T_g$  of REEP/HDDM was above 320 °C, higher than those of most reported epoxy systems, both derived from biomass-based and petroleum-based materials. Moreover, the tensile strength of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were 77.8 MPa, 70.8 MPa and 63.6 MPa, respectively, and the  $T_{d5\%}$  of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were 319.9 °C, 335.1 °C and 348.1 °C, respectively, indicating excellent mechanical performance and thermal stability of the cured epoxy system. Interestingly, the REEP/HDDM exhibited outstanding blocking properties in the range of 220–400 nm (UV-light) and low flammability with compact and continuous char residues. In short, REEP, with a well-defined chemical structure, has a stiffness conjugated stilbene structure to prevent the molecular from motioning in the crosslinked network structure and three epoxy groups, thereby increasing the crosslinked density dramatically, which endows REEP/HDDM network with outstanding comprehensive properties.

## 1. Introduction

The epoxy resin, a typical thermosetting resin, is extensively applied in coating, adhesive, and composite materials, etc, due to its excellent mechanical performance, as well as good thermal stability and easy processability [1–3]. Epoxy resins are usually prepared from crosslinked reaction between resins (such as bisphenol A-based epoxy resins, bisphenol F-based epoxy resins and N, N-digly-Cidyl p-hydroxylaniline glycidyl ether, etc) and curing agents (such as isophorondiamine, 4,4'-diaminodicyclohexyl methane (HDDM), 4, 4-diaminodiphenylmethane (DDM) and diaminodiphenylsulfone (DDS), etc.) [4–6]. And of all the characteristic parameters of an epoxy resin, the  $T_g$  is significant one [7–9]. Generally, the higher  $T_g$  indicates wilder applications in frontier fields [10]. The  $T_g$  of the cured epoxy resin, however, is usually lower than 300 °C, which greatly limit its applications in aerospace engineering and electrical and electronics [11,12].

The  $T_g$  of cured epoxy resins, in fact, is related to its crosslinked density and stiffness of building blocks. Recently, many cured epoxy resins with relatively high  $T_g$  have been investigated. For instance, Wan

et al. [11] prepared a difunctional epoxy resin called TPEU-EP with melting point of 174.1 °C. TPEU-EP had a fully aromatic ester backbone (from rigid eugenol and terephthaloyl chloride) that could be cured by 33DDS, while the aromatic ester backbone (stiffness segment) did not lead to a high- $T_g$  network structure (168.4 °C), due to the low cross-linked density of TPEU-EP/33DDS compared with DGEBA/33DDS (174.4 °C). Besides, Dai et al. [13] prepared a daidzein-based epoxy resin called DGED with melting point of 70–80 °C. And the  $T_g$  of its DDM cured epoxy resin was 205 °C. In addition, Qi et al. [14] prepared a magnolol-based epoxy resin (DEEM) with allylic double bonds. And the  $T_g$  of its DDS cured polymer was up to 279 °C, due to the high cross-linked network and stiffness backbone. This  $T_g$  value was higher than the one of most epoxy systems reported previously, and the authors believed it was an ultrahigh value. And the chemical structures, curing agents,  $T_g$ s, tensile strength and  $T_{d5\%}$  for the epoxy resins systems previously reported are exhibited in Table 1. It can be found that all the  $T_g$  values reported are still lower than 300 °C. Meanwhile, the melting point of DDM and 33DDS used in previous work is up to 93 °C and 170 °C, respectively, resulting in poor processing properties in practical

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applications [6].

Resveratrol, derived from grape skin, peanut, and giant knot weed, etc., is a renewable biomass-based monomer [19,20]. Structurally, the resveratrol obtains three phenolic hydroxyl groups that give its ability of easy chemical modification. Furthermore, its stiff conjugated stilbene structure is expected to provide high heat resistance for the thermosetting resin prepared from resveratrol. Of some previous investigations, Cheng et al. [21] synthesized a resveratrol-based allyl compound (RAE), and the  $T_g$  of RAE/4SH was 71.2 °C. Froimowicz et al. [22] prepared a resveratrol-based benzoxazine resin (RES-fa). And the  $T_{gTMA}$  of a cured RES-fa was up to 312 °C, thanks to the high crosslinked density and rigid building block from resveratrol. Recently, Ao et al. [23] prepared a resveratrol-based epoxy oligomer (TGER) with low epoxide equivalent weight (EEW of 280 g·eq<sup>-1</sup>), while the  $T_g$  of TGER/DDM system (148 °C) was 21 °C lower than that of DGEBA/DDM system (169 °C). Previously,

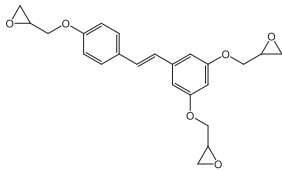
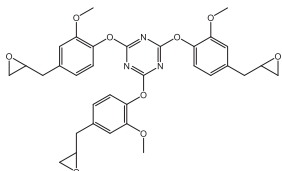
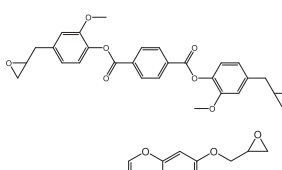
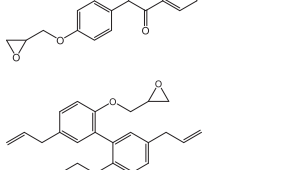
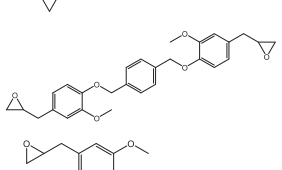
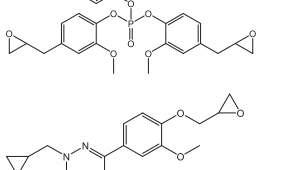
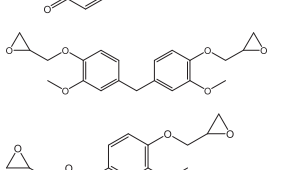
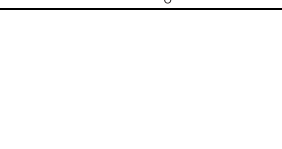
our group prepared a biomass-based epoxy resin with an EEW of 144 g·eq<sup>-1</sup> from the resveratrol (REEP) when it was cured by MeHHPA. And measured by DMTA, the epoxy polymer exhibited a very high  $T_g$  value of 210 °C, which was far higher than those of other reported epoxy/anhydride systems.

At present, few researches on the cured epoxy system with a  $T_g$  higher than 300 °C are reported because it is difficult and complicated to design and select an epoxy resin in which a stiff structure is able to prevent the building blocks motioning at temperature above 300 °C. And in consideration of practical applications, a low-melting-point epoxy and curing agent are needed as well, which could greatly enhance the processing performance of the cured epoxy.

In this work, we introduce low-melting-point curing agent (HDDM) into REEP to prepare a high crosslinked epoxy network with ultrahigh  $T_g$  (>320 °C) and acceptable processing performance. First, REEP was

**Table 1**

Chemical structures, curing agents,  $T_g$ s, tensile strength and  $T_{d5\%}$  for the synthesis of previous studied epoxy resins systems.

Name	Chemical structure	Curing agent	$T_g$ (°C)	Tensile strength (MPa)	$T_{d5\%}$ (°C)	Ref
REEP		HDDM	>320	77.8	319.9	This work
TEU-EP		33DDS	203	–	325.3	[8]
TPEU-EP		33DDS	168.4	–	338	[11]
DGED		DDM	205	83	335	[13]
DGEM		44DDS	279	–	402	[14]
DEU-EP		DDM	114.4	–	341	[15]
TEUP-EP		DDM	203.7	–	320.3	[16]
GSPZ-EP		DDM	187	63.5	331	[17]
DGEBG		HDDM	111	–	–	[18]
DGEVA		HDDM	107	–	341	

synthesized based on our previous investigations [4]; second, the curing behavior of REEP/HDDM and DGEBA/HDDM were respectively investigated by DSC; third, thermal–mechanical properties, as well as mechanical performance and thermal stability of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were respectively studied; finally, the functional properties of REEP/HDDM, including dielectric properties, optical properties and low flammability, were further investigated. Thus, the epoxy system (REEP/HDDM) with ultrahigh  $T_g$  is prepared from the resveratrol. We believe this kind of epoxy system will have a wide range of potential applications in cutting-edge areas such as aerospace engineering and electrical electronics.

## 2. Experimental

### 2.1. Materials

The resveratrol-based epoxy resin (shorted as REEP, equivalent epoxy weight of  $144 \text{ g}\cdot\text{mol}^{-1}$ ) was synthesized in our laboratory [4]; DGEBA (trade name CYD128, EEW:  $192 \text{ g}\cdot\text{mol}^{-1}$ ) was purchased from SINOPEC Baling Company; curing agent 4,4'-diaminodicyclohexylmethane (HDDM) was purchased from Aladdin Reagent (Shanghai) Co.

### 2.2. Preparation of the cured epoxy system

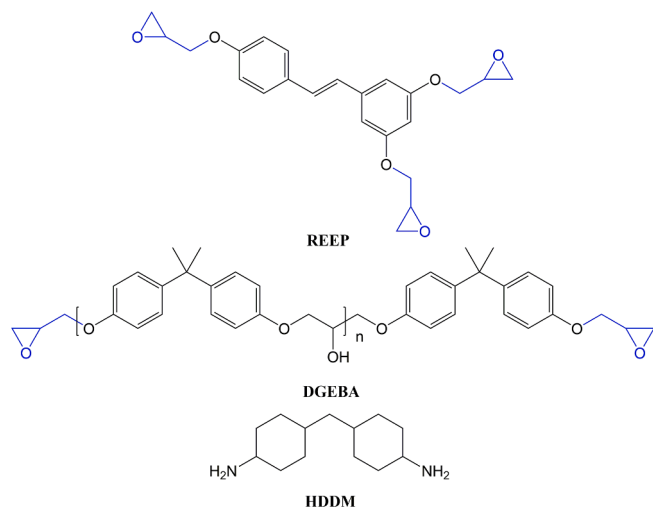
The comparison is carried out with the system of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM (Scheme 1). Relative contents of different resins and curing agents are measured as stoichiometric ratio listed in Table 2. The curing conditions of epoxy/amine system are respectively:  $100^\circ\text{C}$  for 2 h,  $150^\circ\text{C}$  for 2 h and  $200^\circ\text{C}$  for 2 h.

### 2.3. Characterization

FTIR analysis were performed on the Bruker Alpha (Germany). The sample was coated on the KBr pellet with 32 times scanned, and the resolution ratio and the wavenumber range of Bruker Alpha is  $4 \text{ cm}^{-1}$  and  $4000\text{--}400 \text{ cm}^{-1}$ , respectively.

A TA Instrument Q20 DSC was applied to investigate the non-isothermal curing reaction of REEP/HDDM system and DGEBA/HDDM system. The fresh epoxy system roughly 5 mg was sealed in a DSC crucible, and the sample was heated from  $0^\circ\text{C}$  to  $300^\circ\text{C}$  at a heating rate of 5, 10, 15 and  $20^\circ\text{C}\cdot\text{min}^{-1}$  respectively in dry nitrogen at once.

The dynamic mechanical performance of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were respectively tested by using a TA Instruments (DMTA Q800) in a tensile films model from  $25^\circ\text{C}$  to target temperature at a heating rate of  $3^\circ\text{C}\cdot\text{min}^{-1}$  with a constant



Scheme 1. Main chemical structures employed in our work.

Table 2

Formulation of the epoxy/amine system (mass ratio).

Epoxy/amine system	Resin		Curing agent
	REEP	DGEBA	
REEP/HDDM	10	–	3.65
REEP/DGEBA/HDDM	5	5	3.19
DGEBA/HDDM	–	10	2.73

frequency of 1 Hz.

The mechanical performance of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM was respectively performed by applying a Shimadzu AUTOGRAPH at a rate of  $10 \text{ mm}\cdot\text{min}^{-1}$ .

The thermal–mechanical performance of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were respectively confirmed by a TA Instruments Q400 at a heating rate of  $3^\circ\text{C}\cdot\text{min}^{-1}$  in  $\text{N}_2$  atmosphere.

The light transparency of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM films with the thickness of 200  $\mu\text{m}$  were respectively tested by a UV–vis spectrophotometer (UV-3600) ranging from 220 nm to 800 nm.

The thermal stability of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM were respectively tested by the NETZSCH TG 209C (Germany) from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  in  $\text{N}_2$  ( $10 \text{ mL}\cdot\text{min}^{-1}$ ) at the heating rate of 10, 20, 30 or  $40^\circ\text{C}\cdot\text{min}^{-1}$ .

The morphological structure of the carbon layer of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM after combustion were observed by a SEM (S7800). The carbon layer was coated by gold before being observed.

The Limited oxygen index (LOI) of cured epoxy resins was confirmed by a COI oxygen Indicator, and the dimension of sample was  $130 \times 6.5 \times 3.5 \text{ mm}^3$  according to GB/T 2406.2–2009.

The combustion properties of cured epoxy resin were performed on a cone calorimeter under a heat flux of  $50 \text{ kW}\cdot\text{m}^{-2}$ , and the dimension of sample was  $100 \times 100 \times 3 \text{ mm}^3$ .

## 3. Results and discussions

### 3.1. Processability and thermal properties of REEP

The melting point and crystallization properties of REEP are shown in Fig. 1. According to the DSC curves for REEP (Fig. 1a), an obvious endothermic melting peak appears in a relatively low temperature range ( $52\text{--}82^\circ\text{C}$ ) during the heating process, while there is no exothermic peak during the cooling process. And the enthalpies of REEP during the heating process is relatively low ( $49.5 \text{ J}\cdot\text{g}^{-1}$ ). Besides, the REEP becomes a supercooling liquid when the temperature is lower than its melting point, which is favorable for its processability and curing process. The crystallization behavior of REEP and resveratrol are respectively shown in Fig. 1b and supporting information S1. As shown in Fig. 1b, the crystallization peaks of REEP are unsophisticated and simple compared with those of resveratrol. As far as we know, because its molecules are bounded together by very strong hydrogen bonds and intermolecular forces (like  $\pi\text{--}\pi$  interactions), the resveratrol possess high melting point ( $223\text{--}226^\circ\text{C}$ ), which greatly limits its applications in the biological medicine, health products and maquillage products. When the resveratrol is epoxidated, however, the strong hydrogen bonds are destroyed and thereby a supercooling phenomenon and relatively low melting point of REEP generated. The result indicates that REEP is a biobased epoxy resin with solid state at room temperature, which is beneficial to the transportation and storage. Besides, the low melting point and supercooling phenomenon of REEP is good for its processing and applications.

The miscibility of the REEP-DGEBA is displayed in Fig. S2, it can be found that the mixture of REEP/DGEBA is a transparent liquid with primrose yellow, suggesting the good miscibility of REEP and DGEBA.

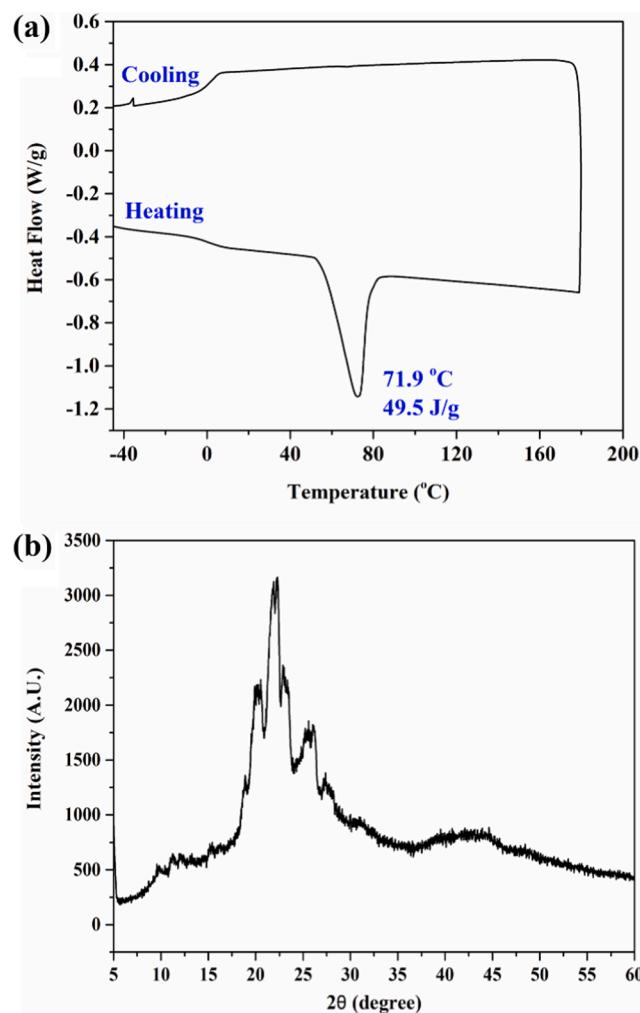


Fig. 1. Melting point (a, DSC curves) and crystallization properties (b, XRD curve) of REEP.

### 3.2. Non-isothermal model-fitting kinetics

The non-isothermal DSC curves for REEP/HDDM and DGEBA/HDDM system at a heating rate of 5, 10, 15 and 20 °C·min<sup>-1</sup> are respectively exhibited in Fig. 2. And relevant data on REEP/HDDM and DGEBA/HDDM are collected in Table 3. The initial curing temperature ( $T_i$ , at a heating rate of 10 °C min<sup>-1</sup>) of REEP/HDDM and DGEBA/HDDM are 59.7 and 60.4 °C, respectively. The peak curing temperature ( $T_p$ ) of REEP/HDDM and DGEBA/HDDM are respectively 101.1 and 116.6 °C. And it can be found that the  $T_p$  of REEP/HDDM is lower than that of DGEBA/HDDM at a heating rate of 10 °C·min<sup>-1</sup>, due to the higher concentration of epoxy functional groups and amidogen groups in REEP/HDDM system versus those in DGEBA/HDDM system. The fact that REEP/HDDM system has higher concentration of amidogen groups may accelerate the reaction between epoxy groups and active hydrogen at low relatively temperature.

The FTIR curves for REEP and REEP/HDDM are exhibited in Fig. 3. From Fig. 3, the peaks at 1459, 1504, and 1604 cm<sup>-1</sup> correspond to the aromatic nucleus [24]; the peaks at 912 cm<sup>-1</sup> match up with stretching vibration of functional groups for epoxy [25]; and the peaks at 965 cm<sup>-1</sup> is attributed to the characteristic absorption for the trans-stilbene. After the reaction between epoxy groups and —NH, the peaks for the epoxy groups cannot be observed, and the broad peaks at 3430 cm<sup>-1</sup> corresponding to the —OH can be found, indicating complete reaction between the epoxy groups and curing agent.

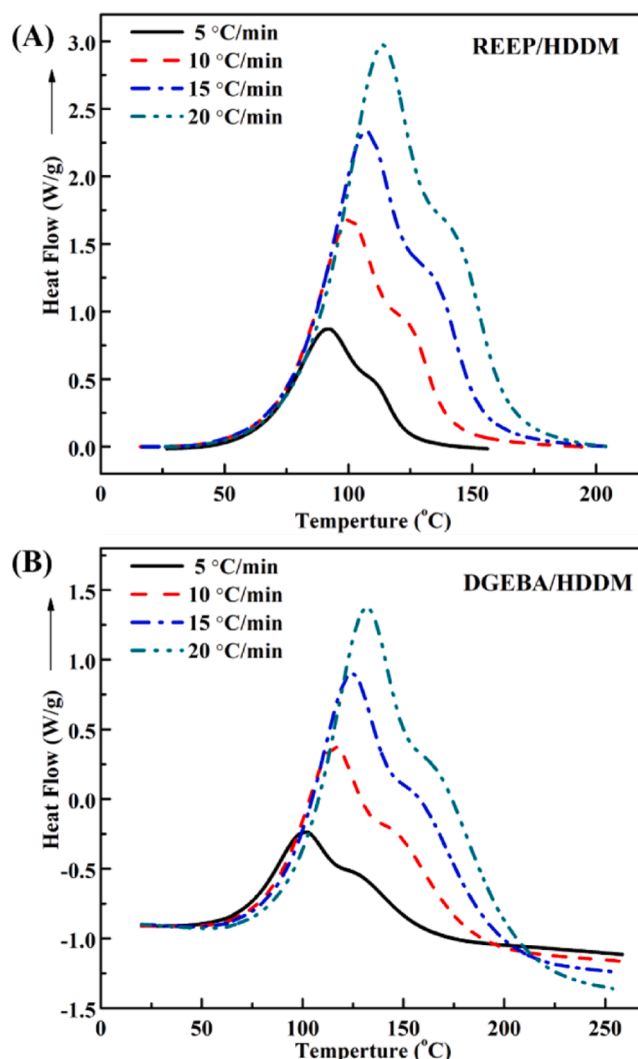


Fig. 2. DSC curves for (A) REEP/HDDM and (B) DGEBA/HDDM at a heating rate of 5, 10, 15 and 20 °C·min<sup>-1</sup>, respectively.

Table 3

Parameters from DSC curves at a heating rate of 5, 10, 15 and 20 °C min<sup>-1</sup>, respectively.

System	$\beta$ /°C·min <sup>-1</sup>	$T_i$ /°C	$T_p$ /°C	$T_f$ /°C
REEP/HDDM	5	55.6	87.2	120.8
	10	59.7	101.1	138.6
	15	63.7	107.6	149.1
	20	72.0	115.2	155.9
DGEBA/HDDM	5	46.3	104.2	156.4
	10	60.4	116.6	173.4
	15	71.3	123.7	179.4
	20	76.9	132.1	188.8

### 3.3. Dynamic mechanical properties of the cured epoxy resins

The dynamic mechanical properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems were respectively investigated by a DMTA measurement. The storage modulus ( $E'$ ) and  $\tan \delta$  versus temperature for REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems are shown in Fig. 4, and the relevant data are collected in Table 4. As shown in Fig. 4a, the  $E'$  of REEP/DGEBA/HDDM and DGEBA/HDDM system are related to temperature. Specifically speaking, the  $E'$  at 25 °C of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM

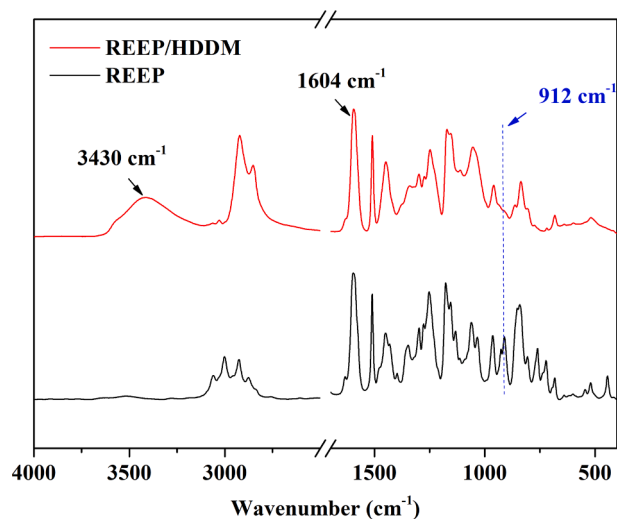


Fig. 3. FTIR curves for REEP and REEP/HDDM.

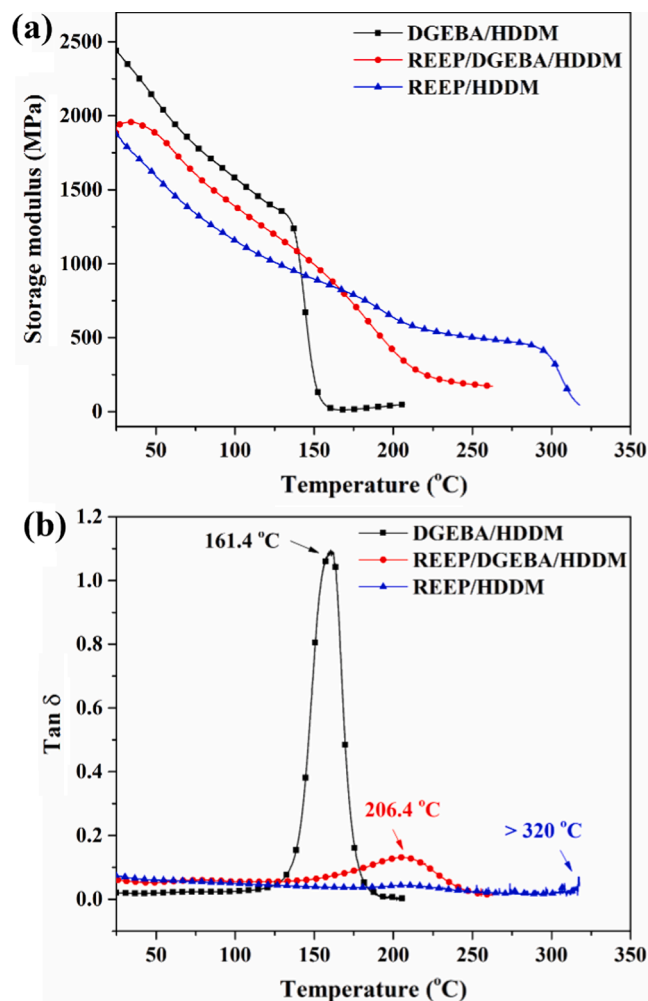


Fig. 4. DMTA curves for REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems: (a) Storage modulus ( $E'$ ); (b)  $\tan \delta$  curves.

HDDM systems are 1864 MPa, 1928 MPa and 2445 MPa, respectively. A sharp drop of  $E'$  can be found in the transition region from glass state to rubber state, as the temperature increases. And as for REEP/HDDM system, the transition region from glass state (427.9 MPa, 292.0 °C) to

Table 4

Crosslinking density of REEP/HDDM and REEP/DGEBA/HDDM systems.

System	$T_{gDMA}/$ °C	$E'$ at 25 °C/ MPa	$E'$ at 200 °C/ MPa	$E'$ at 300 °C/ MPa	$T_{gTMA}/$ °C
REEP/ HDDM	>320.0	1864	637.4	363.0	149.4
REEP/ DGEBA/ HDDM	206.4	1928	407.3	–	187.5
DGEBA/ HDDM	161.4	2445	40.6	–	301.9

rubber state (49.6 MPa, 317.1 °C) can be observed, indicating higher heating resistance of REEP/HDDM system compared with those of REEP/DGEBA/HDDM and DGEBA/HDDM system.

The  $\tan \delta$  curves for REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems are displayed in Fig. 4b. The  $T_{gDMA}$  of REEP/DGEBA/HDDM and DGEBA/HDDM system are 161.4 and 206.4 °C, respectively. And the precise  $T_{gDMA}$  value for REEP/HDDM cannot be determined, because the REEP/HDDM begins to degrade when the temperature reaches up to above 320 °C.

To further investigate thermal properties of cured epoxy system, TMA curves for REEP/HDDM and DGEBA/HDDM are exhibited in Fig. 5, and thus the  $T_{gTMA}$  of the cured epoxy system is calculated. From Figs. 5 and S3, the  $T_{gTMA}$  of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are 301.9 °C, 187.5 °C and 149.4 °C, respectively, which is consistent with the DMA results, indicating excellent

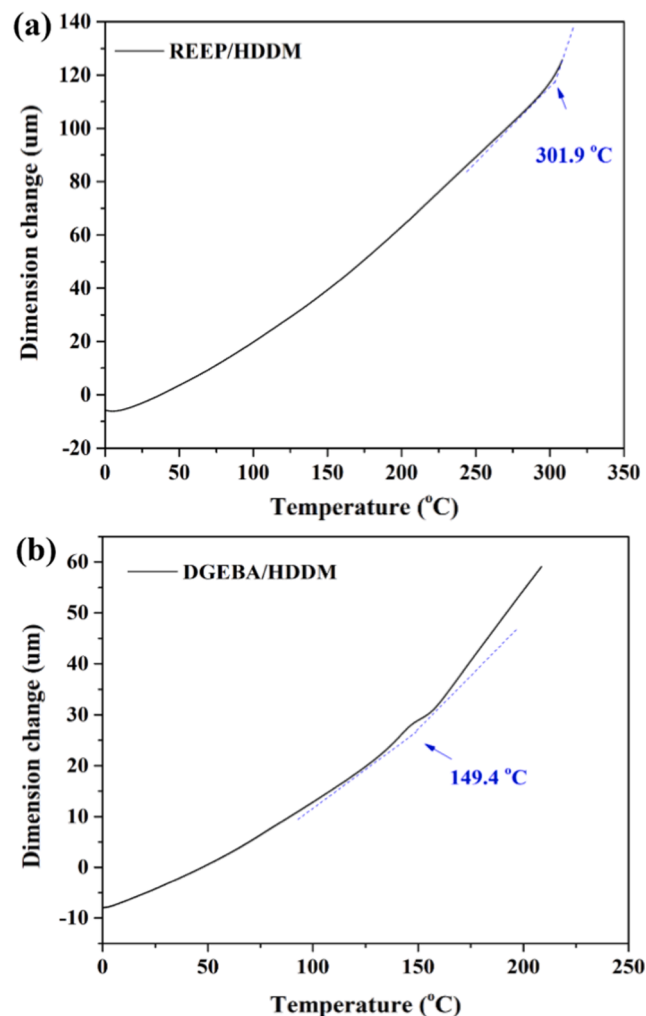


Fig. 5. TMA curves for (a) REEP/HDDM and (b) DGEBA/HDDM.

thermal–mechanical properties of REEP/HDDM.

Actually,  $T_g$  is a fundamental characteristic of the epoxy resins in practical applications. The  $T_g$ s of reported epoxy resins are exhibited in Table S1, Table 1 and Fig. 6. It can be found that the  $T_g$  of REEP/HDDM is higher than 320 °C, which is rarely researched in a precious study. Therefore, it can be believed that this kind of epoxy resin system will have a wide range of potential applications in cutting-edge areas such as aerospace engineering and electrical electronics.

### 3.4. Mechanical properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM

The mechanical performance is usually an important parameter for materials performance in practical applications. Table 5 shows the mechanical properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM. The REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM exhibit a typical brittle fracture behavior, due to the high crosslinked density of cured epoxy systems. The tensile strength of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are 77.8 ± 18.9, 70.8 ± 15.9 and 63.6 ± 9.3 MPa, respectively. Meanwhile, the REEP/HDDM exhibits the highest tensile strength in the cured epoxy system. And the tensile modulus of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are respectively 2.5 ± 0.2, 2.5 ± 0.1 and 2.3 ± 0.1 GPa. In addition, the tensile strain of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are 4.5% ± 1.5%, 3.5% ± 0.7% and 3.7% ± 1.0%, respectively. Thus, the REEP/HDDM, due to its remarkable mechanical properties, has huge applications in building materials and electrical and electronic materials, etc.

### 3.5. Thermal stabilities of the cured epoxy resins

TGA in  $N_2$  atmosphere was performed to confirm the thermal stability of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM. And TGA curves of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM at heating rate of 10 °C·min<sup>-1</sup> are displayed in Fig. S4. From Fig. S4a, the temperature corresponding to 5%, 15%, and 30% weight loss of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM system are listed in Table 6. The  $T_{d5\%}$  of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM system are respectively 319.9 °C, 335.1 °C and 348.1 °C, indicating good thermal stabilities of the cured epoxy resins. And the temperature corresponding to maximum thermal decomposition rate of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems are respectively 340.2 °C, 358.8 °C and 368.8 °C. And the carbon residue rate of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are respectively 12.4%, 9.4% and 4.2%, suggesting potential flame-retardant properties of REEP/HDDM.

**Table 5**

Mechanical properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM.

System	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile strain (%)
REEP/HDDM	77.8 ± 18.9	2.5 ± 0.2	4.5 ± 1.5
REEP/DGEBA/HDDM	70.8 ± 15.9	2.5 ± 0.1	3.5 ± 0.7
DGEBA/HDDM	63.6 ± 9.3	2.3 ± 0.1	3.7 ± 1.0

**Table 6**

Thermal stability parameters for the cured REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems at the heating rate of 10 °C min<sup>-1</sup>.

Sample	$T_{d5\%}$	$T_{d15\%}$	$T_{d30\%}$	$T_s$	Char yield (%)	IPDT	LOI (%)
REEP/HDDM	319.9	334.86	347.83	165.0	12.4	553.8	24.3
REEP/DGEBA/HDDM	335.1	347.70	358.44	171.1	9.4	508.1	22.8
DGEBA/HDDM	348.1	359.35	369.04	176.7	4.2	438.5	21.0

Moreover, the curves for residual weight percentage and derivative residual weight percentage versus temperature at heating rate of 10, 20, 30 and 40 °C·min<sup>-1</sup> are showed in Fig. 7. From Fig. 7-(c), we can find that the  $T_{max}$  increases with the heating rate increases, because there is not enough time for degradation, leading to the DTG curves will move to high temperature to compensate for the reduced time [26].

The temperature index ( $T_s$ ) is used to indicate the long-term service temperature of the thermosetting material, and can also be used as a parameter to characterize the thermal stability of the material. It can be calculated by the following formula [27]:

$$T_s = 0.49(0.4T_{5\%} + 0.6T_{30\%})$$

The  $T_s$  of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are respectively 165.0 °C, 171.1 °C and 176.7 °C. The integral procedural decomposition temperature (IPDT) and activation energy for the decomposition ( $E_a$ ) are usually used as a parameter to assess the lifetime of a material. The IPDT can be calculated as follow [28]:

$$IPDT = A^* \times K^* \times (T_f - T_i) + T_i$$

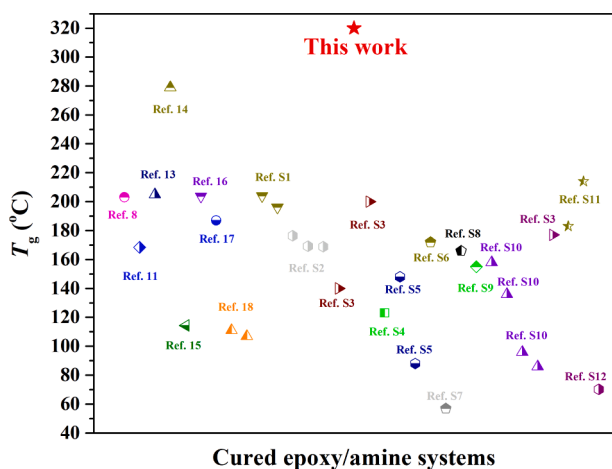
$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3}$$

$$K^* = \frac{S_1 + S_2}{S_1}$$

where  $A^*$  equals to ratio of test area to TGA curve area;  $K^*$  is coefficient of correction;  $T_f$  is the temperature value of terminated TGA test;  $T_i$  is the initial temperature value for the TGA test; the calculation method of  $S_1$ ,  $S_2$  and  $S_3$  is shown in Fig. S11. The IPDT of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are respectively 553.8, 508.1 and 438.5, indicating that with the content of REEP increasing, the lifetime of a material increases.

To further investigate degradation properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM, the Kissinger method is applied to calculate activation energy activation energy of cured epoxy resins, and Eq. (3) is as follows [29]:

$$\frac{d \left[ \ln \left( \frac{\beta}{T_m} \right) \right]}{d \left( \frac{1}{T_m} \right)} = \frac{-E_a}{R}$$



**Fig. 6.** The  $T_g$  of cured epoxy/amine systems.

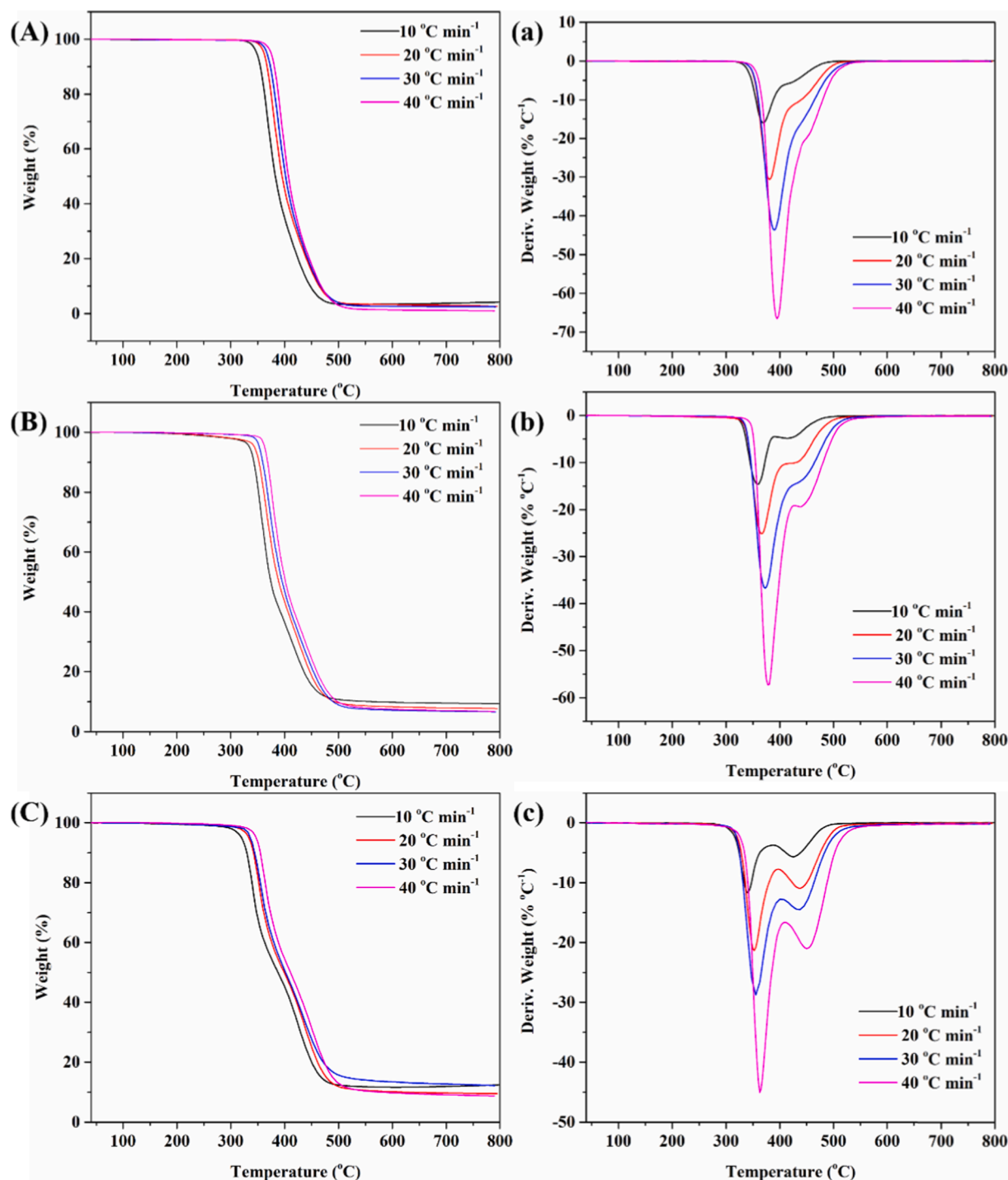


Fig. 7. TGA plots of residual weight percentage (A, B and C) and derivative residual weight percentage (a, b and c) versus temperature for DGEBA/HDDM, REEP/DGEBA/HDDM and REEP/HDDM systems at the heating rate of 10, 20, 30 and 40 °C·min<sup>-1</sup>.

where the  $\beta$  and  $T_m$  is heating rate and peak degradation temperature, respectively. The value of  $E_{\alpha}$  in A and R is exhibited in Table S2. And the Kissinger method of  $\ln(\beta/T_m^2)$  versus  $1/T_m$  for cured epoxy systems is exhibited in Fig. S5. Under thermal degradation process, crosslinked network requires energy for destroying the chemical construction. The  $E_{\alpha}$  of DGEBA/HDDM, REEP/DGEBA/HDDM and REEP/HDDM is 181.61 kJ/mol, 222.30 kJ/mol and 181.08 kJ/mol, respectively.

### 3.6. Flame retardancy of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM

The SEM images of DGEBA/HDDM, REEP/DGEBA/HDDM and REEP/HDDM after combustion are present in Fig. 8. It can be found that, after combustion, DGEBA/HDDM exhibits a carbon layer with loosed round sphere which is discontinuous, indicating that the heat and oxygen accelerate the combustion of DGEBA/HDDM, while REEP/HDDM shows relatively compact and continuous char residues, which serves as an insulative carbon layer to prevent the heat and oxygen from transferring into the epoxy matrix.

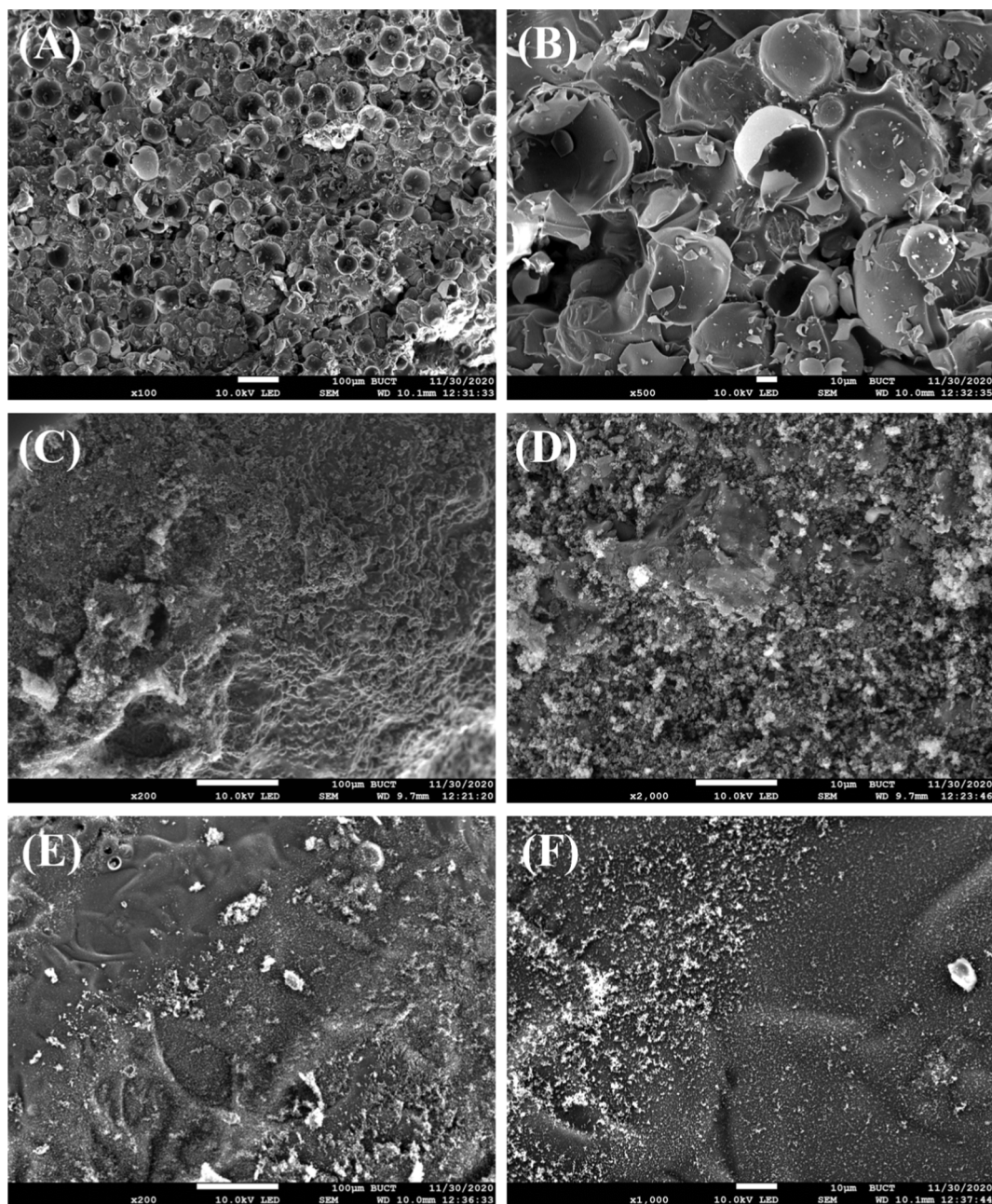


Fig. 8. SEM images of DGEBA/HDDM (A, B), REEP/DGEBA/HDDM (C, D) and REEP/HDDM (E, F) after combustion.

The curves of heat release rate (HRR) of DGEBA/HDDM, REEP/DGEBA/HDDM and REEP/HDDM versus time are exhibited in Fig. 9. It can be found that the curve of HRR of DGEBA/HDDM shows a sharp peak of  $2121.6 \text{ kW}\cdot\text{m}^{-2}$ , while the curve of HRR of REEP/HDDM shows a broad peak of  $1474.2 \text{ kW}\cdot\text{m}^{-2}$ , much lower than that of DGEBA/HDDM. In addition, The DGEBA/HDDM system, with LOI of 21.0%, is usually classified as a combustible material. And with increased content of REEP, the LOI of cured epoxy increases obviously. Compared with DGEBA/HDDM, REEP/HDDM achieves 15.7% increment in the LOI, indicating low flammability of REEP.

### 3.7. Dielectric properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM

The dielectric properties of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are displayed in Fig. 10. DGEBA/HDDM (4.7–4.1)

exhibits relatively high dielectric permittivity over a broad bandwidth range ( $10\text{--}10^7 \text{ Hz}$ ), which is consistent with reported epoxy/amine systems. And REEP/HDDM (3.9–3.2) and REEP/DGEBA/HDDM (4.0–3.3) exhibit lower dielectric permittivity than that of DGEBA/HDDM (4.7–4.1), which favors high frequency signal transmission speed, thereby allowing REEP/HDDM and REEP/DGEBA/HDDM to well adapt to the requirements of miniaturization, as well as high frequency and speed development of electronic products.

### 3.8. UV-blocking properties of the cured epoxy resins

The REEP/HDDM and DGEBA/REEP/HDDM are tested by UV-vis spectroscopy in order to investigate the unique UV-blocking properties. And the transparency of cured epoxy resin is usually a method to characterize the miscibility of thermosetting material. The transmittance properties of the DGEBA/HDDM, DGEBA/REEP/HDDM and



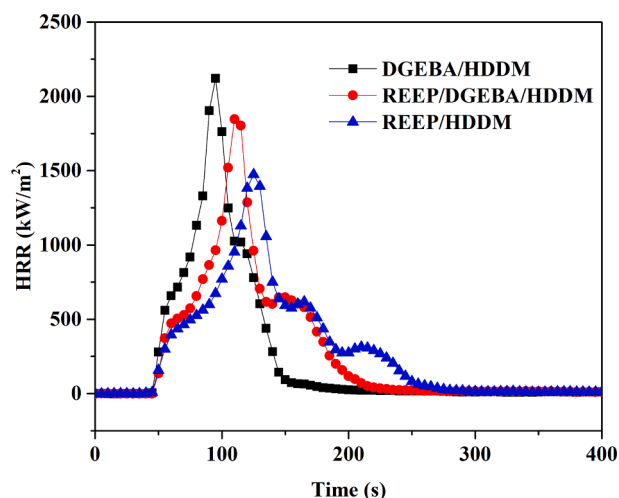


Fig. 9. Heat release rate of different cured epoxy resins versus time curve.

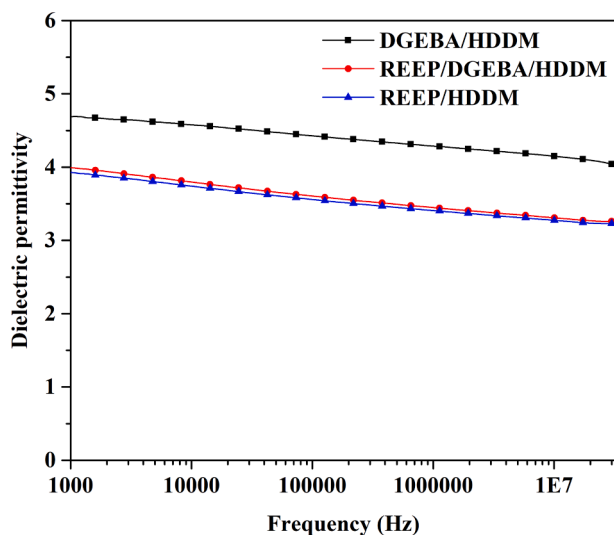


Fig. 10. Dielectric permittivity of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM.

REEP/HDDM films are shown in Fig. 11. The transmissivity of DGEBA/REEP/HDDM and REEP/HDDM at 600 nm is nearly 100%, indicating the good miscibility of REEP-HDDM and REEP-DGEBA-HDDMM. Interestingly, the transmissivity of DGEBA/REEP/HDDM and REEP/HDDM at 220–380 nm is almost 0%, suggesting the excellent UV-blocking properties of DGEBA/REEP/HDDM and REEP/HDDM [30]. And the absorption properties of BPA, DGEBA, resveratrol and REEP are exhibited in Fig. S6. The absorption peaks of REEP at short-, medium-, and long-wavelength UV light is 217 nm, 303 nm and 321 nm, respectively, indicating that the good absorption properties of REEP at UV light, which is consistent with previous transmissivity results.

#### 4. Conclusions

In this work, a trifunctional resveratrol-based epoxy resin (REEP) was prepared. The REEP could be cured by HDDM with acceptable processability. Compared with DGEBA/HDDM, REEP/HDDM shows an ultrahigh  $T_g$  value ( $>320$  °C). And the tensile strength of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM are  $77.8 \pm 18.9$  MPa,  $70.8 \pm 15.9$  MPa and  $63.6 \pm 9.3$  MPa, respectively. Moreover, The  $T_{d50\%}$  of REEP/HDDM, REEP/DGEBA/HDDM and DGEBA/HDDM systems are respectively 319.9 °C, 335.1 °C and 348.1 °C, indicating good thermal

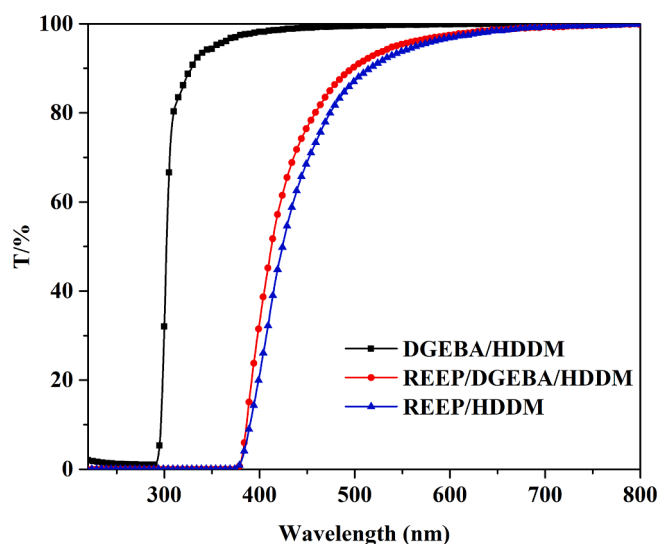


Fig. 11. The transmittance properties of the DGEBA/HDDM, DGEBA/REEP/HDDM and REEP/HDDM films.

stabilities of the cured epoxy resins. And the dielectric permittivity of REEP/HDDM was 3.9–3.2 over a broad bandwidth range ( $10$ – $10^7$  Hz). Interestingly, the REEP exhibited outstanding blocking properties in the range of 220–400 nm (UV-light) and low flammability with compact and continuous char residues. Therefore, due to these excellent comprehensive properties, REEP has great potential to meet the high demand of high-end manufacturing and electronic information industry, especially aerospace materials.

#### CRedit authorship contribution statement

**Yazhou Tian:** Investigation, Data curation, Validation, Writing - original draft, Funding acquisition, Project administration. **Meng Ke:** Investigation, Data curation. **Xiuli Wang:** Data curation, Validation. **Guangdong Wu:** Data curation, Validation. **Junying Zhang:** Writing - review & editing. **Jue Cheng:** Writing - review & editing.

#### Declaration of Competing Interest

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

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2021.110282>.

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