Composites Part B 173 (2019) 106885

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Two Strategies to precisely tune the mechanical properties of plant oil-derived epoxy resins

Jiangjun Zhou [1], Kaijie Xu [1], Mengjia Xie, Haifeng Wu, Zan Hua, Zhongkai Wang *

Biomass Molecular Engineering Center, Anhui Agricultural University, Hefei, Anhui, 230036, China

ABSTRACT

During recent years, the development of mechanically robust epoxy resins from natural abundant plant oils is gaining more and more attention. Herein, two strategies were developed to precisely tune the microstructure of plant oil-derived epoxy polymers and mechanical properties of their thermosets. In strategy 1, plant oil-derived epoxy polymers (EPs) with varied densities of epoxy groups were prepared and epoxy resins with tunable mechanical properties were obtained. Tensile test revealed that the mechanical strength, Young's modulus, and toughness increased with the increase of epoxy group density. In strategy 2, the mechanical performanceof plant oil-derived epoxy resins were greatly improved by introducing vanillin as rigid segments. Moreover, the mechanical properties of plant oil-based epoxy resins could be precisely tuned via either strategy 1 or strategy 2, and thermosets from soft elastomers to rigid plastics were obtained. Due to the existence of well-defined chemical networks, plant oil-based epoxy resins exhibit excellent thermally induced shape memory properties.

1. Introduction

Due to their excellent mechanical properties, chemical resistance, and thermal stability, thermoset materials were widely used in various fields [1,2]. Among them, epoxy resins take possession of approximately 70% of the global thermosets market. Epoxy resins have been widely applied in adhesives, electronics, coatings, and composites [3–6]. Most of the commercialized epoxy resins are derived from non-renewable bisphenol A (BPA) [7,8]. It is worth to mention that BPA may cause serious health issues, such as impair the immune and reproduction system [9,10]. Due to the shortage of fossil resources and serious environmental issues, exploring environmental friendly epoxy resins from renewable biomass has great significance for sustainable development [11–17].

During recent years, various biomass resources such as lignin, sugar, plant oil, isosorbide, rosin, itaconic acid, eugenol, and vanillin have been used to produce bio-based epoxy resins [18–27]. Among them, low-cost, nontoxic, and abundant plant oils are suitable candidates for epoxy resin manufacture [28–30]. Epoxidized plant oils (EPOs) are commercial available, which was usually used as plasticizers or stabilizing agents in plastics, paints, and adhesives [31–33]. EPOs could be easily converted to epoxy thermosets through curing with anhydrides, dicarboxylic acids, diamines, and polyamines [34–37]. However, the ill-defined networks of EPO resins lead to poor mechanical properties [1,36]. This is a result from low reactivity of the internal epoxy groups of fatty acids [38,39]. Recently, plant oil derived epoxy resins with highly reactive terminal epoxy groups was developed to improve the mechanical properties of their thermosets [40]. Moreover, increasing the quantity of internal epoxy groups in one molecule was demonstrated to be an efficient strategy to overcome their low reactivity. For example, epoxidized sucrose ester of fatty acids (ESEFAs) with at least 7 epoxide groups in one molecule can afford thermosets with mechanical strength much higher than EPO-based resins [41–43]. Recently, we reported the development of plant oil-derived epoxy polymers with tens to hundreds of internal epoxy groups in one macromolecular [44]. However, the effect of epoxy polymer characteristics on the performance of epoxy resins is still unknown. We anticipate that by tuning the epoxy group density and the chain rigidity of plant oil-derived epoxy polymers, relevant plant oil-based thermosets with controllable mechanical properties could be acquired.

Two strategies were developed to tune the characteristics of plant oil-derived epoxy polymers and control the mechanical properties of their thermosets. In strategy 1, high oleic sunflower oil (HOSO)-derived epoxy polymers (EPs) with varied epoxy group densities were prepared. Thermosets with controllable epoxy network densities and mechanical properties were then prepared via curing with anhydride. In strategy 2, rigid components were introduced into epoxy polymers to improve their T_g values and mechanical performance of epoxy resins. Vanillin is a kind of small molecule biomass derived from lignin, which can act as rigid segments to manufacture high performance epoxy thermosets [45]. To

---

* Corresponding author.

E-mail address: wangzk6@ahau.edu.cn (Z. Wang).

[1] J. Zhou and K. Xu contributed equally.

https://doi.org/10.1016/j.compositesb.2019.05.096

Received 14 November 2018; Received in revised form 22 March 2019; Accepted 9 May 2019

improve the sustainability, vanillin-derived methacrylate monomer (VM) was used as rigid monomer and copolymerized with sunflower oil-based monomer (SFMA). After epoxidation, high T_g sunflower oil-based epoxy copolymers EP(SFMA-*co*-VM)s were obtained. The DMA and tensile results showed that epoxy thermosets with increasing mechanical performance were obtained. Moreover, the existence of a well-defined network endows these plant oil-derived epoxy resins with unique shape memory properties.

2. Experimental

2.1. Materials

Sunflower oil was purchased from supermarket. 2-(Methylamino) ethanol (99%, Aladdin), sodium methoxide (5.4 M, TCI), methacrylic anhydride (94%, Aladdin), 4-dimethylaminopyridine (DMAP, 99%, Aladdin), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 99%, Aladdin), 3-chloroperoxybenzoic acid (*m*-CPBA, 75%, Aladdin), 4-methycyclohexan-1,2-dicarboxylic anhydride (MCHAn, 98%, Aladdin), methyl methacrylate (MMA, 99%, Aladdin), vanillin (99%, Aladdin), and all other chemicals were used as received. 2,2′-Azobis (2-methylpropionitrile) (AIBN, 98%, Aldrich) was recrystallized before use.

2.2. Synthesis of sunflower oil-derived epoxy polymers

As shown in Scheme S1, sunflower oil amide (SFM), sunflower oil methyl methacrylate (SFMA), and sunflower oil based polymers (PSFMA) were prepared according to our previous work [46]. Epoxy polymers with varied degree of epoxidation were then obtained via epoxidation of PSFMA with *m*-CPBA (Scheme 1). The molar ratios of double bonds (PSFMA) to peroxide were set as 10:1, 5:1, 2:1, 4:3, and 1:1, and defined as EP1, EP2, EP3, EP4, and EP5, respectively. A typical procedure for the preparation of EP5 is shown as follows: PSFMA (2.00 g, 5.00 mol), *m*-CPBA (1.26 g, 5.00 mol), and DCM (20 mL) were placed into a 50 mL bottle. The mixture was stirred at room temperature for 24 h. Pure EP5 was obtained by precipitating the polymer solution (THF as solvent) into methanol for three times and drying under vacuum at room temperature for 12 h.

2.3. Curing of EPs with anhydride

MCHAn was used as the curing agent, DBU was used as the catalyst, and the obtained thermosets were defined as EPs-An. The molar ratio of epoxy to anhydride was 1:0.5. The preparation of EP4-An thermoset is as follows: EP4 (2.8 g), MCHAn (0.44 g, 2.6 mmol), and DBU (2.6 mg, 1.44 mmol) were dissolved in 25 mL THF. The homogenous solution was then cast in a Teflon mold. The solution was dried at room temperature for 48 h and under vacuum for 12 h. Curing reaction was conducted at 100 °C under vacuum for 12 h. The obtained films were cut into dog-bone samples with length of 20 mm, width of 2 mm, and thickness of 0.3 mm.

2.4. Synthesis of P(SFMA-co-VM) copolymers

VM was prepared according to the literature [47]. As illustrated in Scheme 3, AIBN was used as initiator, P(SFMA-co-VM) copolymers were synthesized via copolymerization of SFMA with VM, and defined as CPs. The feed ratio between SFMA and VM were 9.5:0.5, 9:1, 8.5:1.5, 8:2 and 7.5:2.5. A typical procedure is as follows: SFMA (1.72 g, 4.50 mmol), VM (11.3 g, 0.50 mmol), AIBN (8.2 mg, 0.05 mmol), and THF (2 mL) were introduced into a 10 mL round bottle and purged with nitrogen for 15 min. The flask was immersed in an oil bath set at 65 °C. After 12 h, the reaction solution was precipitated into methanol. The obtained copolymers were dried under vacuum at 40 °C for 12 h.

2.5. Epoxidation of P(SFMA-co-VM) copolymers

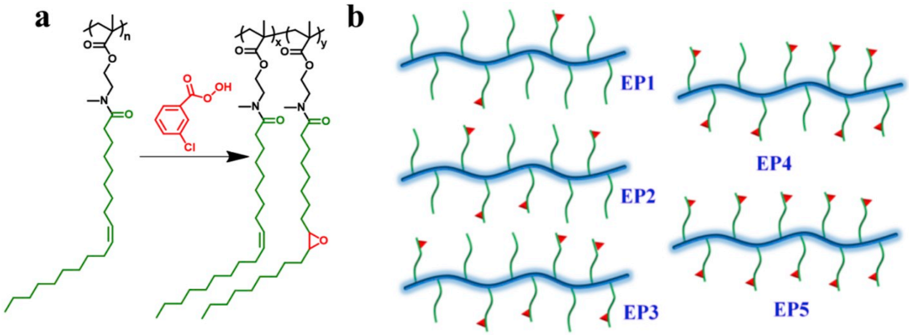
The epoxidation of P(SFMA-co-VM) copolymers was similar to that of EPs. For epoxy copolymers, the degree of epoxidation was maintained at 50%. Take ECP1 as an example, CP1 (2.3 g) and *m*-CPBA (0.71 g) were dissolved in DCM (23 mL). The reaction was stirred at room temperature for 24 h. The solution was dropped into methanol to precipitate the polymer for three times. EPs were then obtained by drying at room temperature under vacuum for 12 h.

2.6. Curing of epoxy copolymers with anhydride

The preparation procedure of ECP-An was similar to that of EP-An, a typical procedure was described follows: ECP2 (1.88 g), MCHAn (0.21 g), and DBU (19 mg) were dissolved in 19 mL THF. The solution was transferred into a cleaned Teflon mold. The solution was dried at room temperature for 48 h and dried under vacuum for 12 h. Subsequently, curing reaction was conducted at 100 °C under vacuum for 12 h. The films were cut into dog-bone specimens with length of 20 mm, width of 2 mm, and thickness of 0.3 mm.

2.7. Characterizations

^{1}H NMR spectroscopy were recorded on an Agilent DD2 600 MHz spectrometer (Agilent Technologies, America) using $CDCl_3$ as solvent with tetramethylsilane (TMS) as an internal reference at 25 °C. Fourier transform infrared spectra (FT-IR) were obtained on a Bruker Tensor 27 FT-IR spectrophotometer (Bruker, Ettlingen, Germany) using the KBr pellet method. Molecular weight and the molecular weight distribution (Đ) of the polymers were measured by size exclusion chromatograph (SEC), which equipped with a PLgel column (MIXED-A in the effective molecular weight range of 200–2,000,000) and using THF (1.0 mL/min) as the eluent. Samples were passed through microporous filtration membrane with average pore size of 0.2 μm before testing. Glass transition temperature (T_g) was characterized through differential scanning



Scheme 1. (a) Synthesis of sunflower oil-derived epoxy polymers (EP1-EP5) via epoxidation of PSFMA with *m*-CPBA; (b) Microstructure models of EP1-EP5 with varied epoxy group densities.

calorimetry (DSC) conducted on a DSC 200 F3 Maia® instrument (METZSCH Instruments) under a nitrogen atmosphere. Firstly, samples were heated from room temperature to 150 °C at a heating rate of 20 °C/min, then cooled down to −100 °C. The second heating and cooling cycle was executed at a rate of 20 °C/min. Dynamic mechanical properties were measured using a DMA 242 E/1/G (METZSCH Instruments). The measurements were conducted at a heating rate of 3 °C/min and a frequency of 10 Hz. Tensile testing was carried out on Suns UTM2502 testing instrument (Suns, China) with the crosshead speed of 20 mm/min at room temperature. The fracture surface morphologies were evaluated by a Hitachi S4800 Scanning Electron Microscope (SEM) and the surfaces were coated with a layer of platinum before testing. Shape memory properties were characterized using a dynamic mechanical analyzer (DMA Q800) by programmed thermomechanical procedure. At low load of 0.001 N, the samples with dimension of 10 mm (length) x 2 mm (width) x 0.6 mm (thickness) was heated to 80 °C and kept for 10 min. Then, the specimen was stretched to 8.6% strain under 0.3 N loading. Next, at a constant loading, the sample was cooled down to 20 °C and kept for 5 min, removal of stress at constant temperature. Finally, the sample was reheated to 80 °C and kept for 5 min. The heating and cooling rate at each cycle was 5 °C/min.

3. Results and discussion

3.1. Synthesis of sunflower oil-derived epoxy polymers (EPs) with different epoxy group densities

In our previous work, epoxy polymers derived from plant oil and their high performance thermosets were prepared [44]. Herein, one of our strategies was to tune the epoxy group density in EPs and mechanical properties of thermosets. As shown in Scheme S1, three steps were applied to prepare sunflower oil-derived polymers. Sunflower oil amide (SFM) was prepared by amidation of sunflower oil with 2-(methylamino)ethanol. Sunflower oil-based monomer (SFMA) was achieved by esterification with methacrylic anhydride. Polymers were then obtained via free radical polymerization of SFMA. The chemical structures of sunflower oil, SFM, SFMA, and PSFMA were confirmed by FT-IR (Fig. S1) and ^{1}H NMR spectra (Fig. S2).

As shown in Scheme 1, sunflower oil-derived polymers were converted to epoxy polymers (EPs) simply via reacting with *m*-CPBA. By controlling the molar ratios of *m*-CPBA/double bond at 1:10, 1:5, 1:2, 3:4, and 1:1, epoxy polymers with varied epoxy group densities were obtained and defined as EP1, EP2, EP3, EP4, and EP5, respectively (Table S1). ^{1}H NMR spectra of PSFMA and EP5 were shown in Fig. 1a, which demonstrated that double bonds of PSFMA were totally converted to epoxy groups. The peak intensity of double bond at 5.32 ppm (CH=CH) gradually decreased and peak intensity at 2.88 ppm (–CH–(O)–CH-) synchronously increased with increasing *m*-CPBA/double bond molar ratio. The degree of epoxidation (Table S1) was calculated according to the following eq (1).

$$\text{Degreeofesterification} = 1 - \frac{I_{5.32}}{I_{2.32}} \cdot 100\% \tag{1}$$

where $I_{2.32}$ and $I_{5.32}$ are the integrated peak intensity at $\delta = 2.32$ and $\delta = 5.32$ ppm corresponding to methylene protons adjacent to the ester and double bond of the protons, respectively. As shown in Table S1, the epoxy group densities of EPs were basically consistent with the feed ratio of *m*-CPBA to double bond. SEC curves of PSFMA and EP1-EP5 were shown in Fig. 1b, which indicated that molecular weight did not change obviously. Molecular weights and molecular weight distributions of PSFMA and EPs were summarized in Table S1.

3.2. Mechanical properties of EP-An epoxy resins

To study the effect of epoxy group density on mechanical properties of plant oil-based epoxy resins, EPs were cured to afford EPs-An according to our previous method (Scheme 2a) [44]. The epoxy/anhydride molar ratio was set as 1:0.5. Fig. 2a and b showed storage modulus (E') and loss tangent (tan δ) as a function of temperature for EPs-An. The E' at room temperature were 151.9, 336.0, 576.6, 823.1, and 1406.6 MPa, T_g values were 42.8, 45.6, 47.6, 53.3, and 56.5 °C for EP1-An, EP2-An, EP3-An, EP4-An, and EP5-An, respectively (Table S2). The results indicated that the storage modulus and T_gs of epoxy resins increased with increasing epoxy group density. The probable reason is that higher epoxy group densities lead to higher crosslinking density. The crosslinking density (ρ) of EP-An were calculated according to the rubber elasticity theory in eq (2) [18,48].

$$\rho = \frac{E}{\phi RT} \tag{2}$$

where E is the storage modulus (E') at T_g+30 °C, ϕ is the front factor (approximated to 1 in the Flory theory [49]), R is the gas constant, and T is the absolute temperature at T_g+30 °C. The calculated crosslinking densities are arranged in sequence of ρ(EP5-An) > ρ(EP4-An) > ρ(EP3-An) > ρ(EP2-An) > ρ(EP1-An) (Table S2). The corresponding microstructure models of EPs-An were shown in insets of Scheme 2b. Finally, we can conclude that higher epoxy group density will lead to higher crosslinking density, therefore having higher storage moduli and T_gs.

The mechanical properties of plant oil-based resins were then characterized via tensile tests. Fig. 2c showed representative stress–strain curves of the EPs-An. EP1-An and EP2-An acted like elastomers, while EP3-An, EP4-An, and EP5-An acted like plastics. Typical parameters were summarized in Table 1. The ultimate tensile strengths, elongation at break, and Young's modulus of EP1-An and EP2-An were 3.1 ± 0.1 and 6.6 ± 0.2 MPa, 76.9 ± 1.6% and 55.4 ± 2.1%, 12.4 ± 0.9 and 49.1 ± 2.4 MPa, respectively. For EP3-An, EP4-An, and EP5-An, the ultimate tensile strength increased from 11.6 ± 0.7 to 28.8 ± 1.6 MPa and

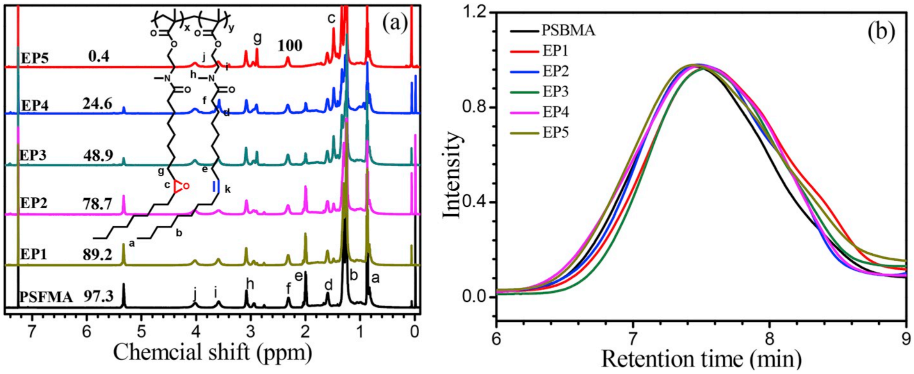
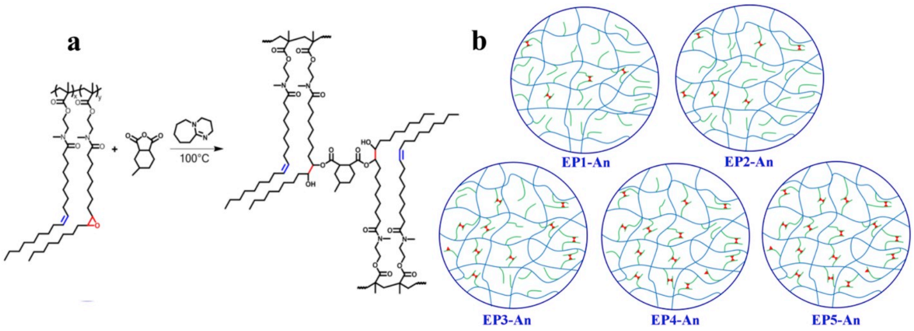


Fig. 1. (a) ^{1}H NMR spectra ($CDCl_3$, 600 MHz) and (b) SEC curves of PSFMA and EP1-EP5.



Scheme 2. (a) Schematic illustration on the curing of EPs with anhydride; (b) Microstructure models of EPs-An thermosets, which possess varied epoxy network density.

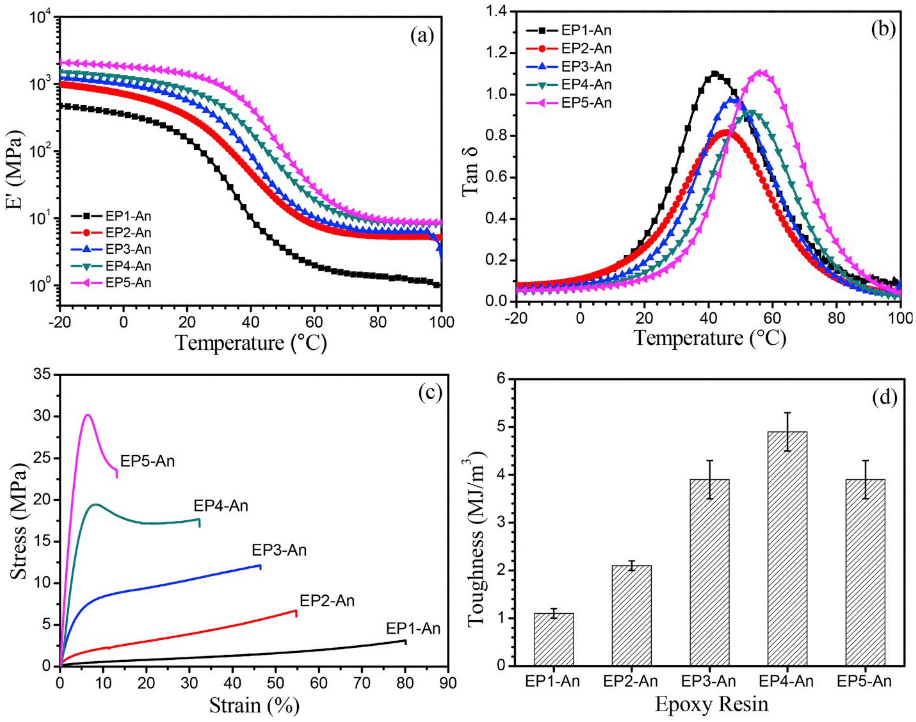


Fig. 2. (a) Storage modulus, E', and (b) loss tangent, Tan δ, as a function of temperature for EPs-An; (c) Stress−strain curves and (d) toughness of EPs-An.

Table 1
Mechanical parameters of EPs-An.

Sample code	Ultimate stress (MPa)	Ultimate strain (%)	Toughness (MJ/m^3)	Young's modulus (MPa)
EP1-An	3.1 ± 0.1	76.9 ± 1.6	1.1 ± 0.1	12.4 ± 0.9
EP2-An	6.6 ± 0.2	55.4 ± 2.1	2.1 ± 0.1	49.1 ± 2.4
EP3-An	11.6 ± 0.7	46.5 ± 3.4	3.9 ± 0.4	174.7 ± 20.1
EP4-An	18.8 ± 0.7	30.3 ± 2.4	4.9 ± 0.4	472.2 ± 29.8
EP5-An	28.8 ± 1.6	17.5 ± 1.0	3.9 ± 0.4	726.3 ± 55.6

Young's modulus increased from 174.7 ± 20.1 to 726.3 ± 55.6 MPa due to increased epoxy group density. Overall, the mechanical strength of EPs-An thermosets increased with increasing epoxy density. Fig. 3S shows the stress-strain curves of bisphenol A based epoxy resin. The tensile strength was as high as 64.8 ± 1.7 MPa, but the failure strain was 6.4 ± 0.4%. The toughness of plant oil based-epoxy resin was about 2.5 times to that of bisphenol A epoxy resin (2.1 ± 0.4 MJ/m^3).

The evolution of toughness as a function of epoxy group density was shown in Fig. 2d, where EP4-An showed highest toughness. As summarized in Table 1, the toughness of EP4-An was 4 times higher than that of EP1-An. However, the toughness of EP5-An slightly decreased to 3.9 ± 0.4 MJ/m^3. We can conclude that EPs with approximately degree of epoxidation of 75% lead to plant oil-based epoxy resins with highest toughness. Fig. 3a–e exhibit the SEM images of tensile fracture surface of the EPs-An. EP1-An showed relative smooth fracture surface, which is similar to that of rubber materials. While the fracture surface of other plant oil-based epoxy resins were rough, with particles or holes were observed. These particles were pulled out from the interface during stretching, which is a very efficient way of energy dissipation. The moderate size and maximum number of particles in the EP4-An lead to efficient energy dissipation during the stretching process, which bring about highest toughness. The average particle diameters were summarized in Fig. 3f. The toughness of EPs-An was positively related to the particle diameters. The above results show that plant oil-based epoxy resins with desired mechanical properties could be acquired by regulating the epoxy group density of plant oil-derived epoxy polymers.

3.3. Synthesis and epoxidation of P(SFMA-co-VM) copolymers

Low T_g of plant oil-derived polymers (Fig. S4, Supporting Information) restricts the mechanical performance of their thermosets. We

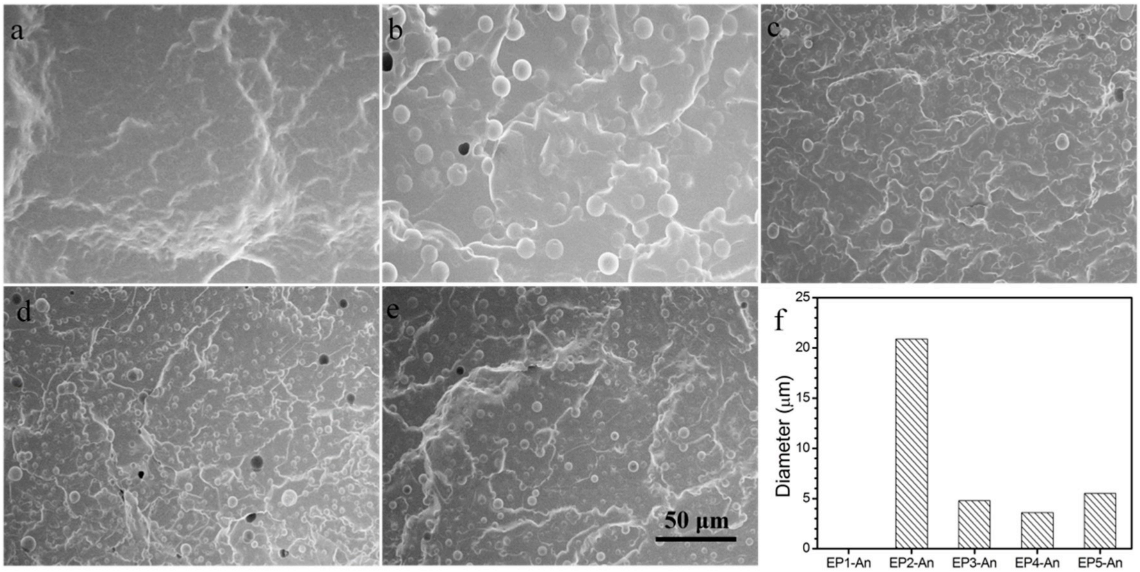


Fig. 3. SEM images of the fracture surface of (a) EP1-An, (b) EP2-An, (c) EP3-An, (d) EP4-An, (e) EP5-An; (f) Diameters of particles on the fracture surface of EPs-An. The scale bar for e was 50 μm and applied to other images.

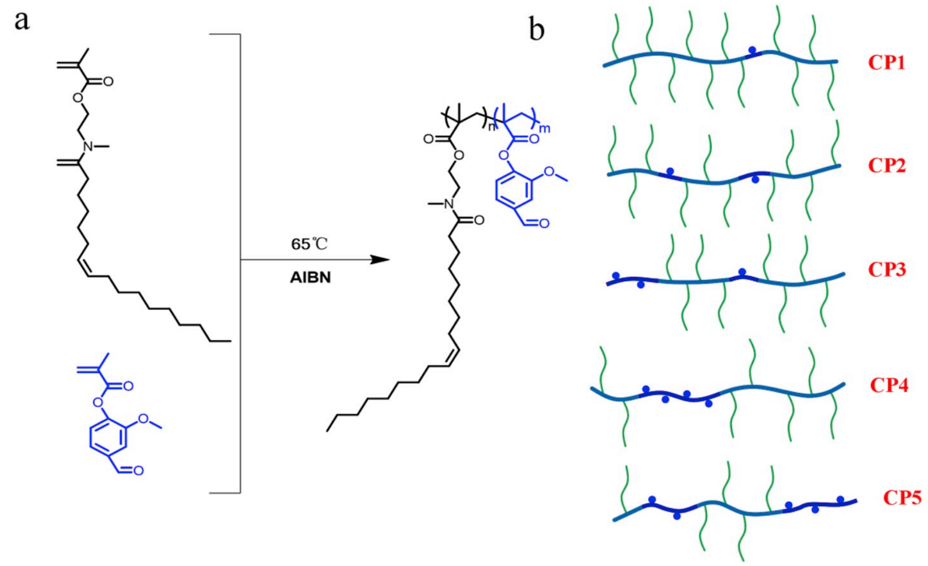
predict that by copolymerizing with rigid monomers, the mechanical performance of plant oil-derived epoxy polymers and their epoxy thermosets could be improved greatly. Poly (vanillin methacrylate) (PVM) derived from lignin showed high T_g value of 130.2 °C (Fig. S5, Supporting Information). To develop sustainable epoxy polymers with higher T_gs, SFMA were copolymerized with VM to afford P(SFMA-*co*-VM) (CPs, Scheme 3). ^{1}H NMR spectra of polymer CP1-CP5 were shown in Fig. 4a. The molar fraction (MF) of VM in CPs was calculated via the following eq (3).

$$MF_{VM} = \frac{I_{9.92}}{I_{9.92} + I_{2.30}/2} \times 100\% \tag{3}$$

$I_{9.92}$ represents the integral value of aldehyde proton peak at $\delta = 9.92$. $I_{2.30}$ is the integration values of methylene protons adjacent to the ester group at $\delta = 2.30$ ppm. The molecular weights and molecular weight distributions ($Đ$) of CPs were characterized by SEC (Fig. S7b) and summarized in Table S3. DSC curves of CP1-CP5 were shown in Fig. 4b. It can be seen that the T_gs of copolymers gradually increased from 2.9 °C to 23.1 °C with the increase of VM contents.

3.4. Mechanical properties of biomass-based ECP-An epoxy resins

CPs were then epoxidized to obtain ECPs with degrees of epoxidation of about 50%. ECP-An with similar network density but varied VM contents were then obtained via curing with MCHAn (Scheme 4). The effect of VM content on mechanical properties of ECP-An was studied via DMA and tensile tests and typical parameters were summarized in Table 2. As predicted, the introduction of VM segments can significantly enhance the mechanical performance of plant oil based epoxy resins. Fig. 5a and b shows the change of storage modulus and tan δ as a function of temperature for ECP-An. Due to the increased VM contents, storage modulus at room temperature dramatically increased from 256.2 MPa, to 452.9 MPa, 623.0 MPa, 2099.9 MPa and 2578.5 MPa for ECP1-An, ECP2-An, ECP3-An, ECP4-An, and ECP5-An, respectively. T_g values for ECP1-An, ECP2-An, ECP3-An, ECP4-An, and ECP5-An were 42.8 °C, 45.6 °C, 47.6 °C, 53.3 °C, and 56.5 °C, respectively. This



Scheme 3. (a) Synthesis of P(SFMA-co-VM) copolymers via free radical copolymerization; (b) Microstructure models of copolymers CPs with varied VM contents.

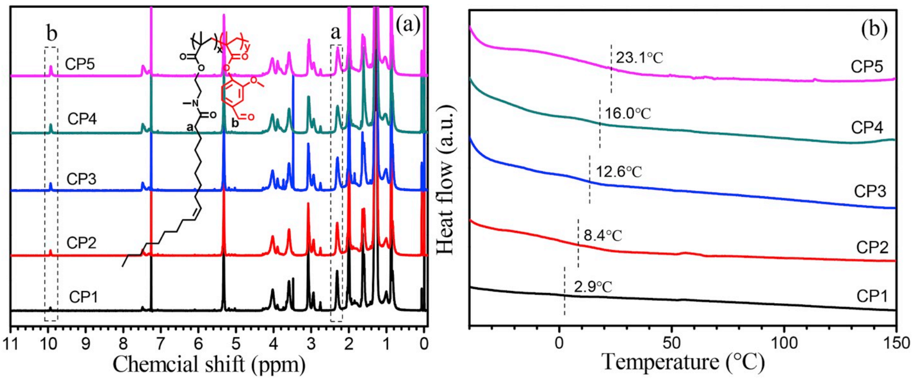
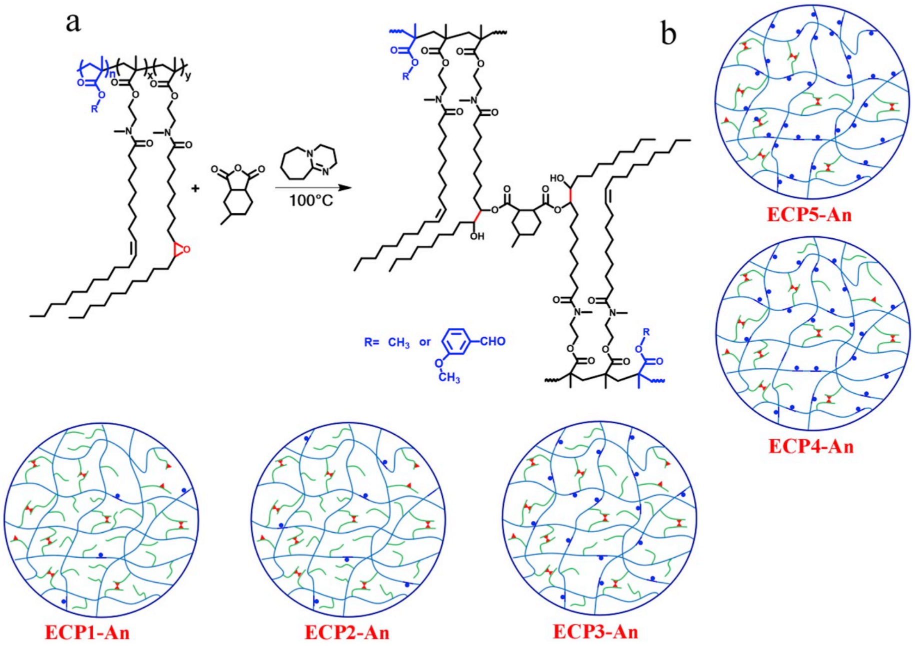


Fig. 4. (a) ^{1}H NMR spectra ($CDCl_3$, 600 MHz) and (b) DSC curves of CP1-CP5.



Scheme 4. (a) Schematic illustration for the DBU catalyzed ECP-An curing; (b) Microstructure models of ECP-An with varied VM contents.

Table 2
Mechanical properties of ECP-An thermosets.

Epoxy resins	Ultimate stress (MPa)	Ultimate strain (%)	Toughness (MJ/m^3)	Young's modulus (MPa)
ECP1-An	9.3 ± 0.2	76.7 ± 2.7	3.9 ± 0.1	73.6 ± 11.5
ECP2-An	10.3 ± 0.5	66.9 ± 3.1	4.6 ± 0.4	138.6 ± 21.1
ECP3-An	12.7 ± 0.5	59.1 ± 1.5	5.5 ± 0.5	188.3 ± 36.2
ECP4-An	15.6 ± 1.9	48.5 ± 3.7	5.9 ± 0.7	330.4 ± 26.1
ECP5-An	24.5 ± 2.9	32.4 ± 6.0	6.4 ± 0.8	532.3 ± 66.1

indicated that the raise of polymer backbone rigidity led to increased T_g values of the final thermosets.

Stress−strain curves of ECP-An epoxy resins were shown in Fig. 5c. With the increase of VM contents, the ultimate tensile stress of the ECP-An was significantly improved, which increased from 9.3 ± 0.2 MPa to 10.3 ± 0.5 MPa, 12.7 ± 0.5 MPa, 15.6 ± 1.9 MPa, and 24.5 ± 2.9 MPa for ECP-An (Table 2). Meanwhile, the ultimate tensile strain decreased from 76.7 ± 2.7 to 32.4 ± 6.0 as the result of the increasing rigid biomass contents. Compared with ECP1-An without rigid components, the toughness of ECP5-An increased 64.1% (Fig. 5d). Therefore, we can conclude that the introduction of rigid biomass component into plant oil-derived epoxy polymer could enhance the mechanical strength and toughness of plant oil-derived epoxy resins. To demonstrate the universality of this strategy, methyl methacrylate (MMA) introduced to improve the performance of plant oil-based epoxy resin (see supporting information). The enhanced performance of epoxy resin confirms the universality, feasibility and efficiency of the strategy.

3.5. *Shape memory properties of EPs-An epoxy resins*

Due to the high chain entanglement molecular weight and low intermolecular friction, elastomers derived from plant oils polymers exhibited high elasticity [50,51]. In this case, the prepared plant oil-derived epoxy resins were expected to exhibit excellent shape memory properties. As presented in Fig. 6a, representative photos of the shape recovery process of EP5-An, which indicated a fast and thorough shape recovery. Spiral shaped samples were prepared at 150 °C and cooled to room temperature to obtain permanent shape. Then a straight strip shape was made at 80 °C and cooled to room temperature to fix the temporary shape. The straight strip was reheated to 80 °C, and photos during shape recovery were taken. The straight strip was recovered to spiral shape within 15 s.

The shape memory behavior of EP5-An was quantitatively characterized via stress-controlled DMA testing (Fig. 6b). Sample was heated to 80 °C and then a constant stress of 0.4 MPa was applied. After cooled to

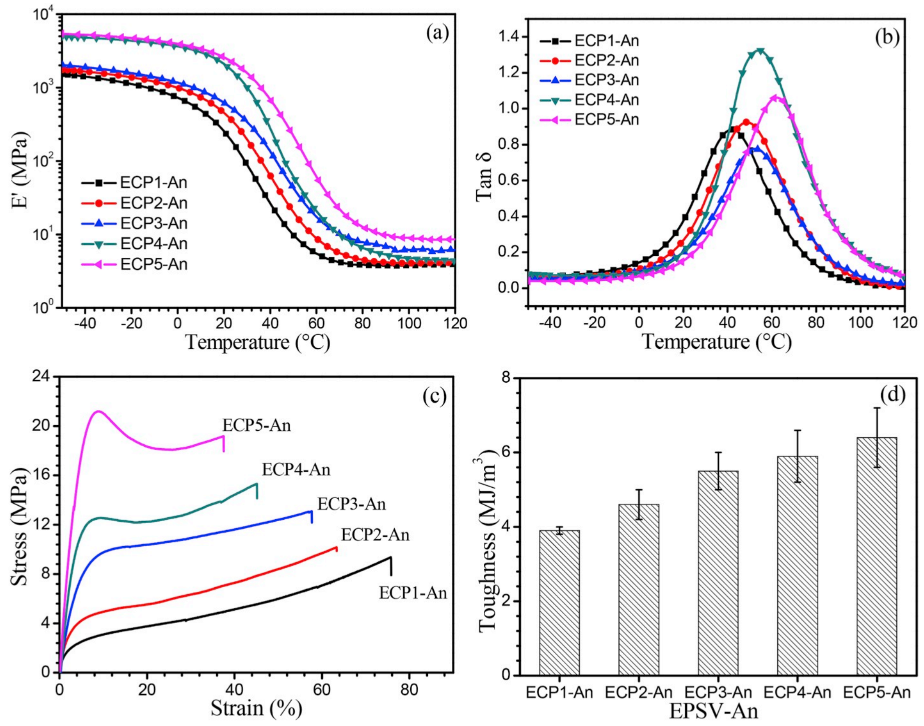


Fig. 5. (a) Storage modulus and (b) tan δ as a function of temperature; (c) Stress-strain curves and (d) toughness for ECP-An epoxy resins.

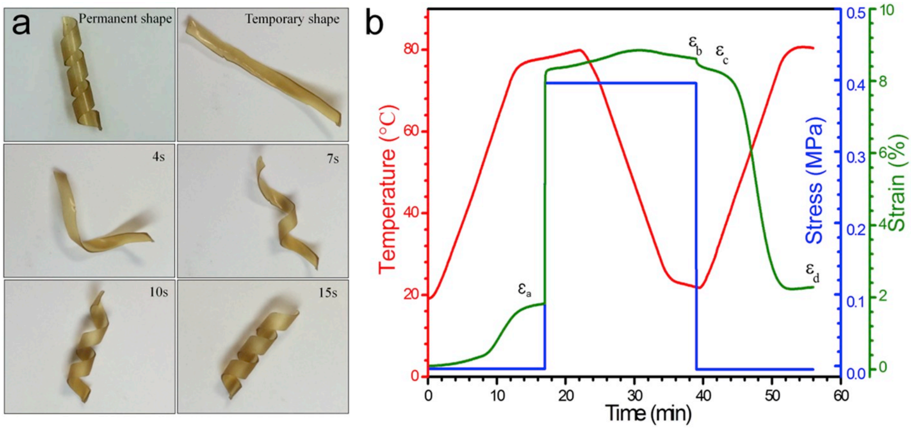


Fig. 6. (a) Representative photos about the shape recovery process of EP5-An at 80 °C; (b) Shape memory programming for EP5-An.

room temperature, a temporary shape with 8.6% strain was obtained. Shape fixity (R_f) reflects the ability of materials to retain temporary shape. Shape recovery (R_r) indicates the ability of materials to recover to permanent shape after stimulation. As shown in equations (4) and (5),

$$R_f = \frac{\varepsilon_c - \varepsilon_a}{\varepsilon_b - \varepsilon_a} \times 100\% \tag{4}$$

$$R_r = \frac{\varepsilon_d - \varepsilon_a}{\varepsilon_c - \varepsilon_a} \times 100\% \tag{5}$$

where ε_a, ε_b, ε_c, and ε_d represent the strain before applying stress, strain after removal of stress, strain after shape fixing, and strain after shape recovery, respectively. The shape fixity and the shape recovery were calculated to be 97.7% and 93.1%, respectively. These results demonstrated that the EPs-An derived from plant oil have very good thermally induced shape memory properties. The excellent shape memory properties of EPs-An originated from well-defined chemical networks, flexible polymer backbone, and low intermolecular friction at elevated temperatures.

4. Conclusion

Sunflower oil-based epoxy resins with high mechanical performances were prepared. Two strategies were then developed to precisely tune the mechanical properties of epoxy resins. By tuning the epoxy group density, the crosslinking density of epoxy resins was well controlled, which impressively controlled the mechanical properties. The introduction of rigid components into plant oil-derived epoxy polymers also helps to increase the T_gs and mechanical properties of their thermosets significantly. Lignin-derived vanillin was used as rigid components to fabricate fully bio-based epoxy resins with high toughness. By using these two strategies, bio-based thermoset resins from elastomers to plastics could be obtained. Moreover, these plant oil-based epoxy resins show excellent thermally induced shape memory properties. Our strategies provide novel insights in the design of high-performance bio-based thermosets.

Acknowledgments

Z. Wang thanks National Natural Science Foundation of China for financial support (Grant 51603002, 51773001). Z. Wang also acknowledges the financial support from Natural Science Foundation for Distinguished Young Scholar of Anhui Province (grant no. 1808085J26). K. Xu acknowledges the undergraduate Training Program for Innovation and Entrepreneurship of Anhui Province (grant no. 201710364073).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2019.05.096.

References

[1] Raquez JM, Deléglise M, Lacrampe MF, Krawczak P. Thermosetting (bio)materials derived from renewable resources: a critical review. Prog Polym Sci 2010;35(4):487–509.

[2] Faruk O, Bledzki AK, Fink H, Sain M. Biocomposites reinforced with natural fibers: 2000-2010. Prog Polym Sci 2012;37(11):1552–96.

[3] Maksym P, Tarnacka M, Dzienia A, Matuszek K, Chrobok A, Kaminski K, et al. Enhanced polymerization rate and conductivity of ionic liquid-based epoxy resin. Macromolecules 2017;50(8):3262–72.

[4] Njuguna J, Pielichowski K, Alcock JR. Epoxy-based fibre reinforced nanocomposites. Adv Eng Mater 2007;9(10):835–47.

[5] Khelifa F, Habibi Y, Bonnaud L, Dubois P. Epoxy monomers cured by high cellulosic nanocrystal loading. ACS Appl Mater Interfaces 2016;8(16):10535–44.

[6] Barbosa AQ, da Silva LFM, Abenojar J, Figueiredo M, Ochsner A. Toughness of a brittle epoxy resin reinforced with micro cork particles: effect of size, amount and surface treatment. Compos B Eng 2017;114:299–310.

[7] Li C, Li YH, Cai XX, Wang HW, Bossmann SH, Sung JG, et al. Competitive nucleophilic attack chemistry based on undecenoic acid: a new chemical route for plant-oil-based epoxies. ACS Sustainable Chem Eng 2016;4(10):5718–29.

[8] Liu T, Hao C, Wang L, Li Y, Liu W, Xin J, et al. Eugenol-derived biobased epoxy: shape memory, repairing, and recyclability. Macromolecules 2017;50(21):8588–97.

[9] Rochester JR. Bisphenol A and human health: a review of the literature. Reprod Toxicol 2013;42:132–55.

[10] Michalowicz J. Bisphenol A–sources, toxicity and biotransformation. Environ Toxicol Pharmacol 2014;37(2):738–58.

[11] Zhu Y, Romain C, Williams CK. Sustainable polymers from renewable resources. Nature 2016;540(7633):354–62.

[12] Xu S, Lamm ME, Rahman MA, Zhang X, Zhu T, Zhao Z, et al. Renewable atom-efficient polyesters and thermosetting resins derived from high oleic soybean oil. Green Chem 2018;20(5):1106–13.

[13] Mashouf Roudsari G, Mohanty AK, Misra M. Green approaches to engineer tough biobased epoxies: a review. ACS Sustainable Chem Eng 2017;5(11):9528–41.

[14] Jian X-Y, An X-P, Li Y-D, Chen J-H, Wang M, Zeng J-B. All plant oil derived epoxy thermosets with excellent comprehensive properties. Macromolecules 2017;50(15):5729–38.

[15] Williams C, Hillmyer M. Polymers from renewable resources: a perspective for a special issue of polymer reviews. Polym Rev 2008;48(1):1–10.

[16] Mohanty AK, Misra M, Drzal LT. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J Polym Environ 2002;10(1–2):19–26.

[17] Wang ZK, Yuan L, Tang CB. Sustainable elastomers from renewable biomass. Accounts Chem Res 2017;50(7):1762–73.

[18] Zhao S, Abu-Omar MM. Renewable epoxy networks derived from lignin-based monomers: effect of cross-linking density. ACS Sustainable Chem Eng 2016;4(11):6082–9.

[19] Kovash Jr CS, Pavlacky E, Selvakumar S, Sibi MP, Webster DC. Thermoset coatings from epoxidized sucrose soyate and blocked, bio-based dicarboxylic acids. Chemsuschem 2014;7(8):2289–94.

[20] Milchert E, Malarczyk K, Klos M. Technological aspects of chemoenzymatic epoxidation of fatty acids, fatty acid esters and vegetable oils: a review. Molecules 2015;20(12):21481–93.

[21] Hong J, Radojčić D, Ionescu M, Petrović ZS, Eastwood E. Advanced materials from corn: isosorbide-based epoxy resins. Polym Chem 2014;5(18):5360–8.

[22] Mantzaridis C, Brocas A-L, Llevot A, Cendejas G, Auvergne R, Caillol S, et al. Rosin acid oligomers as precursors of DGEBA-free epoxy resins. Green Chem 2013;15(11):3091–8.

[23] Ma SQ, Liu XQ, Jiang YH, Tang ZB, Zhang CZ, Zhu J. Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers. Green Chem 2013;15(1):245–54.

[24] Li C, Wan JT, Kalali EN, Fan H, Wang DY. Synthesis and characterization of functional eugenol derivative based layered double hydroxide and its use as a nanoflame-retardant in epoxy resin. J Mater Chem 2015;3(7):3471–9.

[25] Faye I, Decostanzi M, Ecochard Y, Caillol S. Eugenol bio-based epoxy thermosets: from cloves to applied materials. Green Chem 2017;19(21):5236–42.

[26] Shibata M, Ohkita T. Fully biobased epoxy resin systems composed of a vanillin-derived epoxy resin and renewable phenolic hardeners. Eur Polym J 2017;92:165–73.

[27] Li RS, Zhang YC, Xiong ZH, Zheng FY, Meng FR. Liquefied banana pseudo stem-based epoxy composites: incorporation of phenol derivative and its characterization. Compos B Eng 2018;143:28–35.

[28] Stemmelen M, Lapinte V, Habas J-P, Robin J-J. Plant oil-based epoxy resins from fatty diamines and epoxidized vegetable oil. Eur Polym J 2015;68:536–45.

[29] Biermann U, Bornscheuer U, Meier MA, Metzger JO, Schafer HJ. Oils and fats as renewable raw materials in chemistry. Angew Chem Int Ed 2011;50(17):3854–71.

[30] Meier MAR, Metzger JO, Schubert US. Plant oil renewable resources as green alternatives in polymer science. Chem Soc Rev 2007;36(11):1788–802.

[31] Chieng BW, Ibrahim NA, Then YY, Loo YY. Epoxidized jatropha oil as a sustainable plasticizer to poly(lactic acid). Polymers 2017;9(12).

[32] Teng GH, Soucek MD. Epoxidized soybean oil-based ceramer coatings. J Am Oil Chem Soc 2000;77(4):381–7.

[33] Khandelwal V, Sahoo SK, Kumar A, Manik G. Electrically conductive green composites based on epoxidized linseed oil and polyaniline: an insight into electrical, thermal and mechanical properties. Compos B Eng 2018;136:149–57.

[34] Liu ZS, Erhan SZ, Xu JY. Preparation, characterization and mechanical properties of epoxidized soybean oil/clay nanocomposites. Polymer 2005;46(23):10119–27.

[35] Liu ZS, Erhan SZ. Ring-opening polymerization of epoxidized soybean oil. J Am Oil Chem Soc 2010;87(4):437–44.

[36] Li A, Li K. Pressure-sensitive adhesives based on epoxidized soybean oil and dicarboxylic acids. ACS Sustainable Chem Eng 2014;2(8):2090–6.

[37] Ding C, Matharu AS. Recent developments on biobased curing agents: a review of their preparation and use. ACS Sustainable Chem Eng 2014;2(10):2217–36.

[38] Li R, Zhang P, Liu T, Muhunthan B, Xin JN, Zhang JW. Use of hempseed-oil-derived polyacid and rosin-derived anhydride acid as cocuring agents for epoxy materials. ACS Sustainable Chem Eng 2018;6(3):4016–25.

[39] Jian X-Y, He Y, Li Y-D, Wang M, Zeng J-B. Curing of epoxidized soybean oil with crystalline oligomeric poly(butylene succinate) towards high performance and sustainable epoxy resins. Chem Eng J 2017;326:875–85.

[40] Earls JD, White JE, López LC, Lysenko Z, Dettloff ML, Null MJ. Amine-cured ω-epoxy fatty acid triglycerides: fundamental structure–property relationships. Polymer 2007;48(3):712–9.

[41] Pan X, Webster DC. Impact of structure and functionality of core polyol in highly functional biobased epoxy resins. Macromol Rapid Commun 2011;32(17):1324–30.

[42] Pan X, Sengupta P, Webster DC. High biobased content epoxy-anhydride thermosets from epoxidized sucrose esters of Fatty acids. Biomacromolecules 2011;12(6):2416–28.

[43] Pan X, Sengupta P, Webster DC. Novel biobased epoxy compounds: epoxidized sucrose esters of fatty acids. Green Chem 2011;13(4):965–75.

[44] Wang Z, Yuan L, Ganewatta MS, Lamm ME, Rahman MA, Wang J, et al. Plant oil-derived epoxy polymers toward sustainable biobased thermosets. Macromol Rapid Commun 2017;38(11).

[45] Savonnet E, Grau E, Grelier S, Defoort B, Cramail H. Divanillin-based epoxy precursors as DGEBA substitutes for biobased epoxy thermosets. ACS Sustainable Chem Eng 2018;6(8):11008–17.

[46] Yuan L, Wang ZK, Trenor NM, Tang CB. Robust amidation transformation of plant oils into fatty derivatives for sustainable monomers and polymers. Macromolecules 2015;48(5):1320–8.

[47] Stanzione 3rd JF, Sadler JM, La Scala JJ, Wool RP. Lignin model compounds as bio-based reactive diluents for liquid molding resins. Chemsuschem 2012;5(7):1291–7.

[48] Cook WD, Schiller TL, Chen F, Moorhoff C, Thang SH, Bowman CN, et al. Effect of cross-link density on photoplasticity of epoxide networks containing allylic dithioether moieties. Macromolecules 2012;45(24):9734–41.

[49] Nouailhas H, Aouf C, Le Guerneve C, Caillol S, Boutevin B, Fulcrand H. Synthesis and properties of biobased epoxy resins. Part 1. Glycidylation of flavonoids by epichlorohydrin. J Polym Sci, Polym Chem Ed 2011;49(10):2261–70.

[50] Xu Y, Yuan L, Wang Z, Wilbon PA, Wang C, Chu F, et al. Lignin and soy oil-derived polymeric biocomposites by "grafting from" RAFT polymerization. Green Chem 2016;18(18):4974–81.

[51] Yuan L, Wang Z, Ganewatta MS, Rahman MA, Lamm ME, Tang C. A biomass approach to mendable bio-elastomers. Soft Matter 2017;13(6):1306–13.