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Synthesis of unsaturated polyester resins based on rosin acrylic acid adduct for coating applications

Ayman M. Atta *, Ashraf M. Elsaeed, Reem K. Farag, Shymaa M. El-Saeed

Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt

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Abstract

Unsaturated polyester, UP, resins were obtained by reacting the propylene or ethylene glycol, PG or EG, with different acrylopimaric adducts APA, maleic anhydride as a source of double bond, phthalic anhydride and adibic acid as dibasic acids. The molecular weights of UP were determined by end group analysis. The chemical structures of the resulting UP resins were confirmed by ^{1}H NMR analysis. The curing exotherm of UP, vinyl ester resins (VE) and styrene was evaluated at temperatures from 35 to 55 °C using free radical initiator and accelerator. The curing behaviors of cured UP resins with styrene were evaluated by DSC measurements. The prepared UP curable resins were evaluated in the field of steel coating by measuring their mechanical properties and chemical resistance.

Keywords: Unsaturated polyester; Vinyl ester resins; Rosin; Styrene; Coating; Rosin adducts; Chemical resistance

1. Introduction

Rosin, exudates of pine trees, has been developed as a feedstock for synthesis of various chemicals and intermediates for polymers. It is often used in the formulation of adhesives, paints, varnishes and printing inks. It was used to obtain new polymers such as polyesterimides [1] and polyamidimide [2]. It is also incorporated in some formulations of unsaturated polyester, but in small quantities [3]. A large majority of organic coating films in the end-use state exist in the form of a three-dimensional polymer network. Rosin and rosin derivatives are important chemicals in antifouling paint formulations. They may be used either as the vehicle or as the antifouling agent [4,5].

Unsaturated polyester resins, UP, have firmly established themselves as important matrix materials in the field of reinforced plastics and coatings, although phenol formaldehyde type resins are preferred when specific fire and smoke resistance qualities are required [6–8]. Although UP resins are used as organic coatings, they suffer from rigidity, low acid and alkali resistances and low adhesion with steel when cured with conventional "small molecule" reagents. Improvements of resin flexibility can be obtained by incorporating long chain aliphatic compounds into the chemical structure of UP resins. In this respect, we designed both UP resins and hardeners based on aliphatic

* Corresponding author. Tel.: +20 22747917; fax: +20 22747433.
E-mail address: khaled_00atta@yahoo.com (A.M. Atta).

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and cycloaliphatic systems to produce cured UP resins which have good durability with excellent mechanical properties. The aim of this work was to use the rosin as a potential raw material for the production of UP because of its cheaper price and to study its influence on both mechanical properties and chemical resistance of the cured UP resin. In order to fulfill these goals, three steps were distinguished. The first step includes the preparation of Diels Alder adducts of rosin acid to use as dibasic acid material in manufacture of UP resins using ethylene or propylene glycol as diol. On the other hand the produced adducts were used to prepare vinyl ester resin which used as hardener for the prepared UP resins. In the second step, the curing behavior of UP resins and vinyl ester resins used for the production of ambient temperature coatings was investigated. In the final step, the cured resins were evaluated as organic coatings for steel.

2. Experimental

2.1. Materials

Rosin with acid number 183 mg KOH g^{-1} was used. Acrylopimaric acid (APA) adduct was synthesized and purified according to the known method [9,10]. Diacrylate and dimethacrylate vinyl ester resins based on rosin acid MPA were prepared as reported in the previous work [11]. The diacrylate and dimethacrylate resins based on rosin acrylic acid and maleic anhydride adducts were designated as AEMPAE and MEAMPAE, respectively. Maleic anhydride (MA), acrylic acid (AA), ethylene glycol (EG), triphenyl phosphite, epichlorohydrine (EC), *p*-toluenesulfonic acid monohydrate (PTSA) and organic solvents were analytical grade products (Aldrich Chemical Co.). Methyl ethyl ketone peroxide (MEKP) and cobalt octoate (Co) were used as initiator and accelerator, respectively. MEKP was supplied as a 50% paste in dimethyl phthalate. The Co was a 10% solution in styrene. All materials were used without further purification.

2.2. Technique

2.2.1. Synthesis of unsaturated polyester of rosin

The UP resins were prepared by the reaction of 1.1 mole of glycols, such as EG, PG with 0.35 mole of APA, 0.35 mole of MA and 0.35 mole of saturated aromatic and aliphatic acids, such as adipic acid and phthalic anhydride. The polyesterification reactions were carried out under a slow stream of dry nitrogen gas. The reactants were heated to 180 °C in about 1.5 h. The temperature was then persevered at 180 °C for about 3 h and finally raised up to 200 °C and maintained till the expected water quantity was removed. The extent of reaction was determined by monitoring the water volume. The reaction was cooled under nitrogen to 60 °C at the end of reaction. About 1000 ppm of hydroquinone is added as inhibitor to avoid the polymerization of the product.

The unsaturated polyester (UP) resin was dissolved in adequate amount of CH_2Cl_2 and then an equal volume of distilled water was added to the reaction products. The organic layer was separated and the solvent was evaporated. The polyester was viscous liquids having dark yellow to pale brownish color.

2.3. Measurements

The hydroxyl and acid values of the synthesized resins were determined by the conventional acetic anhydride/pyridine method as reported in the previous work [9,10].

Infrared spectra of the prepared compounds were recorded in polymer/KBr pellets using Mattson – Infinity series FTIR Bench Top 961.

^{1}H NMR spectra of prepared resins and polyamide hardeners were recorded on a 270 MHz spectrometer W-P-270 & Y Bruker. The solutions for ^{1}H NMR analysis were prepared by dissolving the prepared compounds in $CDCl_3$.

Transition temperature of epoxy binders was measured with DuPont 2100 differential scanning calorimeter at heating rate of 10 °C/min. Dynamic curing was performed in DSC to observe the curing behavior of epoxy binders. Dynamic curing was performed at a heating rate of 20 °C/min.

2.3.1. Curing exotherms

The curing exotherms of the vinyl ester and styrene resins were measured using MEKP as initiator and Co as accelerator, as described in the previous work [9,10]. The UP was dissolved in 40% (w/w) of styrene monomer. The curing exotherms were determined at temperatures ranging from 35 to 55 °C. The concentrations of MEKP and Co were 2% and 0.2% (w/w) with respect to the total weight of the cured samples.