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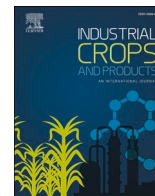
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Sustainable castor oil-based vitrimers: Towards new materials with reprocessability, self-healing, degradable and UV-blocking characteristics

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ABSTRACT

Vitrimers with reversible cross-links are emerging promising sustainable materials with reprocessability and recyclability. Here, castor oil-based epoxy resin (EMCO) with epoxy group and carbon-carbon double bonds was prepared through a two-step process and then cured with itaconic acid (IA) through epoxy-acid ring-opening reaction and free radical polymerization to fabricate fully bio-based epoxy vitrimers containing reversible transesterification bond. The thermal-mechanical properties, reprocessability, repairability, and recyclability could be balanced by varying the molar ratio of EMCO to IA. When the carboxyl group/epoxy group molar ratio reached 1.0, the EMCO-IA_{1.0} vitrimer exhibited the highest tensile strength of 14.39 MPa and T_g of 52.95 °C. Moreover, the vitrimer can be effectively remodeled (2 h at 180 °C) to prepare films and self-healing thanks to a rapid and mild stress relaxation process (2.56 min at 110 °C) and low activation energy (60.94 kJ·mol⁻¹). More significantly, EMCO-IA vitrimer could be degraded in ethanol solution and recycled to prepare films and also exhibited excellent UV blocking ability. Overall, the EMCO-IA vitrimer can achieve a highly efficient closed-loop recycling without significantly sacrificing the mechanical properties, which can extend the service life and facilitate the sustainable development of the castor oil-based polymeric material.

1. Introduction

Conventional thermosets (such as unsaturated polyester, phenolic and epoxy resin) offer numerous merits, including excellent chemical resistance, mechanical robustness, and thermal stability due to their highly cross-linked network structure. They have been extensively employed in the fields of coatings, adhesives, and fiber-reinforced composites (Lebedevaite et al., 2019; Dai et al., 2018; Inciarte et al., 2018). However, due to the presence of a permanent cross-linked network structure constructed by irreversible covalent bonds, conventional unsaturated polyester and epoxy thermosets are challenging to reprocess, repair, reuse, recycle and bio-degrade after the end of service life. It leads to a huge accumulation of waste thermoset materials (Sadler et al., 2014; Liu et al., 2016). Furthermore, most of the building blocks

employed in the preparation of unsaturated polyesters and epoxies are derived from non-renewable petrochemical resources (Bamane et al., 2020; Stuck et al., 2021; Fang et al., 2016). There are mainly three disposal routes for waste thermosets, including mechanically crushed and reused as fillers, landfills as waste and high-temperature incineration as fuels. All of which had disadvantages, such as causing serious environmental burdens, high cost, high energy consumption and wasting resources (Gao et al., 2019; Fidanovski et al., 2018), and thus going against the concept of carbon neutrality and sustainable development. Therefore, developing sustainable, degradable, recyclable, and bio-based polymeric material are highly desirable.

Vitrimers, one of the covalent adaptable networks formulated by introducing associatively exchangeable dynamic covalent bonds (Zhao et al., 2022), such as transesterification bond (Tao et al., 2020; Hao

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et al., 2020; Zhong et al., 2022; Di et al., 2022), disulfide bond (Si et al., 2020; Y.H. Zhang et al., 2018), and carbamate bond (Li et al., 2021; Zhu et al., 2020; Chen et al., 2020) into conventional thermosets networks to obtain reversible cross-links, were firstly pioneered and proposed by Leibler's research group to tackle the unsustainable recycling characteristics of traditional epoxy thermosets (Montarnal et al., 2011). Such vitrimers combined the advantages of both thermosets and thermoplastics, which not only had excellent thermal and mechanical properties similar to conventional thermosets under service conditions but also could rearrange their topological structures under certain stimuli, such as high temperature (Y.Y. Liu et al., 2020), UV light (Lossada et al., 2021), pH (Sun et al., 2022), and chemicals (Yang et al., 2021) via reversible dynamic covalent or non-covalent bond exchange reaction, leading to glasslike viscosity-temperature behavior like a thermoplastic.

An array of petroleum-based vitrimer systems, especially DGEBA-based epoxy vitrimers with dynamic bonds of disulfide bond (Chen et al., 2019), transesterification bond (Li et al., 2020; Xue et al., 2021), and Schiff base bonds (Liu et al., 2019; Memon et al., 2020), were widely investigated to impart material with reprocessability and recyclability. However, the renewability is not fully taken into consideration, as the raw material was usually derived from petrochemical resources. Thus, bio-based vitrimers have received much attention in recent years. A variety of renewable feedstocks, such as vanillin (Memon et al., 2020; Wang et al., 2022), eugenol (Liu et al., 2017), guaiacol (R. Yang et al., 2020), cardanol (Trejo et al., 2020), and lignin (Hao et al., 2019; S. Zhang et al., 2018) with rigid structures have been employed to prepare bio-based vitrimers with high T_g and mechanical properties, while the resulting bio-based vitrimers always exhibited high brittleness, leading to the harsh reprocessing condition. This was mainly attributed to the aromatic structure, and the high cross-linking degree of the vitrimer system limited the mobility and rearrangement of the chain segments. Therefore, researchers tend to develop bio-based vitrimers using raw materials with soft and flexible aliphatic chains. Vegetable oils, such as soybean oil (Wu et al., 2020; Shen, Robertson, 2020; Zhao et al., 2020; Liu et al., 2020), and palm oil (Mu et al., 2020), were reported to prepare bio-based vitrimers owing to their resource abundance, multiple modification strategies, soft chain segments and potential biodegradability. Yang et al. prepared a fully bio-based vitrimer employing epoxidized soybean oil and fumaric acid as raw material. The tensile strength of the soybean oil-based vitrimer was 16 MPa, while the stress relaxation temperature based on dynamic transesterification bonds was in the range of 160–200 °C. The stress relaxation time changed from 10^4 s to 1349 s (X.X. Yang et al., 2020). Xu and colleagues employed citric acid to cure epoxidized tung oil, and obtained a fully bio-based vitrimer with self-healing property and high mechanical strength (tensile strength: 47.05 MPa), moreover, the vitrimer exhibited a stress relaxation behavior from 160 °C to 220 °C, and the stress relaxation time was 2494 s at 160 °C and 79 s at 220 °C (Xu et al., 2021). These vegetable oil-based vitrimers can be reprocessed, repaired and recycled via dynamic transesterification exchange reaction, but they require high recycling temperatures, limiting their future application. Therefore, it is challenging to develop vegetable oil-based vitrimers that can simultaneously balance their high mechanical property and mild closed-loop recyclability.

Castor oil is one of the most widely used inedible vegetable oils with versatile reactive groups, including ester group, hydroxyl group and unsaturated carbon-carbon double bond, which is preferred to develop high value-added polymer (Chauke et al., 2019). At the same time, the non-conjugated carbon-carbon double bonds within castor oil are not reactive enough to undergo free radical polymerization directly. Therefore, researchers attempted to incorporate various reactive groups (such as epoxy, amine, and methacrylate groups) into castor oil to prepare castor oil-based unsaturated polyester or epoxy resin (Yuan et al., 2019; Liu et al., 2018; Sudha et al., 2017). Epoxidized castor oil is obtained using a formic acid/ H_2O_2 system via epoxidation, and is employed as a plasticizer, stabilizer, and intermediates to prepare bio-based epoxy resin or polyurethane (Cayli et al., 2019; Fu et al., 2020;

Li et al., 2017). To the best of our knowledge, few studies involve the development of castor oil-based epoxy resin with reactive epoxy groups and unsaturated carbon-carbon double bonds.

In this study, epoxidized methacrylated castor oil (EMCO) was prepared by methacrylation of castor oil with chloro-free methacrylate anhydride followed by epoxidation using a formic acid/ H_2O_2 system. Subsequently, to take full advantage of the structural characteristics of EMCO with both reactive epoxy groups and methacrylate groups, itaconic acid (IA) was employed as a curing agent to react with EMCO via both epoxy-acid reaction and free radical polymerization, which not only introduced flexible chain segments and dynamic transesterification bond but also contributed to the improvement of the molecular weight of the EMCO-IA material system. Furthermore, IA has several advantages: firstly, IA is regarded as one of the twelve bio-based platform compounds by the US Department of Energy (Sajjad et al., 2021), which can be obtained by biological fermentation of carbohydrates with 100% bio-based carbon content, and thus meeting the needs of sustainable development (Sano et al., 2020). Secondly, each IA molecule has one vinyl group and two carboxyl groups, and the carboxyl group was conjugated to the vinyl group, endowing IA with high reactivity to react with EMCO to form cross-linking networks; thirdly, IA is widely produced in China and the United States of America with low price (Trotta et al., 2018). Therefore, IA is one of the most promising sustainable building blocks to compete with the petroleum-based resource to fabricate polymer material.

Herein, EMCO bearing epoxy group and methacrylate group was firstly designed and prepared via methacrylation of castor oil followed by epoxidation, then itaconic acid, an unsaturated dicarboxylic acid, was reacted with EMCO to construct castor oil-based epoxy vitrimer containing dynamic reversible transesterifications bonds. The resulting castor oil-based epoxy vitrimer can rearrange network topology via reversible transesterification bonds, thus offering the material with reprocessability, recyclability and repairability. In addition, the degradation of the material was also evaluated in an ethanol solution, and the desired mechanical property and mild recycling condition were balanced by controlling the molar ratio of EMCO to IA. This work provides a sustainable solution to develop castor oil-based epoxy vitrimers with balanced mechanical properties and closed-loop recyclability.

2. Experimental section

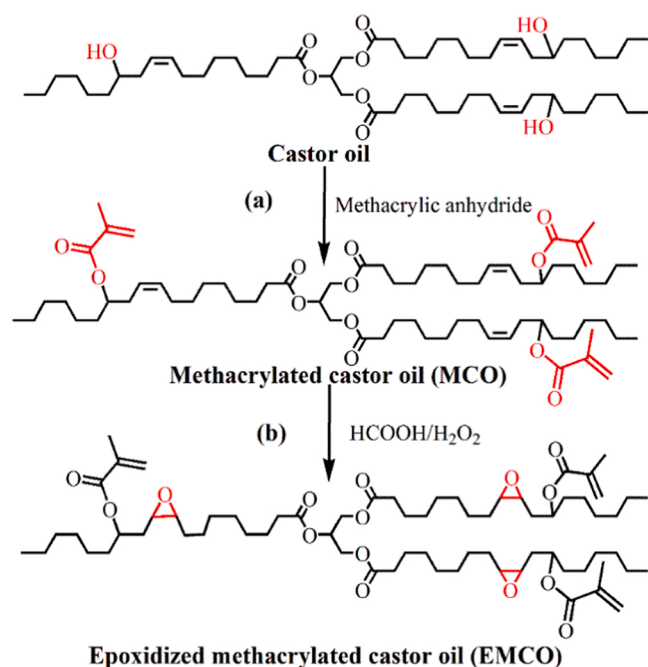
2.1. Materials

Castor oil (CO) and hydrogen peroxide solution (30%) were purchased from Tianjin Kemeiou Chemical Reagent Co., Ltd (China). Methacrylic anhydride, 4-Dimethylaminopyridine, *tert*-Butyl peroxybenzoate (TBPB, 98%), and 1-Methylimidazole (1-MI, 99%) were bought from Shanghai Macklin Biochemical Co., Ltd (China). Itaconic acid (IA, 99%) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd (China). Formic acid, triethylamine (TEA, 99%), dichloromethane, sodium hydrogen carbonate, sodium hydroxide, magnesium sulfate anhydrous and sodium chloride were supplied by Tianjin Tianli Chemical Reagent Co., Ltd (China).

2.2. Synthesis of epoxidized methacrylated castor oil (EMCO)

Step1: Synthesis of methacrylated castor oil (MCO).

MCO was synthesized by the substitution reaction between castor oil and methacrylic anhydride, as shown in Scheme 1(a). Briefly, castor oil (10 g), triethylamine (3.54 g), and 4-dimethylaminopyridine (0.078 g, 0.02 molar equivalents of methacrylic anhydride) were added into a flask and stirred thoroughly at 25 °C until a homogeneous mixture was obtained. Then, methacrylic anhydride (4.96 g) was added dropwise into the flask within 30 min with continuous stirring. Subsequently, the reaction system was heated to 45 °C for 22 h. After the reaction, the crude product was dissolved in dichloromethane, washed with saturated



Scheme 1. (a) Synthesis route of MCO and (b) EMCO.

NaHCO₃, 0.5 mol/L NaOH, 0.5 mol/L HCl and saturated brine, respectively, dried over anhydrous MgSO₄, and removed dichloromethane by rotary evaporation. Finally, MCO (10.31 g) was obtained, and the yield was calculated to be 84.93%.

Step 2: Synthesis of EMCO.

EMCO was obtained by the epoxidation reaction of MCO with the formic acid/H₂O₂ system, as shown in Scheme 1(b). The prepared MCO (10.04 g) was mixed with formic acid (2.43 g) in a flask at 30 °C and stirred for 30 min. Then, 30% hydrogen peroxide solution (5.98 g) was added dropwise over 1 h into the flask, and the mixture was reacted for 18 h. The crude product was extracted with dichloromethane and purified with saturated NaHCO₃ to remove formic acid. Then the organic layer was washed with distilled water and saturated brine, dried over anhydrous MgSO₄, and eliminated dichloromethane by rotary evaporation. Thus, EMCO (8.72 g) was obtained with an epoxy value of 0.302 mol/100 g (measured by hydrochloride acid-acetone titration) (Qi et al., 2018), and the yields were 84.16%.

2.3. Preparation of castor oil-based vitrimers

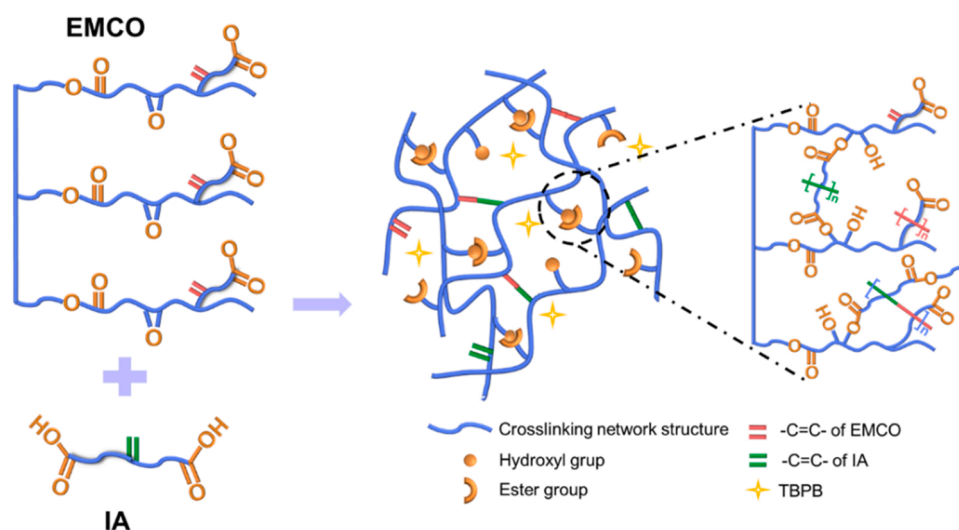
Castor oil-based vitrimers were prepared via the epoxy-acid curing reaction, as shown in Scheme 2. EMCO, IA, and TBPB (a free radical initiator) with different ratios (Table 1) were mixed in a beaker and stirred at 60 °C for 30 min. Then, 1-MI was added to the mixture and stirred to obtain a homogeneous pale-yellow solution. The solution was then poured into the preheated metal mold and degassed at 70 °C in a vacuum oven. Subsequently, the mold was heated at 150 °C for 2 h, 170 °C for 4 h, and 190 °C for 2 h in an argon gas atmosphere. Finally, all samples were cooled to room temperature. The resultant sample was named EMCO-IA_x, where x is the molar ratio of the carboxyl group to epoxy group. The composition of the EMCO-IA_x (x = 0.25, 0.50, 0.75, 1.00 and 1.25) vitrimers is shown in Table 1.

2.4. Characterization

The structure of CO, MCO, EMCO and cured EMCO-IA vitrimers were evaluated by Fourier transform infrared (FTIR) spectra using a Bruker Vertex70 equipment, and the scanning range was 4000–400 cm⁻¹. The ¹H NMR and ¹³C NMR spectra of CO, MCO and EMCO were detected by a Bruker Avance NEO 600 MHz instrument with CDCl₃ as the solvent. The viscosity of MCO and EMCO was measured by a DHR-1 rheometer (TA Instruments) equipped with a 25 mm circular parallel plate, and the test temperature was 30 °C, and the shear rate was in the range from 1 to 200 s⁻¹. The curing process of the liquid EMCO-IA resin systems in the presence of a TBPB initiator was investigated by a Q2000 differential scanning calorimeter (DSC) from 30 °C to 230 °C at a heating rate of

Table 1
Composition of the EMCO-IA vitrimers.

Sample	Epoxy group /carboxyl group (mol/mol)	EMCO (g)	IA (g)	TBPB (g)	1-MI (g)
EMCO-IA _{0.25}	1:0.25	1	0.028	0.0205	0.0411
EMCO-IA _{0.50}	1:0.50		0.057	0.0211	0.0423
EMCO-IA _{0.75}	1:0.75		0.086	0.0217	0.0434
EMCO-IA _{1.00}	1:1.00		0.1145	0.0223	0.0446
EMCO-IA _{1.25}	1:1.25		0.1432	0.0229	0.0457



Scheme 2. Reaction mechanism between EMCO and IA.

10 °C/min under an N₂ atmosphere. Furthermore, the curing degree of the EMCO-IA vitrimers was also evaluated using DSC from 30 °C to 230 °C at a heating rate of 10 °C/min under an N₂ atmosphere.

The gel content of the cured EMCO-IA vitrimers was analyzed by Soxhlet extraction. Approximately 2 g of sample was weighed (m_0) and extracted with dichloromethane in a Soxhlet extractor for 24 h. After that, the insoluble residue was dried to a constant weight (m_1). The gel content was calculated as Eq. (1):

$$\text{Gel content(\%)} = \frac{m_1}{m_0} \times 100\% \quad (1)$$

The curing degree of the EMCO-IA vitrimers was measured by an equilibrium swelling experiment, and the swelling ratio was calculated using dichloromethane as the solvent. Approximately 2 g of sample was weighed (m_2) and subsequently immersed in dichloromethane at 25 °C until reaching an equilibrium. Finally, excess dichloromethane on the surface of the sample was removed using filter paper and then weighed (m_3). The swelling ratio was calculated as Eq. (2):

$$\text{Swelling ratio(\%)} = \frac{m_3 - m_2}{m_2} \times 100\% \quad (2)$$

The dynamic mechanical properties of the cured EMCO-IA vitrimers were measured by a Q800 dynamic mechanics analyzer (DMA, TA Instruments) in the tension film geometry. The sample bar (12 mm × 6 mm × 2 mm) was firstly balanced at -50 °C for 10 min with stress of 0.5 MPa and a frequency of 1 Hz. After that, the sample was heated to 120 °C at a heating rate of 5 °C/min. The cross-linking degree (ν) of the cured EMCO-IA vitrimers was calculated using Eq. (3) according to the elastic theory of rubber.

$$\nu = \frac{E'}{3RT} \quad (3)$$

Where E' is the rubber modulus ($T_g + 45$ °C), MPa; T is the absolute temperature, K; R is the gas constant (8.314), J/(mol·K); ν is the cross-linking degree, mol/m³.

The tensile properties of the cured EMCO-IA vitrimers with dumbbell-shape were conducted by an AI-7000-NGD servo material multi-functional testing machine at a test speed of 10 mm/min, and at least three parallel measurements for each sample were performed to obtain the average value of the tensile properties.

The stress relaxation of the cured EMCO-IA vitrimer samples (6.5 mm × 5 mm × 1.2 mm) was evaluated using a Q800 DMA. The sample was firstly preloaded by 0.001 N, heated and equilibrated at different selected temperatures (70 °C, 90 °C, 110 °C, 130 °C and 150 °C) for 10 min. Meanwhile, a constant 1% strain was applied, and the change of the relaxation modulus was monitored over time. Moreover, the stress relaxation modulus of the EMCO-IA samples at 150 °C was measured. The relaxation modulus (G_t) was normalized by the initial value (G_{t_0}). The characteristic relaxation time (τ) was defined as the time required for $G_t/G_{t_0} = 1/e$ with exponential decay function in Eq. (4):

$$G(t) = G_{t_0} \exp(-t/\tau) \quad (4)$$

The thermal stability of the cured EMCO-IA vitrimers was evaluated by a Q500 thermal gravimetric analysis (TGA, TA Instruments) at the temperature range from room temperature to 800 °C at a heating rate of 10 °C/min under an N₂ atmosphere.

The reprocessing ability of the as-prepared EMCO-IA_{1.00} vitrimer samples was performed by cutting the sample into small pieces, followed by transferring it into a rectangle stainless steel mold, and then hot-pressing at 180 °C for 2 h under 5 MPa. After cooling to room temperature, the reprocessed samples were obtained, and the tensile properties of 3 reprocessing cycles were monitored.

The chemical degradation behavior of the cured EMCO-IA_{1.00} vitrimer sample was carried out by immersing the sample in ethanol at 75 °C for 6 h with continuous stirring. The degraded products were further

physically reprocessed using the above method and analyzed by FT-IR.

The self-healing properties of the cured EMCO-IA vitrimers were evaluated by surface morphology observation using an ultra-depth of field microscope (HIROX). A scratch of the cured EMCO-IA vitrimer sample was made with a knife. After that, the damaged sample was heated in an oven at 170 °C for 5 h. The 2D and 3D images of the damaged EMCO-IA vitrimers before and after self-healing were observed by ultra-depth of field microscope.

The UV-vis spectroscopy of the cured EMCO-IA vitrimers was recorded using a UV visible spectrophotometer (UV-265 FW) from 200 to 800 nm.

3. Results and discussion

3.1. Synthesis and characterization of MCO and EMCO

EMCO was prepared in a two-step procedure, as shown in Scheme 1. In the synthesis of intermediate MCO, the hydroxyl group of CO was reacted with methacrylic anhydride to afford MCO with the methacrylate group via substitution reaction. As shown in Fig. 1, the peak at 3.60 ppm was belong to the tertiary carbon protons connecting to hydroxyl groups (-CH-OH), and the peak at 1.79 ppm was attributed to the protons of a hydroxyl group (-OH) within CO, after reacting with methacrylic anhydride, the signals of hydroxyl group within the product disappeared, while new proton signals at 6.08 ppm (-C=CH₂), 5.53 ppm (-C=CH₂) and 1.94 ppm (C-CH₃) corresponding to methacrylate group were detected, indicating that the hydroxyl group of CO was successfully converted to methacrylate group. The signals at 3.60 ppm were shifted to 4.93 ppm due to the formation of the electron-withdrawing methacrylate group, confirming the intermediate MCO was successfully obtained. EMCO was further synthesized by epoxidation of MCO with HCOOH/H₂O₂ system, and the peaks at 5.38 and 5.46 ppm ascribed to the protons of carbon-carbon double bonds (-CH=CH-) within MCO disappeared. In comparison, two new peaks at 2.88 ppm and 3.00 ppm emerged, corresponding to the protons of the oxirane ring. The carbon-carbon double bonds within the methacrylate group still existed at 6.08 ppm and 5.53 ppm, indicating that the internal double bonds of CO were selectively epoxidized to epoxide groups, confirming the successful synthesis of EMCO with both reactive methacrylate group and epoxy group. The epoxy value of EMCO was 0.302 mol/100 g (Table S1). Similarly, the structure of MCO and EMCO was further confirmed using ¹³C NMR (Fig. S1) as well as FT-IR analysis (Fig. S2), whose results were in good agreement with that of the ¹H NMR.

The viscosity of MCO and EMCO is evaluated in Fig. 2. Both MCO and EMCO showed shear thinning behavior. This was mainly due to their long flexible aliphatic chains are protons to form entanglement of chain segments. The viscosity of MCO was 0.44 Pa·s at 30 °C at 2 s⁻¹, while that of the EMCO was 1.53 Pa·s, which is about 3.5 times higher than that of MCO. This was mainly attributed to the improved molecular weight of EMCO, leading to higher van der Waals attractions than MCO's. Furthermore, the polar epoxide group and more ester groups within EMCO contributed to improved intermolecular force and steric hindrance of EMCO, which further contributed to improved viscosity of EMCO.

The sustainability of EMCO and IA was estimated by bio-based carbon content, and the bio-based carbon content was defined as the proportion of bio-based carbon to the total organic carbon content in a monomer (Zhang et al., 2020). The bio-based carbon content of EMCO and IA was calculated as 82.1% and 100% (Table S1), respectively. Therefore, the EMCO-IA material systems displayed high bio-based carbon content from the sustainability point of view.

3.2. Curing behavior of the EMCO-IA resin systems

As illustrated in Scheme 2, both epoxy-acid ring-opening curing reaction and free radical polymerization reaction occurred in the EMCO-IA

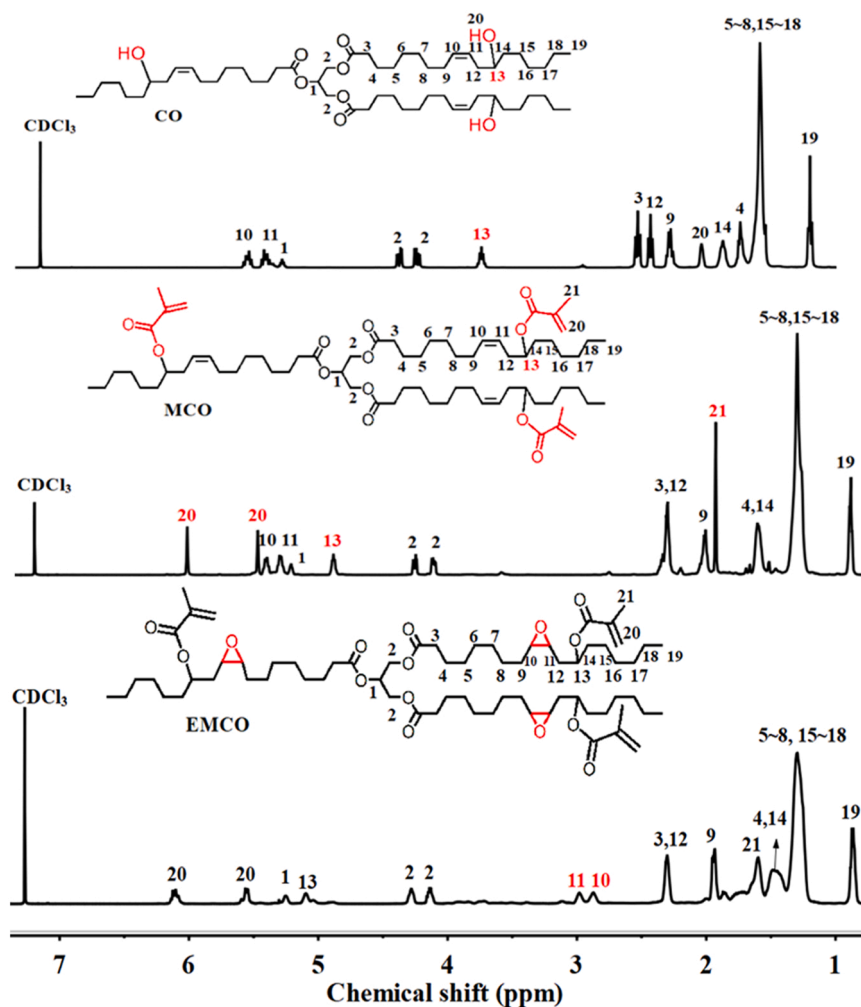


Fig. 1. ^1H NMR spectra of CO, MCO, and EMCO.

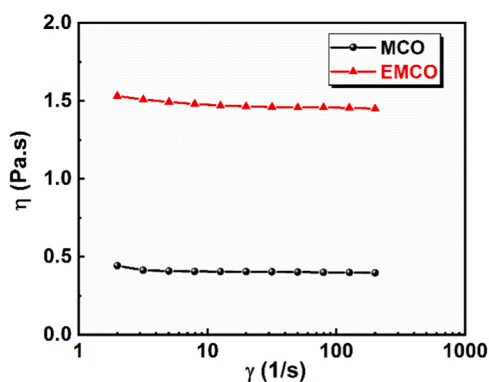


Fig. 2. Viscosity as a function of shear rate for MCO, EMCO at 30 °C.

resin systems in the presence of free radical initiator TBPB. The decomposition of TBPB to generate free radical is generally occurred in the range of 105–205 °C (Lin et al., 2012). Therefore, the curing behavior of the EMCO-IA resin systems with and without TBPB was investigated by DSC in the temperature range of 50–230 °C. As shown in Fig. S3, in the case of the EMCO-IA resin system (the molar ratio of epoxy group/carboxyl group was 1:1) without TBPB, an exothermic peak related to the epoxy-acid ring-opening reaction between EMCO and itaconic acid was observed in the temperature range of 130–165 °C. The cured EMCO-IA material showed a tensile strength of just 2.1 MPa

(Fig. S4), this was mainly due to EMCO owned long and flexible aliphatic chains, the curing of epoxy group within EMCO and itaconic acid in the absence of TBPB lead to a limited cross-linking degree in the EMCO-IA material system.

However, in the EMCO-IA_x resin system with different carboxyl group/epoxy group molar ratios ($x = 0.25, 0.50, 0.75, 1.00, 1.25$) in the presence of TBPB, there were two obvious exothermic peaks observed at about 120 °C and 160 °C in Fig. 3(a). This was mainly due to both free-radical copolymerization and epoxy-acid ring-opening reaction participating in the curing reaction between EMCO and IA in the presence of TBPB. The first curing exothermic peak appeared at 90.75–136.72 °C was derived from the free radical polymerization between the methacrylate group within EMCO and the unsaturated double bonds of itaconic acid, while the second exothermic peak emerged at 136.72–179.12 °C was caused by the epoxy-acid ring-opening reaction between the epoxy group of EMCO and the carboxyl group of itaconic acid. Therefore, the introduction of the initiator TBPB could promote the curing of EMCO-IA resin system by combining the free radical polymerization and epoxy-acid ring-opening reaction. The cured EMCO-IA material systems were subsequently undergoing the DSC test, and no exothermic peak was detected from 30° to 230°C in Fig. 3(b), confirming all the EMCO-IA resin systems were completely cured. Furthermore, in Fig. 3(c), both epoxy peaks at 940 cm^{-1} and unsaturated carbon-carbon double bonds at 1640 cm^{-1} disappeared in the cured EMCO-IA material systems, and new peaks at 3300–3500 cm^{-1} (stretching vibration peak of -OH) emerged, implying complete curing of the EMCO-IA material systems. Meanwhile, Soxhlet extraction and swelling test with dichloromethane

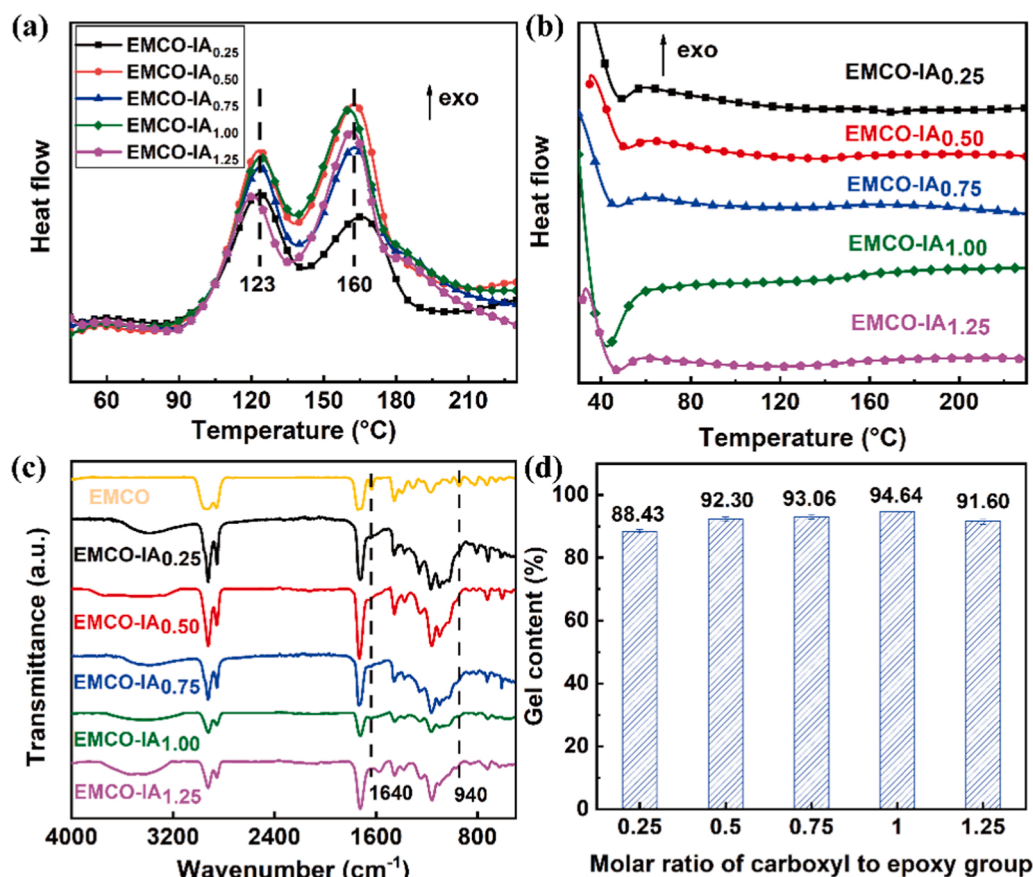


Fig. 3. (a) DSC curves of the uncured EMCO-IA resin systems and (b) cured EMCO-IA material systems; (c) FTIR spectra of the cured EMCO and EMCO-IA material systems; (d) the gel content of the cured EMCO-IA material systems.

as solvent were performed to evaluate the curing degree of the EMCO-IA material systems in Figs. 3(d) and S5, respectively. The gel content of the cured EMCO-IA material systems with different IA loadings was all higher than 88.43%, and the highest value of 94.64% was obtained in the case of the EMCO-IA_{1.0} material. Meanwhile, the swelling ratio of the EMCO-IA materials ranged from 8.11% to 16.42%, and the lowest value of 8.11% was obtained for the EMCO-IA_{1.0} material, indicating that all the EMCO-IA resin systems were cross-linked to form a three-dimensional network structure, and the EMCO-IA_{1.0} material exhibited the highest cross-linking degree.

3.3. Thermal and mechanical properties of the cured EMCO-IA vitrimers

The storage modulus (E') and $\tan \delta$ of the EMCO-IA vitrimers with different IA loadings are shown in Fig. 4. The storage modulus of the EMCO-IA vitrimers showed an increasing trend from 179 to 659 MPa (25 °C), and then decreased to 534 MPa with the carboxyl group/epoxy group molar ratio increased from 0.25 to 1.25, and the EMCO-IA_{1.0} vitrimer obtained the maximum storage modulus of 659 MPa. This was mainly due to with the increase of carboxyl group/epoxy group molar ratio from 0.25 to 1.0, more carboxyl groups and unsaturated carbon-carbon double bonds of IA were available to react with EMCO bearing epoxy group and methacrylate group via epoxy-acid ring-opening

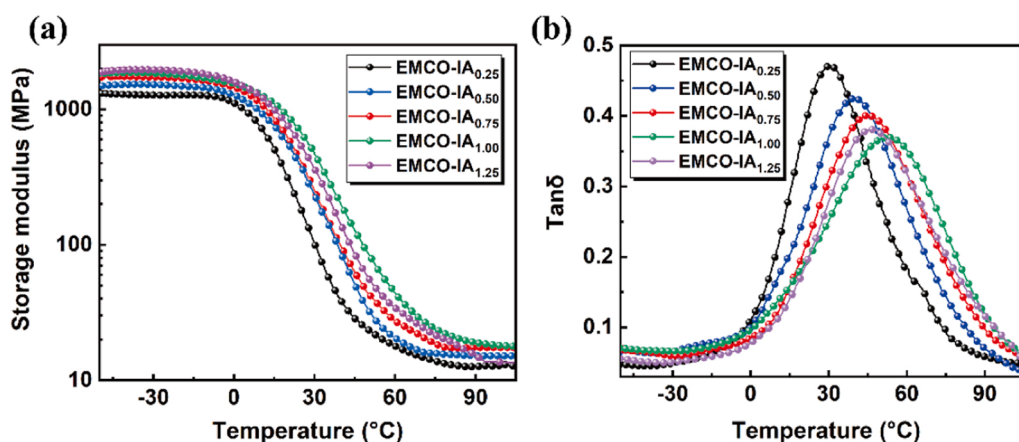


Fig. 4. (a) Storage modulus and (b) $\tan \delta$ of the EMCO-IA vitrimers as a function of temperature.

reaction and free radical polymerization to form a three-dimensional cross-linking network structure, which limited the fluidity of chain segments and increased the storage modulus, and finally, the highest cross-linking degree of 2090.54 mol/m³ was obtained for the EMCO-IA_{1.0} vitrimer (Table 2). While introducing more IA into the EMCO-IA_x vitrimer systems (x = 1.25), excess IA worked as plasticizers and increased the free volume of the network system, leading to decreased gel content (91.60%) in Fig. 3(d), increased swelling ratio (11.75%) in Fig. S5, and decreased cross-linking degree (1523.62 mol/m³). The corresponding temperature of the maximum tan δ is generally regarded as the glass transition temperature (T_g), with the carboxyl group/epoxy group molar ratio increased from 0.25 to 1.25, and the T_g of the EMCO-IA vitrimers increased from 30.36 °C to 52.95 °C, and then decreased to 46.83 °C, when the carboxyl group/epoxy group molar ratio reached 1.0, the maximum T_g of 52.95 °C was obtained. Generally, the height of the tan δ peak represents the mobility of the chain segments, which is related to the cross-linking degree. Similar to the T_g, the height of the tan δ peak also exhibited the same trend. This was mainly due to the EMCO-IA_{1.0} vitrimer with the carboxyl group/epoxy group molar ratio of 1.0 having the highest cross-linking degree of 2090.54 mol/m³ (Table 2), which was consistent with the gel content result in Fig. 3(d) and swelling ratio result in Fig. S5.

The tensile properties of the EMCO-IA vitrimers are shown in Table 2. With the carboxyl group/epoxy group molar ratio increased from 0.25 to 1.25, the tensile strength of the EMCO-IA vitrimers increased from 7.44 MPa to 14.39 MPa, and then reduced to 6.45 MPa. At the same time, the elongation at break increased from 15.23% to 31.31%, and then decreased to 11.34%. This trend agreed well with the cross-linking degree result from DMA (Fig. 4). Furthermore, the EMCO-IA_{0.75} and EMCO-IA_{1.0} vitrimers exhibited obvious yield points and good toughness in Fig. S6. The EMCO-IA_{0.25} and EMCO-IA_{1.25} vitrimers behavior like soft elastomers, while the EMCO-IA_{0.75} and EMCO-IA_{1.0} vitrimers behavior like plastic. The results indicated that the EMCO-IA_{1.0} had the best comprehensive mechanical properties.

Furthermore, the thermal stability of the EMCO-IA vitrimers with different IA loadings is shown in Fig. 5. All samples showed similar decomposition behavior with just one degradation step. The decomposition temperatures at T_{d5%} of all samples were higher than 265 °C, which was significantly higher than the transesterification reaction temperature, implying excellent thermal stability of the EMCO-IA vitrimers due to the formed cross-linking network. The improved thermal stability of the EMCO-IA vitrimers is beneficial to the practical reprocessing application, which can avoid serious decomposition during the reprocessing cycles, since the reprocessing temperature (such as remolding temperature) is generally below 200 °C.

3.4. Dynamic reversible network analysis of the EMCO-IA system

The presence of soft, long, aliphatic triglyceride chains and numerous ester groups and hydroxyl groups are expected to impart the cured EMCO-IA system versatile properties, such as stress relaxation and

plasticity. The stress relaxation test was performed to investigate the dynamic transesterification exchange behavior of the EMCO-IA system in Fig. 6. The epoxy group of EMCO could react with the carboxyl group of IA to form an ester group and hydroxyl group in the EMCO-IA system, and the ester group and hydroxyl group can undergo transesterification exchange reactions in the presence of 1-Methylimidazole at elevated temperature to form vitrimer (Di et al., 2020; Tran et al., 2020). The relaxation time (τ) is generally defined as the time required for the modulus to reach 37% (1/e) of the initial modulus (Zhang et al., 2021), which is a crucial indicator to characterize the transesterification exchange reaction rate within the vitrimer systems. Pure EMCO resin with reactive methacrylate groups can be self-polymerized in the presence of TBPB to obtain EMCO material (control). Such material exhibited no stress relaxation phenomenon due to the presence of only permanent covalent bonds in the cross-linking network structure. While for the EMCO-IA_{1.0} material with abundant ester group and hydroxyl group in the network, a fast stress relaxation rate was observed with a stress relaxation time of only 38 s at 150 °C, this was mainly due to the existence of reversible dynamic transesterification bonds that could rearrange the cross-linking network of the EMCO-IA system at 150 °C, leading to decreased internal stress and stress relaxation.

The stress relaxation curves of the EMCO-IA vitrimers with different IA loadings at 150 °C are shown in Fig. 6(b). For the EMCO-IA_{0.25} material, there was no stress relaxation phenomenon detected within 60 min, this was mainly due to the reaction between the carboxyl group of IA and the epoxy group of EMCO resulting in limited numbers of transesterification bonds in the material system and the free radical polymerization reaction between EMCO and IA was adverse to the stress relaxation of the resulting material. With the carboxyl group/epoxy group molar ratio increased from 0.50 to 1.0, the τ of the EMCO-IA materials decreased from 60 min to 0.57 min, this was mainly due to the increased IA loadings increased the number of free ester group and hydroxyl group, which accelerated the transesterification reaction rate and reduced the relaxation time. While in the case of the EMCO-IA_{1.25} material, the τ further increased to 20.04 min, which was ascribed to excess IA not only resulted in sufficient transesterification reaction, but also irreversibly incorporated into the network and contributed to an improved molecular weight of the EMCO-IA_{1.25} material via free radical copolymerization, and thus decreasing the relaxation time. Furthermore, the stress relaxation of the EMCO-IA_{1.0} networks at different temperatures was investigated in Fig. 6(c). When the temperature reached 70 °C and 90 °C, the EMCO-IA_{1.0} vitrimer exhibited no apparent stress relaxation phenomenon because the temperature was too low to activate the dynamic transesterification exchange reaction. When the temperature increased to 110 °C, 130 °C and 150 °C, the relaxation time of the EMCO-IA_{1.0} networks was 2.56 min, 1.14 min, and 0.57 min, respectively. This was mainly due to the fast transesterification exchange reaction rate, and the rearrangement of the topological network is preferred at elevated temperatures. The relaxation time as a function of temperature can be fitted by the Arrhenius equation in Fig. 6(d), and the activation energy of the material can be calculated according to the Arrhenius equation (Altuna et al., 2013).

$$\ln \tau = \frac{E_a}{RT} - \ln A \quad (5)$$

Where τ is the stress relaxation time, E_a is the activation energy of the transesterification exchange reaction, R is the gas constant (8.314 J/mol·K), and A is the pre-exponential factor. The activation energy of the EMCO-IA_{1.0} networks was calculated to be 60.94 kJ/mol, indicating the EMCO-IA material could undergo fast transesterification exchange reaction upon mild heating.

Table 2

The mechanical properties and thermal stabilities of the EMCO-IA vitrimers.

Sample	T _g (°C)	E' (25 °C) (MPa)	v (mol/m ³)	Tensile strength (MPa)	Elongation at break (%)	T _{d5%} (°C)
EMCO-IA _{0.25}	30.36	179	1480.58	7.44 ± 0.52	15.23 ± 1.72	288.29
EMCO-IA _{0.50}	39.87	358	1725.69	8.54 ± 0.40	20.52 ± 1.58	279.09
EMCO-IA _{0.75}	44.90	395	1886.53	11.68 ± 0.85	23.01 ± 1.51	269.27
EMCO-IA _{1.00}	52.95	659	2090.54	14.39 ± 0.79	31.31 ± 0.96	285.04
EMCO-IA _{1.25}	46.83	534	1523.62	6.45 ± 1.08	11.34 ± 2.01	270.94

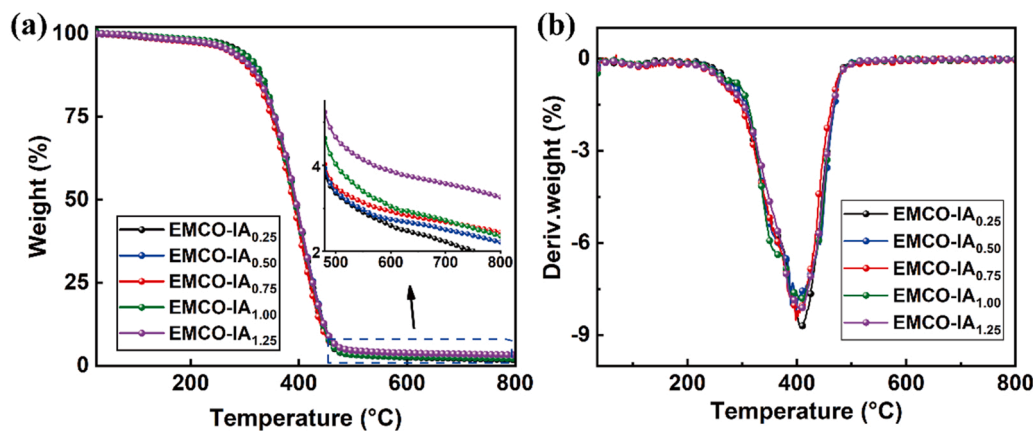


Fig. 5. (a) TG curves and (b) DTG curves of the EMCO-IA vitrimers.

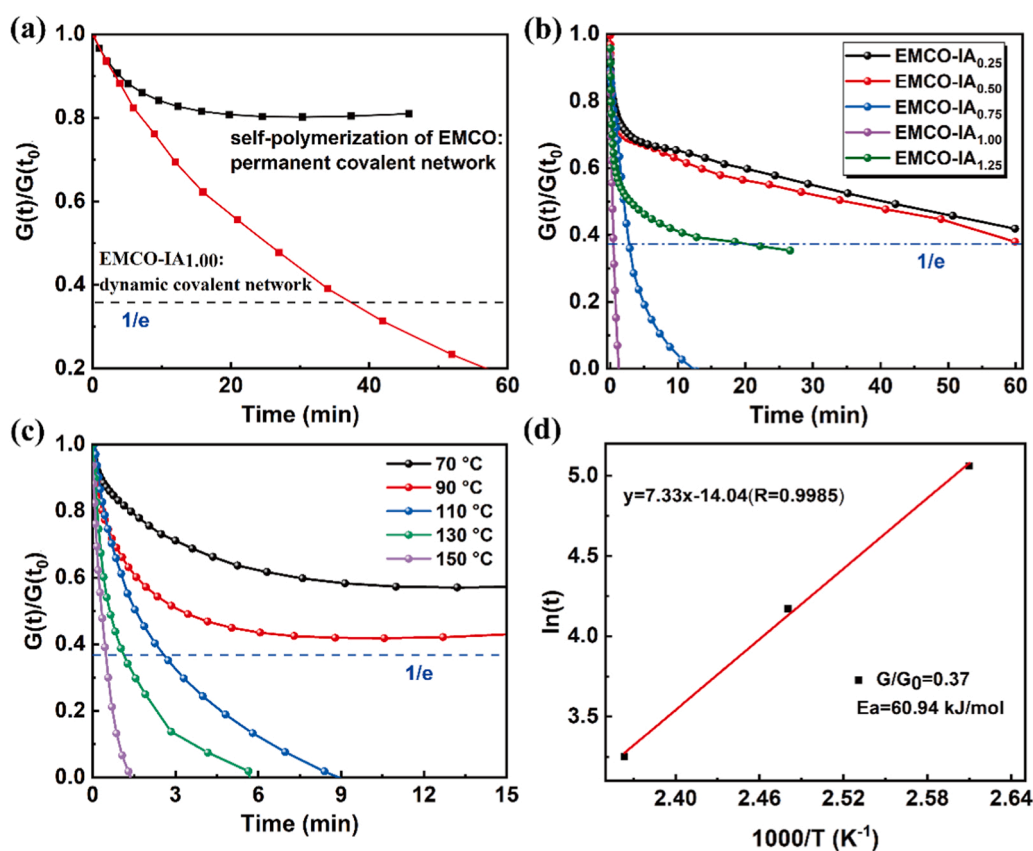


Fig. 6. (a) Stress relaxation curves of EMCO-IA_{1.0} and pure EMCO material; (b) stress relaxation of EMCO-IA_x ($x = 0.25, 0.50, 0.75, 1.00, 1.25$) at 150 °C; (c) stress relaxation of EMCO-IA_{1.0} networks at different temperatures; (d) Arrhenius analysis and the activation energy of the vitrimer.

3.5. Physical recyclability, chemical degradation and self-healing properties of the EMCO-IA vitrimers

The rapid stress relaxation of the EMCO-IA_{1.0} vitrimer confirmed that the dynamic transesterification exchange reaction could occur at elevated temperatures (> 110 °C), which provides evidence for the topological rearrangement of the EMCO-IA cross-linking network. Therefore, both the physical reprocessability and chemical degradation of the EMCO-IA_{1.0} sample is investigated and shown in Fig. 7. The original EMCO-IA_{1.0} sample was firstly cut into small pieces and then remodeled by hot-pressing at 180 °C for 2 h. After that, a uniform and continuous film was reconstructed after hot-pressing, as shown in Fig. 7(a), indicating the EMCO-IA_{1.0} vitrimer had good physical recyclability. And the

remolding mechanism based on the transesterification exchange reaction is illustrated in Fig. 7(b). Nucleophilic hydroxyl groups can react with the ester group under elevated temperature to produce an associate intermediate and then release the exchangeable hydroxyl group and ester group, contributing to revisable transesterification exchange reaction and topological network rearrangement. In addition, the FT-IR spectra of the EMCO-IA_{1.0} material after reprocessing cycles (1st, 2nd, 3rd) were basically the same as that of the original sample in Fig. 7(c). This was mainly due to the chemical structure of the EMCO-IA_{1.0} sample did not change significantly due to the existence of dynamic transesterification reaction during the reprocessing cycles. The influence of reprocessing cycles on the tensile properties of the EMCO-IA_{1.0} vitrimer was revealed in Fig. 7(d). The tensile strength slightly decreased from

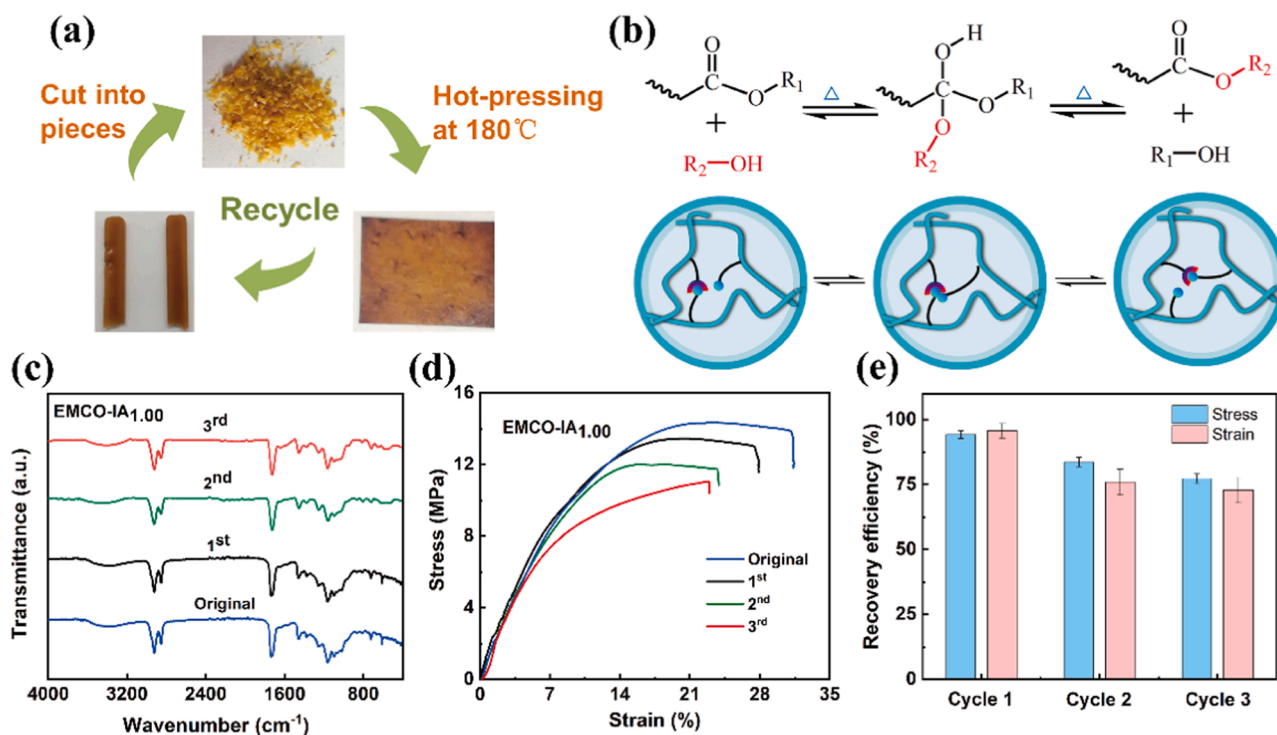


Fig. 7. (a) Schematic of the physical reprocessability of the EMCO-IA_{1,0} material through hot-pressing remolding; (b) schematic of the remolding mechanism based on transesterification exchange reaction; (c) FT-IR spectra; (d) stress-strain curves; and (e) recovery efficiency curves of the original and reprocessed EMCO-IA_{1,0} material.

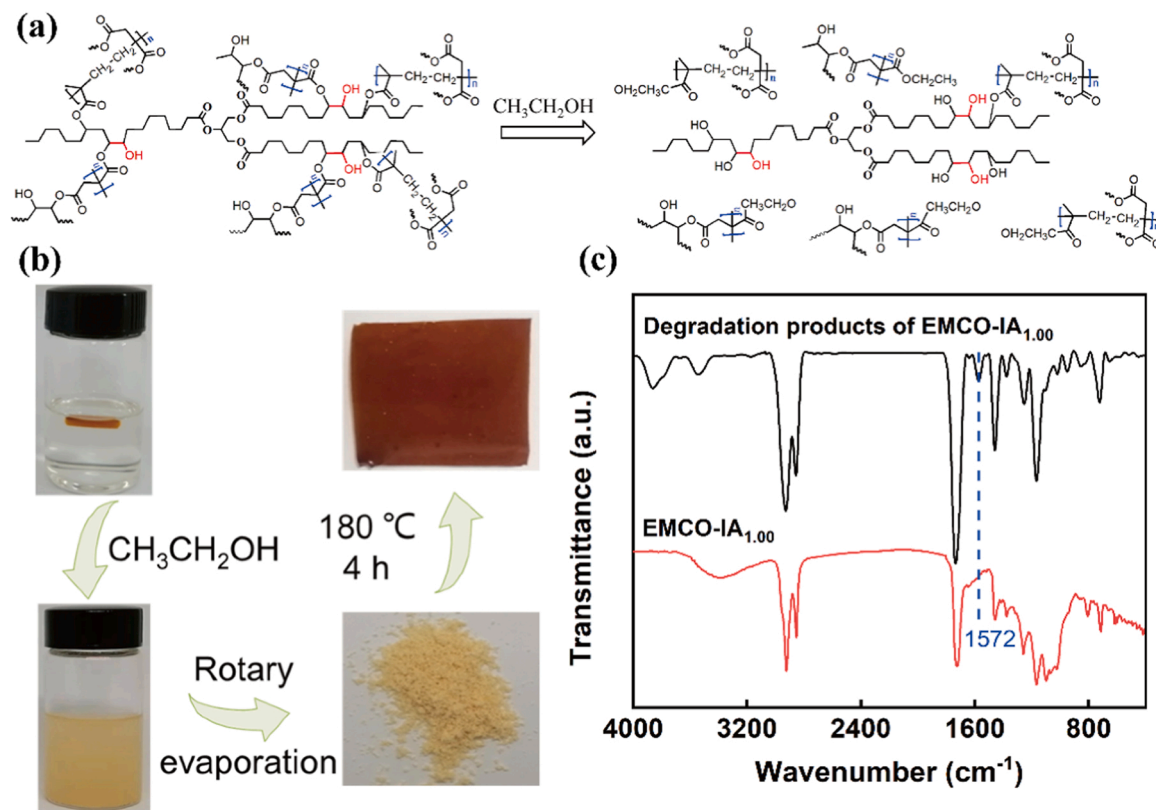


Fig. 8. (a) Illustration of the chemical degradation mechanism of the EMCO-IA_{1,0} vitrimer in ethanol; (b) schematic of the chemical degradation recycling process of the cured EMCO-IA_{1,0} vitrimer; (c) FT-IR spectra of the degradation product and original EMCO-IA_{1,0} vitrimer.

14.39 MPa to 11.13 MPa after reprocessing three times, and the recycling efficiency was maintained at 77.34% in Fig. 7(e). This was mainly due to the dynamic transesterification reaction endowing the EMCO-IA_{1.0} vitrimer with reversible networks and physical reprocessability. The loss of the tensile strength after reprocessing 3 cycles was mainly ascribed to the oxidation reaction or other undesired side reactions during the hot-pressing reprocessing cycles.

The chemical degradation recycling behavior of the cured EMCO-IA vitrimer was evaluated to assess the closed-loop recyclability via alcoholysis reaction, and the chemical degradation mechanism of the EMCO-IA_{1.0} vitrimers in ethanol is shown in Fig. 8(b), due to the presence of abundant ester groups in the EMCO-IA_{1.0} network, it could undergo transesterification with ethanol to obtain new esters and alcohols. The chemical degradation recycling process of the cured EMCO-IA_{1.0} vitrimer is shown in Fig. 8(b), specifically, a rectangular sample was immersed in an ethanol solution and stirred at 75 °C. It was observed that the sample was degraded entirely after stirring for 6 h, and the solution became yellow. After that, the ethanol was removed by rotary evaporation to obtain yellow powders. The FT-IR spectra of the yellow powder showed that the degraded product exhibited absorption peaks at 3652 cm⁻¹ (hydroxyl group) and 1572 cm⁻¹ (ester group) in Fig. 8(c), implying the degradation product could still undergo transesterification exchange reaction and topological network rearrangement. Therefore, the yellow powder was hot pressing at 180 °C for 4 h, and a continuous film was reformed owing to the reversible transesterification exchange reaction, which was consistent with the FT-IR result in Fig. 8(c). All in all, the EMCO-IA_{1.0} vitrimer can achieved a closed-loop recycling, which can extend the service life and facilitate the sustainable development of the material.

The self-healing behavior of the EMCO-IA vitrimer was monitored and observed with a 3D super depth of field microscope, and the results are shown in Fig. 9. Since the ester groups and hydroxyl groups could undergo transesterification exchange reaction, thus endowing the damaged EMCO-IA sample with network rearrangement ability and finally recovering the scratch or crack, as shown in Fig. 9(a). A crack was manually made on the surface of the EMCO-IA_{1.0} vitrimer film sample. After that, clamping the cracked film between two glass slides and heated at 170 °C for 5 h. It can be clearly seen that the EMCO-IA_{1.0} vitrimer exhibited remarkable self-healing ability, as the crack was completely repaired and disappeared in Fig. 9(b). The images of other EMCO-IA_x (x = 0.25, 0.5, 0.75, 1.00 and 1.25) samples before and after self-healing are included in Fig. S7, and all the samples exhibited a certain degree of self-healing ability. The 3D images of the EMCO-IA_{1.00}

vitrimer before and after self-healing are shown in Fig. 9(c). It's observed that the cracked sample exhibited different colors, implying the cracked sample had different plane heights, and the scratch depth was about 430 μm in Fig. 9(d), while the recovered sample exhibited only red color, the scratch depth decreased to 0 μm, further confirming that the prepared EMCO-IA vitrimers had excellent self-healing properties.

3.6. UV-blocking ability of the EMCO-IA vitrimers

Long-term exposure to UV radiation is confirmed to accelerate the degradation and shorten the lifespan of polymer material in outdoors applications. Therefore, there is a great need to monitor the UV-blocking ability of the EMCO-IA material for sustainable development, and the UV-vis transmittance spectra of EMCO-IA_x materials with different IA loadings are shown in Fig. 10. The transmittance of all the EMCO-IA_x materials in the range of 200–455 nm is 0, revealing that the EMCO-IA materials exhibited excellent UV blocking ability in the full wavelength of the UV region (200–400 nm). Therefore, the material can be used as UV-protecting materials.

4. Conclusions

A bio-based epoxy resin EMCO bearing epoxy group and methacrylate group was fabricated through a two-step process and then cured

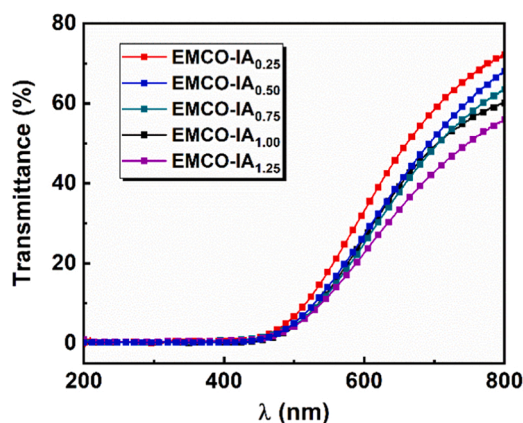


Fig. 10. The UV-blocking ability of the EMCO-IA material.

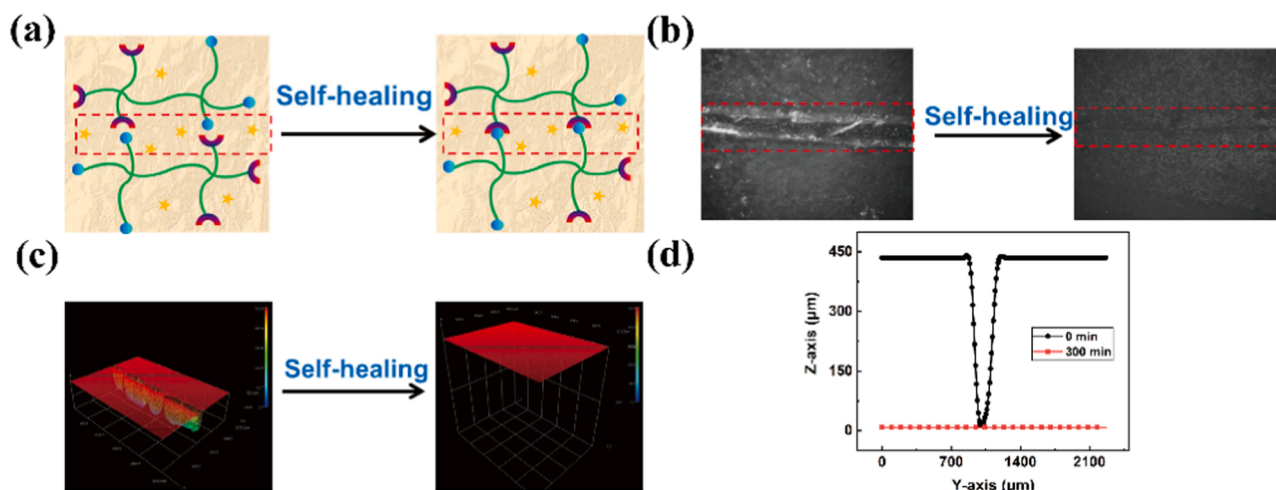


Fig. 9. (a) Schematic of the self-healing mechanism based on dynamic transesterification reaction; (b) the surface changes of the EMCO-IA_{1.0} sample before and after self-healing; (c) 3D images of the EMCO-IA_{1.0} sample before and after self-healing; (d) the corresponding depth profiles of the notched EMCO-IA_{1.0} sample before and after self-healing.

with IA at various loadings to obtain biorenewable and recyclable castor oil-based vitrimers. The EMCO-IA vitrimers offered advantages of balanced thermal-mechanical properties, reprocessability (remolded at 180 °C for 2 h), repairability (170 °C for 5 h), and recyclability (ethanol-degradability) due to fast transesterification reaction at elevated temperature (> 110 °C). Moreover, the material exhibited excellent UV-blocking ability. The bio-based vitrimers demonstrated excellent closed-loop recycling, offering a green and straightforward solution to develop recyclable cross-linked polymeric material.

CRedit authorship contribution statement

Yue-hong Zhang: Supervision, Funding acquisition, Project administration, Writing – review & editing. **Meng-jiao Zhai:** Investigation, Writing – original draft. **Lei Shi:** Methodology, Analysis. **Qin-yang Lei:** Methodology, Analysis. **Shu-tong Zhang:** Data curation, Analysis. **Lei Zhang:** Validation, Analysis. **Bin Lyu:** Writing – review & editing. **Shun-hua Zhao:** Resources, Software. **Jian-zhong Ma:** Conceptualization, Methodology. **Vijay kumar Thakur:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.indcrop.2022.116210](https://doi.org/10.1016/j.indcrop.2022.116210).

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