



Exploration of the complementary properties of biobased epoxies derived from rosin diacid and dimer fatty acid for balanced performance



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ABSTRACT

In this work, a rosin-derived diacid and a dimer fatty acid were converted into diglycidyl ester type epoxies, respectively, and the chemical structures of the products were confirmed by ¹H NMR, FT-IR and ESI-MS. A novel modification was introduced to the two-step synthesis of diglycidyl ester by using CaO as water scavenger in the dehydrohalogenation step. Nadic methyl anhydride was used as curing agent to cure these two biobased epoxies and their mixtures in different weight ratios. The cure behavior was studied using differential scanning calorimetry (DSC). Flexural and dynamic mechanical properties of the cured resins were determined using three point bending test and dynamic mechanical analysis (DMA). Thermal degradation of the cured resins was examined using thermogravimetric analysis (TGA). Results suggest that the rigid rosin-derived epoxy and the flexible dimer acid-derived are complementary in many properties and the combination of them could result in resins with properly balanced properties and overall improved performance.

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1. Introduction

Development of biobased polymers, i.e., polymers from renewable feedstock, has been driven by the growing concerns of long-term sustainability and negative environmental footprint of petroleum-based polymer materials. So far the progress of biobased polymers is usually seen in the sector of thermoplastic polymers. Bernard et al. investigated the structure–properties relationship of biosourced stereocontrolled polytriazoles from click chemistry step growth polymerization of diazide and dialkyne dianhydrohexitols (Besset et al., 2010). The thermoplastic polymers have shown great potential to replace the petrochemical thermoplastics in many applications. On the other hand, the penetration of renewable feedstock into thermosetting polymers has been more

and more popular. Epoxy resin is a kind of thermosetting resin which upon curing generally exhibit high performance in terms of high strength, modulus, heat resistance and other properties. The biobased epoxy resins with different structures had been recently developed from some bioresources, such as isosorbide (Chrysanthos et al., 2011), gallic acid (Aouf et al., 2013b) and catechins (Nouailhas et al., 2011).

Rosin is the exudate from pines and conifers and consists of 90% acidic chemicals called rosin acid and 10% volatile turpentine. Rosin acid is a mixture of different isomers consisting of a hydrogenated phenanthrene ring structure with a carboxylic acid group and two double bonds. Tang's group recently introduced a new type of rosin-derived vinyl monomers and demonstrated the atom transfer radical polymerization (ATRP) of these rosin-derived vinyl monomers (Zheng et al., 2010). They further synthesized a block copolymer of ϵ -caprolactone and rosin-derived vinyl monomer by ROP and ATRP (Yao et al., 2011). We recently also demonstrated that rosin acid could be a potential rigid alternative chemical to petroleum-derived aromatic and cycloaliphatic chemicals for the preparations of epoxies and curing agents (Liu et al., 2009; Wang et al., 2008; Liu et al., 2010). Rosin-derived anhydride (methyl

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maleopimarate, MMP) and acid-anhydride (maleopimaric acid, MPA) exhibited similar curing reactivity to that of their commercial counterparts 1,2-cyclohexanedicarboxylic anhydride and 1,2,4-benzenetricarboxylic anhydride (Liu et al., 2009; Wang et al., 2008), respectively, and the cured epoxy resins displayed comparable mechanical and dynamic mechanical properties as well. However, like most other epoxy resins, these rosin-based epoxies tended to be brittle.

Plant oils are important sustainable chemicals and intermediates. Epoxidized plant oils have found uses in many applications. They were proved to be useful modifiers in epoxy applications but behaved poorly when used alone for epoxy application due to low strength, modulus and T_g of the cured resins (Samper et al., 2012). Czub demonstrated that epoxidized soybean oil (ESO) was an effective reactive diluent in reducing the viscosity of bisphenol A epoxy resins (Czub, 2006). A novel polyamine epoxy curing agent issued from grape seed oil (GSO) was prepared by Lapinte et al., using cysteamine chloride by thiol-ene coupling (Stemmelen et al., 2011). It was found that the thermosets consisted by GSO and epoxidized linseed oil had a very low T_g (-38°C). The study of Shabeer et al. indicated that noise and vibration abatement of commercial epoxy resins could be greatly improved by incorporation of epoxidized ethyl ester of soybean oil fatty acids (Shabeer et al., 2005). Miyagawa et al. (2004, 2005) studied the combination of epoxidized linseed oil (ELO) or ESO and diglycidyl ether of bisphenol F in epoxy application. The izod impact strength increased with increasing concentration of ELO or ESO in the mixed resin. These evidences may also suggest that the flexible plant oil derivatives would significantly regulate the performance of the rigid rosin-derived epoxies. However, the epoxy group in epoxidized oil is an internal oxirane in the middle of the fatty acid chain and is less reactive than the terminal epoxy group of glycidyl ether or ester. The reaction temperature of this hindered epoxy group with anhydride can be as high as 200°C even in the present of a catalyst (Altuna et al., 2011). The low reactivity of the oxirane of epoxidized plant can cause non-homogeneous curing and hence prevent the complete cure of the epoxy network (Boquillon and Fringant, 2000).

In this work, diglycidyl ester of dimer fatty acid was prepared and used to modify the performance of a rigid rosin-derived epoxy, diglycidyl ester of acrylopimaric acid. Dimer fatty acids (DA) are the commercial di-carboxylic acids with 36 carbons resulting from clay-catalyzed, high temperature polymerization of unsaturated fatty acids, usually oleic or linoleic acid from soybean oil, tall oil or cotton seed oil. The products have been commercially available since the 1950s (Leonard, 1979). The structures of dimer acid are very complicated and generally contain non-ring, monocyclic, bicyclic, tricyclic and even aromatic dimers due to the different feedstocks and polymerization methods (Paschke et al., 1964; Wheeler et al., 1970). The monocyclic structure is that of the Diels–Alder reaction between two molecules of monomers, with one molecule acting as diene, and the double bond of the other molecule acting as dienophile (Paschke et al., 1964). This monocyclic structure is believed to be the relatively greater proportion compared to other structures (Leonard, 1979). Sometimes dimer acids are hydrogenated by Pd/C and H_2 to improve the color and thermal stability.

Unlike epoxidized plant oils, the diglycidyl ester of dimer acid has two terminal epoxy groups which are supposed to be more reactive than the internal oxiranes. We introduced a more effective method for preparing the glycidyl esters of rosin acid and dimer fatty acid. As seen in Scheme 1, calcium oxide was added as a water scavenger which reacts with water to form calcium hydroxide, preventing the side reactions such as hydrolysis of epichlorohydrin or saponification of esters. The two epoxies were mixed in different ratios and cured with a commercial curing agent – nadic methyl anhydride. Curing kinetics, flexural properties, dynamical

mechanical properties and thermal stability of the cured resins were studied.

2. Experimental

2.1. Materials

Dimer fatty acid (hydrogenated, Gardner color ≤ 5 , dimers $\geq 95\%$, monomers $\leq 1.5\%$, trimers $\leq 3.5\%$, acid value: 190 mg/g, viscosity at 25°C : 6000–8000 mPa s) was obtained from Shanghai Guxiang Chemical Company. Gum rosin (acid value 170 mg/g) was obtained from Guangxi Wuzhou Richeng Chemical Company. Acrylic acid (99%, Sigma–Aldrich), Epichlorohydrin, sodium hydroxide (98.7%, J.T. Baker), nadic methyl anhydride (99.4%, Electron Microscopy Sciences), benzyltriethylammonium chloride (97%, Aldrich) and 2-ethyl-4-methylimidazole (99%, Acros Organics) were used as received.

2.2. Synthesis

2.2.1. Synthesis of acrylopimaric acid (APA) (Halbrook and Lawrence, 1972)

Gum rosin (300 g) was charged to a flask equipped with a stirrer, dropping funnel, inert gas inlet, thermometer, and reflux condenser. The temperature was raised to 230°C , and acrylic acid (76.5 g) was added slowly. The reaction continued for 3 h at 230°C after all the acrylic acid was added. The crude product 100 g was recrystallized in accordance with Chinese patent using a petroleum ether/ethyl acetate (85/15, v/v) mixture, then 52 g purified acrylopimaric acid was obtained (yield: 52%). The purity of the obtained acrylopimaric acid was 93% (GC).

2.2.2. Synthesis of diglycidyl ester of acrylopimaric acid (DGEAPA)

To a 50 mL flask equipped with reflux condenser, magnetic stirrer and thermometer were charged 3.740 g (10 mmol) APA, 18.500 g (200 mmol) epichlorohydrin and 0.023 g (0.1 mmol) benzyltriethyl ammonium chloride. The reaction temperature was raised to 117°C and the reaction continued at that temperature for 2 h. After the mixture was cooled to 60°C , 0.800 g (20 mmol) sodium hydroxide and 1.120 g (20 mmol) calcium oxide were charged. The mixture was stirred at 60°C for 3 h and then filtered by celite and filter paper. The solid was discarded. After the excess epichlorohydrin was distilled under vacuum at 100°C from the filtrate, 4.2 g yellowish viscous resin was obtained. The product was purified using a silica gel column (ethyl acetate: hexane = 1: 2, v/v) to receive 4 g pure diglycidyl esters (yield: 88% relative to pure APA) with an epoxide equivalent weight 243 g/mol (theory: 243 g/mol). The pure diglycidyl esters contained two isomers corresponding to the two APA isomers. $^1\text{H NMR}$ (CDCl_3 , δ ppm) 5.32 (s, 1H), 4.38–4.43 (q, 1H), 4.24–4.29 (q, 1H), 3.88–3.94 (q, 1H), 3.77–3.83 (q, 1H), 3.17–3.21 (m, 1H), 3.12–3.16 (m, 1H), 2.82–2.85 (t, 1H), 2.78–2.81 (t, 1H), 2.62–2.66 (m, 1H), 2.57–2.60 (m, 1H), 2.55 (m, 1H), 2.30–2.37 (m, 2H), 1.27–1.84 (m, 16H), 1.14 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H), 0.59 (s, 3H). FTIR (cm^{-1}) 764, 849, 910, 1149, 1246, 1728, 2866, 2933. ESI-MS m/z 487.4, $[\text{M}+\text{H}^+]$.

2.2.3. Synthesis of diglycidyl ester of dimer acid (DGEDA)

The method is same to that for the synthesis of acrylopimaric acid diglycidyl esters. The product is a light yellowish liquid with an epoxide equivalent weight 385 g/mol (theory: 351 g/mol calculated by acid value of the dimer acid). Since the dimer fatty acid is a mixture of various isomers with similar structures, DGEDA was not further purified and used as prepared. $^1\text{H NMR}$ (CDCl_3 , δ ppm) 4.42–4.43 (d, 1H), 4.38–4.39 (d, 1H), 3.91–3.93 (d, 1H), 3.87–3.89 (d, 1H), 3.17–3.23 (m, 2H), 2.82–2.85 (t, 2H), 2.63–2.65 (q, 2H),

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