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Rosin based epoxy coating: Synthesis, identification and characterization

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ABSTRACT

Ketone type derivative of rosin was prepared by dehydrocarboxylation of isomerized abietic acid. Coupling of dipimaryl ketone with maleic anhydride was performed by acetic acid catalyzed Diels–Alder reaction. Afterwards, the dipimaryl ketone was epoxidized to get the corresponding tetra glycidyl ester. The chemical structure of the synthesized products was confirmed by UV, FTIR and ^{1}H NMR spectroscopic analyses. Cured resins using a rosin-based crosslinker and p-phenylene diamine (a commercial crosslinker) were evaluated using dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and some preliminary universal coating tests. Results showed that the fully rosin-based epoxy system gave better performance than commercially bisphenol-A based one. This finding was attributed to a liquid crystal behavior of the rosin-based crosslinker. Mesomorphic transition temperature and liquid crystalline texture of the rosin-based crosslinker were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC).

1. Introduction

The increasing demand to maximize bio-based share in various products is now a challenging target. Rosin obtained from exudate of pine and fir trees with annual world-wide production of about 1.27 million tons contains abietic acid as a major component. Low cost, availability and derivatization ability [1] widen application of the latter in many fields. This diterpene acid contains hydrophenanthrene moiety with two conjugated double bonds besides its reactive carboxylic group. Rosin was used in modifying phenol–formaldehyde resins through Diels–Alder cycloaddition of resole to infer oil solubility for surface coating application [2]. The hydrophenanthrene moiety provides resin acids with hydrophobicity, a property that facilitated their use in marine antifouling coating materials for decades [3]. It also found application in printing inks through modification with formaldehyde resins [4,5] and polyester of phthalic anhydride and glycerol [6]. Recently, rosin-based compounds were used as a novel one component i-line molecular glass photoresists [7]. Moreover, a great interest was observed in preparing rosin based polymers for enhanced thermal stability [8,9] as well as polyesters [10,11], epoxy resins [12–15] and epoxy curatives [16–20].

The objective of this research was directed to make use of the rigidity of the tricyclic hydrophenanthrene structure of rosin acids in order to prepare a fully bio-based two component epoxy coating epoxy resin and crosslinker – with enhanced

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performance. In this context, tetraglycidyl dimaleopimaryl ketone (epoxy resin) was prepared and cured with either a rosin acid based crosslinker (RC) or the traditional p-phenylene diamine crosslinker (PPD) for comparison.

2. Experimental

2.1. Materials

Abietic acid (75%) was obtained from Sigma–Aldrich. It is indeed a mixture of rosin acids with abietane type as a main component (75%) where most of the neutral compounds are distilled off [17]. Maleic anhydride (⩾99%), p-toluene sulfonic acid monohydrate (⩾98.5%), 1,1′-(methylenedi-4,1-phenylene) bismalimide (95%) and epichlorohydrin (99%) were purchased from Sigma–Aldrich. Sodium hydride suspension (60% in paraffin oil) was obtained from Loba Chemie chemical company – India and p-phenylene diamine (97%) was obtained from Central Drug House chemical company – India. Acetic acid (99.5%), dimethyl formamide (99.8%) and zinc acetate dihydrate (97+%) were delivered from Acros Organics chemical company – Belguim. 2-ethyl-4-methylimidazole (96%) was purchased from Alfa-Aesar chemical company – USA. A commercial diglycidylether bisphenol-A (DGEBA) sample under the trade name of KEMAPOXY150 was kindly supplied by Chemicals for Modern Building Company (CMB) – Egypt (having epoxy equivalent weight of 182–192 g/mol). All chemicals were used as received without further purification.

2.2. Measurements and characterization

^{1}H NMR spectra were recorded on Varian NMR 300 MHz spectrometer in deuterated chloroform. FTIR spectra were measured on a Mattson-infinity series bench top 961 spectrometer. UV spectra were recorded on Shimadzu UV-1600 series. Elemental analyses were performed on Shimadzu Qp-2010 plus while total acid number was evaluated according to ASTM D-664 on MATi 02 Automated TAN/TBN analysis, Metrohm. Epoxy equivalent weight was experimentaly investigated according to ASTM D-1652 and calculated using ^{1}H NMR analysis data [21]. DMA was carried out on Triton Technology DMA using a three point bending mode. Samples were tested from 30 to 200 °C at a heating rate of 10 °C min^{-1} and frequency of 1 Hz. Thermogravimetric analysis was conducted using Simultaneous DSC–TGA, Q 600 SDT thermogravimetric analyzer. Microscopic observations were investigated using Olympus polarizing microscope (POM) at a magnification of 100 with crossed polarizers. For mechanical, chemical and corrosion analyses of cured epoxy resins, coat samples were mixed and applied with a total dry film thickness (DFT) of 100 μm. As commonly used, mild steel panels (15 cm × l0 cm) were used to evaluate different properties of the coatings. The other side of the panels was coated and protected against corrosive environments by using coal tar epoxy primer. The tested side was blasted and cleaned before coating. The panels were then subjected to different testing procedures for evaluating their mechanical properties and their durability. Mechanical assessments of the coated steel samples including impact resistance and pull-off resistance were evaluated according to ASTM D5420 and ASTM D4541, respectively, while hardness and bending tests were examined using ASD 3363 and D522, respectively.

2.3. Synthesis of tetraglycidyl dimaleopimaryl ketone (TGK)

Synthesis route of tetraglycidyl dimaleopimaryl ketone is presented in Scheme 1. Isomerization of 30.2 g (0.1 mol) abietic acid into levopimaric acid was performed under a continuous stream of nitrogen and carbon dioxide at 180 °C for four hours [16,18,22]. Isomerization was followed up using UV spectroscopy. Dipimaryl ketone was synthesized according to a procedure reported by Bicu and Mustata [23]. Maleodipimalryl ketone was prepared following Diels–Alder cycloaddition protocol using 0.7 g zinc acetate as catalyst and acetic acid as a solvent. After 12 h of reflux a brownish yellow solid was collected. A yield of 85% was obtained after double recrystallization from acetic acid then washed with water. A mixture of maleodipimalryl ketone 21.3 g (0.021 mol) in dimethyl formamide (DMF), purified sodium hydride 1.27 g (0.052 mol) and epichlorohydrin 78.51 ml (0.84 mol) was placed in a three-neck flask and refluxed for 6 h. An extra amount of sodium hydride was added by the end of the reaction. After getting rid of the solid precipitate, the excess of epichlorohydrin and the solvent was evaporated under vacuum. The final product was washed using methanol two times and dried under vacuum at 40 °C. The chemical structure of dipimaryl ketone, maleodipimalryl ketone and tetraglycidyl dimaleopimaryl ketone was confirmed using elemental analysis, melting point (T_m), total acid number (TAN), FTIR and ^{1}H NMR.

2.4. Preparation of a rosin-based crosslinker (RC)

RC was prepared and purified according to a procedure described by Liu and coworkers [16]. Synthesis route of the rosin-based crosslinker is presented in Scheme 2. Thermal transitions of RC were identified by DSC where the sample was heated from room temperature up to 350 °C with a heating rate of 10 °C/min under nitrogen atmosphere. In addition, POM was used to determine the texture during a heating regime.