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A recyclable vanillin-based epoxy resin with high-performance that can compete with DGEBA

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ABSTRACT

In this paper, a high-performance epoxy resin was synthesized from vanillin, and the polyimine-epoxy cross-linked network was prepared via in-situ formation of the Schiff base structure. The chemical structures, thermal and mechanical properties of vanillin-based epoxy resin (DADE) and diglycidyl ether of bisphenol A epoxy resin (DGEBA) were characterized by fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectra (^{1}H NMR), differential scanning calorimetry (DSC), and dynamic thermomechanical analysis (DMA). The results indicated that the DADE showed better thermal and mechanical properties than DGEBA after cured by the same primary amine (D230). The prepared DADE-D230 showed higher Tg (106℃), tensile strength (57.4 MPa) and elongation at break (3.1%) than DGEBA-D230 (98℃, 45.1 MPa, and 2.4%, respectively). Moreover, it can be recycled at a hot pressing, and the reprocessed samples showed a comparable performance with DGEBA.

1. Introduction

Epoxy resin, as an important thermal material, is widely used in various fields, including coatings, adhesives, advanced composites, electronic packaging, etc. due to the exhibit mechanical and thermal properties [1–3]. Nowadays, almost 90% of the world production of epoxy resin is based on the reaction of petroleum-based bisphenol A and epichlorohydrin, producing diglycidyl ether of bisphenol A (DGEBA) [4]. With the overuse of fossil fuels and reservoirs as well as the increase of greenhouse gas emission, causing serious environmental issues, bio-based epoxy resins have attracted significant attention [5–7].

Vanillin, a bio-based monomer derived from lignin [8,9], has shown great potential for the production of high-performance epoxy resins due to its unique structure and good properties. The researchers prepared a series of vanillin-based epoxy resins through chemical modification. Mitsuhiro etc. synthesized a fully bio-based epoxy resin from vanillin and cyclopentanone [10]. Wang etc. prepared a high-performance flame retardant vanillin-based epoxy resins containing phosphorus [11]. Xu etc. reported an epoxy thermosets by vanillin, which combining excellent degradability and antibacterial properties [12]. All of these vanillin-based epoxy resins showed excellent mechanical and thermal properties as good as DGEBA.

Generally speaking, cured epoxy resins are impossible to recycle due to its permanent covalent cross-linking network, which may cause wasting of resources. One way to solve this problem is to introduce reversible covalent bonds into the cross-linked epoxy network. Reversible covalent bonds can be reversibly “broken” and “bound” under the stimulation of certain external conditions (such as heat, pH, light, and catalysts). There are many types of reversible covalent bonds, such as ester bonds [13,14], disulfide linkages,[15,16] Schiff base [17–19], carbamate linkages [20], acetal linkages [21], Diels–Alder addition structures [22,23], boronic ester bond [24], and silicon-oxygen bond [25]. Liu etc. prepared a tri-epoxy resin (TEP) from lignin-based vanillin and guaiacol. The cured epoxy showed high T_g, mechanical properties and self-healing properties due to the presence of dynamic ester bonds [26]. Ma etc. designed an epoxy resin with a monocyclic acetal structure from vanillin and glycerin, which displayed excellent mechanical and degradation performance [27]. Therefore, it is of great significance to develop new recyclable vanillin-based epoxy resin.

In this paper, a vanillin-based epoxy resin (DADE), containing both aldehyde and epoxy groups was synthesized. Imine bonds and the cross-linked network can be formed in situ when DADE cured with primary amine (D230). The cured resin can be reprocessed due to the presence of imine bonds. The thermal, mechanical properties, malleability, reprocessing properties of DADE-D230 were investigated. The prepared DADE-D230 showed better properties than DGEBA-D230. The reprocessed DADE-D230 displayed a comparable performance with DGEBA-D230, and this work provides a new idea for the synthesis of

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recyclable bio-based epoxy resin.

2. Experimental

2.1. Materials

Vanillin (99%), benzyltriethylammonium chloride (98%), sodium hydroxide (98.0%), sodium sulfate (99%) were purchased from Adamas, China. Sormaldehyde solution (37%), hydrochloric acid (36.0%-38.0%), acetone ((≥99.5%), epichlorohydrin (≥97%), sodium chloride (99.5%), ether (≥99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Poly (propylene glycol) bis (2-aminopropyl ether) (average Mn ~ 230), bisphenol A diglycidyl ether (≥85.0%) were purchased from Aladdin Reagent, China.

2.2. Synthesis of 4,4 -dihydroxy-5,5-dimethoxy-3,3-methanediyl-dibenzaldehyde (DHDA)

Synthesis method as described in the literature [28]. Vanillin (178 g, 1.17 mol) and formaldehyde aqueous solution (37%) (56.757 g, 0.7 mol) were placed in a round-bottom flask equipped with a constant pressure funnel and stirred at 110℃. Then sodium hydroxide (50 g, 1.25 mol) was solved in 50 mL of water, and added dropwise to the mixed solution. After the reaction for 3 h, the mixture was poured into 2.5 L of water (75 ℃-80 ℃), then 0.5 L of dilute hydrochloric acid (10%) was added into the solution. After filtered, and washed with water and acetone, the white solid (DHDA) was obtained (yield: 12.4%). ^{1}H NMR (400 MHz, DMSO) δ 9.89 (s, 1H), 9.71 (s, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.22 (d, J = 1.8 Hz, 1H), 3.93 (d, J = 15.4 Hz, 2H), 3.89 (s, 3H). The synthetic routes are illustrated in Scheme 1.

2.3. Synthesis of vanillin-based epoxy resin (DADE)

DHDA (12.65 g, 80 mmol), epichlorohydrin (74.00 g, 0.8 mol), and benzyltriethylammonium chloride (1.82 g, 8 mmol) were placed in a round-bottom flask equipped with a constant pressure funnel and a magnetic stirrer, stirred at 80 ℃ until dissolved. After cooling, NaOH (12.90 g, 0.320 mol) and benzyltriethylammonium chloride (1.82 g, 8 mmol) were dissolved in 64 mL water and was added dropwise and the mixture reacted at room temperature for 3 h. The mixture was washed with saturated saline and dried with anhydrous sodium sulfate. After filtration, the mixture was concentrated by rotary evaporator at 70 ℃. The solution was added dropwise to diethyl ether to obtain a yellow powder (yield: 93.7%). ^{1}H NMR (400 MHz, DMSO) δ 9.95 – 9.63 (m, 1H), 7.51 – 7.31 (m, 1H), 7.33 – 7.15 (m, 1H), 4.45 – 3.97 (m, 2H), 3.95 – 3.87 (m, 2H), 3.81 – 3.67 (m, 3H), 2.82 – 2.70 (m, 1H), 2.67 – 2.54 (m, 2H). The synthetic routes are exhibited in Scheme 1.

2.4. Preparation of cured film

DADE (4.28 g, 10 mmol) and D230 (1.73 g, 7.5 mmol) were dissolved chloroform (5 mL) and stirred for 1 h. The mixture was concentrated by rotary, then poured into the mold. Which was heated at 50 ℃ for 3 h and 110 ℃ for10 h and DADE-D230 was obtained. DGEBA (3.40 g, 10 mmol) and D230 (1.15 g, 5 mmol) were mixed and stirred for 1 h. The mixture was concentrated by rotary, then poured into the mold. Which was heated at 50 ℃ for 3 h and 110 ℃ for10 h and DGEBA-D230 was obtained. The curing mechanism was showed in Scheme 2.

2.5. Reprocessing recycle of DADE-D230

A plate vulcanizer was used to perform the reprocess recycling test. The dog-bone-shaped samples were shattered into powder and placed into dog-bone-shaped mold which covered with two polyimide films and hot pressed at 150 °C under a pressure of 15 MPa for 10 min. After cooling to room temperature, dog-bone-shaped samples were obtained.

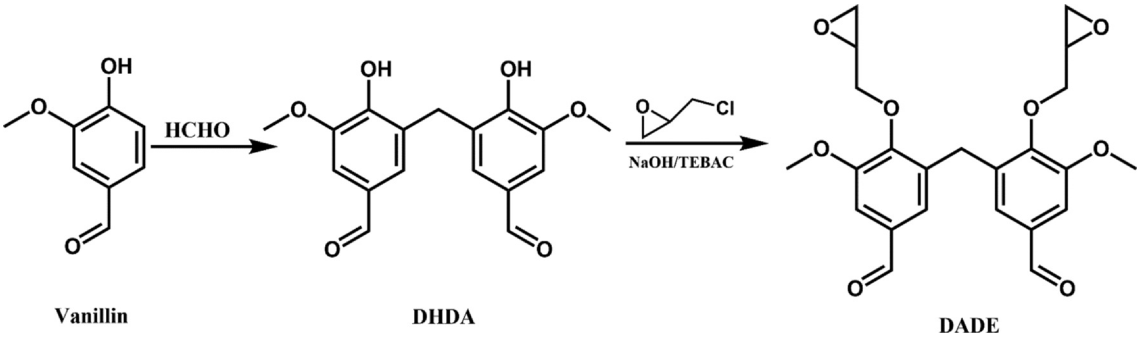
2.6. Characterization.

^{1}H NMR spectra of DHDA and DADE were recorded using an AVANCE III Bruker NMR spectrometer (Bruker, Switzerland) with DMSO-d_6 as solvent, operating at 400 MHz. Thermo Nicolet Nexus FT-IR spectrometer was used to measure FT-IR spectra of DADE, DGEBA, DGEBA-D230, original and reprocessed DADE-D230. The wavenumber ranges from 500 to 4000 cm^{-1}. DMA Q800 (TA Instruments) was used to test the dynamic mechanical properties of the sample. The storage moduli and T_g were examined by heating the samples from 40 ℃ to 180 ℃ at a heating rate of 5 ℃/min. Stress relaxation was tested according to the follow method: the specimen was initially preloaded by 1×10^{-3}N force to maintain straightness. After reaching the testing temperature, is was left for 5 min to reach thermal equilibrium; then the specimen was stretched by 0.5% on a DMA machine and the deformation was maintained throughout the test, the decrease in the tress relaxation modulus was recorded. Expansion experiment was tested according to the follow method: the sample was tested in a constant stress tensile of 24 kPa under controlled force mode at a temperature increase rate of 3 °C/min from 25 °C to 120 °C to observe changes in material strain. Thermal stability was characterized using the TGA 1100SF instrument by heating the samples from 30 °C to 600 °C; the heating rate was 20 °C/min. The tensile tests results were examined by the Instron 5967 at the room temperature; the average stretching rate was 2 mm/min (samples were 25 mm in length and 2 mm in thickness).

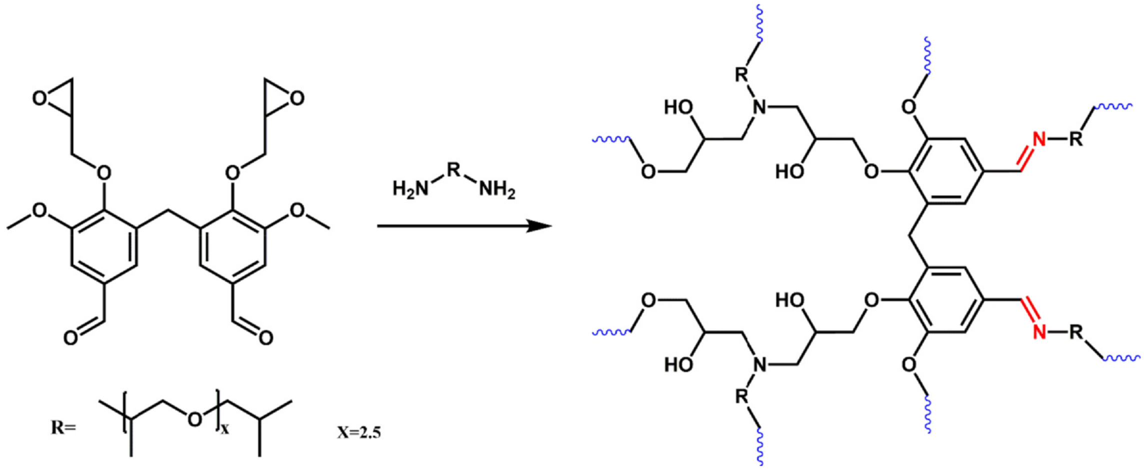
3. Results and discussion

3.1. Structural characterisation of DHDA and DADE

The ^{1}H NMR spectra of DHDA and DADE were showed in Fig. 1a and b. As shown in Fig. 1a, the single peak of 9.89 ppm belongs to the proton of aldehyde group, the peak of 9.71 ppm is ascribed to the proton of phenolic hydroxyl. The protons on benzene ring are dissolved



Scheme 1. Synthetic route of DHDA and DADE.



Scheme 2. Curing mechanism of polyimine- epoxy resin.

at 7.35 ppm and 7.22 ppm, while the protons of methyl and methylene appear at 3.89 ppm and 3.93 ppm. As shown in Fig. 1b, the peak at 9.95–9.63 ppm belongs to aldehyde group, and the peaks at 7.51–7.31 ppm and 7.33–7.15 ppm are ascribed to the protons on benzene ring. The protons of epoxy appear at 4.45–3.97 ppm, 2.82–2.70 ppm, and 2.67–2.54 ppm. The protons of methyl and methylene are dissolved at 3.81–3.67 ppm and 3.95–3.87 ppm. The results indicated that DADE was successfully synthesized. As shown in the Fig. 1c and d, the peak numbers and their chemical shift in the ^{13}C NMR spectrum both match the carbons of DHDA and DADE, indicating that DADE is a single monomer. As shown in the Fig. S1, the peak at around 1685 cm^{-1} belongs to C = O from formyl group, the peak at around 910 cm^{-1} belongs to C-O-C from epoxy group and the peak at around 3192 cm^{-1} corresponds to phenolic hydroxyl. After reacted, the peak of

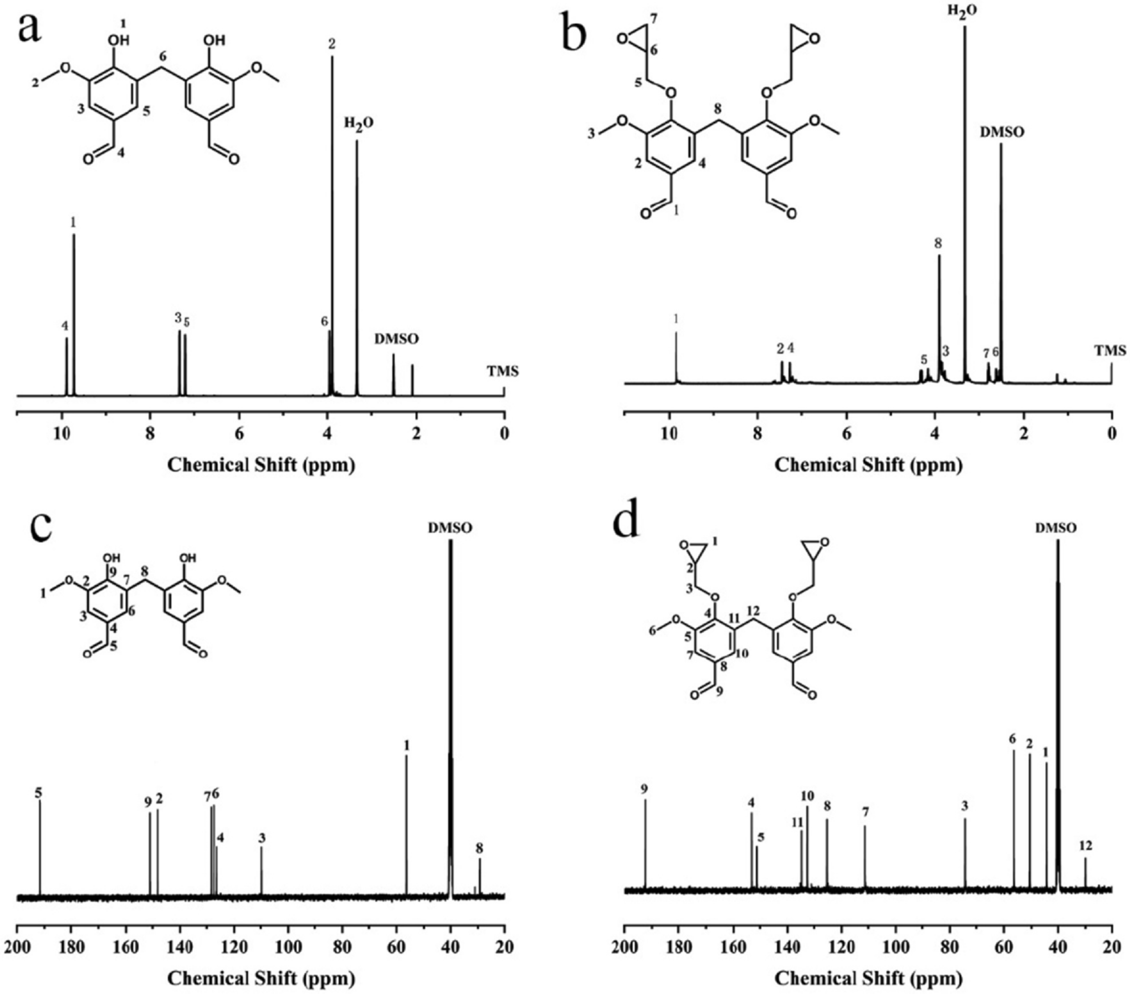


Fig. 1. ^{1}H NMR and ^{13}C NMR spectra of (a), (c) DHDA and (b), (d) DADE.

epoxy group was observed while the peak of phenolic hydroxyl was disappeared, indicating that DHDA and DADE was successfully synthesized. Most vanillin-based epoxy resins are modified by aldehyde groups. This scheme connected two vanillin molecules through the active hydrogen at the ortho position of the phenolic hydroxyl group, thereby the aldehyde group was retained. Compared with the introduction of imine bond and then epoxidation, the imine bond can be formed in situ during the curing process, thus making the preparation process easier.

3.2. *Reprocess recyclability and degradation of DADE-D230*

To determine the recyclability of DADE-D230, the following experiment was done. First, the samples were shattered, then hot-pressed at 150 °C for 10 min to obtain the dog-bone-shaped samples. The result showed that DADE-D230 could be reprocessed under mild conditions through imine exchange (via the excess amine in the network) or imine metathesis. The reason was that as a kind of dynamic reversible covalent bonds, imine bonds involve three equilibrium processes, including imine condensation/hydrolysis, imine exchange, and imine metathesis [29]. There were imine bonds and free amino groups existing in the polyimine- epoxy cross-linked network. Which can promote the exchanges of imine under heating (Fig. 2). Therefore, the prepared polyimine-epoxy cross-linked network can be recycled in a hot pressing after shattered. The color of samples changed from tan to dark brown after reprocessing.

The samples (0.15 g) were put in 15 mL 0.1 M HCl water/THF (1/9–5/5, v/v) solution at 50 °C at different times to investigate the degradation performance. The samples were almost not degraded (< 5%) within 24 h, but the solution turned pale yellow (Fig. S2). In addition, using a variety of organic solvents such as DMSO, DMF, acetone and methanol to conduct degradation experiments at 50 °C, the samples were also degraded slightly. The upper solution and the lower solid were taken separately for infrared characterization (Fig. S3). The peak of C = O was observed whether in solid or solution after degradation, but there still were part of imine bonds remained. This may be because part of aldehyde groups and amino groups reform imine bonds during the drying process. The reason why DADE-230 was almost not degraded may be because the imine bonds were destroyed, but most part of DADE-D230 was still a cross-linked network of difunctional epoxy resin (Fig. 3, structure A), only a small part of D230 (structure E) and small molecule (similar to structure B, C, D) from acid hydrolysis can be dissolved after acidolysis in 0.1 M HCl water/THF solution according to infrared results.

3.3. *FT-IR spectra of DADE, DGEBA, DADE-D230 and DGEBA-D230*

The FT-IR spectra was shown in Fig. 4. The peak at around 1685 cm^{-1} belongs to C = O from formyl group, the peak at around 910 cm^{-1} belongs to C-O-C from epoxy group and the peak at around 1640 cm^{-1} corresponds to C = N after Schiff based reaction. After DADE was cured, the peak of C = N was observed while the peak of C = O was disappeared. The peaks at around 910 cm^{-1} from epoxy group were disappeared and the peak of C-N at around 1261 cm^{-1} was observed after the resins cured by D230. The FT-IR spectra indicated that DADE and DGEBA were fully cured by D230. The chemical structures of DADE-D230 before and after reprocessing were also determined by FT-IR. There was no obvious change in the FT-IR spectrum of DADE-D230 after remodeled, especially for the characteristic peak of C = N at around 1640 cm^{-1} and C = O at around 1685 cm^{-1}, indicating that

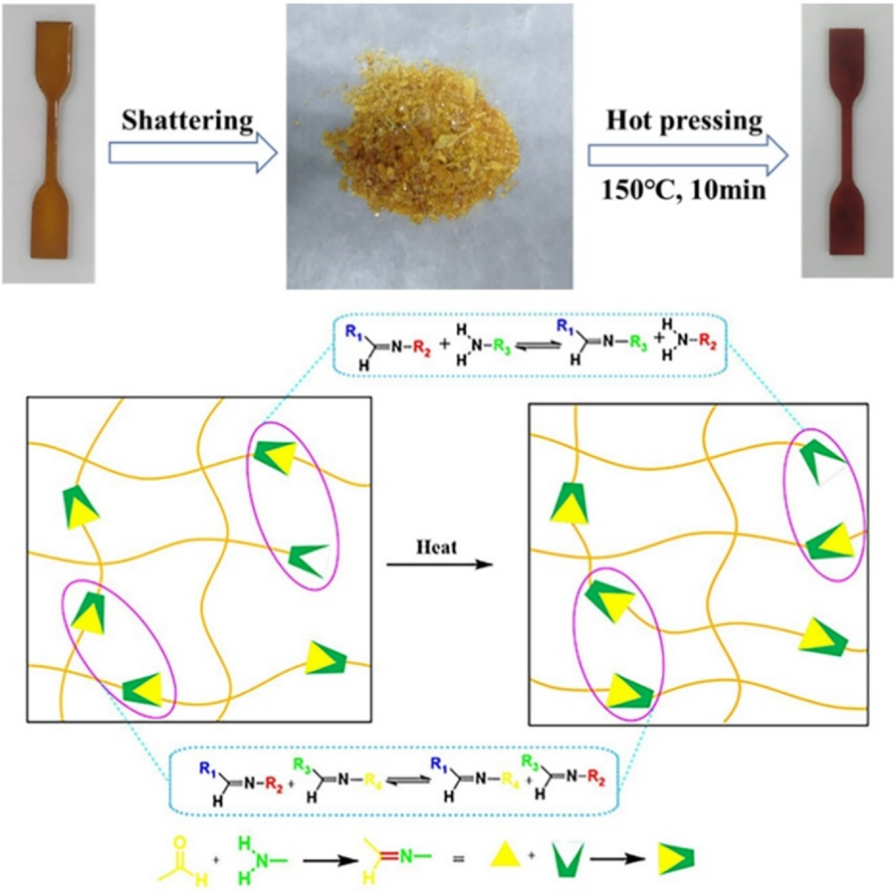


Fig. 2. Reprocessing experiments of DADE-D230 in a hot pressing and recyclable mechanism of DADE-D230.

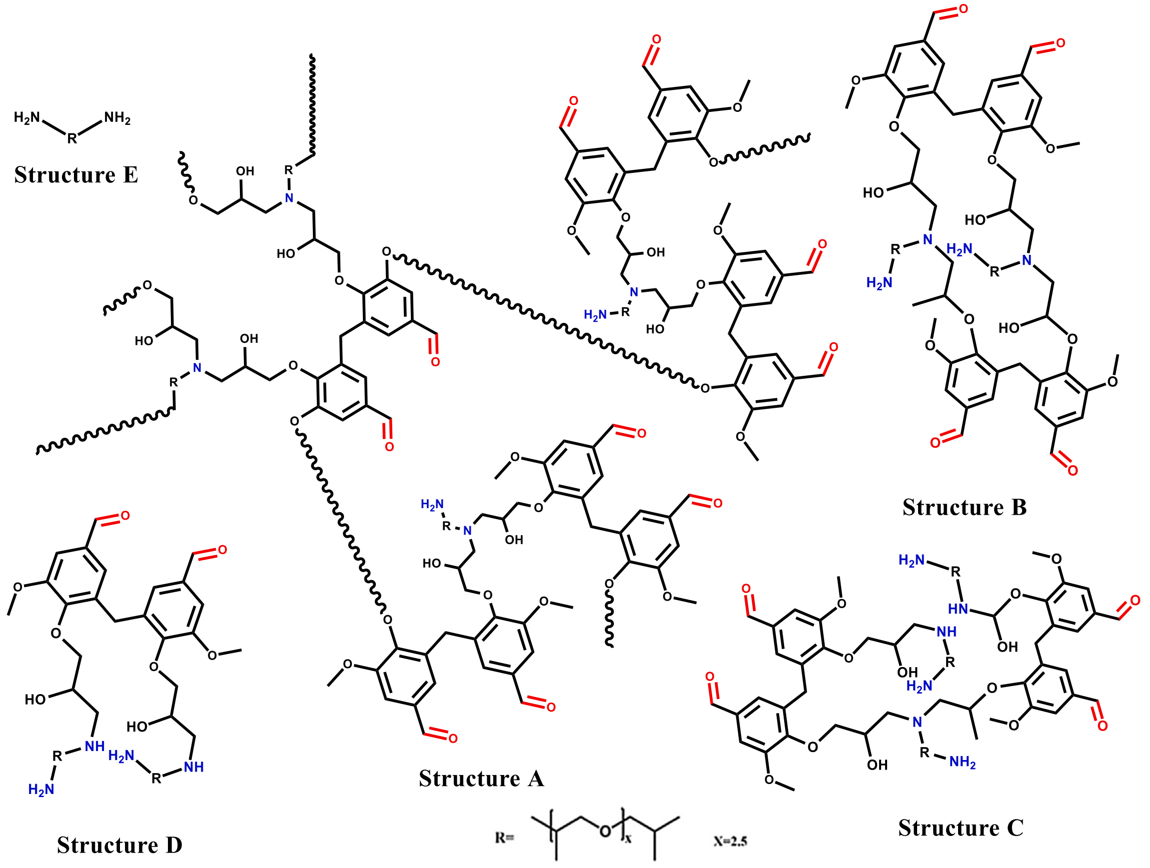


Fig. 3. Potential structure of DADE-D230 after degradation.

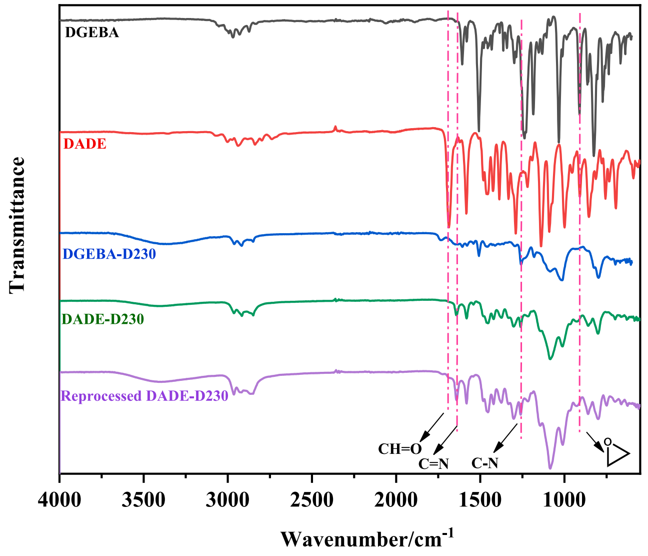


Fig. 4. FT-IR spectra of DGEBA, DADE, DGEBA-D230, original and reprocessed DADE-D230.

the chemical structures were well-preserved during reprocessed.

3.4. Swelling and gel content test of DGEBA-D230, original and reprocessed DADE-D230

To prove the original and reprocessed DADE-D230 were three-dimensional network structure, a swelling test was performed [30]. The original and reprocessed DADE-D230 were cut to a certain size, and the initial sizes were measured with a vernier caliper. The sample was put into a bottle containing an appropriate amount of 1, 2, 4-trichlorobenzene. Kept the temperature at 100 °C for 1 h, then took out the sample to measure the size quickly. The sample was put back into the bottle after measuring, and continue to heat at 120 °C for 1 h, 140 °C for 1 h, 16 0 °C for 1 h, and 180 °C for 1 h. The swelling ratio can be obtained by dividing the swelled volume by the original volume, which were showed in Fig. 5 and Table 1. The DGEBA-D230, as a comparison, was tested as well.

As can be seen from Table 1 the volume of DADE-D230 increased 4% after heating at 100 °C for 1 h. When the temperature raised to 120 °C, the volume rapidly increased to 122%. The sample almost reached equilibrium at 140 °C, the volume reached 127% of the original volume. And the volume of the sample eventually reached 129%. DGEBA-D230 showed the faster swelling rate (117%, 100 °C) and greater swelling ratio (eventually reached 145%) compared with DADE-D230. Obviously, both the swelling rate and swelling ratio of reprocessed DADE-D230 improved rapidly, which may be due to the decrease in crosslink density [31]. In addition, using a variety of organic solvents such as dichloromethane, chloroform, and tetrahydrofuran to conduct swelling experiments on the materials at room temperature, the materials only swelled but not dissolved, which can prove that the three-dimensional crosslinking network was formed. The reprocessed DADE-D230 retained its complete shape after swelling (Fig. 5), indicating that it still kept a crosslinked network structure. The results of gel content test were as shown in the Table S1. The gel content of DGEBA-D230, DADE-D230 and reprocessed DADE-D230 can be reached 100.0%, 99.9% and 99.9% respectively, which can also conform the forming of three-dimensional network structure.

3.5. Malleability of DADE-D230

The malleability of DADE-D230 was characterized via the time-and

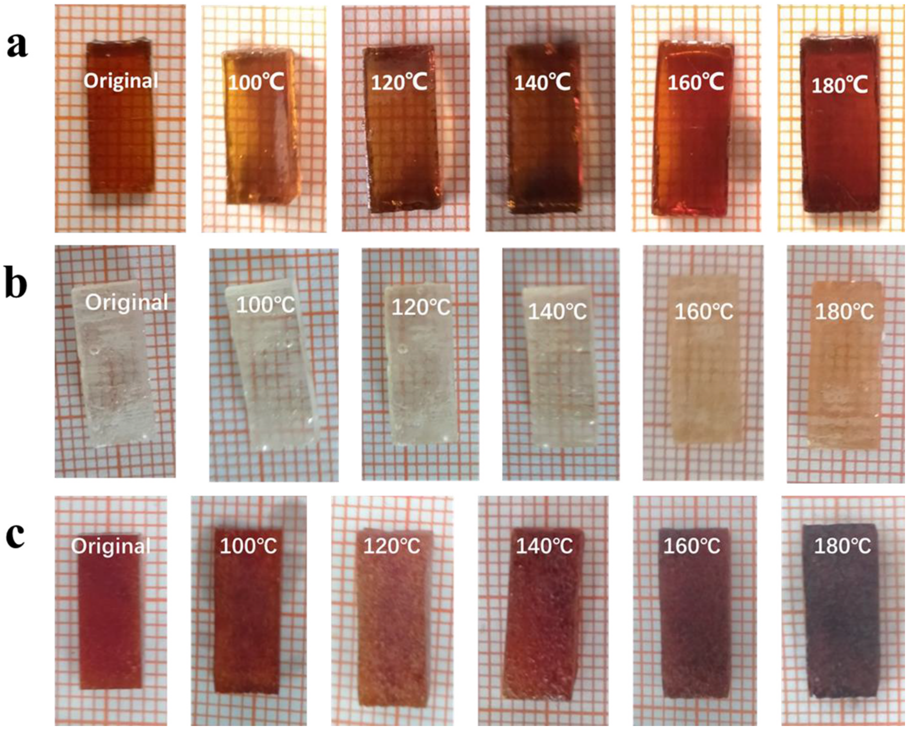


Fig. 5. Digital photos of the swelling result of (a) DADE-D230, (b) DGEBA-D230 and (c) reprocessed DADE-D230.

Table 1
Swelling ratio of the samples.

Swelling step	DADE-D230		DGEBA-D230		Reprocessed DADE-D230	
	Sample size (mm)	Swelling degree	Sample size (mm)	Swelling degree	Sample size (mm)	Swelling degree
Before swelling	5.21 × 11.95 × 1.95	1.00	5.15 × 12.27 × 1.45	1.00	5.20 × 12.04 × 2.17	1.00
100 °C, 1 h	5.30 × 12.06 × 1.98	1.04	5.30 × 13.37 × 1.51	1.17	5.30 × 13.04 × 2.55	1.30
120 °C, 1 h	5.62 × 12.85 × 2.05	1.22	5.73 × 13.91 × 1.54	1.34	5.51 × 12.48 × 2.72	1.49
140 °C, 1 h	5.7 1 × 13.07 × 2.06	1.27	5.72 × 14.20 × 1.63	1.45	5.64 × 13.96 × 2.93	1.70
160 °C, 1 h	5.75 × 13.22 × 2.06	1.29	5.73 × 14.19 × 1.62	1.44	5.67 × 13.97 × 2.96	1.72
180 °C, 1 h	5.75 × 13.25 × 2.05	1.29	5.72 × 14.22 × 1.63	1.45	5.68 × 13.96 × 2.95	1.72

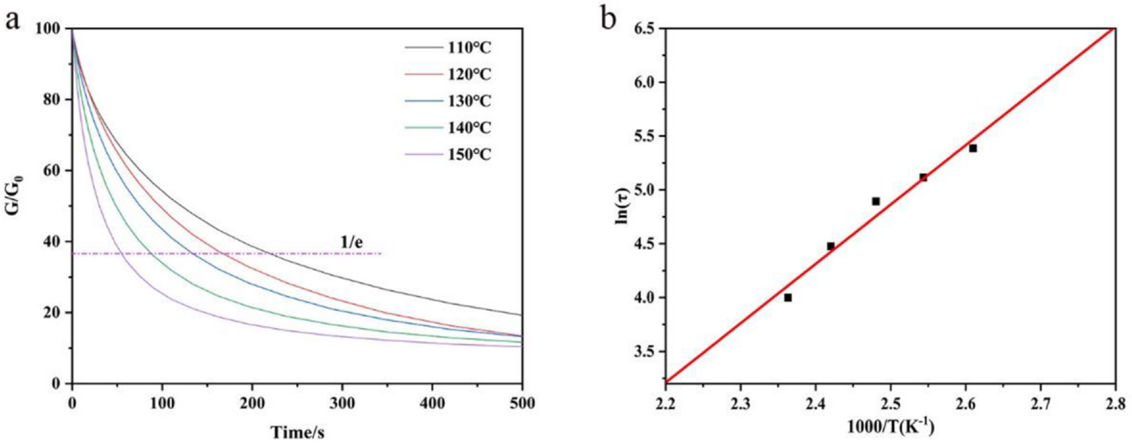


Fig. 6. (a) Normalized stress relaxation curves and (b) Arrhenius analysis of the characteristic relaxation time, ln(τ), versus 1000/T for DADE-D230.

temperature-dependent stress relaxation modulus. The relaxation modulus of DADE-D230 at different temperatures was shown in Fig. 6a. The relaxation time, τ, refers to the time required for the initial modulus to decrease to $1/e$. The τ of DADE-D230 was 54.5 s at 150 °C, 87.7 s at 140 °C, 133.4 s at 130 °C, 166.6 s at 120 °C, and 218.4 s at 110 °C, which were in accordance with the increased temperature and reduced stress relaxation time This can be attributed to the increased exchange rate of Schiff base with an increased temperature. Besides, above T_g (106 °C), ln(τ) followed the Arrhenius law with temperature (eqn (1)) as follows:[32]

$$ln(\tau) = ln\tau_0 + (E_a/\ RT) \tag{1}$$

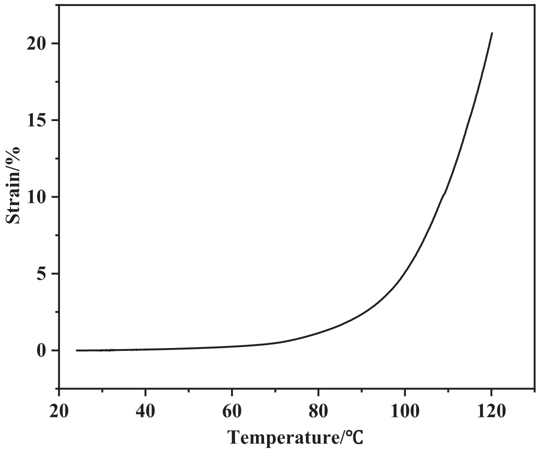


Fig. 7. The expansion curve of DADE-D230.

where, τ_0 is the characteristic relaxation time at infinite temperature, T is the experimental temperature, E_a is the activation energy of the bond exchange process, and R is the universal gas constant. Fig. 6b displayed the Arrhenius analysis of the characteristic relaxation time, ln (τ), versus $1000/T$ for DADE-D230. The calculated E_a was 46.9 kJ mol^{-1}.

DMA expansion method was used to measure the expansion coefficient (strain) versus temperature curve to determine T_v of DADE-D230 [33]. From the results in Fig. 7, the strain rate was increased sharply after 70 °C. That was, below 70 °C, due to the relatively slow imine bond metathesis of the system, DADE-D230 showed the same performance as ordinary thermosetting materials. But above 70 °C, due to the rapid occurrence of imine bond metathesis, the cross-linked network has "fluidity" and the strain of the material was increased sharply. According to Leibler's definition standard, define 70 °C as the solidification transition temperature (T_v) of the topological network [33].

3.6. Mechanical and thermal properties of DGEBA-D230, original and reprocessed DADE-D230

The glass transition temperature (T_g), which usually acts as the upper limit temperature for thermosetting materials, is a major parameter. The T_g of the cured epoxy resins were determined via DMA, as shown in Fig. 8a and b, the data were summarized in Table 2.The cross-linking density (υ_e) can be calculated from the storage modulus E', measured at the rubbery plateau by the theory of rubbery elasticity, which is given by Eq. (2):[34]

$$\upsilon_e = E'/3RT \tag{2}$$

where R is the gas constant, T is the absolute temperature (rubbery plateau modulus at (T_g + 50 K), and E' is the tensile storage modulus corresponding to the T.

The T_g of DADE-D230 was 106 ℃, according to the maximum tan δ peak, which was higher than DGEBA-D230 (97 ℃). Besides, the rubbery platform modulus (T_g + 50 °C) of DADE-D230 was 35.2 MPa, which was higher than that of DGEBA-D230 (16.9 MPa), this was due to the higher cross-link density of DADE-D230. From Table 2, the cross-linking densities (υ_e) of DADE-D230 (3.7), which was twice of DGEBA-D230 (1.8) due to the Schiff based reaction. The result explained why DADE-D230 showed the better mechanical properties than DGEBA-

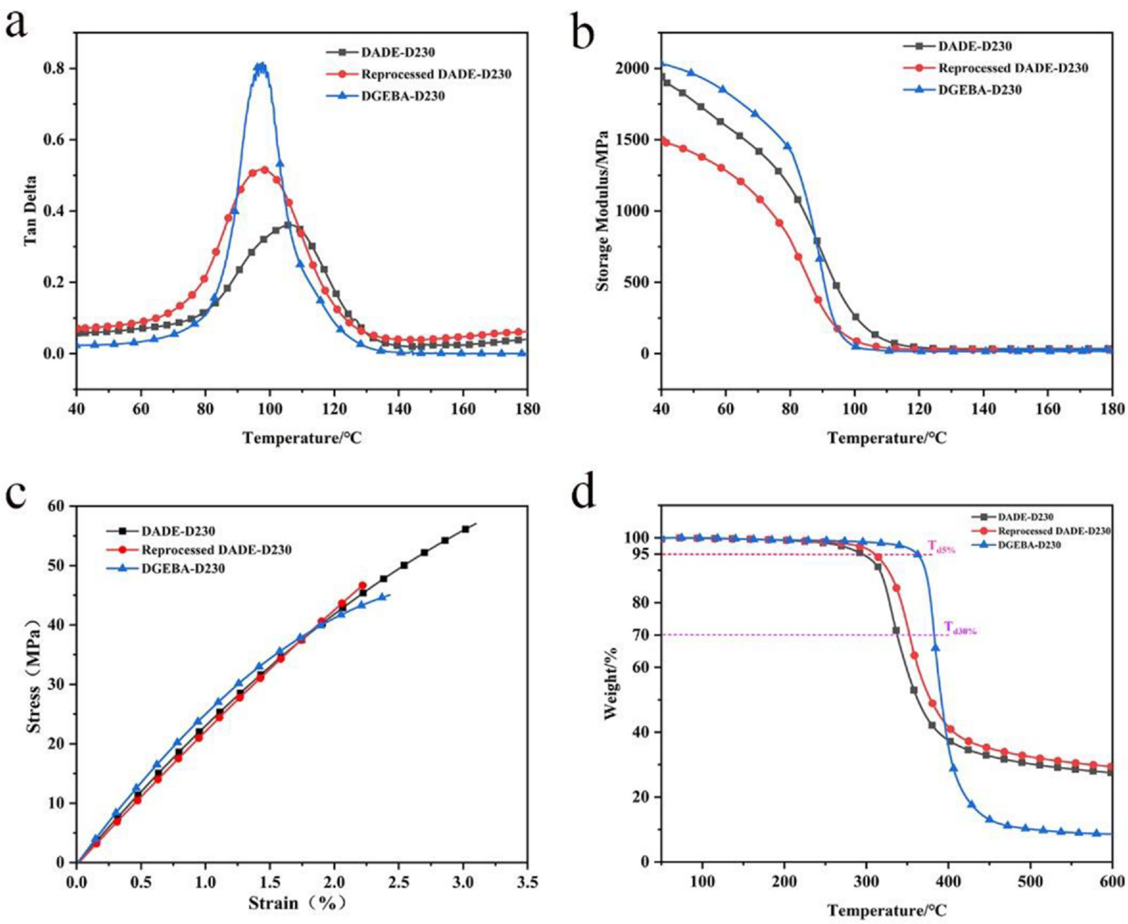


Fig. 8. (a) storage modulus, (b) tan delta, (c) representative tensile stress–strain and (d) TGA curves of DADE-D230, DGEBA-D230 and reprocessed DADE-D230.

Table 2
Thermal and mechanical properties of the samples.

Sample	T_g/°C	E'/MPa	υ_e/×10^{-3}mol/cm^3	Tensile strength /(MPa)	Tensile modulus /(MPa)	Elongation at break/%	$T_{d5\%}$/°C	$T_{d30\%}$/°C
DADE-D230	106	35.2	3.7	57.4 ± 3.6	2523.7 ± 115.1	3.1 ± 0.6	301	346
DGEBA-D230	98	16.9	1.8	44.5 ± 3.4	2660.6 ± 56.9	2.6 ± 0.2	361	382
Reprocessed DADE-D230	97	28.4	3.1	47.0 ± 4.4	2533.5 ± 254.5	2.2 ± 0.2	339	352

D230. It can be seen from Fig. 8b that the storage modulus and T_g of DADE-D230 decreased after remodeled. Among them, the T_g of remodeled DADE-D230 was reduced to 97 °C, the storage and modulus was reduced to 1502 MPa, which decreased by about a quarter. The crosslink density of reprocessed DADE-D230 was calculated to be 3.1, which was just 82% of original samples. The result was similar to the decline in storage modulus. The mainly reason for this result was that after the polyimine-epoxy crosslinked network was destroyed, only the imine crosslinked network can be recombined, but the epoxy crosslinked network cannot be reformed. Thus, making the crosslink density of the material reduced after remolded. But the cross-linking density of reprocessed DADE-D230 was higher than DGEBA-D230.

Fig. 8c presents the representative tensile stress–strain curves of DGEBA-D230, original and reprocessed DADE-D230, the data were displayed in Table 2. The whole samples exhibited rigid tensile behaviors without a yield point. The tensile strength of DADE-D230 (57.4 MPa) was higher than DGEBA-D230 (44.5 MPa). In contrast, the tensile modulus of DADE-D230 was a little lower than that of DGEBA-D230, which may be because DGEBA-D230 contained more rigid structure. At the same time, DADE-D230 showed a higher elongation at break of 3.1% than DGEBA-D230 (2.6%). Obviously, the mechanical properties of DADE-D230 were decreased after remodeled. The tensile strength and elongation at break of DADE-D230 dropped to 47.0 MPa and 2.2%, but it was almost as much as DGEBA-D230, which was consistent with the DMA test. The DMA data and stretch data were mutually confirmed.

Thermal stability is another crucial indicator for thermo-sets, which was characterized via TGA under N_2 atmosphere, and the data are shown in Fig. 8d and Table 2. Both 5% weight loss ($T_{d5\%}$) and 30% weight loss ($T_{d30\ \%}$) of DGEBA-D230 were higher than those of DADE-D230, due to the existence of dynamic imine bond. But the residual carbon of DADE-D230 was higher than that of DGEBA-D230 due to the higher nitrogen content, which has a great advantage in flame resistance. There were not obvious changes of thermal stability found after remolded, this also showed the chemical structures were well-preserved during reprocessed.

4. Conclusion

In this study, a bio-based epoxy resin, containing both aldehyde and epoxy groups was synthesized from vanillin. The cured resin showed excellent mechanical and thermal properties (a high T_g of 106 °C, a tensile strength of 57.4 MPa and elongation at break of 3.1%) after cued, which were better than DGEBA. Moreover, DADE-D230 exhibited superior malleability and reprocessability, with an E_a of 46.9 kJ·mol^{-1}, a T_v of around 70 °C, and it can be recycled at a heat pressing (150 ℃, 10 min) due to the Schiff based bonds. The reprocessed DADE-D230 showed equivalent properties compared with DGEBA-D230. A way was shown to solve the problem of recycling epoxy resin: in-situ introducing reversible bond during resin cured. It is significant for the structural design and recycling of epoxy resins and other cross-linked polymers. And it is also of great significance for future epoxy resin development and resource conservation.

CRediT authorship contribution statement

Xunzheng Su: Conceptualization, Writing - original draft, Investigation. **Zhen Zhou:** Conceptualization. **Jingcheng Liu:** Resources, Data curation, Investigation. **Jing Luo:** Investigation. **Ren Liu:** Writing - review & editin, g.

Declaration of Competing Interest

There are no conflicts to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2020.110053.

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