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# Improved electrical properties, hydrophobicity, and degradability of ortho-vanillin-based epoxy resin: Roles of Schiff base

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ABSTRACT

Conventional diglycidyl ether of bisphenol A epoxy resins (DGEBA) are made from non-renewable fossil resources, which caused severe resource waste and environmental issues. It is of great importance to develop degradable epoxy resins with excellent physicochemical and electrical properties. In this work, a novel vanillin-based epoxy resin (VEP) with Schiff base bond is synthesized from Ortho-vanillin (OVA) and L-phenylalanine (PHE) through a two-step procedure. After cured with 4, 4′-diaminodiphenylmethane (DDM), the vanillin-based epoxy resin (VEP/DDM) exhibits a high char yield of 31.15 %, and 110 % enhancement in storage modulus comparing to DGEBA/DDM. Meanwhile, VEP/DDM presents excellent electrical properties with breakdown strength of 33.16 kV/mm, dielectric constant of 4.00 and dielectric loss of 0.0059 at 50 Hz, respectively. Furthermore, the degradable Schiff base and hydrophobic groups on the side chain of PHE enable the VEP/DDM with good acid-catalytic degradation and hydrophobic properties. This work provides a new route for fabricating bio-based epoxy resins with promising physicochemical and electrical performance in practical engineering applications.

## 1. Introduction

Epoxy resin has been widely used in power industry because of its excellent mechanical properties, adhesion strength, thermal resistance and electrical insulation performance [1,2]. As the core insulating material in solid insulation switchgear, dry-type transformers and power electronic devices, epoxy resin has become the research hotspot in the field of power system. However, conventional epoxy resins are mainly fabricated using an organic diglycidyl ether of bisphenol A (DGEBA), which is one of the nonrenewable petroleum-based compounds. Landfill and incineration are two common methods to dispose its wastes, which inevitably give rise to serious environment pollution as well as considerable waste of resources [3–5]. Consequently, developing sustainable bio-based epoxy resin with great degradability and electrical performance to replace DGEBA becomes urgent for industrial applications and environmental conservation.

Recently, numerous bio-renewable compounds such as vegetable oils, cardanol, isosorbide, gallic acid, lignin and their derivatives have been developed as feedstocks for preparation of epoxy resins [6–9]. The bio-based compounds exhibit various advantages over DGEBA, including high degradability, hydrophobicity and flame retardancy [10], which have been successfully applied in a wide range of composites, coatings and flame retardants [11]. However, it is still a challenge to develop the bio-based epoxy resin with high degradability but not to sacrifice other properties such as thermal stability and electrical insulating capability. Consequently, a strategy that introduces reversible covalent bonds such as ester bonds, disulfide linkages, Schiff base linkages and Diels-Alder addition structures to the cross-linked network of the bio-based epoxy resin is widely adopted to address the recycle issue [12,13].

As a promising dynamic reversible covalent bond, Schiff base was generally produced with Ortho-vanillin to react with amino acids such as L-leucine, L-methionine and L-phenylalanine due to its unique three coordination sites [14–17]. For instance, Zhi et al. [18] synthesized a vanillin-based epoxy resin including a rigid Schiff base structure resulted from vanillin, 1,6-hexanediamine, and epichlorohydrin, which

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shows a large char yield (30.8 %), high glass transition temperature (186 °C) and improved storage modulus (2821 MPa). Yang et al. [19] developed a Schiff base diepoxy compound from vanillin and 9,9-Bis (4-aminophenyl) fluorene. The cured epoxy thermoset demonstrated improved glass transition temperature (197 °C) and flame retardancy. However, current researches on covalent Schiff base epoxy resin mainly focus on its synthetic process and physicochemical properties, neglecting its electrical properties such as electrical breakdown strength and dielectric response. Therefore, the electrical properties of bio-based epoxy resin should be concerned before extending its application in the field of power system.

In this work, a novel vanillin-based epoxy resin (VEP) with Schiff base was synthesized from Ortho-vanillin and L-phenylalanine. The chemical structure, physicochemical, electrical performances and degradability were comprehensively studied comparing with commercial DGEBA.

## 2. Experimental section

### 2.1. Materials

Ortho-vanillin (OVA), L-phenylalanine (PHE), potassium hydroxide (KOH), epichlorohydrin (ECH) and triethylbenzylammonium chloride (TEBAC) were purchased from Shanghai Aladdin Biochemical Technological Co., China. Diglycidyl ether of bisphenol A (DGEBA) and 4, 4′-diaminodiphenylmethane (DDM) were provided by Macklin Biochemical Technological Co., China. Sodium hydroxide (NaOH) and magnesium sulfate ($MgSO_4$) were supplied by Chengdu Chron Chemical Co., China.

### 2.2. Synthesis of Schiff base compound

The chemical reaction mechanism of Schiff base compound (VAL) condensed by OVA and PHE is shown in Fig. 1a. The molar ratio of OVA to PHE is 1:1 (based on the molar ratio of -CHO to -$NH_2$ being 1:1). Firstly, OVA (15.2 g, 0.1 mol) and 150 mL of anhydrous ethanol was mixed in a conical flask. Afterwards, PHE (16.5 g, 0.1 mol), KOH (5.6 g, 0.1 mol) were dissolved in the anhydrous ethanol and mixed through magnetic stirring at 85 °C for 1 h. Subsequently, the OVA and PHE solution were blended together and reacted in a water bath equipment at 85 °C for 3 h, followed by filtration and washing with anhydrous ethanol for three times. Finally, the VAL was produced after drying in a vacuum oven at 80 °C for 12 h.

### 2.3. Synthesis of vanillin-based epoxy compound

Fig. 1b shows the chemical synthesis process of the vanillin-based epoxy compound (VEP) with the solution of VAL (2.99 g, 0.01 mol), excess ECH (100 mL) and TEBAC (0.23 g, 0.001 mol) in a conical flask at 80 °C for 1 h. After the temperature was cooled to 65 °C, 40 wt% NaOH aqueous solution (4.00 g, 0.1 mol) was added dropwise under the magnetic stirring for 1 h. Afterwards, a suspension was obtained, and it was further filtered and washed for three times with deionized water. Finally, the separated organic layer was concentrated under reduced pressure in a rotary evaporator to remove the surplus ECH, and VEP was obtained with a yield of 94 %. To ascertain the yield and purity of the synthesized VEP, the epoxy value was examined via perchloric acid titration. The measured epoxy equivalent was 207.9 g/eq, and the epoxy value was 0.481. This value was in close proximity to the theoretical epoxy equivalent of VEP (0.486).

### 2.4. Synthesis of the cured vanillin-based epoxy resin

DDM was generally chosen as the curing agent to prepare cross-linked VEP because it contains two functional groups including amino and acetylamino that work as both crosslinking agent and catalyst during the curing reaction [20,21]. Fig. 1c shows the curing process of vanillin-based epoxy resin. Firstly, VEP (4.11 g, 0.01 mol) and DDM (0.99 g, 0.005 mol) were mixed according to the stoichiometry ratios (the molar ratio of epoxy groups to N–H bond was 1:1) and blended by

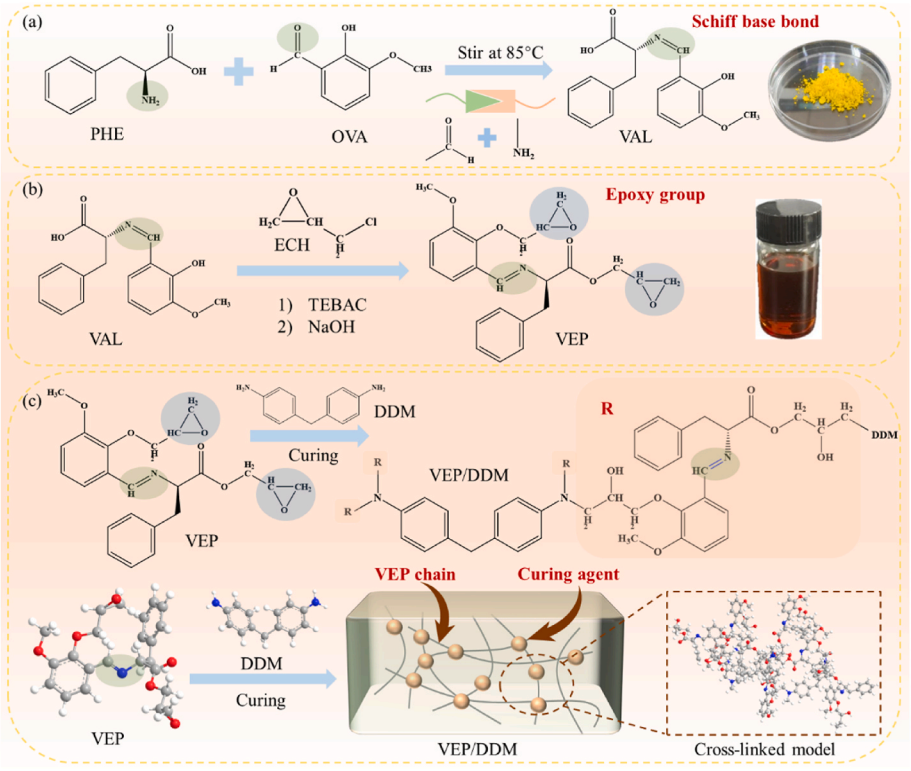


**Fig. 1.** Chemical reaction process of bio-based epoxy composites. (a) VAL, (b) VEP, (c) cross-linked VEP/DDM.

magnetic stirring for 10 min at room temperature. Then, the mixture was poured into a preheated mold for vacuum degassing for 10 min. Finally, the VEP/DDM sample was obtained after continuously curing at 90 °C for 2 h, 110 °C for 2 h and 130 °C for 2 h in a drying oven, respectively. For comparison, DGEBA/DDM was also prepared with the same procedure.

### 2.5. Characterization

The Fourier transform infrared (FT-IR) spectra were obtained using a Thermo Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, America) with a scanning range of 400 $cm^{-1}$–4000 $cm^{-1}$. $^{1}H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were obtained using the Bruker 400 MHz nuclear magnetic resonance spectrometer (Bruker, Switzerland) at room temperature with the deuterium oxide ($D_2O$) as solvent. Differential scanning calorimetry (DSC, TA, America) were carried out from 40 °C to 250 °C under a nitrogen atmosphere to investigate the apparent activation energy of the cured samples. The thermal stability of the samples is measured using thermogravimetric analysis (TGA, TA Q400, America) from 40 °C to 800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed with a heating rate of 5 °C/min and frequency of 10 Hz using a DMA Q800 instrument (TA Q800, America) in a single cantilever mode. The water contact angle (WCA) of the samples was measured via a Drop Meter A-200 contact angle system (Kudos, America). Dielectric properties were evaluated in the frequency range 10–$10^6$ Hz at room temperature using Novocontrol ALPHA frequency-response analyzer (Concept 80, Germany). In accordance with IEC 60423-1-2013, the alternating-current (AC) breakdown strength of the samples is analyzed based on a two-parameter Weibull statistic model,

$$F(x) = 1 - e^{(-x/E_b)^{\beta}} \quad (1)$$

where $x$ is tested discrete breakdown strength, $E_b$ is the Weibull breakdown strength, and $\beta$ is the shape parameter, reflecting the data dispersion.

### 2.6. Calculation method

*The cross-linked models of VEP/DDM and DGEBA/DDM systems were established and the Fractional Free Volume (FFV) were calculated using the Forcite module.* The free volume represents the space for the activity of

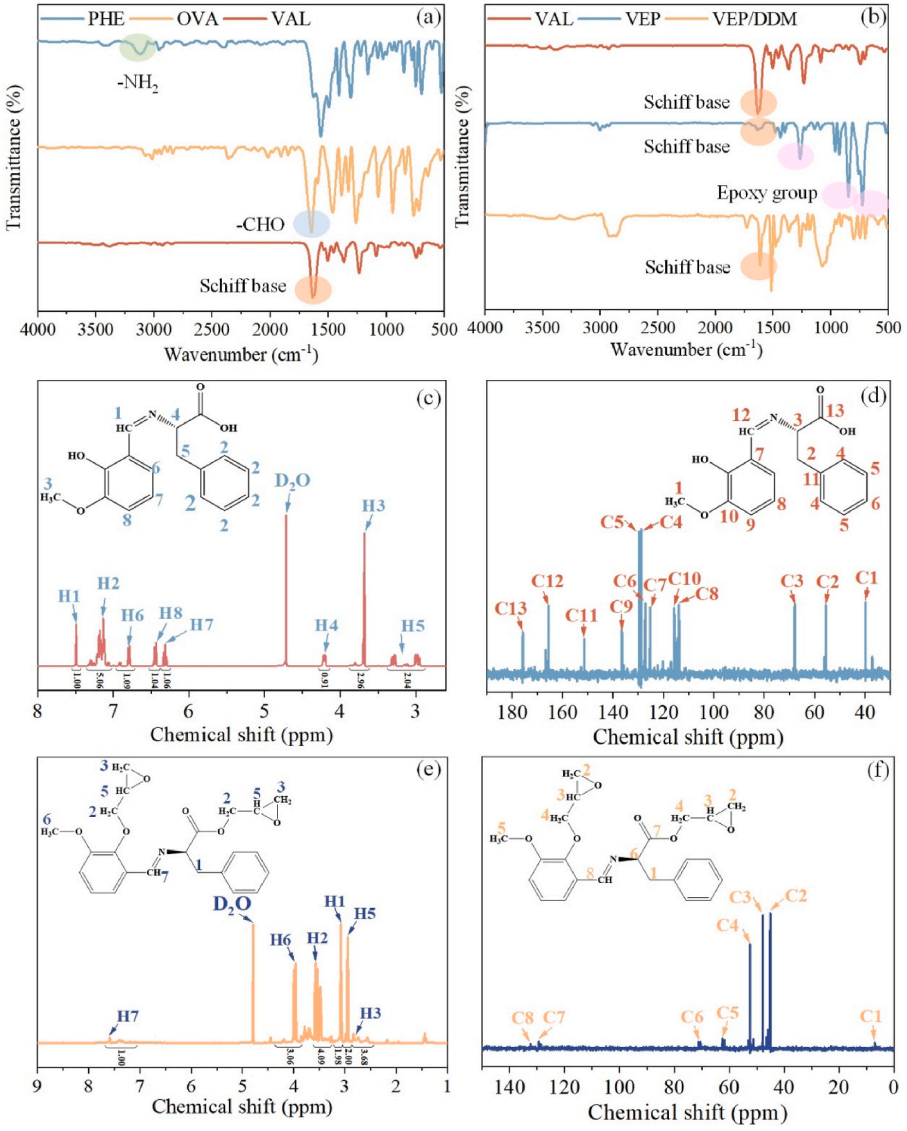


**Fig. 2.** (a) FT-IR spectra of PHE, OVA, VAL and (b) VEP, VEP/DDM. (c)$^{1}H$ NMR spectra of VAL, (d) $^{13}C$ NMR spectra of VAL, (e) $^{1}H$ NMR spectra of VEP and (f) $^{13}C$ NMR spectra of VEP.

the molecular chains, and the FFV represents the packing efficiency of the molecular chains, which can be defined by the following equation,

$$FFV = \frac{V_f}{V_o + V_f} \quad (2)$$

where $V_o$ is the occupied volume and $V_f$ is the free volume. *The density of states was carried out based on the Density Functional Theory (DFT) and the DMol3 module.*

## 3. Results and discussion

### 3.1. Chemical characterization of VAL, VEP and VEP/DDM

Fig. 2a displays the FT-IR spectra of the synthesized monomers such as PHE, OVA and VAL. It is found that the characteristic peaks of -$NH_2$ at 3110 $cm^{-1}$ and -CHO at 1649 $cm^{-1}$ disappear in VAL as a new adsorption peak of Schiff base (-C=N-) is generated at 1632 $cm^{-1}$, indicating that VAL was successfully synthesized from OVA and PHE [22,23]. Fig. 2b illustrated that VEP was synthesized from the reaction between VAL and ECH. The characteristic peaks of epoxy groups can be found at 1263 $cm^{-1}$, 845 $cm^{-1}$ and 724 $cm^{-1}$, which can be attributed to the stretching vibration, bending vibration and deformation vibration of epoxy groups, respectively [24,25]. Moreover, the liquid VEP reacted with DDM powder during the curing process and the epoxy groups in VEP would be consumed to produce the VEP/DDM. As shown in Fig. 2c–f, the VAL and VEP molecules are validated through NMR spectrum to confirm their structure. In Fig. 2c and d, the peak at 7.5 ppm was assigned to the proton in Schiff base bond (-CH=N-). Following epoxidation, the peaks in the range from 2.5 ppm to 3.0 ppm were assigned to the epoxy ring protons [26]. Moreover, the $^{13}C$ NMR spectrum of VAL and VEP showed that the carbon resonances were well-matched with the expected structure. The value of the integral regions within the hydrogen protons further confirms the synthesis of VAL and VEP, which is consistent with the theoretical results of the structure. Along with the results from FT-IR, $^{1}H$ NMR, and $^{13}C$ NMR, the chemical structure of VAL and VEP were verified to be fabricated.

### 3.2. Curing behavior of VEP/DDM

In Fig. 3a and b, the DSC curves were tested to analyze the non-isothermal curing kinetics of VEP/DDM and DGEBA/DDM. It is clear that only one curing exothermic peak can be observed at different heating rate in both epoxy resin samples, which is closely related with the ring-opening crosslinking reaction of epoxy-amines [19]. To obtain a more accurate comparison of the curing reactivity, the apparent activation energy ($E_a$) of the ring-opening reaction is calculated using Kissinger's method [27,28],

$$\ln\left(\frac{\delta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (3)$$

where $A$ is the pre-exponential factor, $\delta$ and $R$ represent the heating rate and the ideal gas constant, $C$ is a constant, $T_p$ is the exothermic peak temperature, respectively. From Fig. 3a and b, the $T_p$ value of VEP/DDM at equivalent heating values is systematically lower than that of DGEBA/DDM, suggesting higher reactivity of epoxy groups in VEP. Additionally, the $E_a$ in Fig. 3c of VEP/DDM calculated is 36.91 kJ/mol, lower than that of DGEBA/DDM (43.16 kJ/mol). These results are attributed to the higher reactivity of Schiff base that promotes the curing reactivity of VEP/DDM and accelerates the curing process [29,30].

### 3.3. Electrical performance of VEP/DDM

Due to the randomness and discreteness of the occurrence of partial discharge during the insulation test, ten breakdown points were tested for each sample, respectively. The Weibull distribution was used to handle the reliability and accuracy of the breakdown strength ($E_b$). In Fig. 4a, it is found that the breakdown strength of VEP/DDM is 33.16 kV/mm, slightly higher than 31.94 kV/mm of DGEBA/DDM, which is mainly attributed to the introduction of nonpolar groups on the side chain of PHE that improves $E_b$ of VEP/DDM [31]. The dielectric constant and dielectric loss of VEP/DDM and DGEBA/DDM samples were tested three times, error bands were presented in Fig. 4b and c, and the average value at low, medium, and high frequency were calculated in Table 1. From Fig. 4b and c, the dielectric constant ($\varepsilon$) and dielectric loss ($\tan\delta$) of VEP/DDM are both lower than that of DGEBA/DDM in a wide frequency range from 10 Hz to $10^6$ Hz. As illustrated in Table 1, $\varepsilon$ and $\tan\delta$ of VEP/DDM are 4.005 and 0.00599 at 50 Hz, respectively, which are 10.31 % and 21.84 % lower than that of DGEBA/DDM [32,33]. It is believed that three substituents on the benzene ring in the OVA portion of VEP/DDM suppress the polarization, and result in the decrease of $\varepsilon$ and $\tan\delta$. Moreover, the *Fractional Free Volume* (FFV) of VEP/DDM is lower at different crosslinking degree as shown in Fig. 4d and e, which reduces the migration efficiency of charge carriers and decreases the contribution of electrical conductivity loss to dielectric loss $\tan\delta$ [34,35].

### 3.4. Thermomechanical properties of VEP/DDM

Glass transition temperature ($T_g$) is closely related with their crosslink density ($\nu_e$) of the segmental chain. The $\nu_e$ of VEP/DDM and DGEBA/DDM was calculated using the rubber elasticity theory [36],

$$E_r = 3RT_r\nu_e \quad (5)$$

where $R$ is the universal gas constant, $E_r$ is the storage modulus of the thermosets in the rubber plateau region at $T_r$ that is 30 °C above the glass transition temperature ($T_r = T_g + 30$ °C).

In Fig. 5a, VEP/DDM showed a higher storage modulus than DGEBA/DDM at 30 °C because of the rigidity of Schiff-base bond in the main chain of the VEP/DDM system, as well as the π-π conjugation between the benzene ring and the Schiff-base. However, in Fig. 5b, the $T_g$ of the

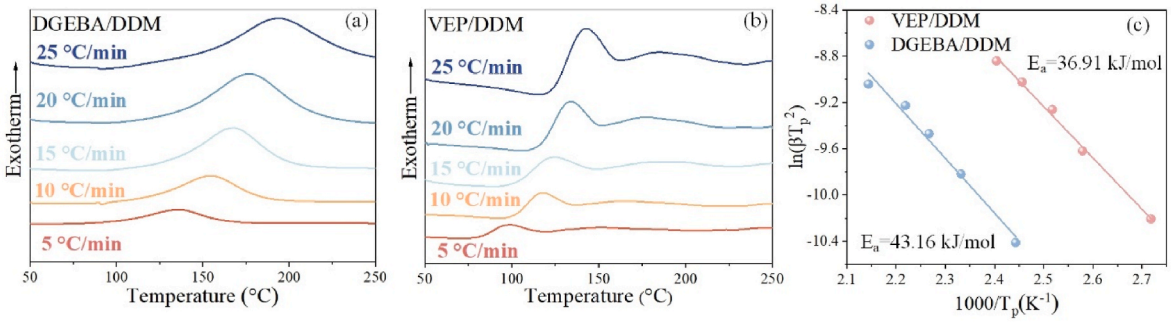


**Fig. 3.** (a) DSC curves of VEP/DDM and (b) DGEBA/DDM, (c) linear plots of $\ln(\delta/T_p^2)$ versus $1/T_p$ based on Kissinger's equation.

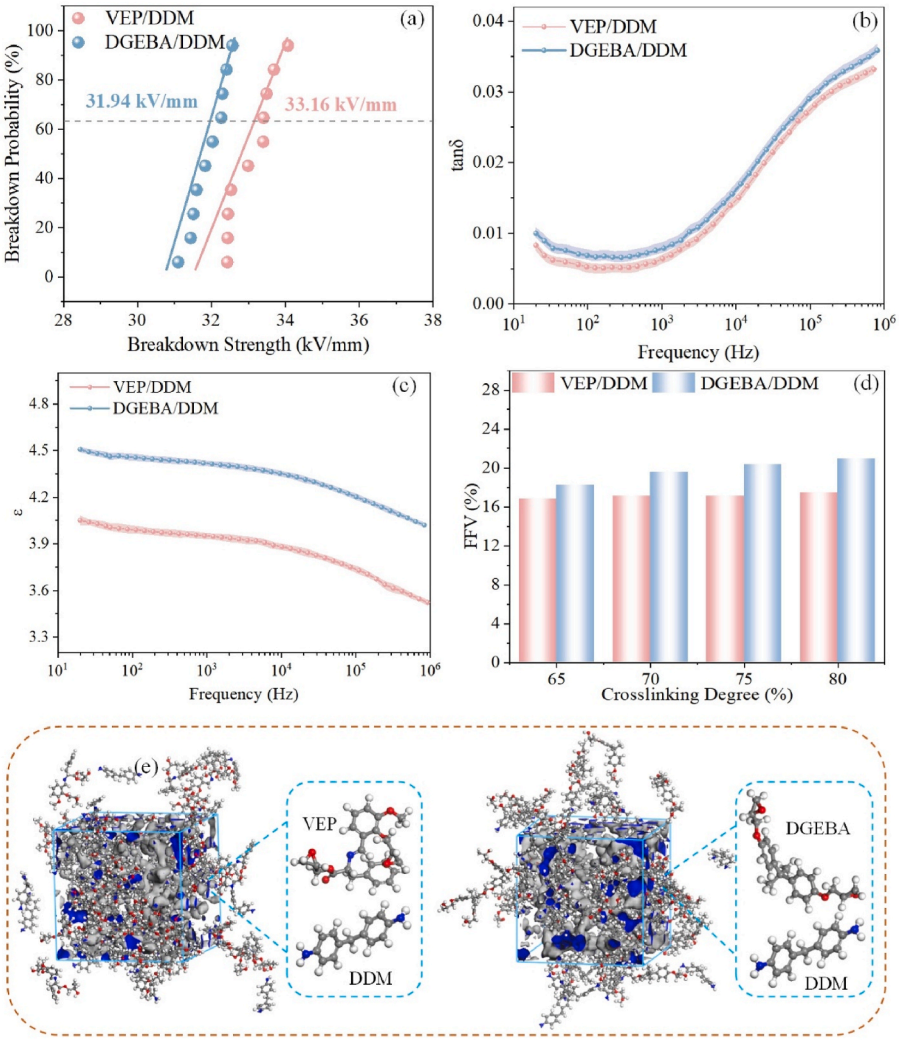


**Fig. 4.** (a) Weibull distribution diagrams of breakdown strength, (b) dielectric loss, (c) dielectric cconstant, (d) FFV at different cross-link degree, (e) free volume distribution of VEP/DDM and DGEBA/DDM.

**Table 1**
Electrical parameters of VEP/DDM and DGEBA/DDM.

| Sample | $E_b$ (kV/mm) | ε | | | tanδ ( × $10^{-3}$) | | |
|---|---|---|---|---|---|---|---|
| | | 50 (Hz) | $10^3$ (Hz) | $10^6$ (Hz) | 50 (Hz) | $10^3$ (Hz) | $10^6$ (Hz) |
| VEP/DDM | 33.16 | 4.005 | 3.947 | 3.523 | 5.990 | 6.468 | 33.248 |
| DGEBA/DDM | 31.94 | 4.464 | 4.415 | 4.022 | 7.525 | 7.850 | 35.798 |

VEP/DDM is only 110.63 °C, lower than 148.75 °C of DGEBA/DDM. The $T_g$ of thermosetting resins is primarily influenced by the rigidity of the molecular structure and cross-link density. As shown in Table 2, the calculated cross-link density of VEP/DDM and DGEBA/DDM is 567.2 mol/$m^3$ and 751.9 mol/$m^3$, respectively. Although VEP incorporates a rigid Schiff base structure, it contains a large number of flexible methoxy groups, which reduce the cross-linking density of VEP/DDM.

### 3.5. Thermal stability of VEP/DDM

The thermal stability of VEP/DDM and DGEBA/DDM are characterized by the statistic heat-resistant index ($T_s$), and the $T_{d5\ \%}$ (degradation temperature of 5 % weight loss) and $T_{d30\ \%}$ (degradation temperature of 30 % weight loss) are calculated with TGA curves [37],

$$T_s = 0.49[T_{d5\%} + 0.6(T_{d30\%} - T_{d5\%})] \quad (6)$$

As shown in Table 3, the temperature corresponding to 5 % loss for VEP/DDM and DGEBA/DDM is 267.55 °C and 317.50 °C, respectively, the lower onset thermal decomposition temperature for VEP/DDM is mainly attributed to the early thermal decomposition of Schiff base and low cross-link density of VEP/DDM structure [37,38]. However, it is found in Fig. 6a that VEP/DDM presented a char residue of 31.51 % at 800 °C, much higher than 15.95 % of DGEBA/DDM. Firstly, the Schiff base structure promotes the formation of residual carbon structures during the thermal decomposition of VEP/DDM. Secondly, the aromatic ring structure within the VEP/DDM molecule can facilitate the formation of the coke layer [39]. In Fig. 6b, VEP/DDM exhibits two degradation stages corresponding to the decomposition of the Schiff-base structure and the degradation of the epoxy resin matrix. Therefore, VEP/DDM exhibits great potential for flame retardant applications in thermosetting epoxy resins [40].

### 3.6. Chemical degradation of VEP/DDM

The reversibility of Schiff base bonds facilitates acid-catalyzed hydrolysis, as evidenced by the formation of aldehyde and amino groups during degradation [19,39]. In this study, VEP/DDM samples were

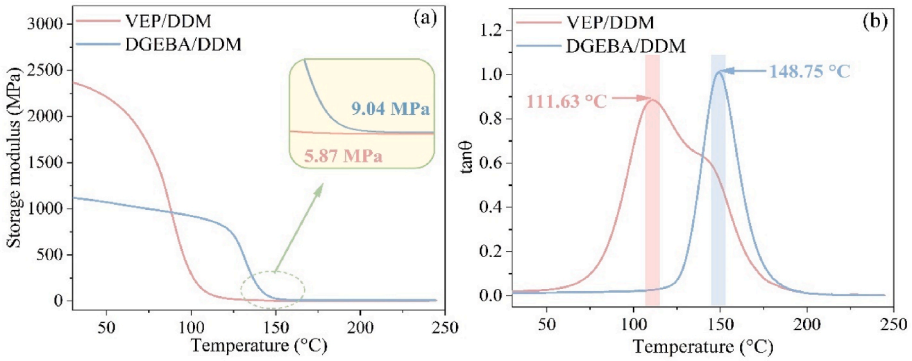


**Fig. 5.** (a) Storage modulus, (b) tanθ of VEP/DDM and DGEBA/DDM.

**Table 2**
Thermodynamic results of VEP/DDM and DGEBA/DDM.

| Sample | Storage modulus (MPa) | $T_g$ (°C) | $\nu_e$ (mol/m$^3$) |
|---|---|---|---|
| VEP/DDM | 2370 | 111.63 | 567.2 |
| DGEBA/DDM | 1123 | 148.75 | 751.9 |

**Table 3**
Thermogravimetric data of VEP/DDM and DGEBA/DDM.

| Sample | $T_{d5\ \%}$ (°C) | $T_{d30\ \%}$ (°C) | $T_s$ (°C) | $C_{y800}$(%) | $T_{max}$ (°C) | $R_{max}$ (%/°C) |
|---|---|---|---|---|---|---|
| VEP/DDM | 267.55 | 337.87 | 157.77 | 31.51 | 300.96, 420.27 | −0.54, −0.26 |
| DGEBA/DDM | 317.50 | 400.89 | 180.09 | 15.95 | 398.14 | −2.19 |

soaked in 20 ml of 0.2 M HCL with various solvents such as Methanol (MeOH), Ethanol (EtOH), Dimethyl sulfoxide (DMSO) and N, N-Dimethylformamide (DMF) for 12 h, respectively. The decomposition process of VEP/DDM under different solutions was carried out at 25 °C and 65 °C as shown in Fig. 7a. After soaking for 12 h, a noticeable swelling of VEP/DDM samples can be observed in solvents at 25 °C, while a significant color variation occurs for the samples in the solution at 65 °C. In Fig. 7b, the degradation rate was used to evaluate the decomposition process of VEP/DDM in different solvents at 25 °C and 65 °C, respectively. It is obvious that high temperature accelerates the decomposition process of VEP/DDM samples. Fig. 7c shows the possible degradation mechanism that the Schiff base can break into aldehyde group and amino group in acidic aqueous solutions.

The density of states (DOS) of VEP/DDM and DGEBA/DDM samples were also calculated to analyze the molecular structural stability. The density of state energy gap ($\Delta E$) between VEP and DDM, DGEBA and DDM are presented in Fig. 7d and e, respectively [41]. The $\Delta E$ of VEP/DDM is obviously lower than that of DGEBA/DDM because VEP/DDM possesses a more active structure, and is more likely to participate in chemical reactions under acidic aqueous solution.

### 3.7. Hydrophobic properties of VEP/DDM

When working in a moisture circumstance, water vapor may diffuse into epoxy resin and deteriorate its mechanical and electrical properties [42,43]. Consequently, excellent hydrophobicity plays a pivotal role in ensuring the stable application of epoxy insulating materials in electrical equipment. The non-polar functional groups of hydrophobic materials are difficult to form hydrogen bonds with water molecules, thus exhibiting hydrophobic properties. When the contact angle (WCA) is over 90°, the surface of the material is hydrophobic, which can be protected from moisture. As displayed in Fig. 8a and b, the VEP/DDM demonstrates an excellent hydrophobic property with an average WCA of 104.87°, which is 22.41 % higher than that of DGEBA/DDM. It is suggested that the hydrophobic groups on the side chain of PHE produces the stable intramolecular hydrogen bonds in VEP/DDM, which restrains the interaction between water molecules and hydroxyl groups, thereby enhancing the hydrophobic properties [44,45].

## 4. Conclusions

In this work, a novel bio-based epoxy resin with Schiff base was successfully synthesized from Ortho-vanillin and L-phenylalanine. In comparison to DGEBA/DDM, VEP/DDM exhibits a high char yield of 31.15 %, and 110 % enhancement in storage modulus. Additionally, the breakdown strength and dielectric constant of VEP/DDM reach 33.16 kV/mm and 4.00, which shows better electric performance than DGEBA/DDM. Furthermore, VEP/DDM is degradable in acid solutions at 65 °C due to the hydrolysis reaction of Schiff base. The hydrophobic PHE

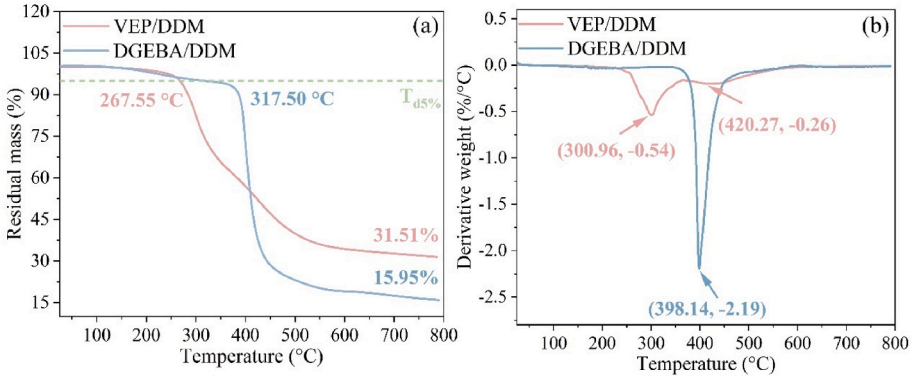


**Fig. 6.** (a) TGA, (b) DTG curves of VEP/DDM and DGEBA/DDM.

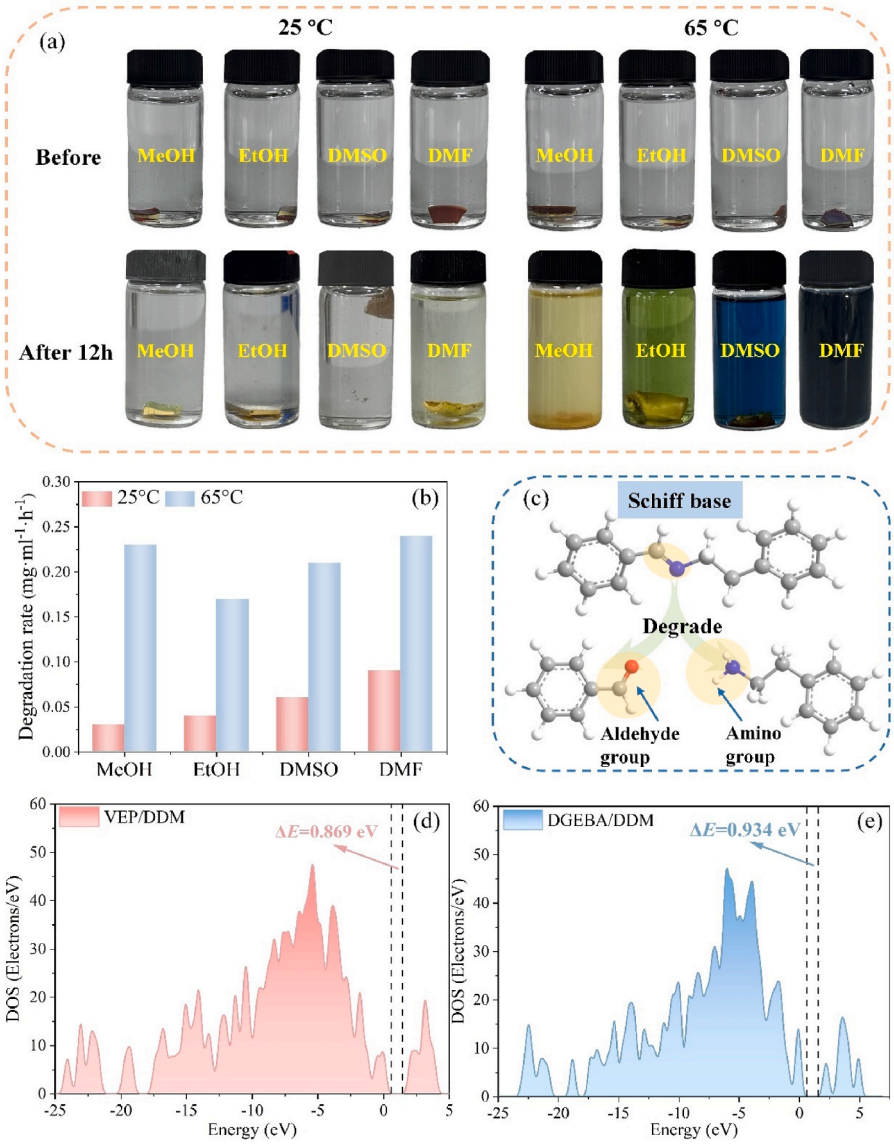


**Fig. 7.** (a) Photographs of VEP/DDM degradation in different solvents, (b) degradation rate of VEP/DDM at 25 °C and 65 °C, (c) degradation mechanism of VEP/DDM, and density of states in (d) VEP and (e) DGEBA.

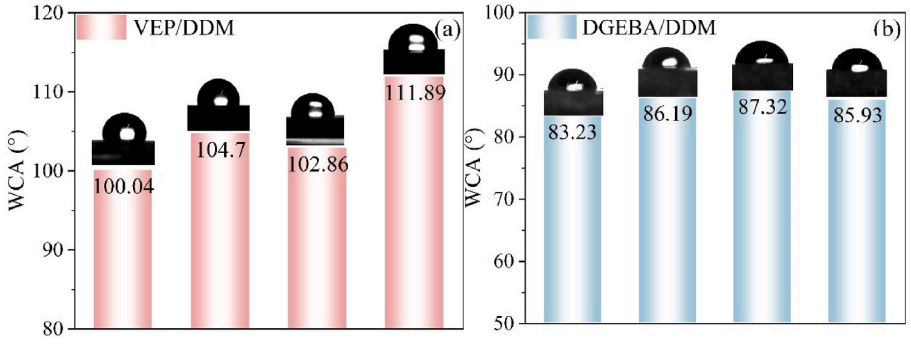


**Fig. 8.** WCA of (a) VEP/DDM, (b) DGEBA/DDM.

enables VEP/DDM an excellent hydrophobic property, with the WCA of 104.87°, which is 22.41 % higher than that of DGEBA/DDM. This work proposes a novel strategy for preparing the bio-based epoxy resin that could be a potential eco-friendly insulating material for engineering application.

## CRediT authorship contribution statement

**Xiao Peng:** Writing – original draft, Methodology, Data curation, Conceptualization. **Xuetong Zhao:** Writing – review & editing, Supervision, Resources, Project administration, Data curation. **Tingyue**

**Dong:** Writing – review & editing, Formal analysis, Data curation. **Yuan Yuan:** Methodology, Investigation. **Li Cheng:** Resources, Methodology. **Lijun Yang:** Resources, Methodology. **Ruijin Liao:** Supervision, Methodology.

## 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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## Data availability

Data will be made available on request.

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