

# Preparation of environmentally friendly bio-based vitrimers from vanillin derivatives by introducing two types of dynamic covalent C=N and S–S bonds

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## ABSTRACT

In this study, a novel self-healing, chemically degradable and recyclable vanillin vitrimers (VF<sub>x</sub>) containing multiple reversible covalent bonds were prepared from vanillin-derived dialdehyde and amine monomers. In order to improve mechanical properties and shorten the relaxation time, we introduced disulfide bonds into the polyschiff vitrimers. Among these VF<sub>x</sub>, VF<sub>10</sub> containing 10 mol % disulfide bonds exhibited the best mechanical properties (*T*<sub>g</sub> = 43 °C, tensile strength = 16.68 MPa), and the mechanical properties were sustained after two cycles of hot pressing. More significantly, VF<sub>x</sub> could be degraded in hydrochloric solution (pH = 2) and recycled to prepare the films. These characteristics of reprocessability, recyclability and bio-based monomer present a feasible way to satisfy the demands of sustainability, which is of great significance for the recycling of resources.

## 1. Introduction

Dynamic covalent chemistry has been used for preparing high performance and reprocessable polymers. Covalent bond adaptability networks (CANs) [1–5] or vitrimers [6] have become a hot topic in polymer and materials science. Many researchers have introduced reversible covalent bonds into the cross-linked polymer [7–10]. These networks can be rearranged by the exchange of covalent bonds upon heat and light without affecting the integrity of the network. This attribute can endow thermosetting resins with many advantages of thermoplastic resins, such as self-healing, reprocessability, recyclability, etc. Such cross-linked polymer do not depolymerize upon heating, but are characterized by a fixed cross-link density due to the associative exchange mechanisms, which makes these networks permanent as well as dynamic. In addition, these materials can be reshaped like traditional glass materials without the need to precisely control the processing temperature [11,12]. Since then several dynamic chemistries such as

transesterification [13–15,25], imine amine exchange [16,17], vinyl-olefin transamination [18], olefin metathesis [19,20,26], disulfide exchange [21–23], transalkylation reactions of triazolium salts [24], boroxine bonds [27], radically exchangeable alkoxyamines [28], and hindered urea bonds [29], were developed. However, quite a few exchange reactions require catalysts and the raw materials are not environmentally friendly chemicals, which limit the application of vitrimers. Thus, it is extremely desirable to develop a method to prepare vitrimers from bio-based materials, which could greatly reduce production costs and environmental problems.

Lignin, a by-product of pulp and paper refining processes, has been widely used because of its polyaromatic structures and bio-based attributes [30–33]. Therefore, in recent years, researchers have turned their attention to lignin-derived phenolic monomers such as vanillin [34–36], guaiacol [37], eugenol [38] and vanillic acid [39]. These non-toxic bio-based compounds were used to prepare epoxy resins and phenolic resins. Recently, construction of vitrimers from bio-based compounds is

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a promising strategy in terms of environmental issues and waste of resources [34,37,40–43]. Ye [34] and his colleagues prepared dialdehyde monomers from vanillin and reacted with polyamines to prepare polyschiff-based vitrimers with reprocessable and self-healing properties. Hu group [43] prepared recyclable thermosetting epoxy resin which was based on a bisphenol that employed isosorbide. However, these vitrimers contain only one kind of dynamic covalent bond. As a result, their dynamic and mechanical properties are largely limited, such as long relaxation time. In order to tune their mechanical properties and self-healing performance, novel vitrimers based on multiple reversible covalent bonds are highly desired.

In this study, we designed a novel vanillin vitrimers ( $VF_x$ ) based on multiple reversible covalent bonds (S–S and C=N) to address the challenge of long relaxation time of vitrimers.  $VF_x$  possessed good thermo-mechanical properties and could be easily reprocessed. Meanwhile,  $VF_x$  had excellent self-healing, degradable, and recyclable properties under simple and mild conditions without the need to add other catalysts, which could greatly reduce production costs, and environmental problems.

## 2. Experimental section

### 2.1. Materials

4-(bromomethyl) benzaldehyde ( $\geq 97\%$ ) was purchased from 3A company; Vanillin ( $\geq 99\%$ ), Tris (2-aminoethyl) amine ( $\geq 96\%$ ), and 4, 4'-disulfanedioldianiline (4-AFD) ( $\geq 97\%$ ) were purchased from Adamas company. All other reagents were commercially available and used without further purification.

### 2.2. Synthesis of 4-((4-formylbenzyl) oxy)-3-methoxybenzaldehyde (VC)

The mixture of vanillin (6.082 g, 40 mmol), 4-(bromomethyl) benzaldehyde (8.71 g, 44 mmol) and  $K_2CO_3$  (16.58 g, 120 mmol) in MeCN (300 mL) were heated at  $50^\circ\text{C}$  for 6 h. Then water was added and extracted with DCM for three times. The combined organic phase was washed with brine, dried over  $Na_2SO_4$  and concentrated in vacuum. The crude product was purified by column chromatography (silica gel) using PE/EA 10:1–1:1 as eluent. Compound VC was obtained as a white solid (Fig. 1) (7.78 g, 72% yield).  $^1\text{H}$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm): 10.02 (s, 1H), 9.85 (s, 1H), 7.91 (d, 2H,  $J = 8.0$  Hz), 7.62 (d, 2H,  $J = 8.0$  Hz), 7.46 (s, 1H), 7.40 (d, 2H,  $J = 8.0$  Hz), 6.96 (d, 2H,  $J = 8.0$  Hz), 5.32 (s, 2H), 3.97 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm): 191.8, 190.9, 153.1, 150.1, 142.9, 136.2, 130.7, 130.1, 127.4, 126.4, 112.4, 109.5, 70.1 and 56.1 (Fig. 2).

### 2.3. Preparation of vanillin vitrimers

Vanillin vitrimers ( $VF_x$ ) were prepared by dissolving VC in an appropriate amount of  $CHCl_3$  (10 wt%), then a precise amount of 4-AFD and tris (2-aminoethyl) amine were added into the solution and stirred at  $40^\circ\text{C}$  for 10 min ( $VF_x$ : “x” means the molar ratio of 4-AFD to tris(2-aminoethyl) amine in the vanillin vitrimers). Immediately, the mixture were poured into a square PTFE mould, and then kept curing overnight at room temperature. The obtained defect-free film was further cured in vacuum at  $50^\circ\text{C}$  for 48 h.

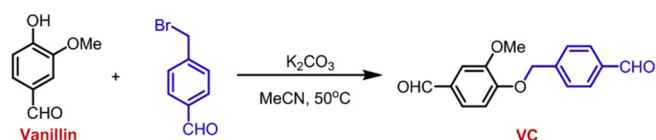


Fig. 1. Synthetic route of compound VC.

### 2.4. Solubility and swelling experiments

Solubility and swelling experiments of  $VF_0$ ,  $VF_5$ ,  $VF_{10}$  and  $VF_{30}$  were performed in DMF, THF, DCM, MeOH and neutral  $H_2O$ . Samples were about 20 mg for each experiment, and were immersed in 15 mL of the corresponding solvent for 48 h at  $25^\circ\text{C}$ . soluble fraction =  $(m_i - m_d)/m_i$ , swelling ratio =  $(m_s - m_i)/m_i$ ,  $m_i$ ,  $m_s$ , and  $m_d$  were the mass of sample in initial, swollen, and dry state, respectively.

### 2.5. Characterizations

Bruker Avance 400 spectrometer was used to measure the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/DSC3+ instrument under nitrogen atmosphere at heating rate of  $10^\circ\text{C}/\text{min}$  from  $35^\circ\text{C}$  to  $900^\circ\text{C}$ . Dynamic mechanical analysis (DMA) and stress–relaxation experiments were performed on Netzsch DMA242E.  $T_g$  analyses have been carried out with samples of dimension ( $30 \times 4 \times 2 \text{ mm}^3$ ) between  $-50$  and  $100^\circ\text{C}$  at  $2^\circ\text{C}/\text{min}$ . Stress–relaxation experiments were conducted with samples of dimension ( $30 \times 4 \times 2 \text{ mm}^3$ ). Samples were initially preloaded at a force of  $-0.01 \text{ N}$  to maintain straightness. After reaching the testing temperature, samples were allowed 30 extra minutes to reach the thermal equilibrium. The specimens were stretched by 4% and the deformation was maintained during the test. The decrease of stress was recorded and the stress relaxation modulus was calculated. Tensile testing was performed on CMT-8502 tensile tester, equipped with a 500 N load cell with samples of dimension ( $30 \times 4 \times 2 \text{ mm}^3$ ) the tensile tests were run at speed of  $10 \text{ mm}/\text{min}$ .

## 3. Result and discussion

### 3.1. Preparation of $VF_x$

Aiming to obtain vitrimers with different dynamic bonds, the molar ratio of tris (2-aminoethyl) amine to 4-AFD was adjusted (Fig. 3). The details for preparing the  $VF_x$  were recorded in Table 1.

### 3.2. Thermal properties of $VF_x$

The detailed results of thermal properties of  $VF_x$  are provided in Table 2. The glass transition temperature ( $T_g$ ) and storage modulus ( $E^0$ ) of  $VF_x$  were characterized by dynamic thermal analysis (DMA). The results shown in Fig. 4 and Table 2 suggested that as the amount of 4-AFD increases, the  $T_g$  of the  $VF_x$  increased gradually, which rose from  $35$  to  $45^\circ\text{C}$ . This is due to the increase in the content of benzene rings in the cross-linked network, as the amount of 4-AFD increased.

The storage modulus of  $VF_0$  ( $E^0 = 353 \pm 30 \text{ MPa}$ ) is lower than that of  $VF_5$  ( $E^0 = 370 \pm 35 \text{ MPa}$ ),  $VF_{10}$  ( $E^0 = 1322 \pm 50 \text{ MPa}$ ) and  $VF_{30}$  ( $E^0 = 1220 \pm 77 \text{ MPa}$ ) at  $25^\circ\text{C}$ , which is obviously attributed to structure of network ( $VF_0$  did not have aromatic amines).

As shown in Fig. 5, the 5% weight loss temperature ( $T_{d5\%}$ ) of  $VF_x$  are from  $221^\circ\text{C}$  to  $227^\circ\text{C}$ . The residual weight percentages of  $VF_x$  could still keep 35% up to  $900^\circ\text{C}$ . All these results demonstrate that  $VF_x$  are thermally stable under conventional modeling approaches.

### 3.3. Solubility and swelling properties

In order to assess the material's resistance to chemical solvents and ensure the robustness of the cross-linked network solubility, swelling experiments were performed on  $VF_{10}$ . The experiment was performed by immersion of samples in dimethylformamide (DMF), tetrahydrofuran (THF), methanol (MeOH), dichloromethane (DCM) and neutral  $H_2O$  for two days at  $25^\circ\text{C}$ . The solubility fraction and swelling ratios were reported in Table 1. After 2 days of immersion,  $VF_{10}$  did not dissolve significantly in these solvents, indicating that  $VF_{10}$  had solvent resistance due to the formation of the cross-linked network (Table 3).

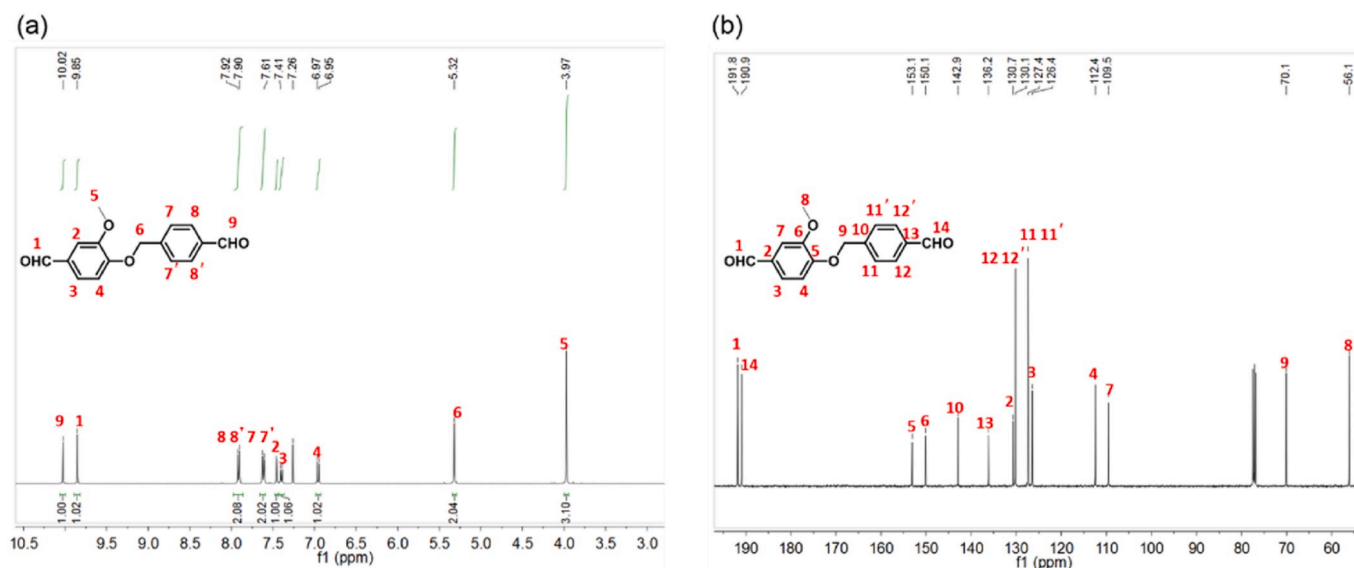


Fig. 2. a)  $^1\text{H}$  NMR spectrum of the VC. b)  $^{13}\text{C}$  spectrum NMR of the VC.

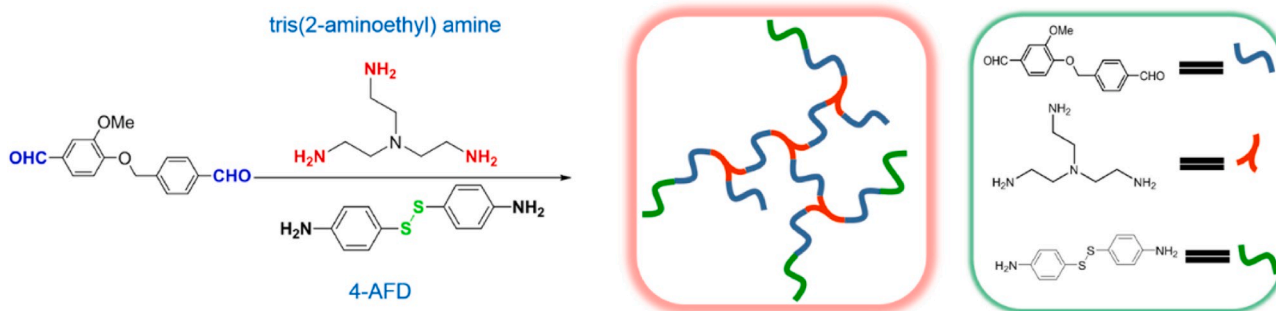


Fig. 3. Synthetic route of  $\text{VF}_x$ .

Table 1

Recipe of VC and amine monomers used for preparing vitrimers.

	VC	4-AFD	tris (2-aminoethyl) amine
$\text{VF}_0$	2.5 g (9.256 mmol)	0	0.902 g (6.171 mmol)
$\text{VF}_5$	2.5 g (9.256 mmol)	0.0743 g (0.299 mmol)	0.8732 g (5.972 mmol)
$\text{VF}_{10}$	2.5 g (9.256 mmol)	0.1437 g (0.579 mmol)	0.8463 g (5.785 mmol)
$\text{VF}_{30}$	2.5 g (9.256 mmol)	0.3832 g (1.543 mmol)	0.7516 g (5.142 mmol)

Table 2

The detailed results of thermal properties and mechanical properties of  $\text{VF}_x$ .

	$T_g$ [ $^{\circ}\text{C}$ ]	$T_{d5\%}$ [ $^{\circ}\text{C}$ ]	$E^0$ (25 $^{\circ}\text{C}$ ) [MPa]	Stress [MPa]	Strain [%]
$\text{VF}_0$	$35 \pm 3$	221	$353 \pm 30$	$7.24 \pm 0.23$	$103 \pm 3$
$\text{VF}_5$	$41 \pm 2$	226	$370 \pm 35$	$11.87 \pm 0.67$	$93 \pm 5$
$\text{VF}_{10}$	$43 \pm 2$	227	$1322 \pm 50$	$16.68 \pm 0.56$	$78 \pm 4$
$\text{VF}_{30}$	$45 \pm 2$	225	$1220 \pm 77$	$15.35 \pm 0.78$	$81 \pm 3$

The crosslink degree has been characterized by equilibrium swelling method (Table 4). Results showed that  $\text{VF}_0$ ,  $\text{VF}_5$ ,  $\text{VF}_{10}$  and  $\text{VF}_{30}$  could not be soluble in DMF and with the addition of 4-AFD, the swelling rate of the material gradually increased, indicating that the crosslink density of the material gradually decreased.

### 3.4. Dynamic properties

As shown above,  $\text{VF}_x$  have the same thermal properties as other bio-based vitrimer films [34,43]. However, because of the introduction of disulfide bonds and change the cross-link density of the network,  $\text{VF}_x$  have exhibited some dynamic characteristics in the following section.

Time and temperature-dependent relaxation moduli of the dynamic network were tested by DMA to characterize their heat-induced ductility. Fig. 6 showed normalized stress relaxation curves at different temperatures (40–70  $^{\circ}\text{C}$ ). The results indicated that  $\text{VF}_x$  were able to relax when the temperature was above  $T_g$ . Based on the Maxwell model equations for viscoelastic fluids, relaxation time was defined as the time required to relax to  $1/e$  (37%) of the initial stress. The obtained relaxation times ( $t^*$ ) of ranged  $\text{VF}_0$  from 10.95 min at 40  $^{\circ}\text{C}$  to 0.95 min at 70  $^{\circ}\text{C}$ ,  $\text{VF}_5$  from 5.52 min at 40  $^{\circ}\text{C}$  to 0.61 min at 70  $^{\circ}\text{C}$ ,  $\text{VF}_{10}$  from 2.51 min at 40  $^{\circ}\text{C}$  to 0.35 min at 70  $^{\circ}\text{C}$  and  $\text{VF}_{30}$  from 0.71 min at 40  $^{\circ}\text{C}$  to 0.33 min at 70  $^{\circ}\text{C}$ . These results showed that  $\text{VF}_{30}$  has the shortest relaxation time at each temperature. This suggested that an increase in the number of disulfide bonds greatly reduces the relaxation time of the  $\text{VF}_x$ . As shown in Fig. 7, the dependence of relaxation time on temperature was in accordance with the Arrhenius equation (Equation (1)) which indicated that the stress relaxation of the  $\text{VF}_x$  was attributed to the exchange reaction of imine and disulfide bonds.

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

The activation energy ( $E_a$ ) of the  $\text{VF}_0$ ,  $\text{VF}_5$ ,  $\text{VF}_{10}$  and  $\text{VF}_{30}$  were

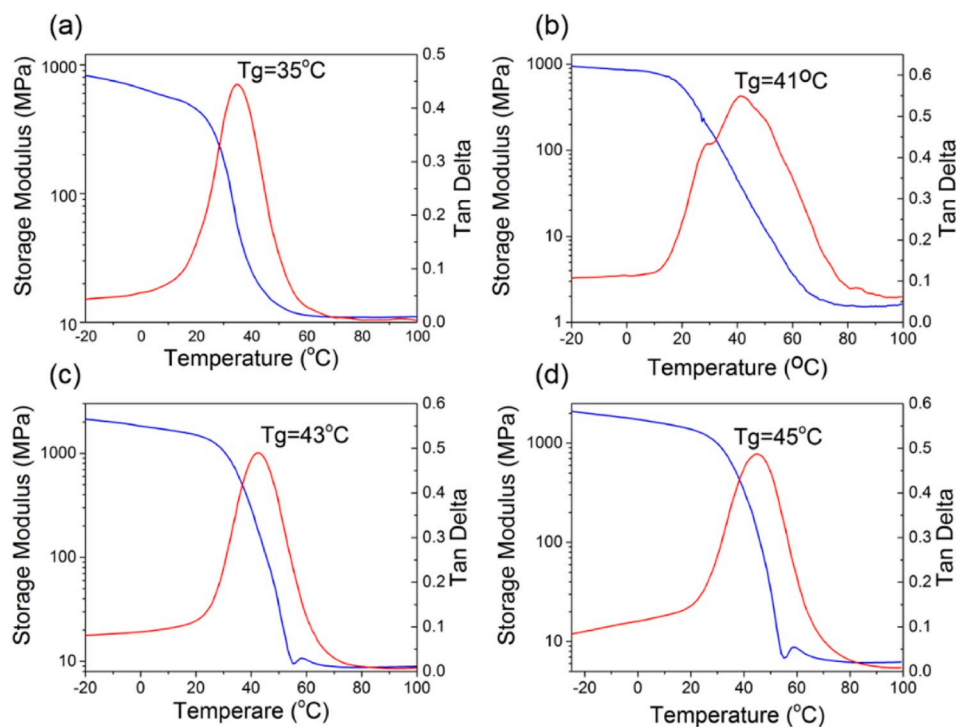


Fig. 4. (a–d) DMA curves of VF<sub>0</sub>, VF<sub>5</sub>, VF<sub>10</sub> and VF<sub>30</sub>.

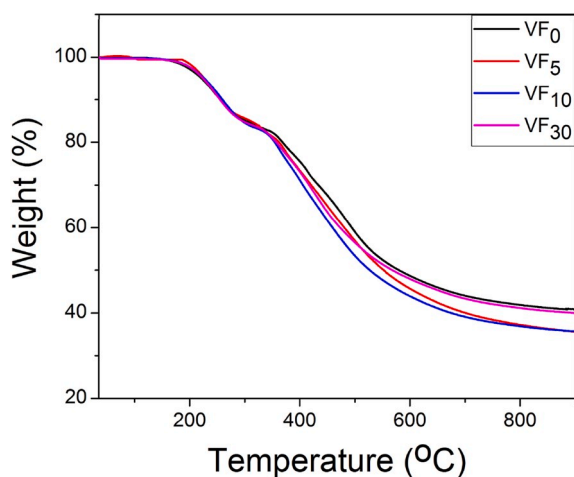


Fig. 5. TGA curves of VF<sub>0</sub>, VF<sub>5</sub>, VF<sub>10</sub> and VF<sub>30</sub>.

Table 3

Soluble fraction and swelling ratio of VF<sub>10</sub> after 48 h immersion in solvent at 25 °C.

Solvent	m <sub>i</sub> (g)	m <sub>d</sub> (g)	m <sub>s</sub> (g)	Soluble fraction (%)	Swelling ratio (%)
DMF	0.0249	0.0232	0.0352	6.83	41.22
THF	0.0202	0.0172	0.0287	14.84	42.47
DCM	0.0120	0.0059	0.0285	50.86	137.53
MeOH	0.0192	0.0179	0.0203	6.85	5.76
Neutral H <sub>2</sub> O	0.0238	0.0229	0.0240	6.34	0.84

respectively 67.12 kJ/mol, 66.18 kJ/mol, 65.77 kJ/mol and 61.17 kJ/mol according to equation (1). The topology freezing transition temperature ( $T_v$ ) was a key characteristic for vitrimers [6], which was the temperature when a transition from solid to liquid occurred owing to the

Table 4

Swelling ratio of VF<sub>0</sub>, VF<sub>5</sub>, VF<sub>10</sub> and VF<sub>30</sub> after 48 h immersion in DMF at 25 °C.

	m <sub>i</sub> (g)	m <sub>s</sub> (g)	Swelling ratio (%)
VF <sub>0</sub>	0.0311	0.0433	39.23
VF <sub>5</sub>	0.0347	0.0497	43.23
VF <sub>10</sub>	0.0431	0.0633	46.87
VF <sub>30</sub>	0.0364	0.0592	62.64

bond exchange reaction in dynamic network. This shift was believed to be a shift that occurred when the viscosity of a dynamic network became higher than  $10^{12}$  Pa s. Based on the result of Fig. 7 the value of  $T_v$  of the VF<sub>0</sub>, VF<sub>5</sub>, VF<sub>10</sub> and VF<sub>30</sub> were −24 °C, −26 °C, −34 °C and −36 °C respectively, which was extrapolated from the Arrhenius fitting line (Fig. 7) to a relaxation time of  $3 \times 10^5$  s and below the  $T_g$  of each VF<sub>x</sub>. It can be concluded that VF<sub>30</sub> greatly increases the number of exchangeable bonds in the system by the introduction of multiple disulfide bond, therefore displays better relaxation properties.

### 3.5. Mechanical and repairing properties

#### 3.5.1. Mechanical properties

The tensile test was conducted to characterize the mechanical properties of VF<sub>x</sub> (Fig. 8, Table 2). It can be seen that the VF<sub>x</sub> had yielding phenomenon during the stretching process. This may be due to the fact that the  $T_g$  of VF<sub>x</sub> are close to room temperature, and molecular chain slip and dynamic bond exchange occur during stretching. Table 3 shown that VF<sub>10</sub> reached the best mechanical properties because at this ratio, the number of benzene rings and the cross-link density of the network are well combined.

#### 3.5.2. Reprocessable properties

It is well known that conventional thermosetting materials could not be reformed when chemical bonds were broken, resulting in cross-linked network that could not be reshaped and thus difficult to repair. However, vitrimers could be easily reprocessed at temperatures above  $T_g$  due

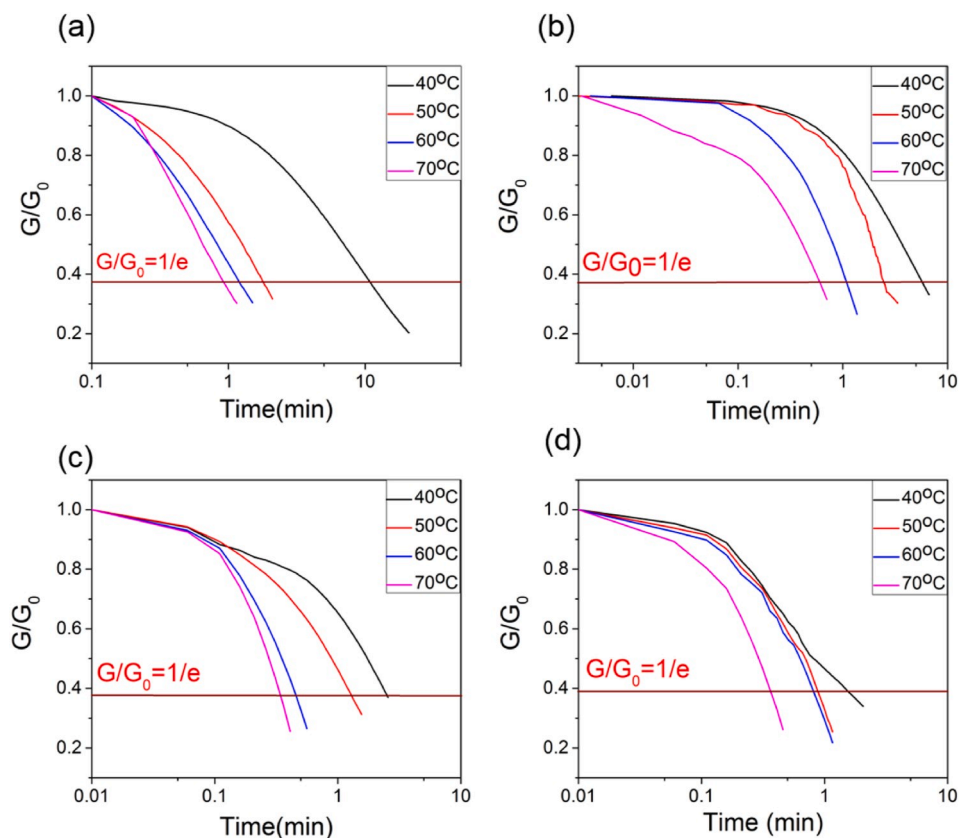


Fig. 6. (a–d). Normalized stress relaxation curves of VF0, VF5, VF10 and VF30 at different temperatures.

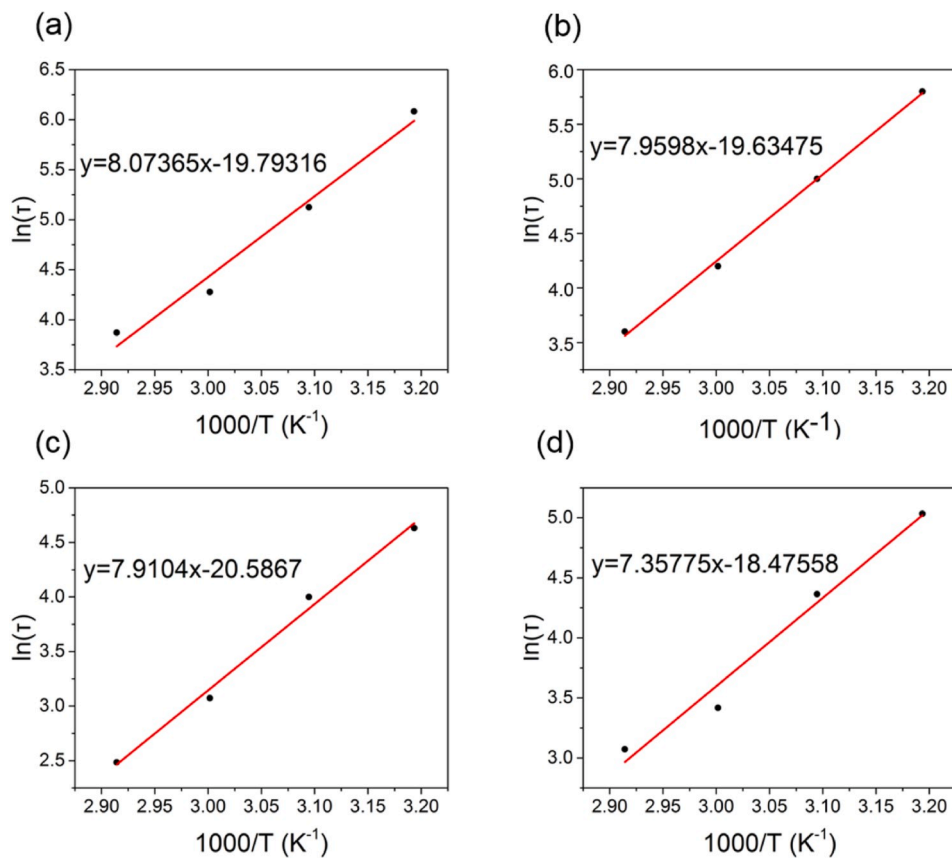


Fig. 7. (a–d). Fitting of the relaxation times to the Arrhenius equation (VF0, VF5, VF10 and VF30).



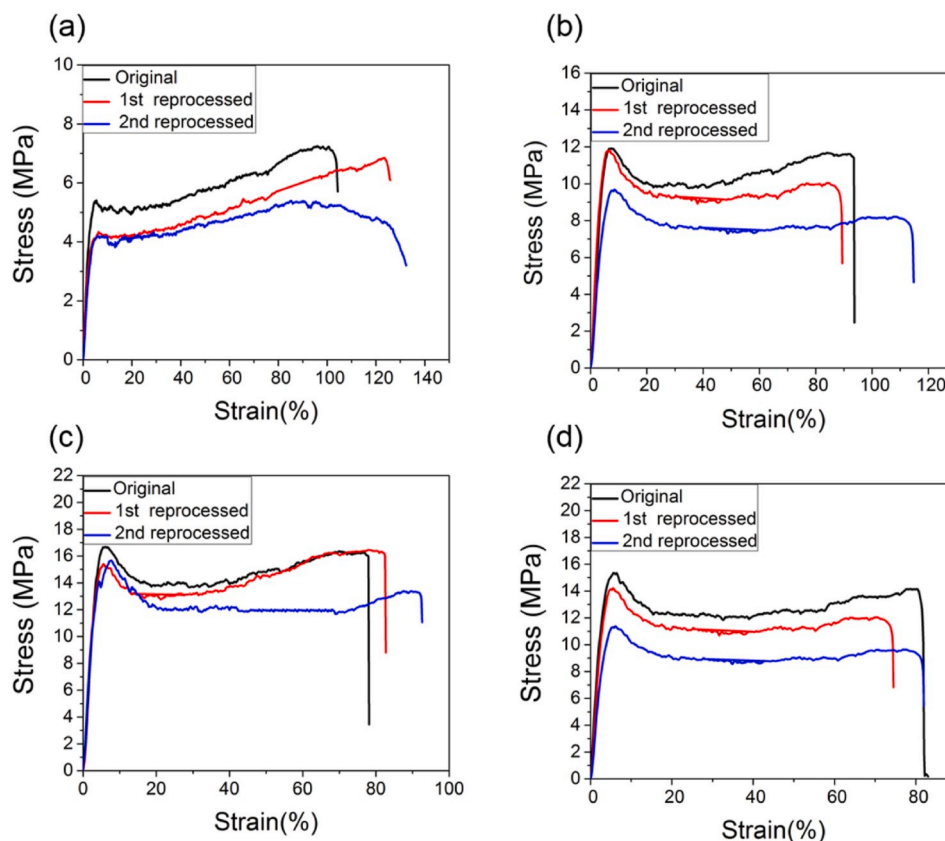


Fig. 8. (a–d). Stress–strain curves of the original and reprocessed VF<sub>0</sub>, VF<sub>5</sub>, VF<sub>10</sub> and VF<sub>30</sub>.

to the joint movement of molecular chains and exchangeable bonds.

As shown in Fig. 9, the VF<sub>x</sub> fragmentation could be reshaped after sandwiched between two glass plates for 20 min at 60 °C. It was repeated twice and the stress and strain curves of the tensile test were used to characterize the difference in the mechanical properties of the reworked material and the original material. As depicted in Fig. 8, the tensile strength of VF<sub>x</sub> closed to initial value after the first processing. When the material was processed twice, the mechanical properties of VF<sub>x</sub> had a slight decline. This may be due to a certain degree of degradation of the imine bond due to prolonged exposure to higher temperatures and water. In summary, VF<sub>10</sub> had good mechanical and reprocessable properties.

### 3.6. Self-healing and recyclable properties

#### 3.6.1. Self-healing properties

As imine metathesis could be effectively catalyzed by minute amounts of primary amines in a kinetically well-behaved process. Fig. 10 shown that the self-healing properties of the VF<sub>10</sub> were

investigated using a small amount of ethylenediamine. 2 mL of ethylenediamine was added to the two-piece-stacked portion, and pressed with a weight of 200 g for 30 min. The two pieces were well repaired and were able to withstand a weight of 500 g. This proved that under very mild and convenient conditions, VF<sub>x</sub> showed excellent self-healing properties due to the occurrence of amine exchange reaction in cross-linked network.

#### 3.6.2. Recyclable properties

Since the hydrolysis reaction of the imine bond under acidic conditions has been reported, it is a significant to investigate the recyclability of the VC under acidic conditions [34]. As shown in Fig. 11a, the VF<sub>10</sub> was stirred in hydrochloric acid aqueous solution (pH = 2) at 50 °C for 24 h, the film was degraded. The white solid was collected by filtration and washed with water and hexane. Fig. 11b shown that the <sup>1</sup>H NMR spectrum of the recycled VC is consistent with the original VC. In addition, the recovered VC could be reformed into film follow the same preparation steps, demonstrating the recyclable performance of VF<sub>x</sub>.

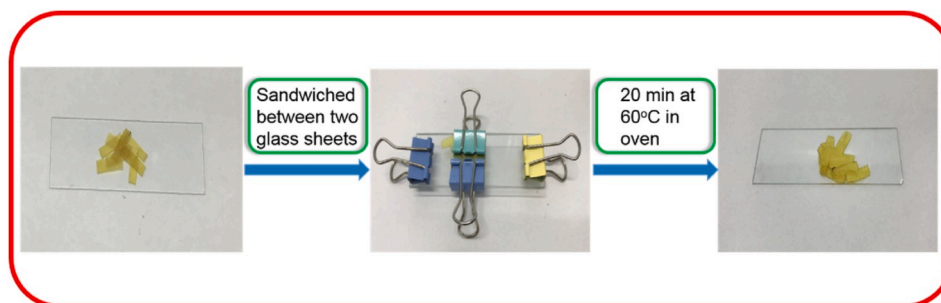


Fig. 9. Reprocessable properties of the grinded polymer network by hot pressing.

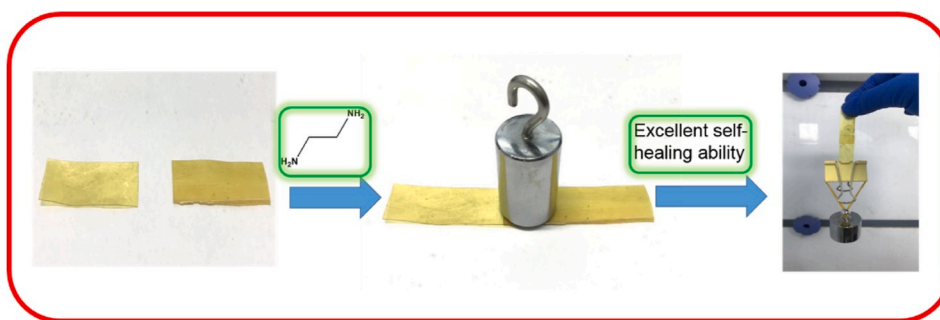


Fig. 10. Self-healing properties of  $VF_x$  after adding a small amount of amine.

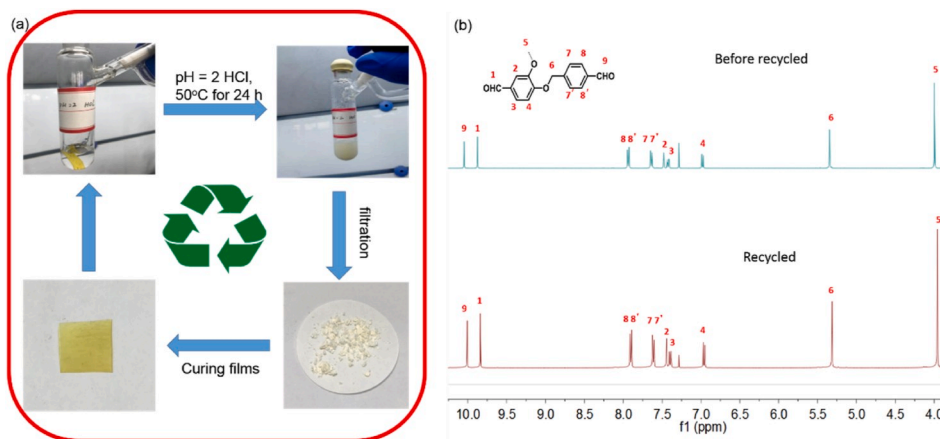


Fig. 11. a) Recyclable diagram of  $VF_{10}$ . b)  $^1H$  NMR spectra of VC and recycled VC from acid hydrolysis.

#### 4. Conclusions

In summary, a novel self-healing, chemically degradable and recyclable vanillin vitrimers ( $VF_x$ ) contained multiple reversible covalent bonds were prepared by vanillin derived dialdehyde and amine monomers.  $VF_x$  containing imine and disulfide bonds were prepared by reaction of VC with tris (2-aminoethyl) amine and a certain amount of 4-AFD. Through thermal and mechanical properties tests,  $VF_{10}$  showed the best performance.  $VF_x$  exhibited excellent self-healing properties under hot pressing or with the addition of a catalytic amount of amine. In addition,  $VF_x$  performed degradability and chemical recyclability under acidic conditions. Such self-healing, chemically degradable and recyclable cross-linked polymer from biomass compounds are of great significance for alleviating the depletion of petroleum resources and environmental pollution, as well as have beneficial prospects of materials science and resource reuse.

#### Declaration of competing interest

There are no conflicts to declare.

#### CRediT authorship contribution statement

**Zijian Guo:** Conceptualization, Methodology, Writing - original draft, Formal analysis, Data curation. **Bangjie Liu:** Resources. **Li Zhou:** Validation. **Lingna Wang:** Data curation. **Kashif Majeed:** Software. **Baoliang Zhang:** Resources. **Fengtao Zhou:** Conceptualization, Methodology, Writing - review & editing. **Qiuyu Zhang:** Conceptualization, Methodology, Supervision, Funding acquisition.

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