Stilbene 구조를 지닌 바이오 기반 에폭시 열경화성 수지의 높은 T_g 및 난연성

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Bio-based Epoxy Thermoset Containing Stilbene Structure with Ultrahigh T_g and Excellent Flame Retardancy

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Abstract: Bio-based epoxy resins with an ultrahigh glass transition temperature (T_g) and excellent flame retardancy are critical for developing sustainable polymers. Herein, a novel trifunctional epoxy monomer triglycidyl ether of resveratrol (TGER) was synthesized from renewable resveratrol. The chemical structure of TGER was confirmed by Fourier transform infrared (FTIR), ^{1}H, and ^{13}C nuclear magnetic resonance (NMR) spectroscopy which was then reacted with 4,4'-diaminodiphenylmethane (DDM) to form resin. The obtained resin was evaluated in terms of flame retardance and thermal properties. The resultant TGER-DDM 240 resin shows excellent flame-retardant properties, presenting a residual char of 42.5% at 800 °C, limiting oxygen index (LOI) of 31.2%, and flammability rating of V-0 in UL94 test. Moreover, the resin possesses an ultrahigh T_g at 294 °C. This work provides a facile method for preparing high-performance flame-retardant epoxy resin from a renewable resource.

Keywords: bio-based, stilbene structure, flame retardancy, epoxy resin.

Introduction

Epoxy resins, one of the most versatile thermosetting polymers, have been widely used in aerospace, electronics, coatings and adhesives due to the excellent thermal stability, chemical resistance, electrical insulation, adhesive and thermomechanical properties.[1-3] The market value of epoxy resins is expected to reach $27.5 billion in 2020 and $37.3 billion in 2025. However, about 90% of the epoxy resins are produced from diglycidyl ether of bisphenol A (DGEBA), which is obtained by the condensation of epichlorohydrin and bisphenol A (BPA).[4,5] BPA is usually obtained from non-renewable petroleum-based phenol and acetone, thus accelerating the depletion of petroleum resources and aggravating global warming.[6] Moreover, BPA is an estrogen-like chemical and causes endocrine-disrupting even at very low doses.[7] Therefore, there is a long-standing interest to replace BPA with renewable bio-based materials. Liu *et al*. prepared a new type of bio-based epoxy resin from itaconic acid. The glass tran-

sition temperature (T_g) and flexural strength of the resulting resin reach 130.4 °C and 152.4 MPa, respectively.[8] Fang's group reported a triepoxy monomer from protocatechuic acid, which gives an epoxy resin with much better thermal and mechanical properties than the BPA-based one.[9] Savonnet *et al.* prepared two kinds of epoxy resins from vanillin derivatives. The resins show high T_g values ranged from 140 to 200 °C, and their thermal degradation temperature was comparable to that of a DGEBA-based resin.[10]

Unfortunately, the bio-based epoxy resins still suffer from high flammability like the petroleum-based counterparts, which impedes their practical application in many fields, such as electronic packaging, construction and transportation.[11-13] Although the introduction of flame retardants can enhance the flame retardant property of bio-based epoxy resins, some emerged problems/risks include the migration of additives, the deterioration in mechanical strength and thermal stability. The covalent attachment of flame retardant elements (halogen, nitrogen, silicon or phosphorus) to polymer network could overcome the above drawbacks of additives, yet accompanied with complicated synthesis, decreased bio-based content, high toxicity or serious melt dripping.[14-16] Thus, it's urgent to develop greener and safer approaches to prepare flame-retardant epoxy resins. As we know, chemical structures with high charring ability are expected to endow corresponding materials with high flame retardancy.[2,17-19] Generally, aromatic structures are introduced to promote char, which decreases the processing performance of the resin materials. Interestingly, some polymers with unique chemical structure have high charring ability and excellent flame retardancy. For instance, daidzein-based epoxy resin and genistein-based epoxy resin contain benzo-pyrone ring structure and exhibit high residual char (above 42% at 800 °C under nitrogen atmosphere), excellent flame retardant properties (limiting oxygen index above 31% and flammability rating of V-0 in UL94 test).[20,21]

The above facts prove that it's a promising strategy to prepare materials with unique properties by using the structural diversity of bio-based monomers. Resveratrol (3,4',5-trihydroxystilbene), a natural and abundant polyphenol in many plants, including nuts, berries and grapes, contains a stilbene structure.[22-24] Compared with the two isoflavones (daidzein and genistein) in our previous work,[20,21] resveratrol has more functional groups and a more rigid molecular structure. More importantly, stilbene structure is easy to form fused-ring under heating, beneficial to char formation and thus flame retardancy. Up to now, there have been several reports on the application of resveratrol in epoxy resins. Still, no detailed research has been conducted on their flame retardant properties in epoxy-amine curing systems.[25-27] Herein, we show the synthesis of stilbene-containing bio-based epoxy resins from resveratrol (Scheme 1). The chemical structure of the resin was characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The flame retardancy and thermal properties of the resin were also investigated. According to the results from scanning electron microscope (SEM) characterization, we also discussed the flame-retardant mechanism of resveratrol-based epoxy thermosetting polymer. This study provides a facile method to develop intrinsically flame-retardant bio-based epoxy thermosets.

Experimental

Resveratrol was supplied by Shanxi Haochen Bio-Technology Co., Ltd. (Xi'an China). Benzyltriethylammonium chloride (TEBAC), sodium hydroxide and dichloromethane were procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Anhydrous sodium sulfate, epichlorohydrin (ECH) and 4,4-diaminodiphenylmethane (DDM) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Bisphenol A-based epoxy resin (DGEBA, trade name DER332) was obtained from Sigma-Aldrich (Poole, Dorset, UK). All the chemical reagents were used as received.

Synthesis of Triglycidyl Ether of Resveratrol. TGER was synthesized by the typical glycidyl etherification reaction between resveratrol and epichlorohydrin (ECH). 15.78 g (103.7 mmol) of resveratrol and 8.59 g (62.1 mmol) of tetrabutyl ammonium bromide (TBAB) as the catalyst was dissolved in 200 mL of ECH in a 500 mL round flask equipped with a
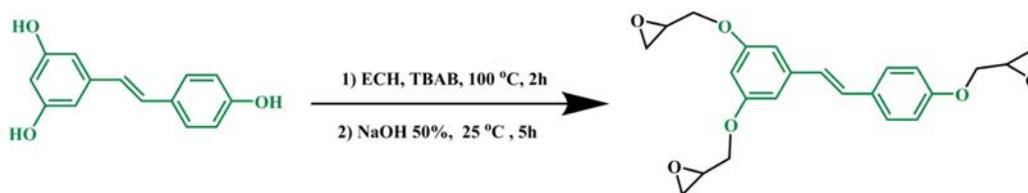
Scheme 1. Synthesis of trifunctional epoxy resin from resveratrol.

magnetic stirring and kept at 100 °C for 2 h. Then, 5 g (14.4 mmol) of sodium hydroxide (NaOH) dissolved in 30 mL deionized water was added dropwise into the flask steadily and slowly over a period of 0.5 h and then stirred at 30 °C for 5 h. Afterwards, the mixture was washed with deionized water 3 times and dried with anhydrous magnesium sulfate. The organic layer was concentrated in a vacuum to remove the excessive ECH. Finally, the light yellow powder TGER with a yield of 92.4% was obtained.

Preparation of Epoxy Thermosets. DGEBA and TGER were respectively mixed with curing agent DDM with a 1:1 molar ratio of epoxy *vs* -NH for curing. The mixtures were stirred at 100 °C for 5 min, degassed under vacuum and poured into the preheated stainless steel moulds at 120 °C for curing with the set curing procedure. Thereafter, the cured epoxy resins were allowed to cool down to room temperature before their unmolding slowly.

Characterizations. FTIR of TGER, and the cured epoxy resins were recorded in transmission mode using a NICOLET 6700 (Thermo-fisher, USA) spectrometer in the wavenumber range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The specimens were prepared by mixing with spectroscopy-grade KBr powder and then compressing to pellet.

The ^{1}H and ^{13}C NMR spectra of the target monomer TGER were collected using a Bruker AVANCE III 400 MHz NMR spectrometer (Bruker, Switzerland) at room temperature. Deuterated chloroform (CDCl$_3$) and tetramethylsilane (TMS) were used as a solvent and internal reference, respectively.

The epoxy value of the target monomer TGER was used to determine by epoxy titration according to ASTM D1652.

Differential scanning calorimetry (DSC) tests were performed on a Mettler-Toledo MET DSC (METTLER TOLEDO, Switzerland) in a high purity nitrogen atmosphere. To determine the activation energy of polymerization for TGER/DDM and DGEBA/DDM system, the samples were scanned at different heating rates of 5, 10, 15 and 20 °C/min in the temperature range of 25 to 350 °C.

Thermal gravimetric analysis (TGA) of the cured epoxy resin was conducted with a Mettler-Toledo TGA/DSC1 (METTLER TOLEDO, Switzerland) in the temperature range from 50 to 800 °C at a rate of 20 °C/min under a nitrogen and air atmosphere, respectively.

Dynamic mechanical analyses (DMA) were investigated on a TA analyzer (TA Q800, USA) in tension mode at a frequency of 1 Hz, from -25 to 350 °C at a heating rate using 3 °C/min.

The vertical burning (UL94) test was conducted on the AG5100B instrument (Suzhou Vouch Testing Technology Co. Ltd., China) according to ASTM D3801-2010 with a dimension of 130 × 13.0 × 3.0 mm.

The limited oxygen index (LOI) values were acquired using an HC-2 Oxygen Index instrument (Jiangning Analytical Instrument Co. Ltd., China) according to ASTM D2863-97 with a dimension of 70 × 6.0 × 3.2 mm^3.

Cone calorimeter test was performed on the 6810 instruments (Suzhou Vouch Testing Technology Co. Ltd., China) according to standard ISO 5660 with dimensions of 100 × 100 × 3.2 mm^3.

Results and Discussion

Synthesis and Characterization of TGER. In this work, the synthetic route of TGER is displayed in Scheme 1. The TGER was readily obtained by glycidylation of resveratrol and ECH under alkaline conditions, in which TBAB was used as the phase-transfer catalyst. Besides, the product was obtained with a high yield (92.4%), which indicates that this method has an excellent potential for large-scale production.

FTIR and NMR spectroscopy analysis were used to confirm the chemical structure and purity of the synthesized TGER monomer. The FTIR spectrum of TGER is consistent with the TGER proposed structure. As shown in Figure 1, the appearance of epoxy groups in TGER is confirmed by the absorption peak observed at 908 cm^{-1}.[28] The signals that appear at 1588, 1506 and 1441 cm^{-1} are attributed to the C=C stretching of vinyl and benzene. The disappearance of the peak between 3250 and 3700 cm^{-1} indicate that phenolic hydroxyl groups are completely glycidylated.[29]
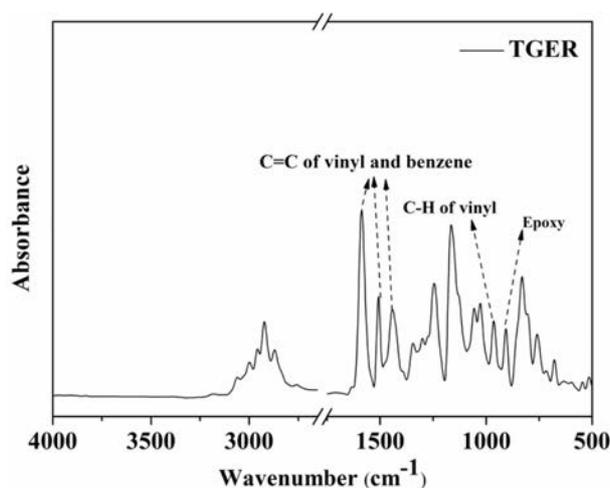

Figure 1. FTIR spectrum of TGER.
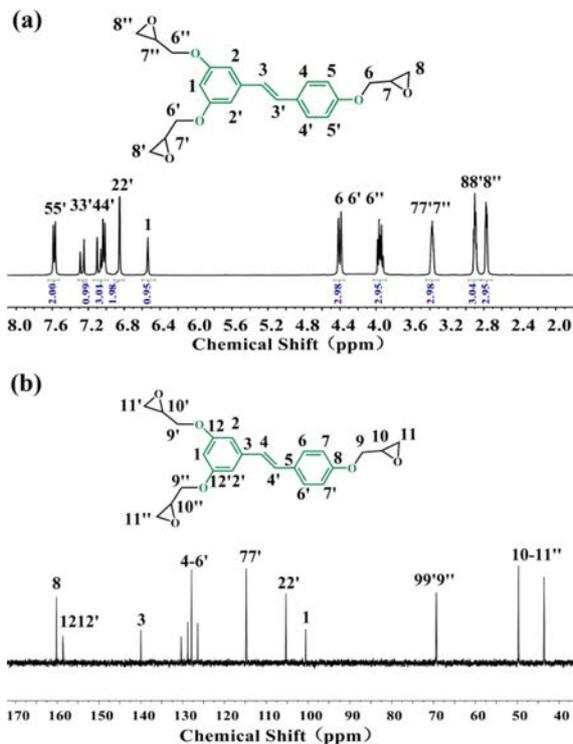
Figure 2. (a) ^{1}H NMR spectra (CDCl₃) of TGER; (b) ^{13}C NMR spectra (CDCl₃) of TGER.

In Figure 2, the peaks at 6.53-7.10 and 7.56-7.58 ppm belong to the protons of the aromatic rings (H1, H2, H2', H4, H4', H5 and H5'), while the peaks at 7.24 and 7.28 ppm correspond to the protons (H3, H3') of C=C of vinyl. The signals of the methylene protons (H6, H6' and H6") are found at 3.92-3.98 ppm and 4.38-4.42 ppm. Furthermore, the characteristic signals of the oxirane ring protons are at 3.35-3.39 and 2.76-2.91 ppm.

According to the FTIR, ^{1}H NMR, and ^{13}C NMR results, we conclude that the TGER is synthesized successfully.

The epoxy value of TGER determined by titration is 0.73 mol/100 g, which is close to the theoretical 0.75 mol/100 g.

Curing Behaviors Investigation. The non-isothermal curing behaviors of DER332-DDM and TGER-DDM systems are determined by DSC. As shown in Figure 3, the heating curves of both DER332/DDM and TGER/DDM system appear a single exothermic peak, which arises from the ring-opening of TGER or DER332 under the attack of the amino group of DDM. As shown in Figure 3(b), TGER/DDM shows the exothermic peak at 125, 140, 149, 156 °C with the heating rate changed from 5 to 20 °C/min. Obviously, the exothermic peak of DER332/DDM are 152, 170, 181, 189 °C, respectively,
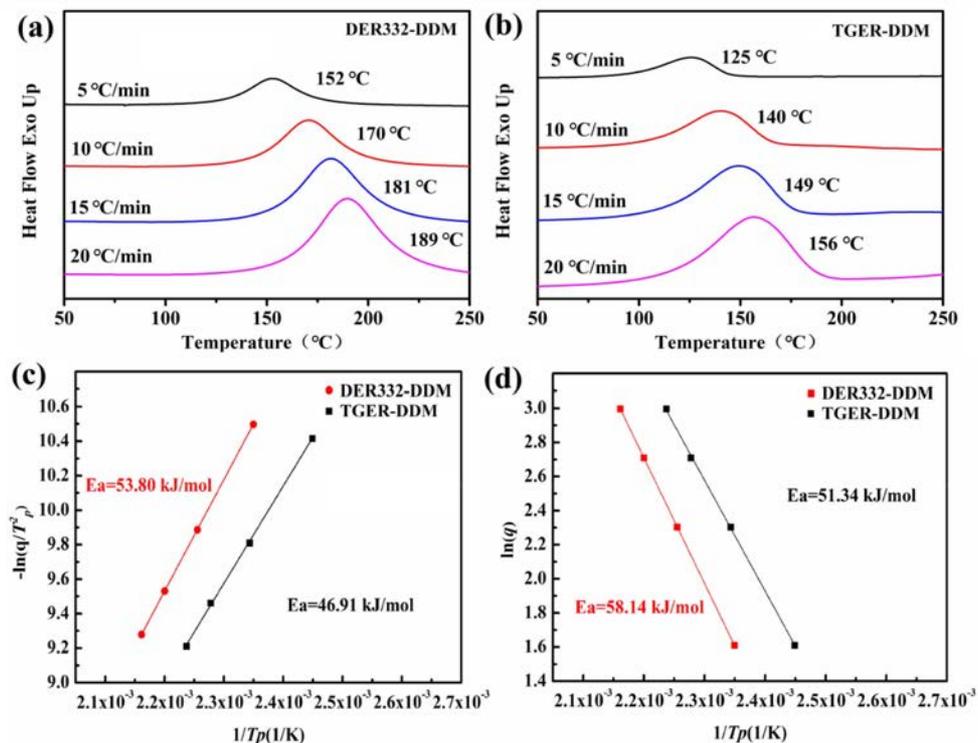
Figure 3. DSC curves for (a) DER332-DDM; (b) TGER-DDM at different heating rates; (c) Linear plots of $\ln(q/T_p^2)$ *versus* $1/T_p$ based on Kissinger's equation for DER332-DDM and TGER-DDM; (d) Linear plots of $\ln(q)$ *versus* $1/T_p$ based on Ozawa's equation for DER332-DDM and TGER-DDM.

under the same condition (Figure 3(a)). The peak temperatures of DER332/DDM are higher than those of TGER/DDM, indicating the lower reactivity of DER332.

The activation energy (E_a) of the two cured systems (DER332/DDM and TGER/DDM) is calculated according to two methods Ozawa's eq. (1) and Kissinger's eq. (2), respectively.[30,31]

$$\ln \beta = -1.052 * E_a / RT_p + \ln(AE_a / R) - \ln(F(x)) - 5.331 \quad (1)$$

$$-\ln(\beta / T_p^2) = E_a / RT_p - \ln(AR / E_a) \quad (2)$$

Here, β is the constant heating rate of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, T_p is the peak temperature of DSC curve corresponding to each heating rate, R is the gas constant with a value of 8.314 J mol^{-1} K^{-1}, E_a is the activation energy of the curing reaction that can be calculated by the slopes of the curves of $\ln(\beta/T_p^2)$ *versus* $1/T_p$ and $\ln\beta$ versus $1/T_p$, respectively.

Figure 3(c) and 3(d) displays the curve fitted by the two methods and the accurately calculated values for two systems of DER332/DDM and TGER/DDM, respectively. Based on the Ozawa's, the activation energy of DER332/DDM and TGER/DDM are 58.14 and 51.34 kJ/mol, respectively. Moreover, the E_a of DER332/DDM and TGER/DDM are 53.80 and 46.91 kJ/mol based on Kissinger's equation.

It can be seen that the activation energy of TGER/DDM system is lower than that of DER332/DDM system, which further indicates that TGER has a higher curing reactivity.

In order to further analyze the curing behavior of TGER-DDM, the ring-opening reaction of the epoxy group and the polymerization of the vinyl group are verified by FTIR technology in addition to DSC technology. As shown in Figure 4(a), two exothermic peaks are observed in the DSC curve for TGER-DDM in the range of 50-400 °C. These two peaks are attributed to the ring-opening reaction of the epoxy group and the polymerization reaction of the vinyl group, respectively. Meanwhile, as shown in Figure 4(b), as the curing temperature increased, the characteristic absorption for epoxy rings shown at 908 cm^{-1} and the C-H of vinyl group absorption appearing at 961 cm^{-1} is gradually decreased. After curing at 200 °C for
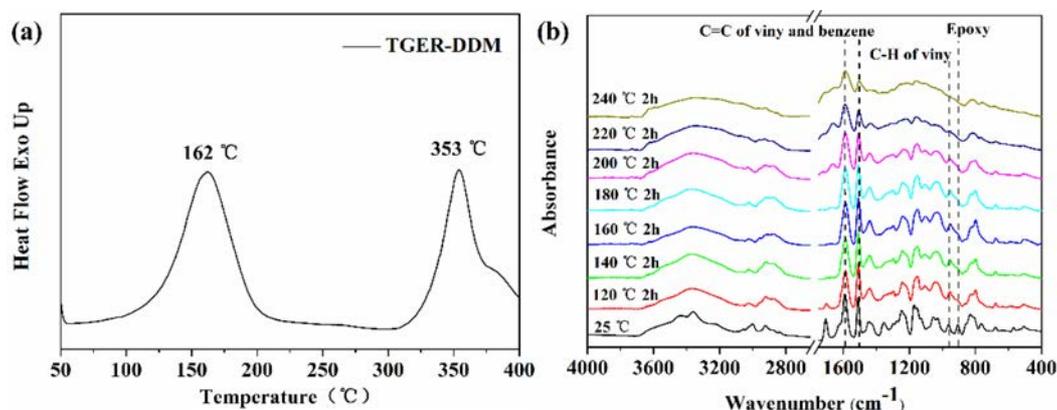
Figure 4. (a) DSC curve for TGER-DDM in the range of 50-400 °C; (b) the FTIR spectra of TGER-DDM at different curing stages.
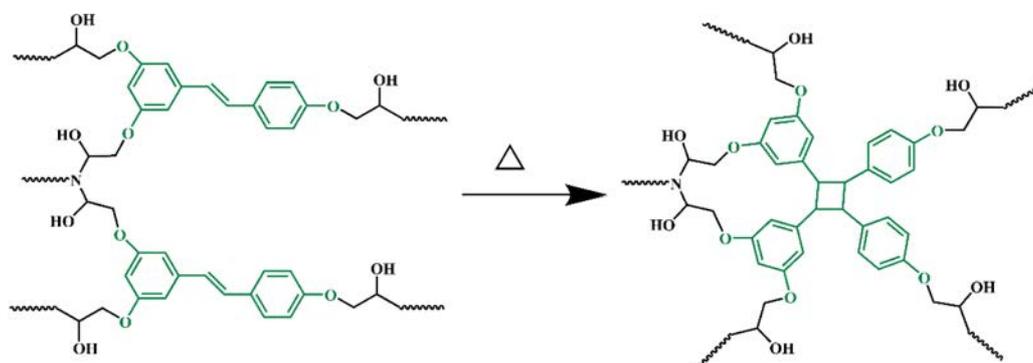
**Scheme 2.** Proposed crosslinked structure of the cured TGER-DDM 240.

2 h, the ring-opening reaction of the epoxy group was completed, as confirmed by the unchanged FTIR spectrum after 220 °C. Besides, it is noted that the characteristic absorption for the C-H of the vinyl group completely disappeared after curing at 240 °C for 2 h, indicating the complete curing reaction.

Based on the above DSC and FTIR results, the two curing conditions for TGER/DDM were applied: (1) 120 °C for 2 h, 140 °C for 2 h, 160 °C for 2 h, 180 °C for 2 h, 200 °C for 2 h; (2) 120 °C for 2 h, 140 °C for 2 h, 160 °C for 2 h, 180 °C for 2 h, 200 °C for 2 h, 220 °C for 2 h, 240 °C for 2 h. The TGER/DDM was cured according to the above conditions and named as TGER/DDM and TGER/DDM 240, respectively.

Thermal Stability. The thermal stabilities and thermal degradation behaviors of the cured DER332-DDM, TGER-DDM and TGER-DDM 240 resins were evaluated from the TGA test. The TGA curves of the cured DER332-DDM, TGER-DDM and TGER-DDM 240 resins under nitrogen atmospheres are presented in Figure 5. The relevant data including the onset of decomposition temperature ($T_{d10\%}$) at 10 wt% weight loss and the residue of the cured resins at 800 °C (R_{800}) are also shown in Figure 5. All cured resins show a temperature of over 350 °C at 10 wt% degradation. Notably, the cured TGER-DDM resin exhibits a higher char yield of 42.5%, in comparison to the cured DER332-DDM resin's 15.4% (Figure 5(a)). This probably because the char yield of the polymers has

a strong tie with its intrinsic chemical structure. The more content of benzene ring and conjugated stilbene structures leads to higher char yields. In addition, as shown in Figure 5(b), the post-curing temperature also has a particular effect on the thermal stability of the TGER-DDM. Compared with the cured TGER-DDM resin, the cured TGER-DDM 240 resin shows almost no change in $T_{d10\%}$, while the R_{800} increases slightly. This should be because the post-curing leads to an increase in the crosslinking density of the cured resin. Generally, the higher the crosslink density is, the higher the char yield.[32]

Flame Resistance. The flame resistance of these cured epoxy resins is evaluated by LOI and vertical burning (UL-94) tests. The related results are collected in Table 1, and the digital pictures during the UL-94 test are presented in Figure 6. According to our previous study,[21] the cured DER332-DDM resin (BPA-based epoxy resin) shows intrinsic inflammability with a low LOI value of 21.5% and failed the UL-94 test. Generally, polymers with LOI less than 22% are classified as combustible, and those with LOI over 22% are self-extinguishing since their combustion cannot be sustained at ambient temperature without the contribution of external energy. When the polymers' LOI values are more than 27%, the polymer is defined as refractory. In conclusion, the polymers with high LOI usually show better flame retardancy.[33] As shown in Figure 6(a), the cured TGER-DDM resin failed to pass the UL-94 vertical burning test. However, it achieves rapid self-extin-
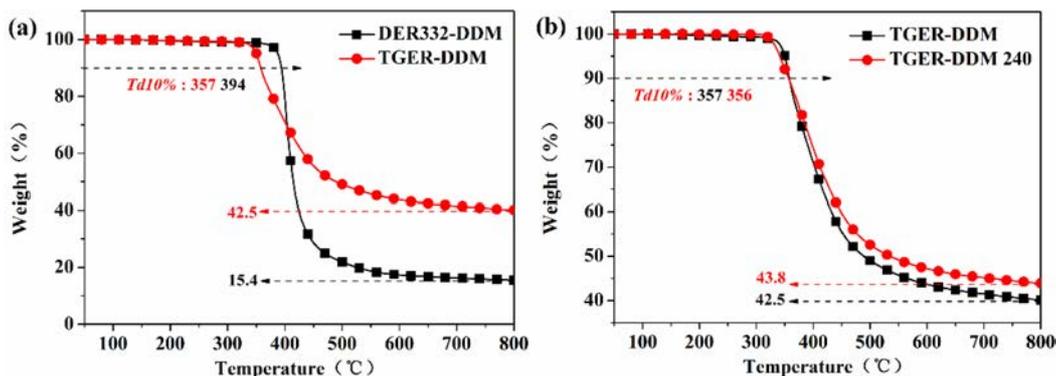
Figure 5. The TGA curves of the cured (a) DER332-DDM and TGER-DDM; (b) TGER-DDM 240 and TGER-DDM.

Table 1. The UL-94 and Cone Data of the Cured TGER-DDM, TGER-DDM 240 and DER332-DDM Resins

| Samples	LOI (%)	UL-94	Flaming drips	PHRR (KW/m²)	THR (MJ/m²)	TSP (m²)
DER332-DDM	21.1	Failed	yes	1077	71.4	20.8
TGER-DDM	27.4	Failed	none	/	/	/
TGER-DDM 240	31.2	V-0	none	259	33.9	5.9
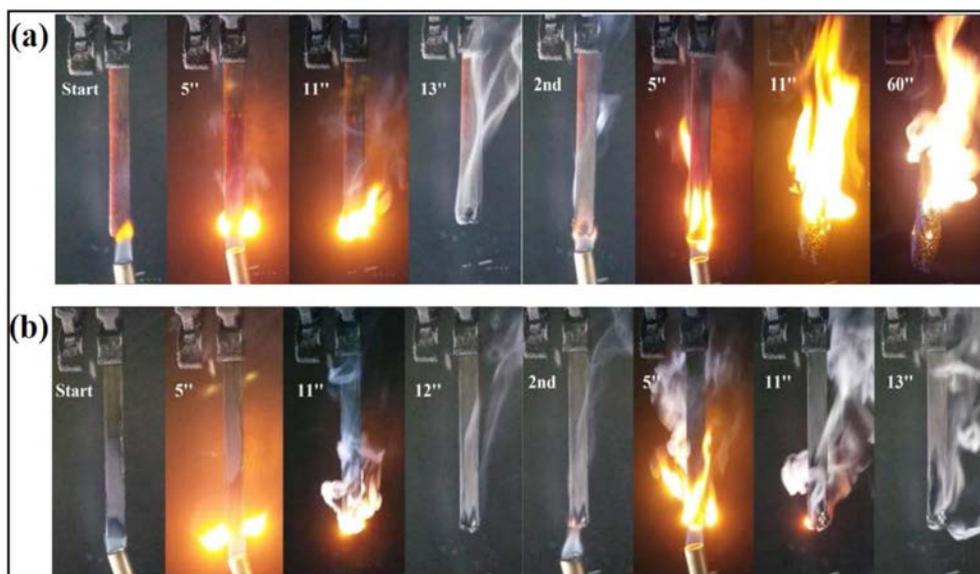
**Figure 6.** Digital photographs of the UL-94 test for the cured (a) TGER-DDM; (b) TGER-DDM 240 resins.

guishing during the first combustion process, and its LOI value reaches 27.4%, which is in line with the aforementioned definition. More importantly, as shown in Figure 6(b), we are surprised that the cured TGER-DDM 240 resin shows the highest flame retardant rating at UL-94 V0 in the UL-94 test with the

LOI up to 31.2%. The above results demonstrate that the flame retardant performance of TGER-DDM system is closely related to its post-curing temperature.

To further evaluate the flame-retardant performance of the cured TGER-DDM 240 resin, the cone calorimetry test was
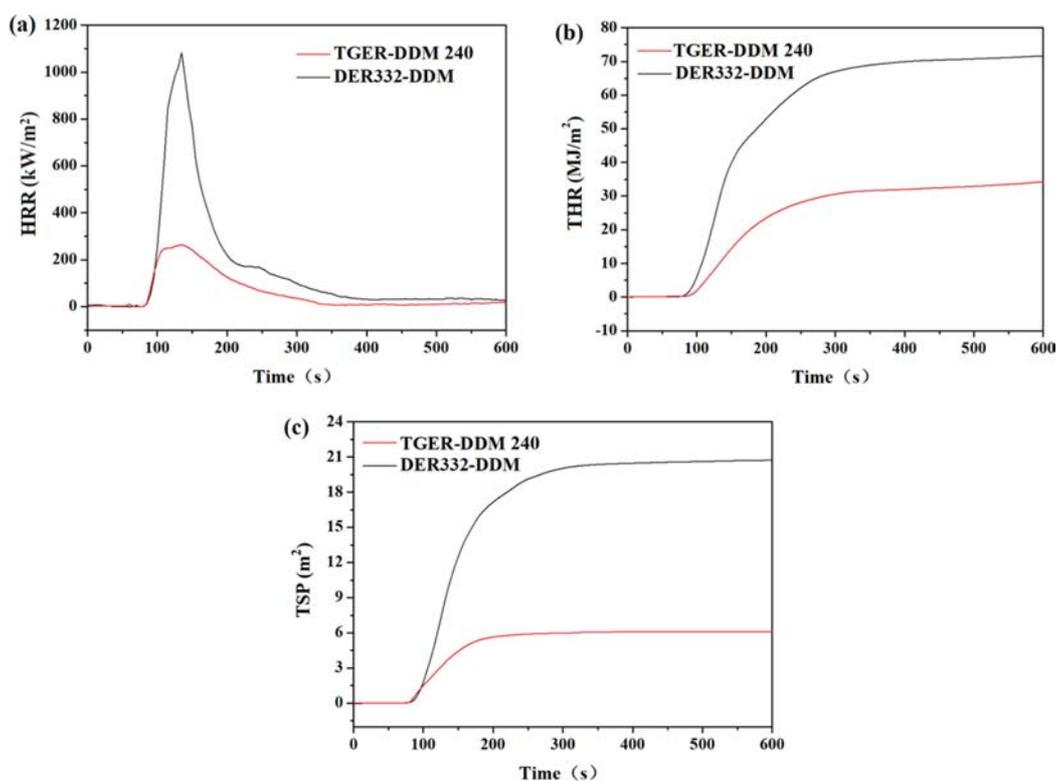
Figure 7. The curves of the cured DER332-DDM and TGER-DDM 240 resins: (a) HRR; (b) THR; (c) TSP.
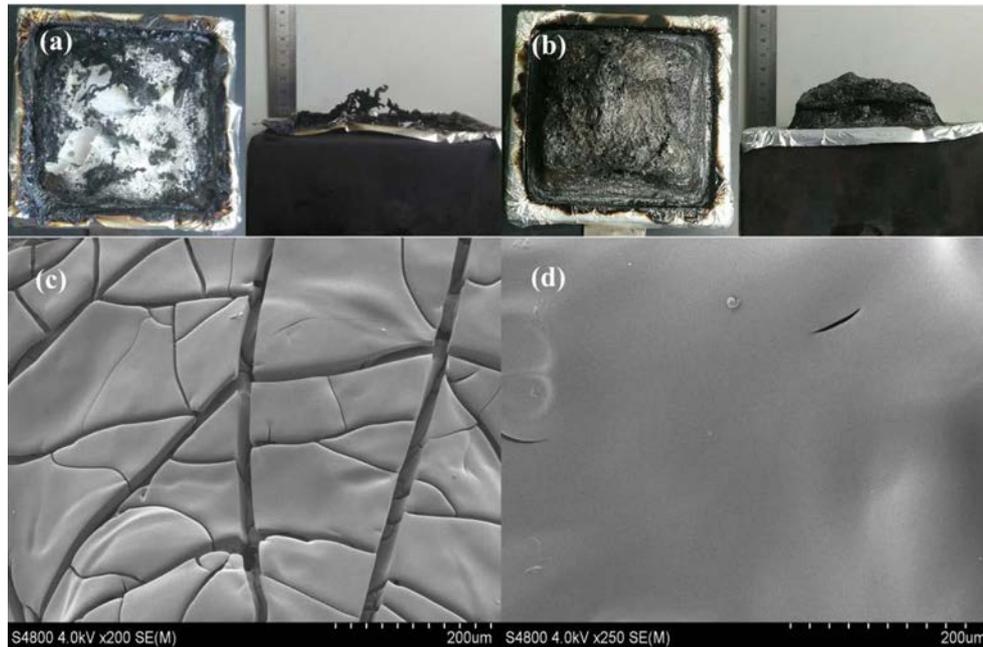
Figure 8. The photos of the cured (a) DER332-DDM; (b) TGER-DDM 240 resins after cone calorimetry test. The SEM images of the residual chars ((c) DER332-DDM; (d) TGER-DDM 240) collected from the test bars after cone calorimetry tests.

employed. The cone calorimeter (CC) test is an efficient technology to evaluate the flammability of epoxy resins in real fires, which provides many important flammability parameters such as heat release rate (HRR), total heat release (THR), as well as total smoke production (TSP). The curves of the HRR, THR and TSP *vs* time are shown in Figure 7. As seen, it indicates that the peak heat release rate (PHRR) and THR values of the cured TGER-DDM 240 resin are much lower than that of DER332/DDM resin. The peak total heat release (PTHR) of the cured TGER-DDM 240 resin is 259 KW/m^2, while the cured DER322/DDM resin gives a much higher value of 1077 KW/m^2. Notably, the cured DER322/DDM resin also exhibits a higher TSP value of 20.8 m^2, whereas the cured TGER-DDM 240 resin shows decreased TSP values of 7.4 m^2. These results demonstrate the superior flame resistance of the cured TGER-DDM 240 resin.

The digital images of the residual chars of the cured epoxy resins after cone calorimeter tests are presented in Figure 8. The fragmentary residue of the cured DER332-DDM resin is very thin and even unable to the cover the underlying foil (Figure 8(a)). In contrast, the residue char of the cured TGER-DDM 240 is thicker and more intumescent (Figure 8(b)). Typically, the quality of the charring residue formed in the combustion process is a key factor in the determination of the flame retardant properties of polymers. Therefore, to further explore the flame-retardant mechanism, the morphology of the residual chars of the samples was characterized by SEM. The SEM digital images of the cured DER332-DDM and TGER-DDM 240 resins after combustion were also shown in Figure 8. Obviously, the carbon layer of the DER332-DDM cured resin is loose and discontinuous, which indicates that the heat and oxygen accelerate the combustion of the DER332-DDM cured resin during the combustion process. Meanwhile, the TGER-DDM 240 cured resin gives dense and continuous carbon layers, acting as an insulator to prevent heat and oxygen transfer.

Dynamic Mechanical Analysis. The dynamic mechanical analysis (DMA) was applied to determine the thermomechanical properties of the cured epoxy resins. The produced DMA curves are depicted in Figure 9, and the corresponding values are collected in Table 2. Generally, the storage modulus of glassy plateaus at 25 °C is corresponding to the polymer's stiffness. As shown in Table 2, the storage modulus of the cured DER332-DDM resin and the cured TGER-DDM 240 resin are 2.4 and 2.8 GPa, respectively. Moreover, in the whole experimental temperature range, the cured TGER-DDM 240 resin has a higher storage modulus than that of the cured DER332-DDM resin (Figure 9(a)). This result indicates that the cured TGER-DDM 240 resin has higher stiffness than the cured DER332-DDM resin.
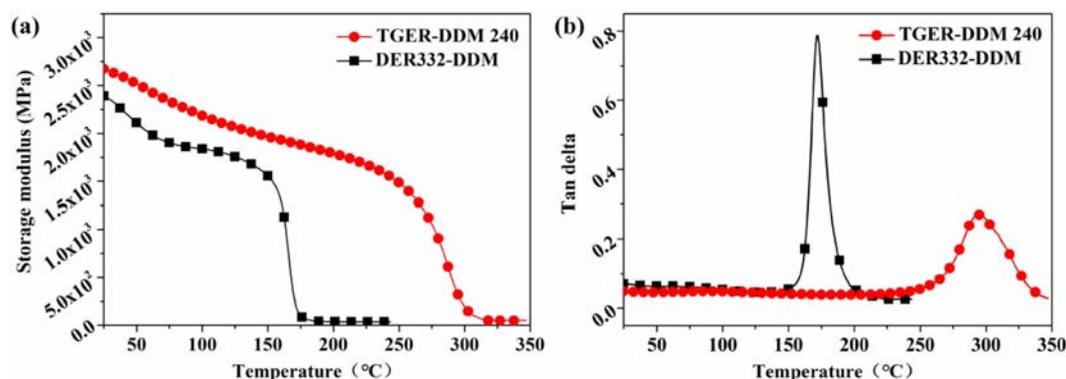
Figure 9. DMA curves of the cured DER332-DDM and TGER-DDM 240 resins: (a) storage modulus; (b) tan δ.

**Table 2.** T_g and Storage Modulus of Cured Epoxy Resins from DMA

Sample	T_g (°C)	E' (GPa) at 25 °C	width of tan δ peaks (half-height)	v_e 10^3 (mol/m^{-3})
DER332-DDM	172	2.4	19	3.1
TGER-DDM 240	294	2.8	46	5.3

The glass transition temperature (T_g) is an essential characteristic parameter of thermosets. As shown in Figure 9(b), the cured TGER-DDM 240 resin's T_g determined by the peak temperature of the tan δ is 294 °C, which is much higher than that of the cured DER332-DDM resin (172 °C). The tan δ peak width at half-height of the cured TGER-DDM 240 resin (46 °C) is broader than that of the cured DER332-DDM resin (19 °C), indicating the lower molecular segmental mobility in the cured TGER-DDM 240 resin. The greater the tan δ peak width at half-height is, the greater the range of glass transition temperature, and the more complex the transition of polymer from glass state to rubber state.[20,21] That is consistent with its relatively higher T_g. Generally, the T_g of the cured epoxy resin is determined by its structural rigidity and the crosslinking density (v_e). The v_e of these cured epoxy resins is calculated according to the rubber elasticity theory (3).[34]

$$v_e = E'/3RT \tag{3}$$

Where E' is the storage modulus in the rubbery plateau region shown in Figure 9(a), R is the universal gas constant and T is the absolute temperature. Here, the absolute temperature of T_g + 30 K was selected for the calculation of v_e. As shown in Table 2, it's obvious that the v_e of the cured TGER-DDM 240 resin (5.3) is greater than that of the cured DER332-DDM resin (3.1). Besides, according to the DSC test results
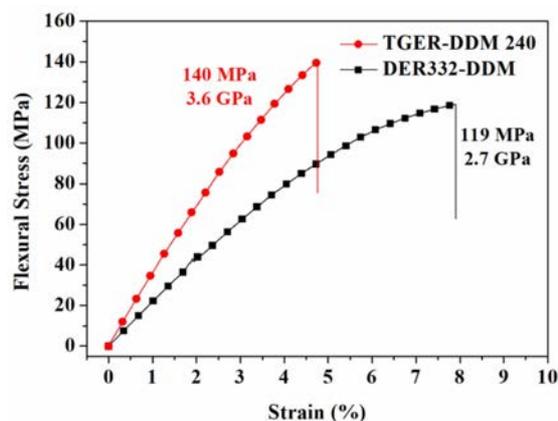
Figure 10. Flexural stress-strain curves of the cured DER332-DDM and TGER-DDM 240 resins.

mentioned above, an additional crosslinking reaction exists in the post-curing stage of the TGER-DDM system, which results in an elevated v_e. Therefore, the ultra-high T_g of the cured TGER-DDM 240 resin should be attributed to its high v_e. All the results support the higher storage modulus and T_g of the cured TGER-DDM 240 resin.

Mechanical Properties. Mechanical properties are usually a vital parameter to characterize the properties of polymers, especially in practical applications. The flexural properties of the cured DER332-DDM and TGER-DDM 240 resins are evaluated by Instron universal testing machine. The flexural stress-strain curves and the related data (flexural strength and modulus) are all presented in Figure 10. As shown in Figure 10, compared with the cured DER332-DDM, the cured TGER-DDM 240 resin exhibits excellent mechanical properties; the flexural strength and modulus are 140 MPa and 3.6 GPA, respectively. The flexural strength and modulus of the thermosetting resins are closely associated with molecular

rigidity and crosslinking density. As mentioned in the DMA discussion, the molecular segment stiffness and crosslink density of the cured TGER-DDM 240 resin is much higher than that of the cured DER332-DDM be the reason for its higher mechanical properties.

Conclusions

In conclusion, a novel trifunctional epoxy monomer TGER was successfully synthesized from renewable resveratrol. With DDM as the curing agent, TGER shows a higher curing reactivity than the petroleum-based DER332. The cured TGER-DDM 240 resin gives a char yield of 42.5% at 800 °C, which is much higher than that of the cured DER332-DDM resin (15.4%). More impressively, the cured TGER-DDM 240 resin without the addition of any extra flame-retardant elements shows excellent flame-retardant properties (LOI: 31.6% and UL94: V-0). Besides, compared with the cured DER332-DDM resin, the cured TGER-DDM 240 resin leads to a 75.9, 52.5 and 71.6% decrease in HRR, THR, and TSP, respectively, during the cone calorimetry test. In addition, the cured TGER-DDM 240 resin has excellent thermodynamic properties, such as an ultrahigh T_g of 294 °C and a storage modulus of 2.8 GPa (25 °C). Thus, resveratrol is an ideal bio-based compound for the synthesis of high-performance flame-retardant epoxy resins.

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