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Vanillin-based degradable epoxy vitrimers: Reprocessability and mechanical properties study

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ABSTRACT

The preparation of vanillin-based epoxy thermosets has attracted great attention in recent years, however, most of them could not be reprocessed once after curing procedures. In the present work, a vanillin-based epoxy vitrimer (Van-Ep/IPDA) with dynamic imine covalent bonds was prepared by curing mono-glycidyl structure of vanillin (Van-Ep) with isophorone diamine (IPDA) hardener, which simultaneously exhibits the excellent reprocessability and acid degradable behavior. The mechanical properties of Van-Ep/IPDA vitrimers and cured bisphenol A (E51) epoxy are kept at the same level, which the Young's modulus, elongation and tensile strength at break of Van-Ep/IPDA vitrimers reach 2.30 GPa, 4.4% and 65.0 MPa, respectively. Importantly, compared with these of original vitrimers, all reprocessed Van-Ep/IPDA vitrimers exhibit the same level of mechanical properties even after three times of hot pressing. Thanks to the imine structure, epoxy vitrimers also exhibit degradable property under acid solution. This facile approach of imine chemistry for preparing vanillin-based epoxy vitrimers sets up an important framework for designing sustainable polymer materials with excellent reprocessability and degradability.

1. Introduction

Cured epoxy resins are thermosets with stable networks of covalent bonds, high mechanical properties and chemical resistance. They are extensively utilized in the fields of composites, adhesives, coatings, and electrical materials. With the depletion of fossil fuel resources, bio-based epoxy resins have become increasingly important, partially or fully bio-based epoxy monomers have been prepared to replace or supplement bisphenol A (BPA) type of epoxy monomers. For example, vegetable oils [1], tannins [2] and furan [3] have been reported for preparing bio-based epoxy resins.

Lignin, the only biopolymers with aromatic structure, direct use of it [4] and its-derived phenol monomers, such as vanillin [5,6], guaiacol [7], eugenol [8] and vanillic acid [9] etc, have been extensively studied as BPA epoxy alternatives. It is still challenging to prepare lignin based epoxy without deconstructing the inhomogeneous and complex aromatic structures of lignins, due to their poor reactivity and solubility [10]. Until now, great efforts have been focused on designing the structures of epoxy from lignin derived monomers, mainly including tailoring the epoxy content by converting reactive groups (methoxy and aldehyde) into hydroxyl groups [11–13] and using bridging regents [5,14]. Despite of the huge progress reported in the above fields, it should be recognized that their applications as commercial epoxy alternatives are still hindered by the high cost. Therefore, it is desirable that the epoxy thermosets could be mechanically reshaped without deterioration on their mechanical properties even after several times of break. Once this problem has been resolved, the cost will be hugely reduced.

Thermoset vitrimers which is a class of a covalent adaptive network with exchangeable chemical bonds [15,16] still have being a hot topic in recent years, showing wonderful properties, such as self-healing and remendable ability. The vitrimers concept, pioneered by Leibler et al, was achieved by transesterification which is conveniently applied to epoxy/acid and epoxy/anhydride curing systems [16]. Until now,

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Abbreviations: TEBAC, triethylbenzylammonium chloride; IPDA, isophoronediamine; Van-Ep, vanillin-derived epoxy; SR, swelling ratio; GF, gel fraction; E′, storage modulus; ν_e, cross-linking densities; E_a, activation energy; T_v, topology freezing transition temperature; τ, stress relaxation time

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varieties of vitrimers or vitrimer-like materials based on carboxylate transesterification [17], transamination of vinylogous urethanes [18], transcarbamoylation [19], olefin metathesis [20], disulfide exchange [21] and imine amine exchange [22], etc have been reported. By introducing the above dynamic covalent bonds into crosslinking networks, the traditional thermosets could be hot reprocessed like thermoplastic does. As for epoxy vitrimers, transesterification and disulfide exchange are the most adopted vitrimers chemistry [16,23–28]. For example, the epoxy vitrimers obtained from DEGBA and glutaric anhydride show stiff properties with ~1.8 GPa modulus and stress at break of ~55 MPa at room temperature [16]. Recently, siloxane equilibration catalyzed with potassium silanolate end groups has been firstly introduced into epoxy networks, the stress at break and Young's Modulus reach up to 46.6 MPa and 2.2 GPa, respectively [29]. Until now, the stiffest epoxy vitrimer is the one that Young's Modulus, stress and elongation at break reach 2.6 GPa, 88 MPa and 7.1%, respectively [24], which was prepared by curing the DEGBA with 4,4′-disulfanediyldianiline (aromatic disulfide). However, there are still several problems needed to be solved. For example, zinc catalyst is necessary for transesterification in most cases, but it might cause the risk of catalyst instability and toxicity. Besides, the widely used aromatic disulfide (4-aminophenyl disulfide) hardener is too expensive. Very recently, lignin based vitrimers have also been reported, such as recyclable polyschiff thermosets [30,31] and recoverable adhesive [32]. With respect to lignin based epoxy vitrimers, only Zhang et al. have done some pioneering works until now. For example, anhydride-cured eugenol and vanillin-derived di/trifunctional epoxy resins were prepared [7,13]. The Young's Modulus, stress and elongation at break of trifunctional epoxy resins are ~1.95 GPa, ~69 MPa and 4.9%, respectively [7].

Imine bond is classic dynamic covalent bond, which is formed by the condensation reactions between aldehydes and amines. Three equilibrium processes, imine condensation/hydrolysis, imine exchange and imine metathesis, are commonly involved in this system [33]. Recently, self-healing Li-Ion electrolyte membrane and repairable woven carbon fiber composites have been reported by using imine chemistry [34,35]. Besides, taking advantage of its instability under water solution, self-healing hydrogel [22,36,37] and drug release carrier [38,39] have also been designed based on this property. However, this approach has remained underused for designing thermoset resins except for recently reported polyschiff vitrimers [30,31].

The aim of this study is preparing a lignin based epoxy vitrimers from vanillin using imine chemistry. The aldehyde group is neither reduced to hydroxyl group [9] nor oxidized to phenol [40], but the phenol group of vanillin was epoxidized. Finally, this vanillin-based epoxy monomer with aldehyde group was reacted with amine hardener to form dynamic imine covalent bond. Through simple imine chemistry, the reprocessable and degradable ability are simultaneously achieved. In this work, the mechanical properties, stress relaxation behaviors and degradation ability were extensively characterized.

2. Experimental

2.1. Materials

Vanillin (≥99%), triethylbenzylammonium chloride (TEBAC) (98%) and isophoronediamine (IPDA, ≥99%) were purchased from Aladdin Company. Epichlorohydrin and anhydrous sodium hydroxide are commercial chemicals and used without further purification. E51 epoxy resin (epoxy value = 0.51 mol/100 g) was supplied by Wuhan Shenshi chemical company.

2.2. Synthesis of vanillin-derived epoxy (Van-Ep)

Vanillin (7.608 g, 1.0 eq), TEBAC (1.139 g, 0.1 eq) and epichlorohydrin (46.26 g, 10 eq) were added to a 150 mL three-necked bottle under magnetic stirring. Then, the mixture was stirred for 1.5 h at 80 °C, after which the solution was cooled down to room temperature. A mixed solution of TEBAC (1.139 g, 0.1 eq) and NaOH (8 g, 4.0 eq, 5.0 mol/L) was added and then stirred for 30 min at room temperature. After the reaction was completed (monitored using TLC), ethyl acetate and distilled water were added and stirred for a while, and then the aqueous phase was washed three times with ethyl acetate. The organic phase was collected and dried over anhydrous M_gSO_4 before the solvent was condensed by a rotary evaporator in vacuum. After being vacuum dried in an oven over night, Van-Ep with a yield of 92% was obtained as a light yellow solid (m.p. about 88 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.84 (s, 1H, Ar—C$\underline{H}$O), 7.50–7.05 (3H, Ar—$\underline{H}$), 4.45–4.03 (m, 2H, ArsbndCH2—), 4.00–3.85 (s, 3H, —O—C$\underline{H}_3$), 3.48–3.35 (m, 1H, —CH_2—C$\underline{H}$—), 2.99–2.74 (m, 2H, —CH—C$\underline{H}_2$—O—).^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 190.80, 153.37, 149.90, 130.60, 126.36, 112.27, 109.53, 69.91, 55.94, 49.84 and 44.62.

2.3. Preparation of vanillin-based epoxy thermosets

The vanillin-based epoxy vitrimers were prepared by dissolving Van-Ep (2.4985 g, 12 mmol) in 20 mL CH_2Cl_2 solvent, and then IPDA (1.6647 mL, 9 mmol) was dropped into the above solution under slow stirring. The mixed solution was poured into a square PTFE tray (10 cm length), and a glass plate was used to cover it. After most of solvent was evaporated in an oven at 50 °C for 12 h (0.5 MPa), it was further cured at 80 °C for 2 h and another 2 h at 100 °C. The film was recorded as Van-Ep/IPDA. Besides, a controlled sample of E51/IPDA was obtained using the same procedures. The IPDA (6 mmol —NH_2, 0.5549 mL) was introduced into E51 (12 mmol epoxy, 2.3529 g) with 1:1 M ratio of epoxy vs. —NH for curing. After the pre-curing film obtained, it was further cured at 80, 100 and 120 °C for 2 h, respectively.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 560 FTIR spectrometer using the ATR model. Each spectrum was recorded with 32 scans in the frequency range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 (400 MHz) spectrometer, using $CDCl_3$ as a solvent.

The thermal properties of Van-Ep/IPDA and E51/IPDA were performed on a differential scanning calorimeter DSC (NETZSCH, DSC 214). The sample was heated from room temperature to 200 °C to remove the heat history and then the temperature was immediately dropped to −40 °C and kept at equilibrium in this state for 3 min. Finally, it was increased to 200 °C at 10 °C/min. All the above temperature control was performed under nitrogen atmosphere (60 mL/min flow rate).

The thermal stability of the films was measured by thermal gravimetric analysis (TGA; TA instrument, model Q-500) at a heating rate of 10 °C/min from room temperature to 600 °C under nitrogen atmosphere (50 mL/min flow rate).

Dynamic mechanical properties were characterized using a DMA (TA-Q800) using a film-tension mode. The thickness average values of films with 4 mm width and 30 mm length were measured with a micrometer at five times. The measurements were conducted from −20 to 200 °C at a heating rate of 3 °C/min. The frequency was set at 1 Hz, and the oscillating amplitude was 15 um.

Swelling ratio and gel content were measured as the previous reported methods [41]. Both Van-Ep ad IPDA can well dissolve in xylene, thus swelling experiments were carried out by immersing crude sample (W_0) into xylene at 165 °C for 24 h to get a swollen sample (W_1). The crude sample (W_0) was extracted with xylene at 170 °C for 24 h using a Soxhlet extractor, and then it was dried at 100 and 130 °C for 24 h under vacuum respectively until a constant weight was reached (the dry weight sample was recorded as W_2). The swelling ratio (SR) and gel fraction (GF) were calculated as the formulas: SR = $W_1/W_0 \times 100\%$; GF = $W_2/W_0 \times 100\%$.

Stress relaxation was also measured on a DMA Q800 instrument. Samples were initially preloaded at a force of 0.001 N to maintain straightness. The sample was kept at testing temperature for 5 min, after which it was stretched by 3% and the deformation was maintained. The decrease of stress was recorded and the stress relaxation modulus was calculated.

The mechanical properties of epoxy vitrimers and controlled samples were measured on a 5567 Universal Testing machine with a 1 kN sensor. The gauge length was 25 mm, and the test was performed at a 10 mm/min cross-head speed. The average thickness values of films with 4 mm width were calculated with a micrometer over five measurements. At least eight species were tested for each sample.

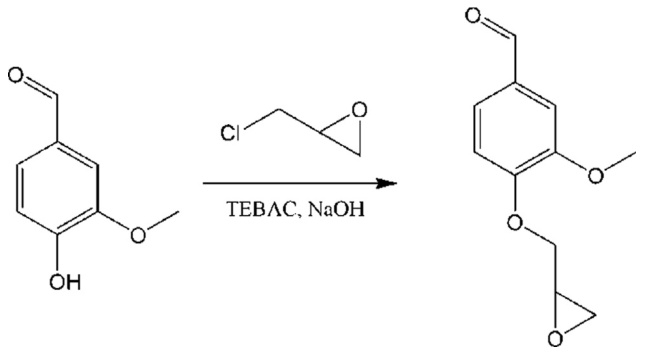
Reprocessing test was performed on a hot pressing machine. The films were firstly cut into large pieces with scissor, and then they were broken into small pieces using a machine mixer with two blades for about 30 s. The pieces were hot reprocessed at 130 °C for 5 min at 10 MPa. After cooling to room temperature, the reprocessed films were obtained. The stress–strain tests were conducted to evaluate their self-healing ability as previously described.

Chemical degradation of the epoxy vitrimers were performed by immersing samples into hydrochloric acid solution (1 mol/L, 10^{-2} mol/L, 10^{-5} mol/L) at 70 °C for 24 h under continuous stirring. The insoluble residuals were collected, vacuum-dried, and characterized by FTIR methods. Finally, the residual weight percentages were calculated.

3. Results and discussion

3.1. Structure characterization of Van-Ep

Almost all of lignin based epoxy monomers have been synthesized through at least two tedious steps [42–44], mainly including pre-modification and epoxidation. Here, Van-Ep monomer was prepared via just one simple step as shown in scheme 1. Its structure was confirmed by FTIR and NMR methods as shown in Figs. S1 and S2, respectively. The absorption peak of phenol —OH group, centered near 3165 cm^{-1}, disappears after epoxidation. A new peak at 908 cm^{-1} is emerged, which confirms the formation of epoxy groups. Besides, the aromatic aldehyde absorption peak is also observed near 1670 cm^{-1}. As shown in the NMR spectra, the absorption signal corresponding to the methylene proton (3a + 3b), which is adjacent to the phenolic ether (Ph-O-CH_2-) group, is detected at 4.38 and 4.30 ppm, respectively. Van-Ep monomer exhibits epoxy protons H4, H5b and H5a at δ 3.42, 2.93 and 2.79 ppm, respectively. The absorption peaks locating at 9.84 and 190.80 ppm are confirmed as the aromatic aldehyde groups. These similar results have also been reported [5,45], thus van-Ep monomer from vanillin was successfully synthesized.



Scheme 1. Synthetic route of Van-Ep monomer from vanillin.

3.2. Curing of Van-Ep/IPDA and their structures characterization

Traditionally, the C—N bonds are formed when di-epoxy monomers are cured with amine hardeners, thus resulting into the stable covalent bonds. In our system, the preparation of vanillin based epoxy vitrimers was illustrated as Scheme 2. Obviously, the dynamic imine covalent bonds could be formed due to the presence of aromatic aldehyde groups in Van-Ep monomer. Meanwhile, the epoxy groups are reacted with amine group of IPDA to form stable C—N covalent bonds. Considering the mono-glycidyl structure of Van-Ep monomer, it is obviously concluded that the numbers of imine dynamic covalent bonds are up to half of total cross-linked networks, which is apparently beneficial to the self-healing and degradation behaviors of Van-Ep/IPDA vitrimers.

The curing reactions of epoxy thermosets are usually monitored using DSC method. However, a homogeneous mixture of Van-Ep and IPDA is hardly obtained, due to the solid property of Van-Ep at room temperature. We tried to immediately mix them together after Van-Ep (m.p. about 88 °C) melting, but the rapid imine reaction was happened, proved by the absorption peak near 1641 cm^{-1} in the FTIR spectrum (results are not showed). Therefore, this curing process was finally characterized by FTIR method and compared with that of referenced sample of E51/IPDA [46]. Here, the epoxy conversion using the method reported by Abu-Omar [6]. Specifically, The conversion ($C_{epoxy}\%$) was then calculated using the following equation:

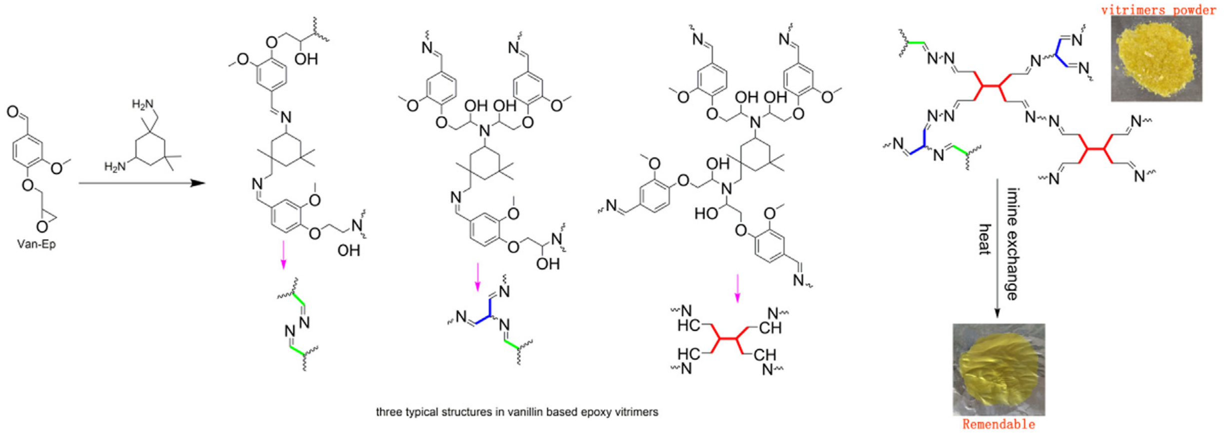
$$C_{epoxy}\% = 1 - \frac{A_{918}(t)/A_{1509}(t)}{A_{918}(0)/A_{1509}(0)} \tag{1}$$

A_{918} (0) and A_{1509} (0) are the areas of the epoxide peak at 918 cm^{-1} and reference peak at 1509 cm^{-1} at time zero, while A_{912} (t) and A_{1509} (t) are the areas of the epoxy and reference peaks at time t (min). Peak fitting was conducted using peak fit software with the residuals fitting method, as shown in Figs. S4 and S5. The consumption of aldehyde group was also determined by using the equation 1 except for the replacement of A_{918} with A_{1674}.

The new formation of imine bond, hydroxyl group and disappearing of epoxy peaks, which are centered near 1641 cm^{-1}, 3359 cm^{-1} and 918 cm^{-1}, respectively, demonstrates the successful curing of Van-Ep with amine hardener, as shown in Fig. S3. As shown in Fig. S6, the results indicate that the epoxy conversion of Van-Ep/IPDA reaches 84.7% and 93.4% at stage of 1 and 2, respectively. In contrast, its conversion in E51/IPDA thermoset is only up to 54.5% and 89.3% respectively. These results suggest that the epoxy groups in Van-Ep show higher reactivity than those of traditional E51 epoxy resin. With the further curing of Van-Ep/IPDA, it is weird that epoxy conversion becomes slightly lower, which is possibly caused by the red shift of epoxy absorption band from 918 to 921 cm^{-1} (seen from peak fitting results). It is noticed that there is a fitting peak at around 926.2 cm^{-1} in Van-Ep monomer. Thus, it is deduced that the shift of epoxy peak at further curing process (stage 3, 4 and 5) is might partially overlapped with the above fitting band of Van-Ep, finally leading to the error of calculation. Overall, FTIR is only a semi-quantitative method. From the above results, it is still can be concluded that the most of epoxy group is reacted with amine and aldehyde. With respect to the aldehyde group, its conversion goes up to 93.5% at the first stage and finally reaches 96.7% when the curing temperature was raised to 140 °C. Considering the conversion of epoxy and aldehyde groups, it could be concluded that there are about 10% residuals of amine groups in Van-Ep/IPDA vitrimers at the 3rd stage. It can be proved by the absorption band of —N—H which is located around 1584.2 cm^{-1} as shown in Fig. 1.

3.3. Thermal properties characterization

The thermal properties of epoxy vitrimers and E51/IPDA were studied by DSC method, as illustrated in Fig. 2a. It is indicated that the glass transition temperature (T_g) of Van-Ep/IPDA is slightly lower than that of E51/IPDA, which are 109 and 117 °C, respectively. Their



Scheme 2. Imine exchange reaction for dynamic epoxy networks.

thermal stabilities were characterized by TG method as shown in Fig. 2b. The temperatures of 5 wt% and 30 wt% weight loss (T_{d5} and T_{d30}) as well as the residual weight percentages at 600 °C (R_{600}) were presented in Table 1. Obviously, all samples are thermally stable up to a temperature of 222 °C (T_{d5}). Interestingly, the residual weight of Van-Ep/IPDA is much higher than that of controlled epoxy derived from E51. In order to quantitatively compare their thermal stability, the statistic heat-resistant index (T_s) was calculated according to reported method [43], as the following equation:

$$T_s = 0.49[T_{d5} + 0.6 \times (T_{d30} - T_{d5})] \tag{1}$$

It is found that the T_s value of Van-Ep/IPDA is slightly lower than that of E51/IPDA, indicating the relatively inferior thermal stability.

Fig. 3 illustrates the dynamic mechanical properties of epoxy vitrimers. The storage modulus of Van-Ep/IPDA (E′ = 3.56 GPa) is slightly higher than that of referenced sample of E51 epoxy (E′ = 2.44 GPa) at 25 °C, indicating that the renewable epoxy vitrimers derived from vanillin are stiffer than that of E51/IPDA. The tanδ peak is often used to determine the T_g. It is noticed that the T_g of Van-Ep/IPDA (121 °C) is relatively lower than that of E51/IPDA (145 °C), which is consistent with the DSC results. Besides, the tanδ peak of Van-Ep is much wider than that of reference sample. This wide transition may be due to the differences of motion ability in each polymer components as illustrated in scheme 2. The presence of crosslinking networks in these systems could be proved by the rubbery plateau above T_g temperature. The rubbery phase modulus for E51/IPDA and Van-Ep/IPDA are 6.05 MPa and 4.58 MPa, respectively, indicating the lower cross-linking degree of Van-Ep/IPDA. Here, the cross-linking densities (ν_e) of Van-Ep/IPDA and E51/IPDA epoxy thermosets were calculated according to the following equation [47]:

$$E' = 3\nu_e RT \tag{2}$$

where E′ is the storage modulus of the thermosetting resin in the rubbery plateau region (T_g + 40 °C), R is the universal constant, and T refers to the absolute temperature.

It is found the crosslinking density of Van-Ep/IPDA (423.25 mol/m^3) is relatively lower than that of E51 epoxy thermoset (529.32 mol/m^3). These results can be explained by the GF and SR of thermosets. It was observed that Van-Ep/IPDA vitrimers and E51/IPDA thermosets still retained their original shape without being broken up into small particles, with approximately 91.3% and 99.1% residual weight percentage, respectively. The swelling ratio is often closely related to the crosslink density. Compared with the swelling ratio of E51/IPDA thermosets (114.5%), the higher value of Van-Ep/IPDA vitrimers (250.5%) is obviously due to mono-glycidyl structure of vanillin.

3.4. Thermal stress relaxation of Van-Ep/IPDA

The time and temperature dependent relaxation modulus of the Van-Ep/IPDA dynamic networks was measured by DMA method in order to study its heat induced malleability. The normalized stress relaxation curves at different temperatures (noted as 125, 130, 135, 140,

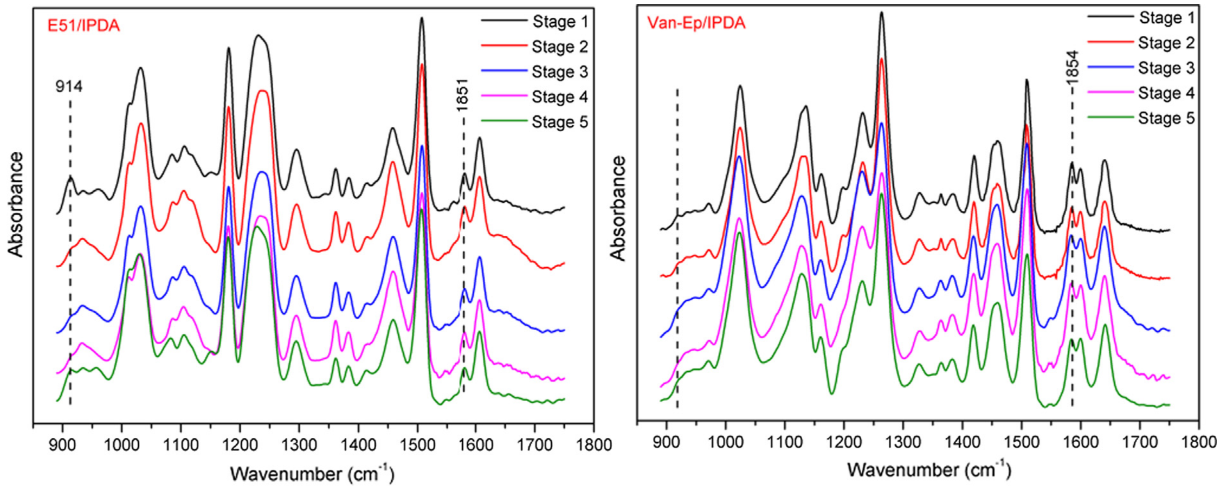


Fig. 1. FTIR spectra from 890 cm^{-1} to 1750 cm^{-1} for E51 (a) and Van-Ep (b) epoxy monomers which were cured with IPDA at different stages (stage 1: cured at 50oC for 12 h; stage 2: cured at 50 °C, 12 h + 80 °C, 2 h; stage 3: cured at 50 °C, 12 h + 80/100 °C, 2 h; stage 4: cured at 50 °C, 12 h + 80/100/120 °C, 2 h; stage 5: cured at 50 °C, 12 h + 80/100/120/140 °C 2 h, respectively).

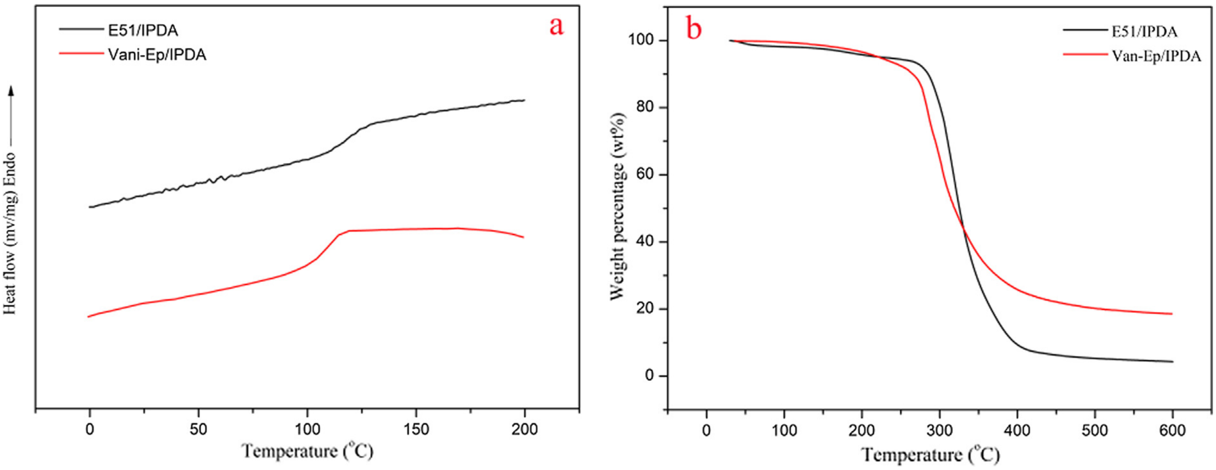


Fig. 2. DSC (a) and TGA (b) curves of the cured epoxy resins (Van-Ep/IPDA and E51/IPDA).

Table 1
Details of thermal properties for epoxy thermosets.

	T_{d5} (°C)	T_{d30} (°C)	R_{600} (wt%)	T_s(°C)	T_g (°C)[a]	T_g (°C)[b]
Van-Ep/IPDA	222	294	18.6	130	109	121
E51/IPDA	227	311	4.30	136	117	145

[a] Determined by DSC method.
[b] Determined by DMA method.

145 and 150 °C), are illustrated in Fig. 4a. It is clearly concluded that the vanillin based epoxy networks are able to completely relax stress and flow above its T_g (120 °C). Based on the Maxwell model for viscoelastic fluids, relaxation time is defined as the time required relaxing 63% of the initial stress. It is found that the τ is ranged from 309 s at 125 °C to 50 s at 150 °C, indicating that the stress relaxation triggered by the imine exchange in our system is faster than other cross-linked vitrimers to our knowledge. For example, up to 197 s of the relaxation time is observed in the aromatic disulfide dynamic covalent bond even at temperature of 130 °C (~70 °C higher than its T_g) [23]. Diglycidyl ether of bisphenol A (DGEBA) epoxy curded with 4-aminophenyl disulfide exhibits about 300 s relaxation time at the relaxation temperature of 150 °C (T_g ~130 °C) [24]. The relaxation time for classic transesterification in vitrimers that synthesized from DGEBA and fatty acids at 150 °C (T_g ~50 °C) with 10 mol% zinc acetate catalyst reaches high up to 10^3 s [26]. It is acknowledged that the dynamic feature which is studied by the model of molecular compounds could be used as a proof to explain the stress relaxation behaviors at some extent. As reported in previous literature [16,48,49], the equilibrium time for the model molecular metathesis reactions between aromatic disulfide, transesterification exchanges and Schiff are 22 h (at room temperature), 58 h (100 °C) and 8 h (25 °C), respectively. Thus, it is theoretically deduced that the imine metathesis reactions are much easier. Besides, the chemical structures are apparently responsible for this fast stress relaxation. Compared with E51 epoxy, the mono-glycidyl structure of Van-Ep cured with amine hardener would lead to the lower cross-linking densities and much higher content of dynamic imine bonds (illustrated as Scheme 2.), which are beneficial to the rearrangement of dynamic covalent bonds networks.

As illustrated in Fig. 4b, the value of the relaxation time τ as a function of the temperature follows the Arrhenius' law, which was calculated as the following equation:

$$\mathrm{Ln}\tau = \mathrm{Ln}\tau_0 + E_a/RT \tag{3}$$

From this equation, the activation energy (E_a) of 90.25 KJ/mol was obtained for Van-Ep/IPDA vitrimers, which was at the same level of the values (80–90 KJ/mol) reported by Leibler et al for transesterification reactions in epoxy vitrimers [16,26].

Another key characteristic of vitrimers is the topology freezing transition temperature (T_v), which is defined as the temperature at which the transition from solid to liquid due to the bond exchange reactions in the network. This transition is considered at the point at which the viscosity becomes higher than 1012 Pa s. As for Van-Ep/IPDA vitrimers, T_v can be determined by the extrapolation of the Arrhenius' fitted line (Fig. 4b) when $\tau^* = 6.55 \times 10^5$ s [47]. The hypothetical T_v is 36 °C that is much lower than its T_g, indicating that a fast exchange

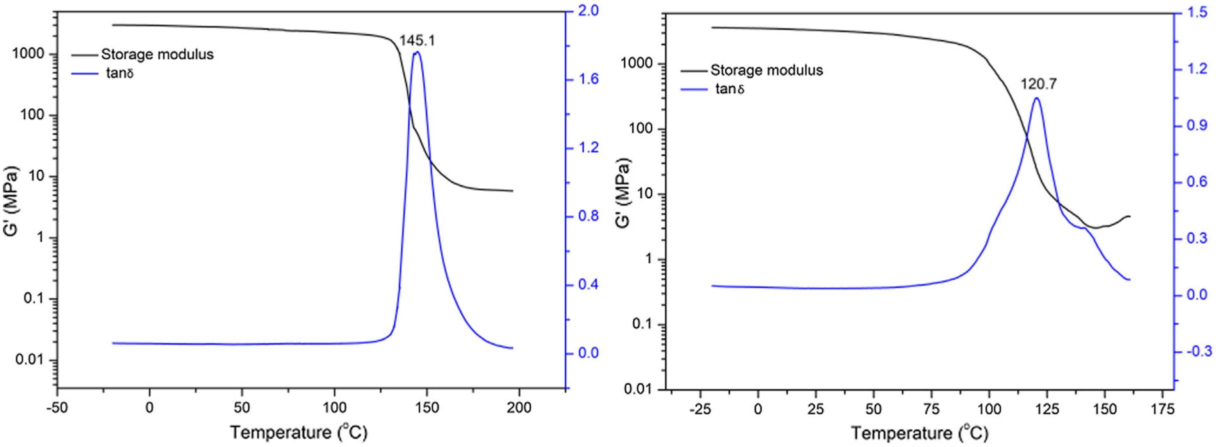


Fig. 3. DMA curves of the cured epoxy resins: E51/IPDA (a) and Van-Ep/IPDA (b).

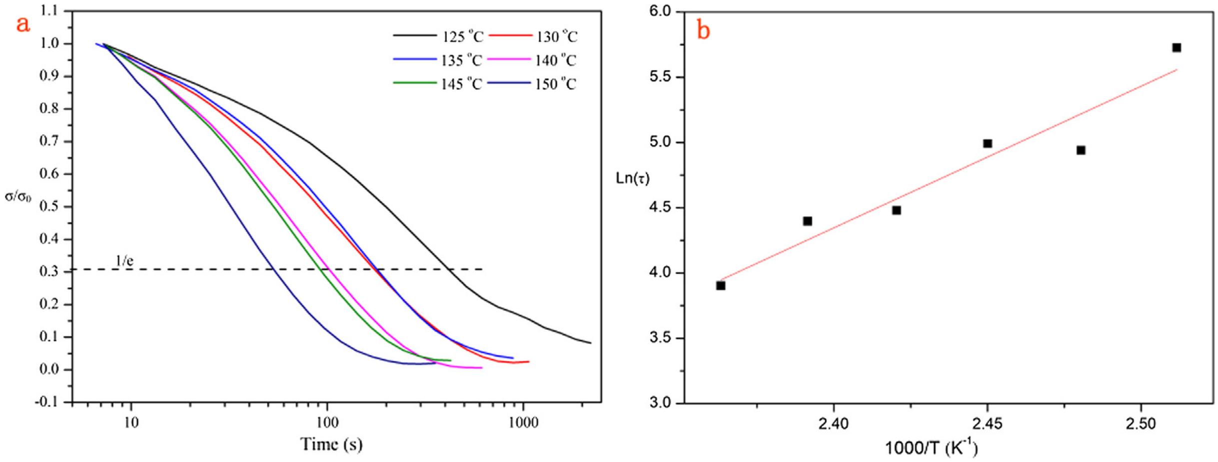


Fig. 4. (a) Normalized stress relaxation curves of dynamic epoxy network of Van-Ep/IPDA at different temperatures. (b) Fitting of the relaxation times to the Arrhenius' equation.

reaction is trapped in a rigid polymer matrix. Theoretically, the reaction kinetics for imine metathesis are not frozen, but the segmental motion is restricted under T_g [24]. Once the temperature goes up to T_g, the stress relaxation of this system is very fast.

3.5. *Reprocessing of Van-Ep/IPDA*

After the stress relaxation behaviors of vanillin based epoxy vitrimers was confirmed, the reprocessability which is endowed by the dynamic covalent network was studied here. Considering the very short relaxation time (309 s at 125 °C) at the temperature above T_g, it is expected that Van-Ep/IPDA can be easily hot-reprocessed. As shown in the Fig. S7, the fragmentized pieces of bulk materials could be reshaped into dog-bone shape of samples using a hot press machine at 130 °C for 5 min at 10 MPa. More importantly, even after three hot-pressing recycles, all reprocessed vitrimers exhibit the same level of mechanical properties, which are extremely critical to the vitrimers practical utilization. As shown in Fig. 5, the pristine vanillin based epoxy exhibits a rigid property with about 2.30 GPa of Young's modulus. Correspondingly, its elongation at break is only up to 4.4%, and the tensile strength reaches 65.0 MPa. Compared with original vitrimers, the Young's modulus of recycled sample is slightly higher, which reaches about 2.60 GPa after three recycles. It is deduced that the further of curing during hot pressing could be responsible to the increased modulus. As shown in Fig. S8, the absorption peak of —NH, centering around 1584.2 cm^{-1}, is disappeared with the increasing remendable recycles, indicating that the residual amine groups could be reacted with epoxy at higher processing temperature. Another possible reason is the self-cross-linking reaction of Schiff base which leads to the formation of nitrogen-containing hexatomic ring at high temperature [50]. The gel content, relating to the cross-linking degree, was added to test whether further crosslinking is occurred after hot reprocessing. As for original vitrimers, GC is up to 91.3%. After the 1st reprocessing, the GC is increased to 94.5%, finally to 96.2% for the 3rd reprocessing vitrimers. Therefore, the Young's Modulus shows an increasing trend with the reprocessing times. Meanwhile, their tensile strength and elongations at break is still kept above 60.0 MPa and 3.3%, respectively. These high recovery efficiency of mechanical properties maybe is attributed to the fast stress relaxation and low T_v [35]. Moreover, it was interestingly found that the imine bond is not decayed during hot press, proved by the presence of aromatic aldehyde absorption peak around 1641 cm^{-1} even after three reprocessing cycles, as shown in Fig. S8.

In order to explore its potential ability as an alternative to commercial epoxy, their mechanical properties were compared with those of E51/IPDA. The Young's modulus, tensile strength and elongation at break of traditional epoxy are about 2.3 GPa, 76.7 MPa and 5.2%, which are almost at the same level of Van-Ep/IPDA vitrimers. The detailed mechanical properties of epoxy vitrimers from vanillin are shown in Table 2. Moreover, their mechanical properties were compared with other types of epoxy vitrimers and traditional lignin based epoxy thermosets, as listed in the following Table S1. It was concluded that Van-Ep/IPDA vitrimers show superior mechanical properties than most of epoxy vitrimers except for the vitrimers that were prepared from DGEBA and aromatic amine [24]. Apparently, the mechanical properties can be further improved through tuning amine hardener types. Compared with traditional lignin based epoxy thermosets, the mechanical properties of Van-Ep/IPDA are slightly lower, but the advantage is their reprocessability.

3.6. *Chemical degradation of Van-Ep/IPDA vitrimers*

Taking advantage of the unstable imine structure under acid condition [51], it is interesting to test the degradability of Van-Ep/IPDA vitrimers. Here, the samples were immersed in hydrochloric acid solution (1 mol/L, 10^{-2} mol/L, 10^{-5} mol/L) at 70 °C for 24 h under continuous stirring, and then the residual weight percentages of film were recorded. As illustrated in Fig. S9, after acid hydrolysis using 1 mol/L HCl, the epoxy vitrimers become yellow oil adhering to bottle wall; in contrast, the incompletely acid hydrolysis (using 10^{-2} mol/L, 10^{-5} mol/L HCl solution) leads to a white powder. Therefore, it was concluded that strong acid solution is desirable for Van-Ep/IPDA vitrimers degradation, proved by only 19.25 wt% residuals at 1 mol/L of hydrochloric acid solution. These results are attributed to the breakage of unstable imine bond [22], leading to the disappearing of imine bond and the new generation of aromatic aldehyde group which is confirmed by the new 1678 cm^{-1} absorption peak in the FTIR spectrum of residuals (Fig. 6b). We tried to extract the yellow oil with CH_2Cl_2 or ethyl acetate, but it was failed. Besides, it is partially dissolved into dimethylformamide and dimethyl sulfoxide, thus further characterization methods, such as NMR and GPC, cannot be adopted. Compared with the lignin-based degradable epoxy thermosets which are based on the breakage of ester linkages under sodium hydroxide [52] or phosphotungstic acid [53] aqueous solutions, our work firstly demonstrated the possibility of using imine chemistry to design degradable epoxy.

4. Conclusions

In the present work, a vanillin-based epoxy vitrimers (Van-Ep/IPDA) was prepared by curing mono-glycidyl structure of vanillin (Van-Ep) with isophorone diamine (IPDA). The vitrimers exhibit comparable

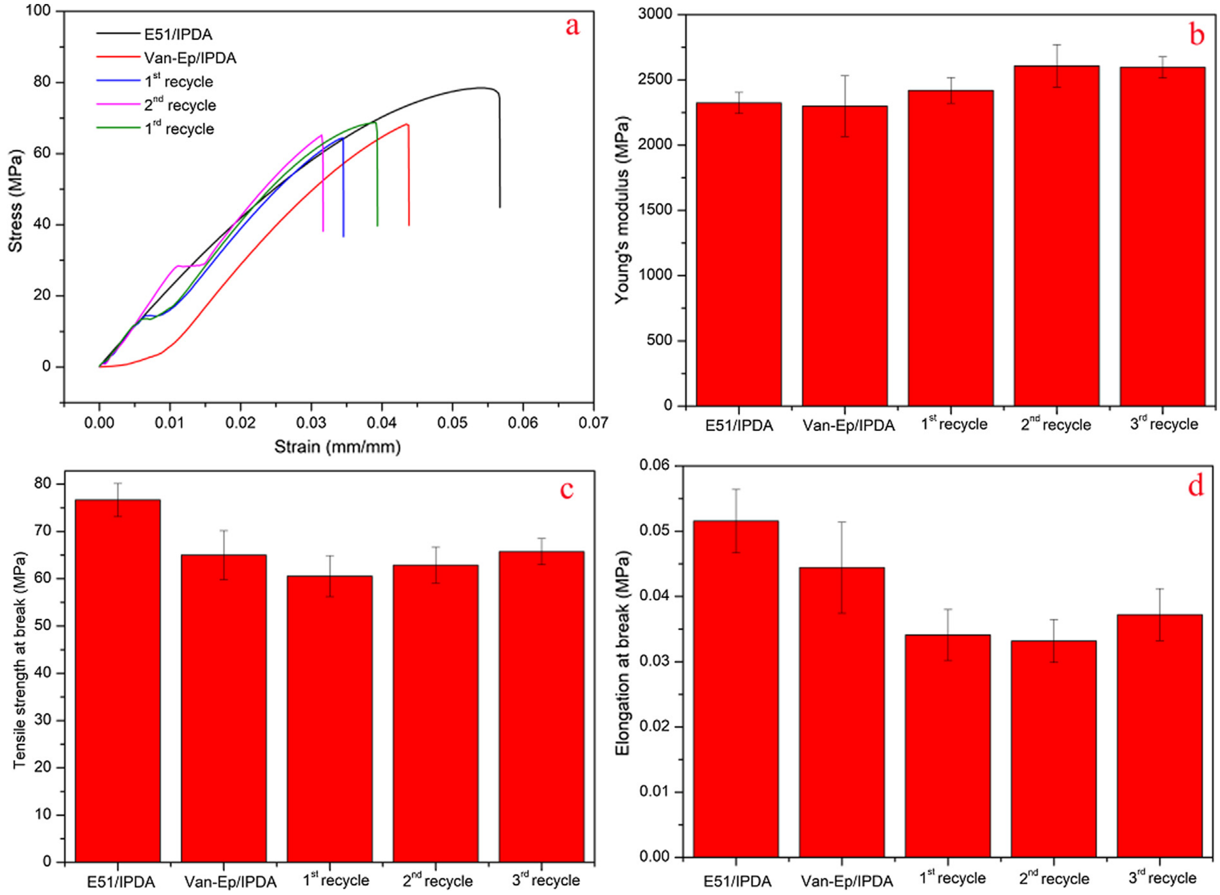


Fig. 5. Comparison of the mechanical properties of reprocessed Van-Ep/IPDA vitrimers with commercial E51 epoxy: (a) the typical stress-strain curve of virgin and reprocessed Van-Ep/IPDA vitrimers and E51/IPDA; (b), (c) and (d) are the Young's modulus, tensile strength and elongation at break for virgin and reprocessed Van-Ep/IPDA vitrimers and E51/IPDA.

Table 2
The detailed mechanical properties of virgin and reprocessed epoxy vitrimers from vanillin.

Samples	Young's modulus (GPa)	Tensile strength at break (MPa)	Elongation at break (%)
Virgin	2.30 ± 0.23	65.0 ± 5.2	4.4 ± 0.7
1st recycling	2.40 ± 0.10	60.5 ± 4.3	3.4 ± 0.4
2nd recycling	2.61 ± 0.16	62.9 ± 3.8	3.3 ± 0.3
3rd recycling	2.60 ± 0.08	65.7 ± 2.8	3.7 ± 0.4

Young's modulus, elongation at break and thermal stability with those of cured bisphenol A epoxy (E51). The glass transition temperature (T_g) of Van-Ep/IPDA reaches 121 °C. The tensile strength at break of original Van-Ep/IPDA reaches about 65.0 MPa, which is 11.7 MPa lower than that of E51/IPDA. The relatively low cross-linking densities and high content of dynamic imine bonds in the networks are beneficial to the fast stress relaxation behaviors of vitrimers, proved by the short relaxation time, 50 s, at the temperature of 30 °C above T_g. Importantly, even after three reprocessing cycles, all reprocessed vanillin based epoxy vitrimers exhibit the same level of mechanical properties that could be compared with these of originals. Thanks to its Schiff structure, this epoxy vitrimers is degradable under acid solution. This facile approach of imine chemistry for preparing vanillin-based epoxy vitrimers sets up an important framework for designing sustainable polymer materials with excellent reprocessability and degradability.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary material

Fig. S1. FTIR spectra of Van-Ep and vanillin monomer; Fig. S2. NMR spectra of Van-Ep monomer; Fig. S3. FTIR spectrum of Van-Ep/IPDA vitrimers after curing at 50 °C/12 h + 80 °C/2h + 100 °C/2h; Fig. S4. Peakfitting of the FT-IR spectrum of Van-Ep/IPDA at different curing stages from 890 to 1750 cm^{-1} wavenumber; Fig. S5. Peak fitting of the FT-IR spectrum of E51/IPDA at different curing stages from 890 to 1750 cm^{-1} wavenumber; Fig. S6. The epoxy conversion in E51 and Van-Ep curing system (left) and the aldehyde (right) conversion in Van-Ep/IPDA at different stages; Fig. S7. The digital pictures of dog-bone shape of Van-Ep/IPDA vitrimers after several hot press cycles at 130 °C for 5 min at 10 MPa; Fig. S8. FTIR spectra of Van-Ep/IPDA vitrimers after several hot press cycles at 130 °C for 5 min at 10 MPa; Fig. S9. Chemical degradation of vanillin based epoxy vitrimers before (a) and after (b) acid hydrolysis under different concentration of HCl solution (left: 1 mol/L; middle: 10^{-2} mol/L; right 10^{-5} mol/L) at 70 °C for 24 h; Table

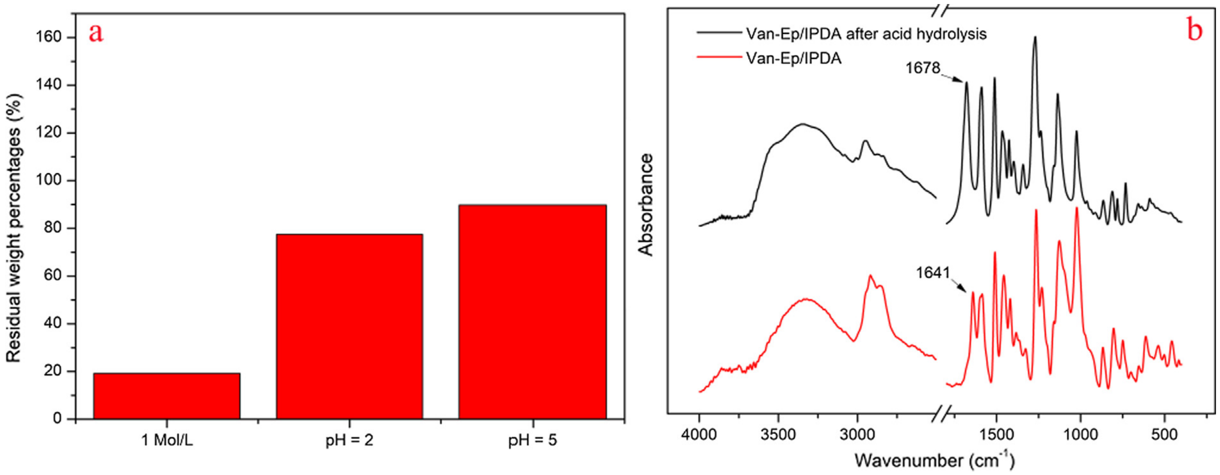

Fig. 6. (a) The residual weight percentages of Van-Ep/IPDA vitrimers after acid hydrolysis at 70 °C for 24 h; (b) The FTIR spectra of Van-Ep/IPDA vitrimers before and after hydrolyzed at 10^{-2} mol/L HCl solution at 70 °C for 24 h.

S1. Comparison of the mechanical properties of our epoxy vitrimers with other reported epoxy vitrimers and lignin based epoxies. Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2019.04.053.

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