

Preparation of a bio-based epoxy with comparable properties to those of petroleum-based counterparts

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Abstract. In this paper a bio-based epoxy with outstanding thermal and mechanical properties was synthesized using a rosin-based epoxy monomer and a rosin-based curing agent. The chemical structures of rosin based epoxy monomer and curing agent were confirmed by Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FT-IR) spectra. The flexural mechanical and dynamic mechanical properties as well as thermal stability of the cured epoxy were investigated. The results showed that the cured epoxy exhibited a glass transition temperature (T_g) of 164°C and its flexural strength and modulus were as high as 70 and 2200 MPa, respectively. This indicated that a wholly bio-based epoxy resin possessing high performance was successfully obtained.

Keywords: thermosetting resin, bio-based, rosin, thermal properties, mechanical properties

1. Introduction

In recent decades, more and more attention has been directed to the bio-based materials because of the diminishing petroleum oil reserves and serious environmental pollution [1]. The conversion of biomass to useful polymers or composites has considerable economical and environmental value. With the rapid development of bio-based materials, more and more natural resources, such as vegetable oil [2, 3], starch [4, 5], soy protein [6] and cellulose [7] have been used as the renewable feedstock to produce polymeric materials. Furthermore, these polymers based on renewable resources have often possessed similar properties compared with their petroleum-based counterparts. Up to now, a large quantity of bio-based polymeric materials, such as polylactic acid (PLA) [8], poly(hydroxyalkanoates) (PHA) [9], and castor oil based polyamide [10], have already been commercialized. However, compared with the achieved progress on bio-based thermoplastics, the

research on bio-based thermosetting resins, especially the thermosetting resins with high glass transition temperature (higher than 100°C) and comparable mechanical properties with petroleum-based counterparts are very limited.

To the best of our knowledge, plant oil might be the most popular renewable resource in the synthesis of bio-based thermosetting resins [3, 11–13]. But unfortunately, due to the long soft aliphatic chain in triglyceride and its low crosslink density, the resulting resin always has a low glass transition temperature (lower than 100°C) and disappointing mechanical properties. For example, Park *et al.* [3] synthesized epoxy from soybean oil and castor oil. The results showed that the glass transition temperature of the cured epoxy was lower than 50°C. Javni *et al.* [11] and Can *et al.* [12] also prepared unsaturated polyester or polyurethane from soybean oil derivatives. But their results indicated that the properties of the oil-based resin strongly depended on the

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incorporation of rigid petroleum chemicals [11–15]. In order to obtain the acceptable mechanical and thermal properties for practical application, the content of the rigid co-monomer was usually as high as 50% or beyond. Obviously, they were only partly bio-based materials and the petroleum based component played a critical role in determining the properties of these materials. As we know, the thermosetting resin with satisfactory performance (T_g is higher than 100°C and modulus is higher than 2000 MPa) derived from bio-based feedstock has seldom been reported [16–18].

Rosin is an important natural product. It is composed of ca. 90% acidic and ca. 10% neutral compounds. The hydrogenated phenanthrene ring structure in rosin acids is similar in rigidity to rigid petroleum chemicals. Therefore, we could make use of this bio-based feedstock to synthesize high performance polymeric materials. In our previous works, several kinds of rosin based anhydride type [19] or diimide-diacid type epoxy curing agents [20] were synthesized and their potential in improving the properties of thermosetting resins was demonstrated. In this paper, a rosin based epoxy with three functional groups was synthesized and it was cured with a rosin based curing agent. The objective of this research is to make the full use of rosin rigidity to synthesize a wholly rosin-based thermosetting resin with satisfactory properties, so as to inspire us to explore more and more renewable alternatives to petroleum based polymeric materials.

2. Experimental section

2.1. Materials

Rosin acid ($C_{20}H_{30}O_2$, purity of 75%, yellow crystals or chunks, soluble in acetone, petroleum ether, Et_2O and $EtOH$, melting point of 139–156°C) was obtained from Aladdin Reagent Co., Ltd. Shanghai. It is actually a mixture of abietic acid and other rosin neutral compounds. Sodium hydroxide, acetic acid, epichlorohydrin, maleic anhydride, *p*-toluenesulfonic acid, 2-ethyl-4-methylimidazole, tetrabutyl ammonium bromide and the common solvents were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the chemicals were used as received.

2.2. Characterization

NMR spectra was recorded on the Bruker (Germany) 400 MHz spectrometer. The samples were dissolved in deuterated chloroform ($CDCl_3$). 1H -NMR and ^{13}C -NMR were obtained at room temperature using Tetramethylsilane (TMS) as the internal standard. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet 6700 FTIR spectrometer. The collecting wavelength was from 4000 to 400 cm^{-1} . Samples were prepared by dissolving a small amount of compound in CH_2Cl_2 , followed by smearing the solution onto a KBr crystal plate and evaporating the solvent at room temperature completely. Dynamic mechanical properties were measured by SDTA861e DMA using three-point bending method. Samples were heated from 40 to 250°C with a heating rate of 2°C/min. and frequency of 1 Hz. Thermogravimetric analysis was performed on Perkin-Elmer Diamond TG/DTA with high purity nitrogen as a purge gas at a scan rate of 10°C/min. Elemental analyses were performed by Perkin-Elmer PE2400 elemental analyzer. Flexural properties were determined by Instron model 5567 (Made in UK) with a 30 kN load cell at the crosshead speed of 2 mm/min. Unnotched izod impact testing was conducted on XJ-50Z impact testing machine and (Made in Chengde, China). For the mechanical testing, at least five specimens were tested for each sample to obtain the average value for properties.

2.3. Synthesis of maleopimaric acid (MPA)

The synthesis, collection and purification of MPA were done according to the procedure described in our former paper [19, 20]. 1H -NMR (CD_3Cl , δ ppm) 5.5 (1H), 3.1 (2H), 2.7 (1H), 2.5 (1H), 2.2 (1H), 1.78–1.24 (13H), 1.2(3H), 1.0(6H), 0.6(3H). ^{13}C -NMR (CD_3Cl , δ ppm) 185, 173, 171, 148, 125, 54, 53, 52, 49, 47, 45, 40, 38, 37, 36, 35, 33, 27, 22, 20, 20, 17, 15.76 FT-IR (cm^{-1}) 850, 930, 944, 1010, 1090, 1140, 1280, 1235, 1390, 1465, 1730, 1782, 1842, 2860, 2942, 3500–3100. Elemental analysis: Calculated %: C: 71.97, H: 8.05; Found %: C: 71.42, H: 8.11.

2.4. Synthesis of triglycidyl ester of maleopimaric acid

Into a three-necked round flask equipped with magnetic stirrer, thermometer and reflux condenser,

30 mL of distilled water and 20 g (0.05 mol) of maleopimaric acid were charged. After it was heated to 130°C, 6 g (0.15 mol) of sodium hydroxide was added gradually and the reaction was maintained at this temperature for 4 h under nitrogen atmosphere. To this mixture, 46.5 g (0.5 mol) of epichlorohydrin and 0.5 g of tetrabutyl ammonium bromide were added before the reaction was refluxed for another 6 h. It was cooled to 70°C after the addition of excess sodium hydroxide. By cooling the reaction to room temperature, the solid precipitation was removed via filtration. The filtrate was diluted by 200 mL of hexane and washed with distilled water twice. The upper hexane layer was concentrated by rotary evaporator and dried at 60°C in the vacuum oven for 12 h to get the triglycidyl ester of maleopimaric acid weighting 22 g (Yield: 75%). ¹H-NMR (CDCl₃, δ ppm) 5.4 (1H), 4.3–4.5 (3H), 3.9–4.0 (2H), 3.70–3.72 (1H), 3.11–3.32 (3H), 2.78–2.87 (6H), 2.55–2.70 (4H), 2.40–2.42 (1H), 2.18–2.3 (1H), 1.78–1.24 (13H), 1.15 (3H), 1.00–0.98 (6H), 0.59 (3H); ¹³C-NMR (CDCl₃, δ ppm) 178.2, 173.5, 172.6, 148.1, 127.4, 65.1, 56.4, 53.5, 52.4, 49.5, 47.2, 45.9, 40.6, 38.2, 37.9, 36.6, 35.6, 35.0, 32.7, 27.1, 21.9, 20.8, 20.2, 17.2, 16.9, 15.8. FT-IR (cm⁻¹) 466, 620, 721, 759, 849, 908, 1020, 1071, 1103, 1173, 1249, 1384, 1453, 1730, 2869, 2954, 3446. Elemental analysis: Calculated %: C: 67.55, H: 7.90; Found %: C: 67.23, H: 7.82.

2.5. Cured resin preparation

Maleopimaric acid and triglycidyl ester of maleopimaric acid in a 1:1 stoichiometric ratio together with catalyst 2-ethyl-4-methylimidazole (1 wt% on the basis of total weight) were dissolved in acetone

to get the uniform mixture. The solvent was removed in the vacuum oven at 60°C for 30 min. The solvent free mixture was transferred to the steel mold with the inner dimension of 64 mm × 10 mm × 5mm to prepare the specimens for mechanical and DMA test. The curing reaction was carried out at 120°C for 2 h, 150°C for 2 h and 180°C for 2 h at normal pressure. The cured samples were left still at room temperature for 12 h prior to mechanical and DMA testing.

3. Results and discussion

The reaction scheme and chemical structure for the triglycidyl ester of maleopimaric acid were shown in Figure 1. The synthesis of maleopimaric acid from rosin acid was described carefully in our former paper [19] and its triglycidyl ester was prepared by the reaction with epichlorohydrin and aqueous sodium hydroxide with tetrabutyl ammonium bromide as the phase transfer catalyst. It is easy to notice that maleopimaric acid was the intermediate product to prepare the rosin-based epoxy monomer. In our previous work, [19] maleopimaric acid was demonstrated to have great potential to replace some of conventional petroleum-based curing agents in synthesis of high performance epoxy resin. Naturally, it was also employed as a curing agent to cure its resulting triglycidyl ester and so as to prepare the wholly rosin-based epoxy resin in this research.

Figures 2a and 2b show the ¹H-NMR and ¹³C-NMR spectra for triglycidyl ester of maleopimaric acid, respectively. In Figure 2a, the peak at 5.4 ppm was assigned to the proton 1 on the unsaturated carbon. The multiple peaks appearing at 4.3–4.5, 3.9–4.0

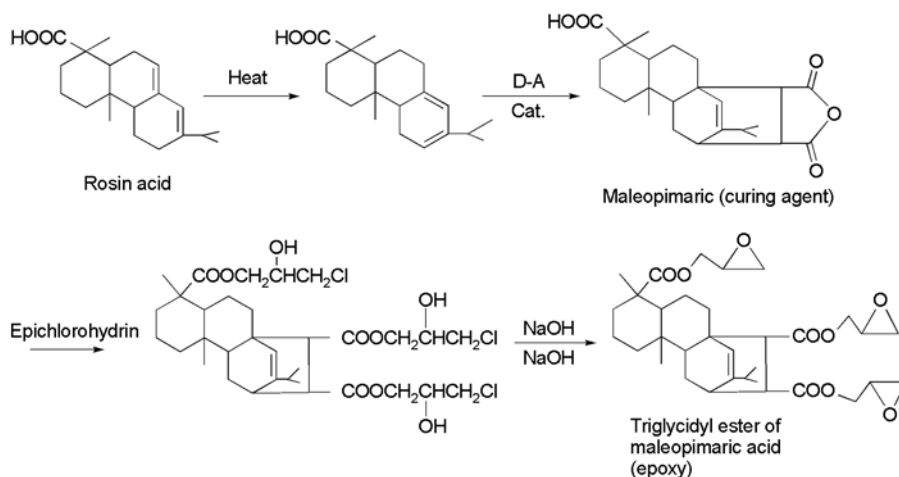


Figure 1. Synthetic route for maleopimaric acid and its triglycidyl ester

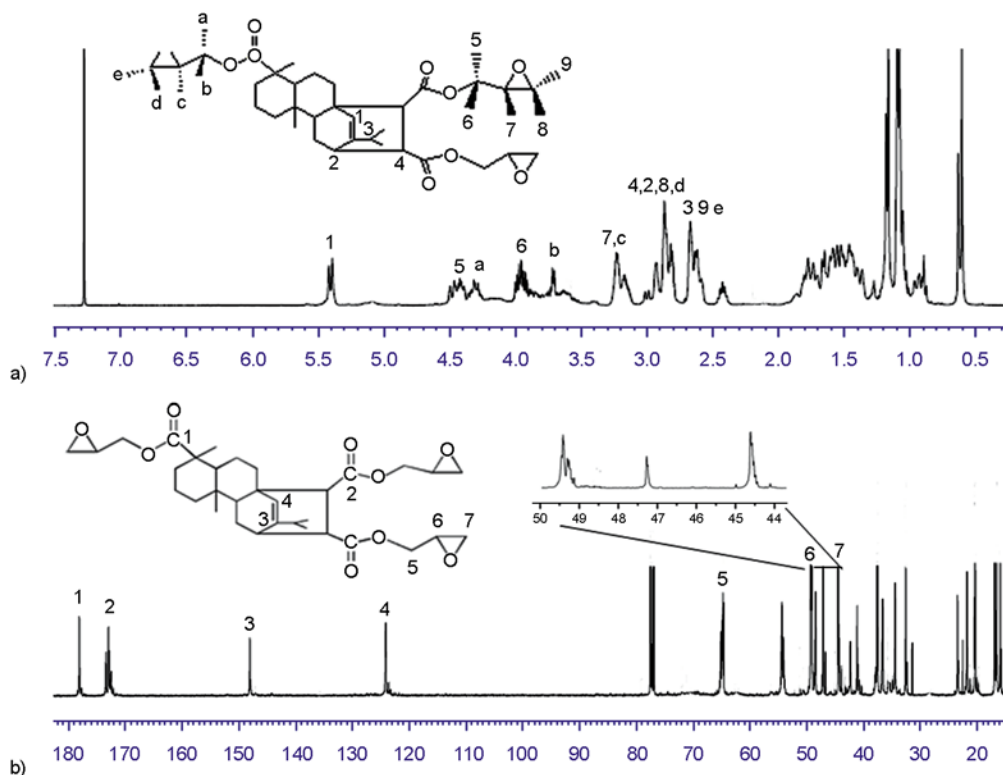


Figure 2. ^1H -NMR and ^{13}C -NMR spectra for tirglycidyl ester of maleopimaric acid

and 3.70–3.72 ppm were attributed to the proton 5, a, 6, b due to the presence of chiral carbon in the ethylene oxide ring. Other specific peaks at 3.1–3.3, 2.78–2.87 and 2.5–2.70 ppm were also identified accordingly. In Figure 2b, all the characteristic chemical shift assignments for different carbons in tirglycidyl ester of maleopimaric acid were made. Especially, from the expansion between 45 and 50 ppm, the peaks for carbon 6 and carbon 7 on the ethylene oxide ring were clearly observed.

FT-IR is useful to monitor the epoxy curing reaction. Figure 3 is the FT-IR spectra for the mixture of maleopimaric acid and tirglycidyl ester of maleopimaric acid before and after curing reaction. In the unreacted mixture, the bands at 1782 and 1842 cm^{-1} were assigned to the characteristic peak of anhydride group; the band at 1730 cm^{-1} was attributed to the carbonyl stretch ($\text{C}=\text{O}$); the peak at 908 cm^{-1} indicated the presence of oxirane rings. After curing reaction, the bands at 1782, 1842 and 908 cm^{-1} were disappeared completely, which represented the conversion of anhydride and epoxy group as well as the formation of the cured resin.

Dynamic mechanical analysis is a popular method to determine the dynamic elastic modulus of polymeric materials and observe the emergence of their

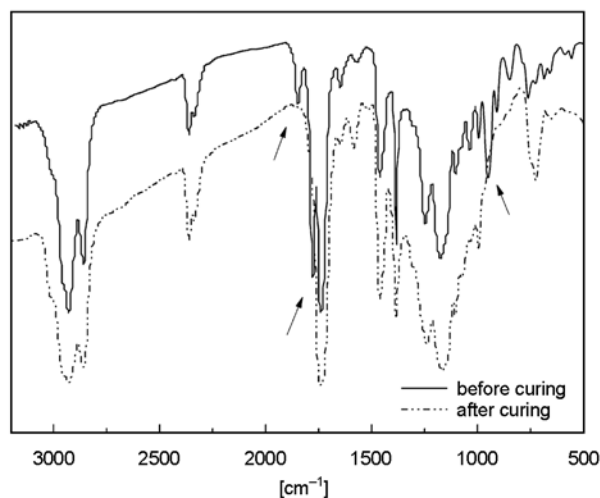


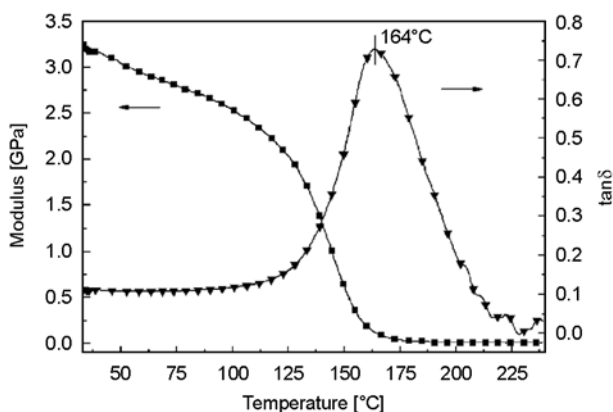
Figure 3. FT-IR spectra for the mixture of maleopimaric acid and tirglycidyl ester of maleopimaric acid before and after curing reaction

molecular mobility transition such as glass transition. Figure 4 shows the dynamic mechanical properties of tirglycidyl ester of maleopimaric acid cured with maleopimaric acid. Apparently, its glass transition temperature (T_g) and storage modulus at room temperature was as high as 164°C and 3.2 GPa, respectively. As we know, the plant oil based thermosetting epoxy, unsaturated polyester or polyurethane were widely studied [11–13, 21–23], but their

Table 1. Mechanical properties and thermal stability of cured triglycidyl ester of maleopimaric acid and petroleum-based counterparts DEGBA

Sample	Flexural modulus [MPa]	Flexural strength [MPa]	Impact strength [kJ/m ²]	Strain at break [%]	Thermal stability ^a [°C]
rosin-based epoxy	2200±30	70±1	2.1±0.2	1.9±0.3	$T_{5\%} = 328$
DGEBA	3000±200 [24]	80±3 [24]	3.2 [25]	2.6 [24]	$T_{2\%} = 319$ [26]

^atemperature of 5% or 2% thermal degradation

**Figure 4.** DMA curves for cured triglycidyl ester of maleopimaric acid

glass transition temperatures and modulus were very low (lower than 50°C). In order to increase their T_g or modulus, more than 50% petroleum-based rigid monomers must be introduced. To the best of our knowledge, this is the first wholly bio-based thermosetting resin which demonstrated outstanding dynamic mechanical properties and thermal properties

To evaluate the properties of this bio-based epoxy resin, the mechanical properties and thermal stability were also investigated. The flexural properties and impact strength were summarized in Table 1. The flexural modulus and flexural strength were about 2200 and 70 MPa, respectively, which are comparable with those of petroleum-based bisphenol A epoxy cured with different curing agents [24]. It meant that this wholly bio-based epoxy resin could be used as an engineering thermosetting resin. Although the resin shows a little bit brittleness according to the lower values of the impact strength and strain at break compared with the reported results [24, 25], it is still acceptable. The low impact strength might be due to the high crosslink density of the cured epoxy, since the epoxy monomer and curing agent both have three crosslinkable functionalities.

The thermal stability is also one of the important properties for polymeric materials and TGA is the most convenient method to determine the thermal stability and degradation behaviors of polymers. In Table 1, the TGA result for the cured triglycidyl ester of maleopimaric acid indicated that its 5% weight loss occurred at 328°C, which is also competitive with the petroleum-based bisphenol A epoxy [26]. As we know, the common cured bisphenol A epoxy usually show their 5% weight loss temperature at about 350°C.

4. Conclusions

A novel bio-based thermosetting resin was developed using a rosin based epoxy monomer and rosin based curing agent. It demonstrated high T_g and modulus. Also its flexural properties and thermal stability were comparable to those of the conventional petroleum-based epoxy. Our results indicated the possibility to synthesize wholly bio-based thermosetting resin with high performance and inspired us to explore more and more renewable alternatives to petroleum based polymeric materials.

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