



## Rosin-derived imide-diacids as epoxy curing agents for enhanced performance

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### ABSTRACT

Two rosin-based imide-diacids were synthesized and studied as epoxy curing agents. In comparison, a similar imide-diacid based on trimellitic anhydride was also prepared. The chemical structures were confirmed by  $^1\text{H}$  NMR and FT-IR. The curing of a commercial epoxy with these imide-containing diacids was studied by differential scanning calorimetry (DSC). Thermal stability, tensile and dynamic mechanical properties of the cured epoxies were investigated. The results indicate that rosin-based imide-diacids used as curing agents resulted in significantly higher glass transition temperature, tensile and dynamic mechanical properties than the imide-diacid derived from trimellitic anhydride. Rosin acids have a great potential to replace some of current petroleum-based compounds in the synthesis of epoxy curing agents.

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### 1. Introduction

Rosin is an abundantly available natural material composed of ca. 90% acidic and ca. 10% neutral compounds. The acidic components, rosin acids, are also a mixture mainly consisting of isomeric abietic-type acids (40–60%) and pimaric-type acids (9–27%) on the basis of total rosin weight. Rosin and its derivatives are traditionally used in adhesive pacifiers, vanishes, and other niche applications. The hydrogenated phenanthrene ring structure of rosin acids is a rigid entity and could make the derivatives of rosin acid important alternatives to current petroleum-based rigid monomers. In recent years, rosin acids have also received attention as a renewable feedstock in polymer synthesis. For example, the Diels–Alder adduct of levopimaric acid and maleic anhydride–maleopimaric acid, was used as a rigid building block in the main chains of aliphatic polyesters to manipulate their mechanical properties and crystallization behaviors (Liu et al., 2005, 2006a,b). Other Diels–Alder adducts of rosin acid with acrylic acid, acrylonitrile, or diallyl maleate were used as monomers in the synthesis of polyamides (Ray et al., 1985; Ioan and Fanica, 2000), polyamideimide (Ray et al., 1988, 1990), saturated polyesterimide (Barabde et al., 2005; Das and Maiti, 1982; Ioan and Fanica, 2004), and unsaturated polyesters (Hoa et al., 1993; Ioan and Fanica, 1997).

Rosin acid derivatives have also been used for the preparation of thermosetting resins. Matynia (1980) synthesized epoxies from the reaction of epichlorohydrin with the Diels–Alder adducts of terpene and maleic anhydride. Atta et al. (2004, 2005) prepared epoxy resins by reacting hydroxymethylated rosin acid with the adduct of diabietyl ketone/maleic anhydride or acrylic acid. However, de-

tailed information on their mechanical and thermal properties, which were the important data to evaluate the properties of new materials, was not given in those studies. Recently, we also investigated the utilization of rosin acids for the synthesis of epoxies and curing agents (Wang et al., 2008, 2009; Liu et al., 2009). Dynamic mechanical properties and thermal stability of the epoxies cured by rosin-based curing agents and their petrochemical analogs were compared (Liu et al., 2009). The introduction of the hydrogenated phenanthrene ring into an epoxy or a curing agent molecule resulted in increases in  $T_g$  and modulus but slightly lower thermal stability. Furthermore, the molecular flexibility of rosin-based anhydride curing agents was manipulated by introducing a flexible spacer between two terminal maleopimarate entities (Wang et al., 2009), hence the flexibility of the cured epoxies. The results from these studies suggest that rosin could be used as a major feedstock in the place of aromatic or cycloaliphatic compounds for the synthesis of both epoxy resins and curing agents.

In recent years, combining the structural versatility of epoxy resins with the high thermal stability of aromatic imide for advanced application has received considerable attention. This goal can be achieved by either using imide-containing epoxy or curing agent in the curing systems. For example, Serra et al. (1986), Cadiz et al. (1987) prepared a series of epoxy–imide resins by modifying the backbone structure of epoxy resins with imide units. Ginu et al. (2007) synthesized diimide-diacids as curing agents. The cured epoxies showed that the properties of the epoxy–imide system were influenced by many factors, such as the imide content, structure of the diimide-diacid, and the epoxy resin used.

In this study, two rosin-based curing agents containing imide groups were synthesized. For comparison, an imide-diacid derived from trimellitic anhydride was also prepared. Curing of a commercial epoxy resin with these imide-diacids, and mechanical and

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thermal properties of the cured resins were studied. The objective of this study is to investigate thermal stability, tensile and dynamic mechanical properties of the epoxies cured with rosin-based curing agents, hence to develop novel rosin-based curing agents for enhanced performance of epoxy and further broaden the family of rosin derivatives. As a part of our continued research, this study also intended to provide important information on relationship between molecular structure of rosin-based curing agent and the properties of the cured epoxy, especially thermal stability.

## 2. Methods

### 2.1. Materials

A solid epoxy, DER 6224 with an epoxide equivalent weight of 675–725 g/eq, was obtained from Dow Chemical Company. Abietic acid (75%), maleic anhydride (powder, 95%), *p*-toluene sulfonic acid (98.5%), *p*-aminobenzoic acid (97%), trimellitic anhydride (97%), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (95%), and 2-ethyl-4-methylimidazole (95%), were obtained from Aldrich. Solvents of reagent grade (acetic acid, acetic anhydride, dimethylformamide, ethyl ether, chloroform, and methanol) were used as received. Maleopimaric acid was synthesized in our previous work. (Liu et al., 2009).

### 2.2. Synthesis of *N*-(4-carboxyphenyl)trimellitimide (NCPT) (Liu et al., 2006)

To a 250 mL three-necked flask equipped with a magnetic stirrer, reflux condenser, and thermometer, was charged 13.7 g (0.1 mol) of 4-aminobenzoic acid and 50 mL of DMF. After 4-aminobenzoic acid was dissolved, 19.2 g (0.1 mol) of trimellitic anhydride was added gradually. The reaction was continued at room temperature for 24 h, and then 20 mL of acetic anhydride and 5 mL of pyridine were added. The reaction was heated to 150 °C and continued at this temperature for another 5 h. By cooling the reaction, a solid product was precipitated and collected by filtration. The raw product was recrystallized twice in DMF and dried at 80 °C in vacuum oven to receive 26.7 g of white product (yield 86%).

### 2.3. Synthesis of rosin–maleic anhydride imidodicarboxylic acid (RMID)

To a three-necked round flask was charged 20 g (0.05 mol) of maleopimaric acid, 7.2 g (0.0526 mol) of *p*-aminobenzoic acid,

and 60 mL of dimethylformamide. After the mixture was heated to 160 °C and maintained at this temperature for 4 h under Ar atmosphere, it was cooled to room temperature and poured into 400 mL of water. The precipitate was washed with water thoroughly and dried in vacuum oven at 90 °C. The white product was recrystallized in dimethylformamide twice, washed with diethyl ether and dried in a vacuum oven at 70 °C for 12 h to get a constant weight. Yield 87%.

### 2.4. Synthesis of dirosin–maleic anhydride imidodicarboxylic acid (D-RMID)

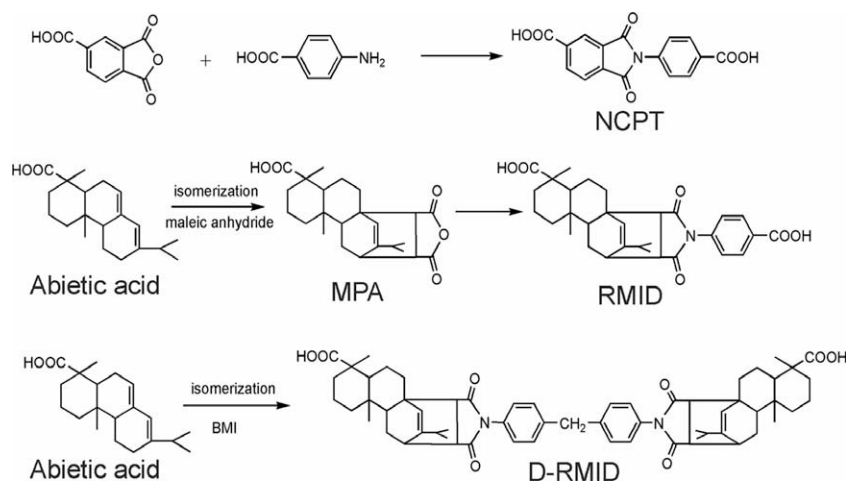
In a 100 mL three-necked round flask equipped with a magnetic stirrer and reflux condenser, 10 g abietic acid (24 mmol) was heated to 180 °C and maintained at this temperature for 3 h to complete the isomerization from the abietic structure to the pimelic structure under the protection of Ar. The reaction was cooled to 120 °C, and 30 mL of acetic acid was added. To this mixture, 4.3 g 1,1'-(methylenedi-4,1-phenylene)bismaleimide (12 mmol) and 0.46 g *p*-toluene sulfonic acid (PTS) (0.24 mmol) was added and the reaction was refluxed for 12 h before it was cooled to room temperature. The precipitate was collected via filtration and purified by several reprecipitations from warm chloroform to hexane. At last, the yellowy powder was dried in the vacuum oven at 70 °C for 12 h and the pure product weighting 10 g was obtained (yield: 87%).

### 2.5. Curing procedure

Epoxy resin (DER 6224), curing agent (NCPT, RMID or D-RMID), and 2-ethyl-4-methylimidazole (1 wt.% on the basis of the total weight of curing agent and epoxy) were first dissolved in a small amount of chloroform and methanol mixture to achieve good mixing. The solvents were removed under vacuum at 50 °C for 3 h. Epoxy and curing agent was in a 2:1 equivalent ratio for all samples. The reactant mixture was transferred into a mold with cavity dimensions of 60 × 5 × 2 mm and held under a constant pressure on the hot plate. The curing reaction was conducted at 100 °C for 1 h, 130 °C for 1 h, 160 °C for 2 h, and 180 °C for 2 h. The cured samples were carefully removed from the mold and used for tensile, dynamic mechanical and thermal tests.

### 2.6. Characterizations

<sup>1</sup>H NMR spectra were recorded using a Bruker 300 MHz spectrometer at room temperature. Fourier transform infrared spectra



**Scheme 1.** Synthesis route of NCPT, RMID and D-RMID.

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