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Research Article

Hempseed Oil-Based Covalent Adaptable Epoxy-Amine Network and Its Potential Use for Room-Temperature Curable Coatings

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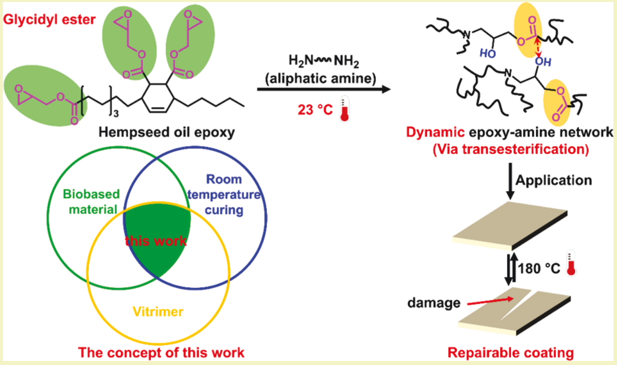

ABSTRACT: Conventional thermoset coatings are prepared from petrochemical feedstocks, which are nonrenewable, and the resulting coatings are not repairable. To extent the service life and meet the sustainable demands, it is desirable to develop repairable coatings prepared from renewable feedstocks. Dynamic covalent chemistry can impart thermosetting polymers the repairability. However, such alternative polymers that are also room-temperature curable are rare. In this work, a room-temperature curable epoxy vitrimer is introduced by curing a mixture of hempseed oil-based glycidyl ester-type epoxy (HOEP) and a bisphenol A-based digycidyl ether-type epoxy with diethylenetriamine (DETA). The resulting cross-linked network possesses abundant ester bonds and hydroxyl groups, which can undergo dynamic transesterification reactions at elevated temperatures and provide typical vitrimer behaviors such as stress relaxation and reparability to the cured resin. Coatings of this resin system on tin plates prepared at room temperature exhibit satisfactory glass transition temperature (>40 °C), scratch hardness (5H), gouge hardness (6H), adhesive strength (5B), and solvent resistance. The renewable HOEP accounts for up to 67.5 wt % in the composition. This work has demonstrated a simple method for the preparation of a room-temperature curable epoxy vitrimer using a glycidyl ester epoxy as a co-monomer and an aliphatic amine as the hardener, which is readily pluggable into current epoxy commercial products.

KEYWORDS: *vitrimer, room-temperature curing, coating, hempseed oil, transesterification reaction, internal catalysis, amine cured epoxy*

■ INTRODUCTION

Room-temperature curable epoxy coatings (RTEC) have been widely seen in our daily life for decoration and protection of substrates such as concretes and metals. Most of the RTEC are based on the room-temperature curable epoxy-aliphatic amine system due to their convenient processability and low manufacturing cost.[1,2] During curing, each active hydrogen of the amine curing agent is capable of reacting with one epoxy group to form a stable C−N bond and a hydroxyl (−OH) group. The abundant high polar −OH groups promote strong adhesion between the coating and the substrate,[3] and the use of the curing agent of a high amine value enables the formation of a high-cross-link density network that displays excellent chemical resistance and dimensional stability. However, the permanent and stable cross-linked network also makes the cured epoxy not easily repairable. The common way to deal with the damaged coating is to remove the old coating and apply a new one onto the substrate, which generates a lot of polymer waste and is costly. To extend the service life and reduce the waste and cost, it is desirable to develop repairable and room-temperature curable epoxy coatings.

Dynamic covalent chemistry provides a likely solution to address the unrepairability of the cross-linked polymers. Vitrimers are a class of the cross-linked polymers that consist of dynamic covalent bonds, and they behave like conventional thermosets at service temperature but can undergo topological changes at elevated temperatures owing to the dynamic covalent bond interchange reactions.[4] Therefore, vitrimers exhibit certain degrees of repairability and malleability. A variety of dynamic covalent bonds, such as hydroxyl-ester (transesterification),[5,6] imine,[7−9] disulfide,[10,11] siloxane,[12] etc., have been introduced to the cross-linked network of epoxy materials. Among them, hydroxyl-ester is the most studied one as it commonly presents in the epoxy-acid and epoxy-anhydride curing systems that are widely used in the epoxy industry.[13] Some epoxy vitrimers reported in the literature with hydroxyl-ester linkages exhibit excellent dimensional stability/mechanical resistance and satisfactory repairability and have demonstrated potential applications for adhesives,[14,15] polymer

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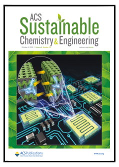

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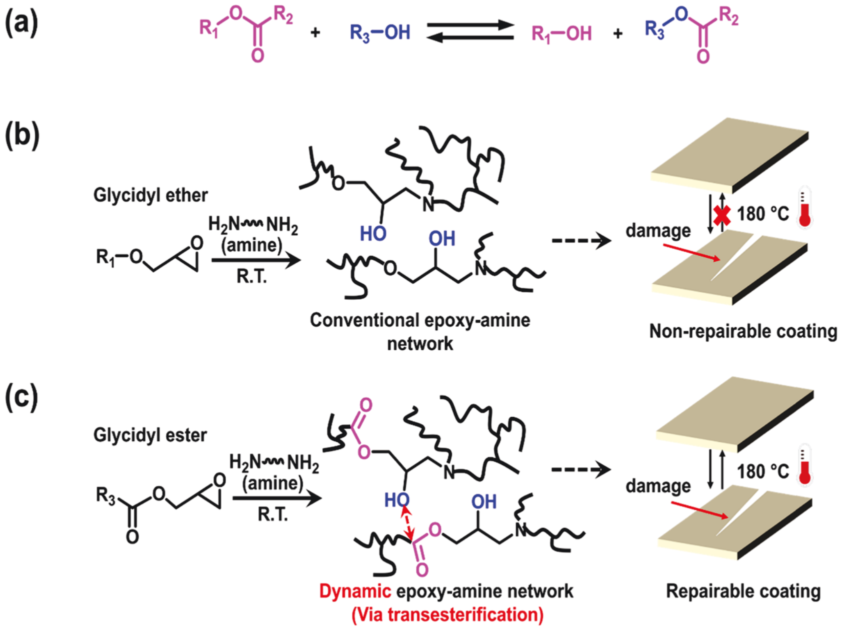
Scheme 1. Schematic Illustration of (a) Dynamic Transesterification Reactions (DTERs); (b) Conventional Epoxy-Amine Cross-linked Network from the Curing Reaction of Glycidyl Ether With Amine; and (c) Dynamic Epoxy-Amine Cross-linked Network from the Curing Reaction of Glycidyl Ester With Amine[a]



[a]Compared with the glycidyl ether epoxy-amine thermoset, the glycidyl ester-based epoxy-amine thermoset endowed thermal repairability by introducing ester linkages to the cross-linked network.

composites,[16,17] three-dimensional (3D) printing resins,[18] etc. However, to the best of our knowledge, there has not been a study of using epoxy vitrimers for room-temperature coatings. This is because both the epoxy-acid and epoxy-anhydride systems require curing at elevated temperatures.

In the literatures, effective dynamic transesterification reaction (DTER, Scheme 1a) in epoxy vitrimers has been demonstrated when the network structure contains sufficient −OH groups, ester bonds, and/or internal tertiary amines.[19,20] An amine cured epoxy possesses abundant −OH groups and tertiary amines (Scheme 1b); however, the DTER cannot take place due to the lack of ester bonds in the system. This problem could be addressed using an ester bond containing epoxy resins (e.g., 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (ECC), diglycidyl hexahydrophthalate (DHDP), and diglycidyl phthalate) (Scheme 1c). However, ECC exhibits low reactivity,[21] while DHDP and diglycidyl phthalate are often used as reactive diluents rather than the major resins.

On the other hand, commercial epoxy resins are derived from petrochemicals, which are nonrenewable. Preparation of alternative epoxies from renewable feedstocks has received extensive investigations. Especially, a series of epoxy vitrimers based on vegetable oil (VO) derivatives, such as dimer acid[20] and sebacic acid,[22] have been reported in the literature. However, curing of the epoxy-fatty acid system requires elevated temperature, and the resulting vitrimers generally exhibit low glass transition temperatures (T_g's) due to the flexible backbone structures. These issues make them not suitable for room-temperature coatings. In our previous work, we demonstrated the preparation of a VO-based glycidyl ester triepoxy via a simple Diels−Alder addition of tung oil fatty acids with fumaric acid and subsequently converting the adduct to triglycidyl esters.[23] The triepoxy had a similar reactivity during curing, and the cured resin exhibited comparable mechanical properties to that of conventional BPA epoxies.

In this work, a room-temperature curable and repairable epoxy vitrimer based on the curing of a mixed hempseed oil (HO)-derived epoxy (HOEP) and BPA epoxy with an aliphatic amine curing agent was studied. Hempseed oil (HO) contains about 80% polyunsaturated fatty acids, which enable the facile chemical modification for the preparation of epoxy resin. The cross-linked network possessed abundant −OHs and catalytic tertiary amines in addition to abundant ester bonds that came with HOEP. DTER took place effectively at elevated temperatures (>150 °C). The cured epoxy exhibited typical vitrimer behaviors such as stress relaxation and repairing properties. The curing system was then assessed for room-temperature coatings on tin plates. After curing at room temperature for 7 days, the resulting coatings showed comparable adhesion, hardness, and solvent resistance properties to the diethylenetriamine (DETA)-cured BPA epoxy (DER 331), which is a representative commercial coating with high T_g and stiffness.

■ EXPERIMENTAL SECTION

Materials. Hempseed oil (HO, Hemp Oil Canada Inc.), sodium hydroxide (AR, Macron Fine Chemicals), hydrochloric acid (35−37%, EMD Millipore Corporation), potassium hydroxide (AR, Macron Fine Chemicals), maleic anhydride (MA, 99%, Acros Organics), ethylene glycol (Certified, Fisher Scientific), glacial acetic acid (99.7%, Fisher Scientific), hydroquinone (99%, TCI), magnesium sulfate anhydrous (99%, Acros Organics), epichlorohydrin (ECH, 99%, TCI), tetrabutylammonium bromide (TBAB, 98%, TCI), diethylenetriamine (DETA, 98%, Acros Organics), triethanolamine (TEOA, 99%, Sigma-Aldrich), adipic acid (99%, Acros Organics), and 1,4-butanediol diglycidyl ether (BDE, 60%, Acros Organics) were used as received. DER 331 epoxy resin (epoxy value = 0.53 mol/100 g) was provided by the Horn company. All of the solvents were GR grade and used as received without further purification.

Synthesis of HO-Polyacid-Derived Epoxy (HOEP). HOEP was prepared via four reaction steps as described as follows:[23,24]

(1) Hydrolysis of HO: HO (200.0 g) was hydrolyzed in 280 mL of ethanol−H_2O solution (1:1, v/v) with 32.0 g of NaOH at 70 °C for 2 h under mechanical stirring. At 70 °C, the resulting mixture was acidified to pH 2−3 using a 6 M HCl aqueous and subsequently extracted by 100 mL of hexane three times. The organic layer was collected, washed with DI water, dried by anhydrous $MgSO_4$, and concentrated by a rotary evaporator. The concentrated mixture was dried in a vacuum oven at 70 °C for 12 h. The received product, HO fatty acid (HOFA), was a yellow liquid with a yield of ∼93% and a viscosity of 0.2 Pa s at 30 °C.

(2) Preparation of conjugated hempseed oil fatty acid (C-HOFA): HOFA (100.0 g) in 500 mL of KOH−ethylene glycol solution (25%, w/v) was heated at 200 °C for 10 h under mechanical stirring. Then, the reaction solution was cooled down to 100 °C. A hundred milliliters of DI water was added, and the reaction was continued for 1 h. At room temperature, the resulting mixture was acidified to a pH value of 2−3 using a 6 M HCl aqueous and subsequently extracted by 100 mL of hexane three times. The organic layer was collected, washed with DI water, dried by anhydrous $MgSO_4$, and concentrated by a rotary evaporator. The concentrated mixture was dried in a vacuum oven at 70 °C for 12 h. The received product, C-HOFA, was a light-yellow liquid (0.2 Pa s at 30 °C) with a yield of ∼92%.

(3) Synthesis of hempseed oil polyacid (HOPA): The solution containing C-HOFA (98.0 g), maleic anhydride (82.3 g), hydroquinone (1.8 g), and 294 mL of acetic acid was refluxed for 9 h. Subsequently, 50 mL DI water was added and the solution was refluxed for 1 h. At room temperature, the resulting mixture was extracted by 100 mL of ethyl ether three times. The organic layer was collected, washed with DI water, dried by anhydrous $MgSO_4$, and concentrated by a rotary evaporator. The concentrated mixture was dried in a vacuum oven at 70 °C for 12 h. The received product, HOPA, was a brown and viscous liquid (33.1 Pa s at 30 °C) with a yield of ∼87%. The acid value was titrated as 0.434 mol/100 g.

(4) Synthesis of HOEP: HOPA (100.0 g, 1.0 equiv) and TBAB (7.0 g, 0.05 equiv) were dissolved in ECH (401.5 g, 10.0 equiv) and refluxed for 3 h under mechanical stirring and an argon atmosphere. The resulting solution was cooled down to 50 °C, and a 30 wt % NaOH aqueous (19.1 g of NaOH in 44.6 g of H_2O) was added dropwise. Then, the solution was continuous to react at 50 °C for 6 h. The resulting solution was washed with water, dried by anhydrous $MgSO_4$, and concentrated by a rotary evaporator to remove the unreacted ECH. The concentrated mixture was dried in a vacuum oven at 70 °C for 12 h. The received product, HOEP, was a brown liquid (0.2 Pa s at 30 °C) with a yield of ∼88%. The epoxy value was titrated as 0.383 mol/100 g.

Typical Procedures for the Preparation of Room-Temperature Curable Coatings. Standard tin plates with a dimension of $120 \times 50 \times 0.28$ mm^3 were used as the coating substrates. The tin plates were polished by a sandpaper (220-grit) and cleaned with DI water and isopropanol. The resin system was prepared as follows: under mechanical stirring, HOEP, DER 331, and TEOA were mixed at room temperature. DETA as a curing agent was then added. The molar ratio of epoxy/NH was fixed at 0.8/1. Table S1 gives the formulations. Until a homogeneous mixture was formed, epoxies were coated onto the tin plates. The thickness of the applied coating was controlled using a film applicator. The coatings were allowed to cure at room temperature (∼23 °C) for a predetermined time. After curing, the coating thickness was measured using a thickness gauge.

Characterizations. The Fourier transform infrared (FTIR) spectra were collected on a NICOLET iS50 FTIR spectrometer. The sample (∼1.0 mg) was mixed with KBr (∼100.0 mg) using a mortar, and the resulting mixture was compressed to a disk in a mold. Subsequently, the sample was scanned for 64 times from 4000 to 400 cm^{-1} with a resolution of 4.0 cm^{-1}. The UV−vis spectra were collected on a Lambda-25 UV−vis spectrophotometer. The cured films with a dimension of $\sim 14 \times 32 \times 0.15$ mm^3 were scanned from 400 to 700 nm. The ^1H NMR spectra were collected on a Varian 400-MR spectrometer (400 MHz) using deuterated $CDCl_3$ as solvent. T_g values and the curing behavior were examined using a differential scanning calorimeter (DSC1, Mettler-Toledo, Switzerland). The sample (∼5 mg) was sealed in a 40 μL aluminum crucible and heated from −50 to 200 °C at a rate of 5 K min^{-1} under a nitrogen atmosphere. Thermal stability was examined using a TGA/DSC1 thermogravimetric analyzer (TGA, Mettler-Toledo, Switzerland). The sample (∼10 mg) was added into a ceramic crucible and heated from 50 to 800 °C at a heat rate of 10 K min^{-1} under a nitrogen atmosphere.

The viscosity of the sample was examined using a Discovery HR-2 rheometer (TA Instruments) equipped with a pair of 25 mm parallel plates. The sample was scanned at room temperature (22 - 23 °C) with a frequency of 10 rad s^{-1} and a constant strain of 0.5%. The stress relaxation behavior was measured using the same rheometer equipped with a pair of 8 mm parallel plates. The sample with uniform thickness was heated to the set temperature and equilibrated for 10 min. A constant force of 2 N was then loaded to ensure good contact of the sample with the parallel plate. During the test, a 3% strain was applied to the sample, and the change of the relaxation modulus with time was recorded.

The swelling ratio and gel content were determined according to ASTM D2765-16 standard. The sample (0.500 ± 0.05 g, W_s) was wrapped in a filter paper and extracted with xylene in a Soxhlet extractor. After refluxing for 12 h, the extracted sample was collected, and the solvent remaining on the surface of the sample was removed by a filter paper. The swollen sample was weighed and recorded as W_g. The swollen sample was subsequently dried in a vacuum oven at 100 °C until reaching a constant weight, and the dry weight of the extracted sample was recorded as W_d. The swelling ratio and gel content were calculated according to the following equations

$$\text{swelling ratio} = 1 + K(W_g - W_d)/W_d \tag{1}$$

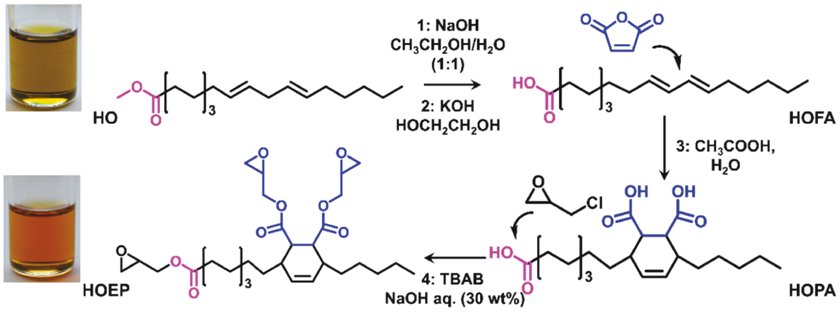
$$\text{gel content}(\%) = W_d/W_s \times 100 \tag{2}$$

where K represents the density ratio of the sample to solvent at the extraction temperature.

Dynamic mechanical properties were determined using a dynamic mechanical analyzer (Q800 DMA, TA Instrument) in a single cantilever mode. The specimen with a dimension of $\sim 35.0 \times 12.8 \times 3.0$ mm^3 was scanned from 0 to 170 °C at a heating rate of 3 °C min^{-1}. The oscillation amplitude was 15 μm, and the frequency was 1 Hz. The tensile properties of the samples were measured on an Instron 4466 test machine according to the ASTM D638 standard. The crosshead speed was set at 1 mm min^{-1}. The impact strength was measured using a pendulum impact tester (TTE-3097, Dynisco BPI), according to ASTM D256. At least, five repeats were tested for each composition.

Characterizations of the coating related properties are described as follows. The adhesion property was measured according to the ASTM D3359-17 standard. A lattice pattern with six cuts in each direction was made by cutting through the coating using a sharp blade. Subsequently, a standard pressure-sensitive tape was used to peel off the lattice pattern. 5B level represents the highest adhesion level that no coated area is peeled off. 0B level represents the lowest adhesion level, in which over 65% of the coated area is peeled off. The hardness of the coating was measured by the pencil test according to the ASTM D3363 standard. A set of standard wood pencils of different hardnesses (from 9B to 9H) were used for the test. The hardest pencil that cannot cut through the coating was recorded as gouge hardness, and the hardest pencil that cannot scratch the coating was recorded as scratch hardness. The solvent resistance of the coating was determined according to the ASTM D5402-15 standard (method A). Water, ethanol, and methyl ethyl ketone (MEK) were used to rub the coating. One forward and back motion was considered as one double rub. The number of double rubs was recorded until the substrate was exposed or 400 double rubs reached.

Scheme 2. Synthetic Route of HOEP from Hemp Seed Oil[a]



[a]The drawing is based on linoleic acid (C18:2), which is the major component of HOFA.

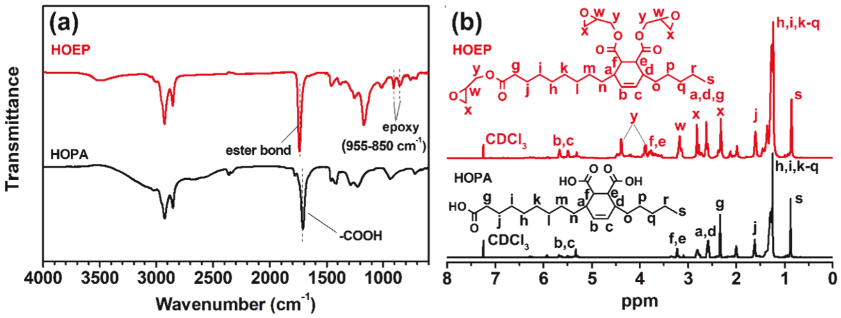


Figure 1. (a) FTIR spectra and (b) ^{1}H NMR spectra of HOPA and HOEP.

RESULTS AND DISCUSSION

Synthesis and Characterizations of HOEP. First, HOFA was prepared following a previously reported method (Scheme 2), which is a two-pot reaction.[24] HO was hydrolyzed to receive fatty acids (HOFAs), in which the unsaturated fatty acids (i.e., linoleic acid and linolenic acid) were subsequently conjugated by heating at 200 °C. The conjugated HOFA (C-HOFA) obtained was then reacted with maleic anhydride through Diels−Alder reaction and hydrolyzed to assure the product, which is HOPA, in acid form (−COOHs). The acid value of HOPA was titrated as 0.434 mol/100 g. Finally, HOPA was converted to a glycidyl ester epoxy (HOEP). Figure 1a shows the FTIR spectra of HOPA and HOEP. After glycidylization, the absorption in the range of 3000−3500 cm^{-1} attributed to the −COOH groups decreased significantly, and new peaks at ~955 and 850 cm^{-1} attributed to the epoxy group appeared. The peak at ~1700 cm^{-1} corresponding to the carbonyl of −COOH shifted to ~1780 cm^{-1} attributed to the carbonyl of the ester bond. The formation of HOEP was also confirmed by the ^{1}H NMR spectra (Figure 1b). The peak signals at 2.32, 2.81, and 3.17 ppm attributed to the protons of the epoxy group were noted after glycidylization. These results suggest the successful conversion of −COOHs to the epoxy groups. The epoxy value of HOEP was found to be 0.383 mol/100 g by titration, which was lower than the theoretical value (0.434 mol/100 g) on assuming complete conversion of −COOHs to epoxy. The lower titration value was probably due to the incomplete ring closing as well as the coupling reaction during synthesis (Scheme S1), as reflected from the small peak observed at ~3500 cm^{-1} attributed to −OHs in the FTIR spectrum of HOEP. It should be mentioned that the structures shown in Scheme 2 and Figure 1b are based on linoleic acid, which is the major component of HO. We have demonstrated in our previous study that the HO used is a mixture that contains about 80% unsaturated fatty acids including 58.1% linoleic acid (C18:2), 19.3% linolenic acid (C18:3), and 2% stearidonic acid (C18:4).[24] Ideally, these polyunsaturated fatty acids can be turned into triepoxy. HO also contains ~20% of saturated fatty acids, which only result in monoepoxy compound after reaction. Because the separation process to remove the unsaturated fatty acids is complex and could significantly add cost to the final product, the fatty acids (HOPA) were used as a whole during the synthesis of HOEP.

According to the literature,[25] the most influential factor for the viscosity of the organic compound is H-bond. HOEP showed a much lower viscosity than HOPA (0.2 vs 56.7 Pa s), which was because the strong H-bond forming among the −COOH groups in HOPA was converted into lesser polar glycidyl ester groups in HOEP. It is worth noting that DER 331, the most widely used commercial BPA epoxy resin for coating application, exhibited a relatively high viscosity of 10.9 Pa s. The viscosity of HOEP is much lower than that of DER 331 (0.2 vs 10.9 Pa s). This is because HOEP is mainly composed of C−C segments and possesses few H-bond donors and/or acceptors, such as −OH and C−O−C, thereby exhibiting low viscosity. In industry practice, the diluents are often added to lower the viscosity of a BPA epoxy resin. In this study, the low viscosity of HOEP is an advantage over BPA epoxy resin.

Curing of HOEP/DER With DETA. Curing of HOEP alone with DETA resulted in a cross-linked polymer of relatively low modulus and glass transition temperature (T_g) due to the flexible backbone structure of the epoxy compound. In this study, HOEP was used together with a commercial BPA epoxy (DER 331). As expected, the viscosity decreased with the increase of the HOEP content in the HOEP/DER resin system. For example, the viscosity remarkably decreased from 10.9 Pa s for DER 331 to 1.7 Pa s for the mixed epoxy resin containing only 25.7 wt % HOEP (Table 1). DETA, an

Table 1. Compositions and Viscosity of the Resins and the Gel Contents and Swelling Ratios of the Postcured Samples

	formulation				
sample	HOEP/DER[a]	HOEP[b] (wt %)	viscosity[c] (Pa s)	swelling ratio[d]	gel content[d] (%)
HOEP/DER-10/0	10:0	100	0.2	1.576 ± 0.008	91.5 ± 0.1
HOEP/DER-8/2	8:2	84.7	0.5	1.149 ± 0.015	97.2 ± 0.1
HOEP/DER-6/4	6:4	67.5	0.8	1.079 ± 0.001	98.6 ± 0.1
HOEP/DER-4/6	4:6	48.0	1.2	1.049 ± 0.003	99.1 ± 0.2
HOEP/DER-2/8	2:8	25.7	1.7	1.020 ± 0.003	99.1 ± 0.1
HOEP/DER-0/10	0:10	0	10.9	1.019 ± 0.001	99.2 ± 0.1

[a] Molar ratio of HOEP/DER by the epoxy groups. [b] Weight percentage of HOEP in the HOEP/DER mixture. [c] Viscosity of the HOEP/DER mixture at room temperature (23 °C). [d] The epoxy was cured at room temperature (~23 °C) for 24 h and 190 °C for 3 h.

aliphatic amine hardener, was used to cure the epoxy resins. Theoretically, each reactive hydrogen (NH) of an amine group can react with one epoxy group. However, compared with the primary amine, the secondary amine exhibits lower reactivity that is mainly due to the steric hindrance effect.[26] In this study, the molar ratio of the epoxy group to the −NH group (epoxy/NH) was fixed at 0.8/1, because the material prepared with this ratio exhibited the highest T_g among all compositions after curing at room temperature for 7 days (Figures S1 and S2). It is understood that the highest T_g of a completely cured epoxy-amine is usually achieved at the epoxy/NH of 1/1. However, the purpose of this work is to demonstrate a room-temperature cured epoxy vitrimer for repairable coatings, so the T_g achievable at room temperature is a more important factor to be considered.

Without a catalyst, the reaction of epoxy-amine could not efficiently take place at room temperature, as it took over 10 h for the curing system to reach the gelation point, which is defined as the intersection of the G' and G'' curves from the rheological test (Figure 2a). To accelerate the curing reaction, triethanolamine (TEOA) that was miscible with the epoxy curing system was used as a catalyst. It is well known that both −OHs and tertiary amine of TEOA efficiently catalyzed the epoxy curing reaction.[27] Our previous study also demonstrated that addition of TEOA to an epoxy-anhydride system effectively catalyzed the DTER in the resulting epoxy vitrimer network.[28] As shown in Figure 2a, when 3 mol % TEOA (on the basis of the epoxy group) was added to the formulation, the gelation time at room temperature was reduced from ~10 to ~5 h. However, a further increase in TEOA loading did not shorten the gelation time. Therefore, 3 mol % TEOA was applied in the subsequent study.

Based on the molar ratio of the epoxy groups between HOEP and DER 331, the samples were denoted as HOEP/DER-10/0, -8/2, -6/4, -4/6, -2/8, and -0/10 (Table 1). Figure 2b shows that the exothermal peak during DSC heating scan shifted to higher temperatures with the increase in lower reactive HOEP content. All of the postcured compositions exhibited one T_g (Figure S3), suggesting good miscibility of the two epoxies during curing. HOEP/DER-0/10 (neat BPA epoxy) exhibited a T_g of 103 °C. The postcured mixed epoxies showed a T_g that decreased almost linearly with the increase in HOEP content (Figure 2c), because the aliphatic backbone of HOEP flexibilized the cross-linked network. As the HOEP loading increased, gel content decreased but the swelling ratio increased (Table 1). These results indicate that the cross-link density of the cured epoxies decreases with HOEP content. TGA results (Figure S4) indicate that the 5% weight loss temperature (T_{d5}) for all samples exhibits at above 200 °C, suggesting that the thermal degradation during the following stress relaxation test at 180 °C is negligible. As the increase in HOEP loading, T_{d5} shifted from 324 to 266 °C. This was probably attributed to the decreased cross-linked density and the increased amount of less stable ester bonds in the network structure.[29,30]

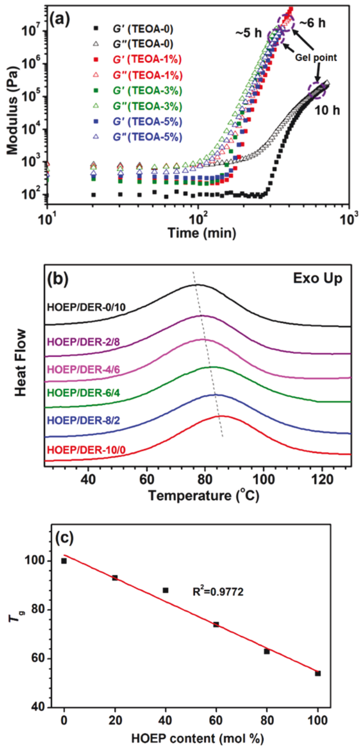


Figure 2. (a) Effect of triethanolamine (TEOA) content on the chemorheological behavior of HOEP/DER-4/6 during curing at room temperature. TEOA content was loaded according to the mole of the epoxy groups in the resin system; (b) DSC thermograms of different HOEP/DER compositions at a heating rate of 5 K min^{-1} under a nitrogen atmosphere; (c) plot of the T_g's of the postcured epoxies (room temperature for 24 h and 190 °C for 3 h) vs HOEP content.

Dynamic Mechanical and Mechanical Properties. Figure 3a shows the storage modulus (E') vs temperature curves of the postcured epoxies from the DMA test. All compositions exhibited a one-step drastic drop associated with the transition from a glassy state to rubbery state. At the glassy state (25 °C), the E_g' of DETA cured DER (HOEP/DER-0/10) was 3.1 GPa. The E_g' of HOEP/DER-2/8 decreased to 2.5 GPa, due to the soft backbone structure flexibilized the cross-linked network. Further increase in the HOEP content only slightly decreased the E_g'. As shown in Table 2, the E_g' values

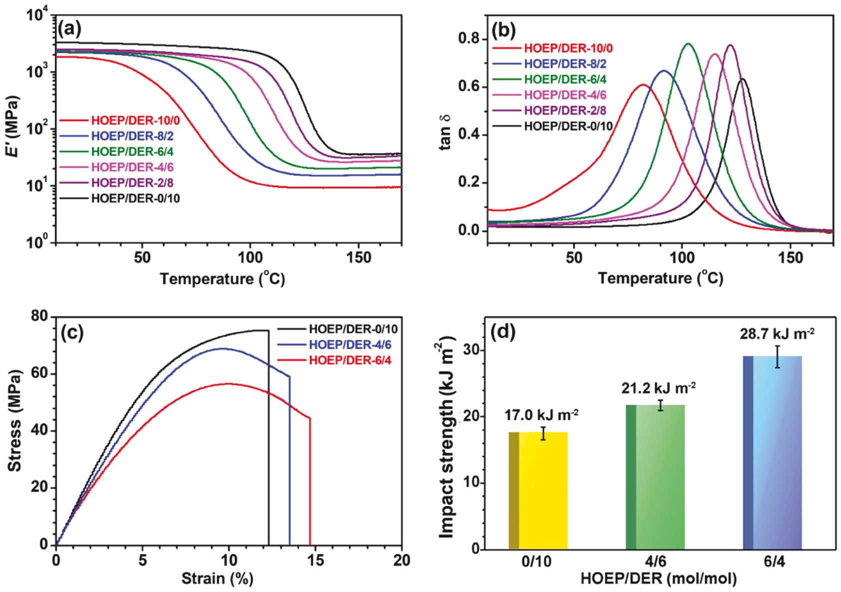


Figure 3. Effect of HOEP content on (a) storage modulus (E'), (b) tan δ curves, (c) stress−strain curves, and (d) impact strength of the postcured epoxies.

Table 2. Thermal and Mechanical Properties of Different Postcured Epoxies

	DMA		tensile properties			
sample	$E_g'^{a}$ (MPa)	$E_r'^{b}$ (MPa)	strength (MPa)	elongation (%)	modulus (GPa)	impact strength (kJ m^{-2})
HOEP/DER-10/0	1560	9				
HOEP/DER-8/2	2140	16				
HOEP/DER-6/4	2240	21	54.8 ± 1.2	15.5 ± 0.9	1.02 ± 0.04	28.7 ± 1.6
HOEP/DER-4/6	2380	26	69.0 ± 0.2	13.7 ± 1.0	1.15 ± 0.05	21.2 ± 0.8
HOEP/DER-2/8	2470	32				
HOEP/DER-0/10	3140	36	75.4 ± 1.5	12.6 ± 0.4	1.29 ± 0.03	17.0 ± 0.9

[a] E_g' at 25 °C;. [b] E_r' at 150 °C.

of HOEP/DERs -2/8, -4/6, -6/4, and -8/2 were at a similar level ranging from 2.5 to 2.1 GPa. The cured epoxy without DER epoxy (HOEP/DER-10/0) only exhibited an E_g' of 1.6 GPa, which was significantly lower than the E_g' of the cured epoxies containing both HOEP and DER epoxy. In addition, the E_r' at the rubbery state, which is proportional to the cross-link density of the network, decreased regularly as the increase in HOEP content, which is consistent with the results from the solvent extraction test. HOEP possessed long carbon chains and lower epoxy value than DER epoxy, so an increase in HOEP loading in the resin system would increase the average distance between two cross-links of the network structure resulting in the decease of cross-link density. Figure 3b shows the tan δ curves. As the increase in HOEP content, the peak shifted to lower temperature correlating to the decrease of T_g, which is consistent with the DSC results (Figure S3). At higher HOEP content, the peak became broader, which could be related to the complicated structure of HOEP originally derived from a mixture of fatty acids, making the network structure less uniform.

Figure 3c shows the stress−strain curves of the postcured epoxies. With consideration of T_g, cross-linked density, and biocontent, HOEP/DERs -4/6 and -6/4 were mainly investigated in this section. The cured HOEP/DERs -8/2 and -10/0 exhibited relatively low T_g, modulus, and cross-linked density, which may limit their practical applications. HOEP/DER-0/10 as a reference exhibited a tensile strength of 75.4 MPa. The tensile strengths of HOEP/DER-4/6 and HOEP/DER-6/4 were 69.0 and 54.8 MPa, respectively. In addition, HOEP/DER-0/10 exhibited a brittle failure, while a clear yield point was observed for both HOEP/DERs -4/6 and -6/4, indicating their better toughness, which was further confirmed by their impact strength (Figure 3d). The impact strengths of HOEP/DERs -4/6 and -6/4 were, respectively, 20.9 and 28.7 kJ m^{-2}, which were much higher than that of HOEP/DER -0/10, which exhibited an impact strength of 12.8 kJ m^{-2}. As a result, the addition of HOEP slightly lower the tensile strength but significantly improve the toughness of the cured epoxy.

Dynamic Interchange Reactions Within the Cross-linked Network at Elevated Temperatures. The reaction of epoxy and aliphatic amine results in the formations of −OH and C−N bonds. Therefore, amine cured glycidyl ether-type BPA epoxies are chemically and thermally stable. If a glycidyl ester-type epoxy reacts with an aliphatic amine, the resulting cross-linked network will contain −OH groups and ester bonds available for DTER and may exhibit vitrimer behaviors when the contents of these functional groups are sufficiently high in the system.

To verify this assumption, a glycidyl ether-type epoxy, 1,4-butanediol diglycidyl ether (BDE), and a diglycidyl ester-type epoxy, adipic acid diglycidyl ester (ADE), were used as two model epoxies and cured with DETA for comparison (Figure 4a). BDE and ADE both have aliphatic linear molecular chains

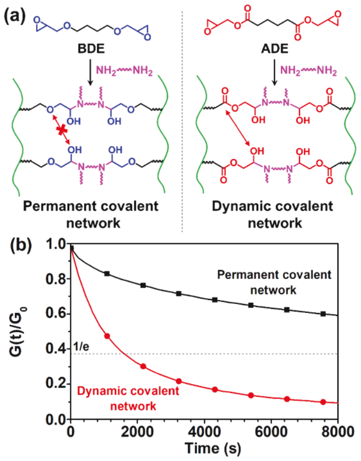


Figure 4. (a) Permanent covalent network and dynamic covalent network were prepared from the curing reactions of 1,4-butanediol diglycidyl ether (BDE) and adipic acid diglycidyl ester (ADE) with DETA, respectively; (b) stress relaxation curves of the epoxy films prepared by curing at room temperature for 24 h and postcuring at 190 °C for 3 h.

of approximately the same lengths. To assure the high purity of the model compounds, the BDE and ADE received were purified by column chromatography to achieve high-purity model compounds.[31,32] As shown in the ^{1}H NMR spectra of BDE and ADE (Figure S5), all of the peak signals were well assigned. The epoxy values of BDE and ADE were, respectively, 0.94 and 0.71 mol/100 g, which were very closed to their theoretical values. The DTER within the cross-linked network can be indirectly detected by the stress relaxation test, which examines the decrease of internal stress induced by an external applied strain to the sample. The relaxation time (τ) is defined as the internal stress relaxes to 37% or $1/e$ of the initial stress. Figure 4b shows the stress relaxation curves of the cured BDE and ADE at 180 °C. Because the stress relaxation test was performed at 180 °C at which cross-linking reaction in the room-temperature cured sample would likely continue to compromise the relaxation process, a postcuring process at 190 °C for 3 h was applied to those samples subjected to the relaxation test. The relaxation of the cured ADE is much faster than that of the cured BDE. The stress of the cured ADE relaxed to 37% at ~1700 s and 10% at 8000 s of the initial stress. In contrast, the cured BDE only relaxed to 53% at 21 000 s (Figure S6). The fast stress relaxation of the cured ADE is because it contains abundant ester bonds and −OHs available for DTER. In contrast, there are no ester bonds in the cured BDE to induce the DTER, so only slow stress relaxation was observed. To investigate the relaxation phenomenon of the amine cured epoxy with no ester bonds, a monoepoxide, phenyl glycidyl ether, was introduced to a BPA epoxy-DETA resin system with an epoxy/NH molar ratio of 0.8/1. At 180 °C, the stress relaxation rate of the fully cured epoxies increased with the increase in the loading of phenyl glycidyl ether (Figure S7). This is because the addition of monoepoxide increased the danging chains in the network and acted as network defects, resulting in an increase in chain mobility and thus faster stress relaxation of the network structure. In addition, we also observed that TEOA in the resin system contributed to the stress relaxation behavior, as the epoxy-amine network with TEOA relaxed faster than that without TEOA.

When the glycidyl ester-type epoxy HOEP and a glycidyl ether-type BPA epoxy (DER) were used together to cure with DETA, notable stress relaxation was observed. Figure 5a shows the stress relaxation curves of the cured HOEP/DER epoxies at 180 °C. Because the network structure of HOEP/DER-0/10 has no ester bonds, it exhibited a slow relaxation rate, which was consistent with the slow relaxation observed in the DETA cured BPA epoxy and the cured BDE (Figures 4b and S7). As the HOEP content increased, the relaxation of the resulting materials became faster. For example, the cured HOEP/DER-2/8 exhibited a τ of ~7600 s; in contrast, the τ of the HOEP/DER-10/0 without DER epoxy in the composition was as short as ~1900 s. The continuous increase of the relaxation rate with the increase in HOEP loading was due to the following reasons: (1) the increase in the content of the ester bonds originated from HOEP in the network structure accelerated the DTER within the network structure; (2) the soft backbone structure of HOEP increased the mobility of the polymer chains, which could also promote the DTER and relaxation. Figure 5b shows the effect of temperature on the relaxation curves of HOEP/DER-4/6 at different temperatures. The stress relaxation rate increased with the temperature increased, which was a consequence of accelerated DTER with an increase in temperature.

The reparability of the postcured coatings of HOEP/DER-4/6 and HOEP/DER-0/10 on the tin plates (~23 °C for 24 h and 190 °C for 3 h) was compared. The coating was cut with a knife to make a scratch on the surface, and then the damaged coating was heated at 180 °C with an applied pressure of ~10 kPa. The healing of the scratch with heating was monitored using an optical microscope (Figure S8). As shown in the inset of Figure 6b,c, after heating for only 10 min, the scratch of

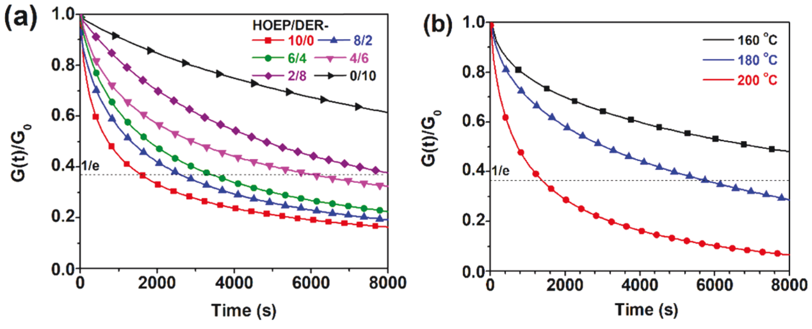


Figure 5. (a) Stress relaxation curves of different HOEP/DER compositions; (b) stress relaxation curves of the HOEP/DER-4/6 at different temperatures. All test samples were prepared via curing at room temperature for 24 h and 190 °C for 3 h.

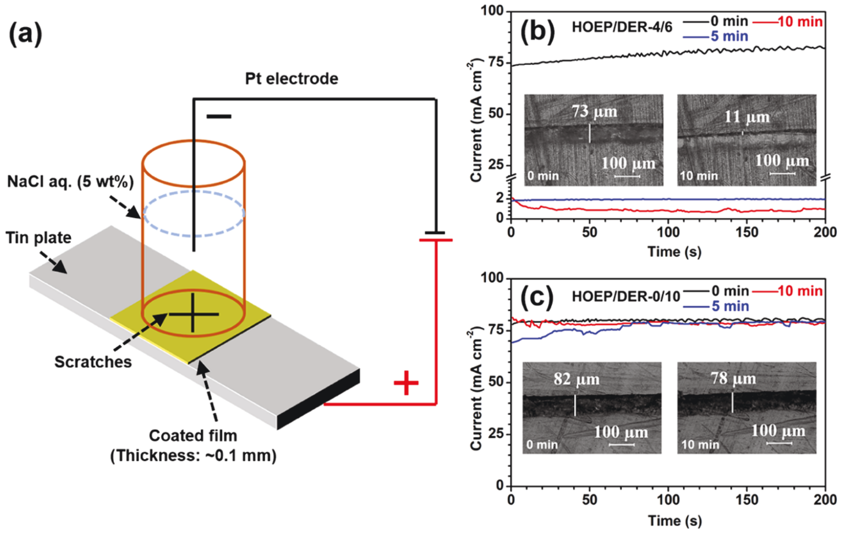


Figure 6. (a) Scheme of the electrochemical test of the coating on the tin plate; current curves of (b) HOEP/DER-4/6 and (c) HOEP/DER-0/10 after repairing at 180 °C for different times. The inset images were the cracks on the coated films before and after repairing at 180 °C on a rheometer with a pressure of ~10 kPa. Prior to the test, the resin system was coated onto a tin plate and cured at room temperature for 24 h and 190 °C for 3 h. The coating thickness was ~100 μm.

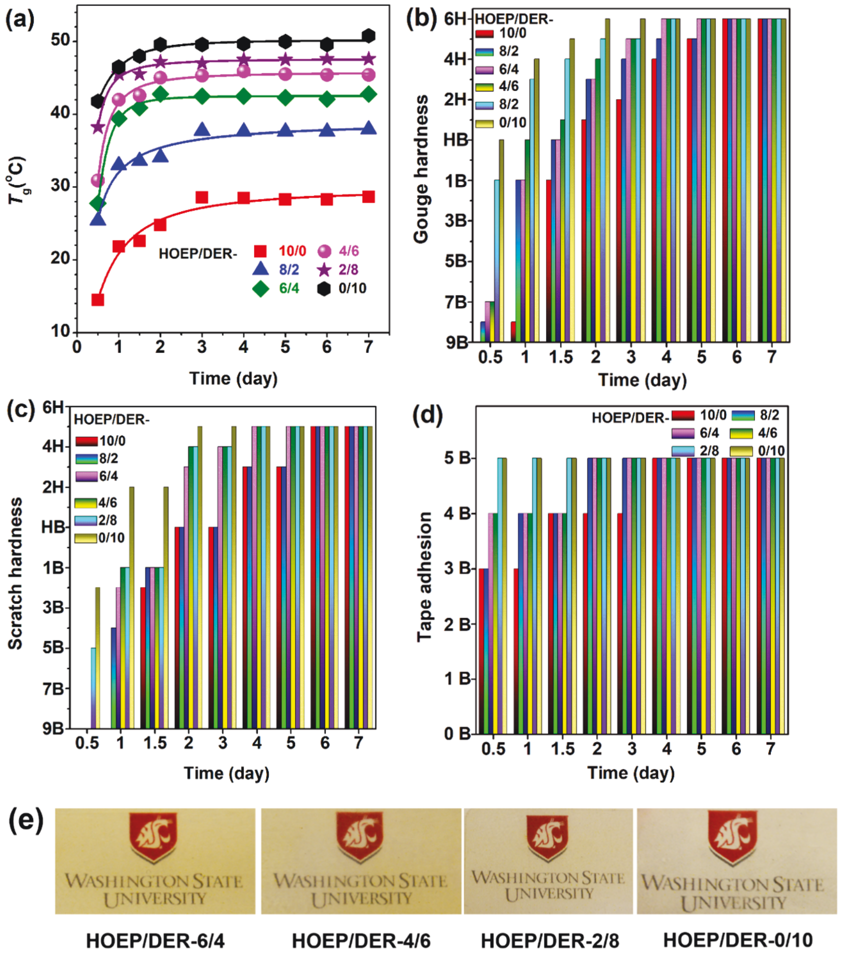


Figure 7. (a) T_g, (b) gouge hardness, (c) scratch hardness, (d) tape adhesion of epoxy coatings after curing at room temperature for different reaction times, and (e) digital photos of the cured epoxy films prepared via curing at room temperature for 7 days. The thickness of all films was ~0.15 mm.

HOEP/DER-4/6 was recovered for ~85%, indicating the excellent repairing property. In contrast, no obvious repairing phenomenon was observed for the tin plate coated with HOEP/DER-0/10 due to lacked ester bonds for DTER. It is noted that HOEP/DER-4/6 exhibited a much shorter repairing time (10 min) than the stress relaxation time (~100 min) at 180 °C. This was because an axial pressure of ~10 kPa was applied to the sample during repairing, which promoted the flow of the sample and improved the repairing efficiency.

More evidence of the repairing property was provided by the electrochemical test using an electrochemical workstation. During the test, the coated tin plate and a platinum electrode, respectively, served as working and counter electrodes, and 5% NaCl solution served as the electrolyte (Figure 6a). A voltage of 3 V was applied, and the change of current with time was recorded. In the beginning, the coating was cut through to the substrate, so the current with an intensity of ~80 mA cm^{-2} directly passed through the tin plate. After heating the coated tin plate at 180 °C for 10 min, almost no current was detected for the tin plate coated with HOEP/DER-4/6, because the coating was repaired and prevented the current from passing through the tin plate. In contrast, the current detected from the tin plate coated with the damaged HOEP/DER-0/10 almost remained unchanged after heating for 10 min, suggesting that the coating was not repaired.

Room-Temperature Coatings with Repairability. The use of the HOEP/DER vitrimers for room-temperature coatings was investigated. Figure 7a shows the changes of the T_g's with reaction time for different HOEP/DER compositions cured at room temperature. The T_g's of HOEP/DERs -6/4, -4/6, -2/8, and -0/10 continually increased with time and reached a steady value after reaction for 2 days. For the compositions with relatively high HOEP content (i.e., HOEP/DERs -10/0 and -8/2), it took more than 4 days for their T_g's to reach steady values. This is because the rate of curing reaction slows down significantly in the glassy state as the reaction becomes controlled by the diffusion of reactants.[33] The curing reaction still happens when the T_g of the epoxy is above the room temperature, but the reaction rate is very slow. As the T_g increases, the reaction rate becomes even slower. This explains why the T_g of the cured epoxies slowly reached to a steady value and could not go higher after curing at room temperature (22−23 °C) for several days (Figure 7a). In addition, the T_g of a cross-linked material is related to the conversion of the reactive groups and the stiffness of the backbone structures. Compared with that of DER 331, the epoxy groups of HOEP possessed lower reactivity, as reflected in an increase in peak temperature with an increase in HOEP loading in the DSC tests (Figure 2b). Therefore, it took a longer time at room temperature for the cured epoxy to reach a steady state at higher HOEP loadings. On the other hand, HOEP is much more flexible than DER 331 in terms of chemical structure. For these reasons, the cured epoxy with a higher content of HOEP exhibited a lower T_g.

The hardness of the coating was assessed by a scratch test (pencil hardness). Figure 7b,c shows that both gouge hardness and scratch hardness increased with reaction time and then reached a steady level of 5H. It took 2 days for HOEP/DER-0/10 to reach the hardness level of 5H, 4 days for HOEP/DERs -4/6 and -2/8, and even longer time for the other compositions with higher HOEP contents. Adhesion property was evaluated by the tape test. Figure 7d shows the changes of adhesion of the coatings with curing time. Within 2 days of curing, the adhesion level of the cured HOEP/DERs except for HOEP/DERs -10/0 reached 5B, which is the highest adhesion level. In commercial practice, the resin is required to achieve a decent T_g (>40 °C), hardness and adhesion after curing at room temperature within 2 days before moving things onto the coatings.[34] Evidenced by the aforementioned results, HOEP/DERs -4/6 and -6/4 are considered appropriate for room-temperature curable coatings. Moreover, the solvent resistance of the coatings was also investigated via the rub test. Table S2 shows the number of rubs for each coating during the test. Water, ethanol, and methyl ethyl ketone were used as solvents. All of the HOEP/DER coatings exhibited the tolerance >400 rubs, indicating their satisfactory solvent resistance.

Figure S9 shows the DSC heating thermograms of the samples before and after room-temperature curing. The samples cured at room temperature for 7 days showed no obvious exothermic peaks, indicating a better completion of curing. The gel contents of the room-temperature cured HOEP/DER-0/10, -4/6, and -6/4 were, respectively, 96.4, 96.1, and 94.2%, which were slightly lower but close to the values of the postcured samples (Table 1). At room temperature, the −OHs of TEOA may not be capable of effectively reacting with epoxy resin due to the low reactivity.[35] However, only weak peak signals attributed to TEOA were observed in the ^{1}H NMR spectra (Figure S10) of the extractables after solvent extraction, indicating that TEOA was firmly bonded to the network structure via hydrogen and/or covalent bond.

To investigate the repairability, the coatings obtained from the curing at room temperature for 7 days were scratched to have a crack on the surface, then the damaged coatings were repaired using the same method as described in the section of Dynamic Interchange Reactions within the Crosslinked Network at Elevated Temperatures. Figure S11 shows the photos of the coatings repaired at 180 °C for different times. The widths of the scratch were recovered by ~87 and ~85% for HOEP/DER-4/6 and -6/4 within 10 min, respectively. After heated for 30 min, the scratch of HOEP-6/4 was almost completely recovered. In contrast, no obvious change was observed during the repairing of the HOEP/DER-0/10 coating due to the lack of ester bonds in the cross-linked network. This result was consistent with the repairing result of the postcured epoxies shown in Figure 6.

Figure 7e shows the digital photos of the cured epoxy films, which were prepared via curing at room temperature for 7 days. The cured epoxies containing HOEP exhibited a light-yellow color, which could be related to the absorption of visible light of the double bonds in HOEP (Figure S12). Nevertheless, the color was not significant, and all of the films were clear and transparent. Based on the above results, HOEP/DERs -4/6 and -6/4 are more suitable for room-temperature curable coatings. More importantly, these coatings containing high contents of renewable components are repairable and display comparable properties to current commercial epoxy coatings.

■ CONCLUSIONS

In this work, a novel room-temperature curable biobased epoxy vitrimer with a simple design of the chemical structure was introduced. A hempseed oil-derived glycidyl ester-type epoxy (HOEP) was synthesized and then blended with a bisphenol A epoxy (DER 331) to manipulate the properties of the resulting vitrimers. An aliphatic amine, diethylenetriamine (DETA), was selected as the hardener to realize the room-temperature curing in the presence of triethanolamine (TEOA) as the catalyst. Unlike the traditional glycidyl ether epoxy-amine thermosets, which are based on stable C−N and ether linkages, the epoxy vitrimer in this work contains ester bonds that came with HOEP and hydroxyls formed from the reaction of amine and epoxy in its cross-linked network. Dynamic transesterification (DTER) between the ester bonds and hydroxyls could take place at elevated temperatures, imparting the vitrimer significant stress relaxation behavior and repairability. TEOA is an effective catalyst for the curing during the preparation of vitrimers because both its hydroxyl and tertiary amine groups promote the reaction of epoxy and amine. Furthermore, the tertiary amine moiety of TEOA catalyzes the DTER in the cross-linked network of the vitrimer. The vitrimer (HOEP/DER-10/0) exhibited a short τ of ∼1900 s and complete healing of cracks within 10 min at 180 °C, while the one prepared with DER 331 showed a longer τ value. After curing at room temperature for 4 days, the cured HOEP/DERs (-6/4, -4/6, and -2/8) all exhibited T_g's of above 40 °C, satisfactory scratch hardness (5H), gouge hardness (6H), adhesive strength (5B), and solvent resistance property, which satisfied the requirements for the room-temperature coating applications. The low-viscosity HOEP (0.2 Pa s, 22 °C) can mix very well with and dilute the viscous commercial BPA epoxy (10.9 Pa s). For example, the mixed HOEP/DER-6/4 (i.e., with 60 mol % HOEP), which corresponded to 67.5 wt % of biocontent in the resulting vitrimer, exhibited a low viscosity of 0.8 Pa s, which is beneficial for the leveling of the coating during processing. This study has provided a viable method to produce room-temperature curable epoxy vitrimers. Further, the tunability of the HOEP/DER composition and the resulting performance ensures its applications in practical fields, especially room-temperature coatings and adhesives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c05223.

> Possible side reaction of HOPA with epichlorohydrin (ECH) during glycidylization; onset T_g's of the room-temperature cured DER/DETA; onset T_g's of the room-temperature cured HOEP/DETA; DSC thermograms and TGA curves of different postcured samples; stress relaxation curves of the postcured films; NMR spectra of triethanolamine; formulation of HOEP/DER compositions; solvent resistance of the epoxy coatings on the tin plates; photos of the cracks on the room temperaure cured coatings before and after repairing; UV-vis absorption spectra of the room temperature cured films (PDF)

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Notes

The authors declare no competing financial interest.

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