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Synthesis and characterization of high thermally stable poly(Schiff) epoxy coatings

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Abstract

Epoxy resins were prepared from Schiff base monomer and polymer through two steps. The first step is based on reaction of salicyladehyde or $5,5^{-}$-methylene-bis-salicylaldehyde with *o*-phenylene diamine. The second step includes the reaction between Schiff base monomer or polymer with epichlorohydrine (EC) to produce epoxy resins. The chemical structures of both Schiff base monomers and polymers were determined by elemental analysis, IR and ^{1}HNMR spectral analyses. The molecular weights of the produced epoxy resins were determined by GPC technique. The chemical structures and epoxy functionality were determined by ^{1}HNMR analysis. The prepared epoxy resins were cured with diamine based on pentaethylene hexamine (PEHA) and *p*-phenylene diamine (PDA). The thermal stability of the cured resins was evaluated by DSC and TGA analysis. Thermal stability data indicate that the cured epoxy resins with aromatic amine possess higher thermal stability than that cured with aliphatic amine. The cured epoxy–amine systems were evaluated in coating applications of steel by measuring the mechanical properties and chemical resistance of the cured films.

Keywords: Schiff base epoxy; Thermal stability; Polyamine; Poly(Schiff base); Coating

1. Introduction

Among the different resinous materials utilized in polymeric applications, epoxies exhibit excellent electrical properties, good adhesion to a material having polar groups, low curing temperature, shrinkage on curing, good impact resistance and moisture resistance [1–5]. The development of new epoxy resins has been carried out on two aspects of the epoxy resins namely, development and modifications of newer epoxy resins, and their applications in manufacturing composites, coatings, adhesives, paints, varnishes, construction materials [6–8] and some other advanced fields.

Schiff base inhibitors have been previously reported as effective corrosion inhibitors for steel, copper and aluminium [9–11]. The mechanism of corrosion protection of these materials was referred to adsorption of these substances on the metal surface. It was reported that, the adsorption depends not only on the nature and charge of the metal but also on the chemical structure of the inhibitor. The main drawback of these materials was referred to poor thermal stability and solubility. In this respect, this work aims to prepare Schiff base epoxy resins to enhance their thermal stabilities. The thermal characteristics and curing exotherms were measured in the presence of aromatic and aliphatic amines as curing agents. On the other hand, the cured Schiff base epoxy derivatives were evaluated as protective coating systems for steel. The chemical resistances were also evaluated to use these epoxy resins in the coating of petroleum equipments.

2. Experimental

2.1. Materials

Salicylaldehyde, *o*-phenylene diamine, epichlorohydrine (ECH) and trioxane were obtained from Aldrich Chemical Co., and used without purification. *p*-Phenylene diamine (PDA) and pentaethylenehexamine (PEHA) were used as curing polyamines and purchased from Aldrich Chemical Co. Acetic acid glacial, sodium hydroxide, sulphuric acid were obtained from ELNASR PHARMACEUTICAL Co. (Egypt). All solvents were purchased from Aldrich Chemical Co. (Germany).

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2.2. *Methods and techniques*

2.2.1. *Synthesis of Schiff base of monomer*

The dibasic Schiff base monomer was prepared by refluxing *o*-phenylenediamine (27 g, 0.25 mol) and salicylaldehyde (61 g, 0.5 mol) in 200 ml absolute ethanol. The reaction temperature was gradually increased up to reflux and maintained at this temperature for 3 h. The reaction mixture was cooled at room temperature to filtrate the solution. The precipitate was washed and dried in vacuum oven to give the product as a fine yellow powder. The reaction yield, melting point were 61% and 163.5 °C, respectively.

2.2.2. *Synthesis of Schiff base (5,5⁻-methylene-bis-salicylaldehyde)*

Salicylaldehyde (80 g, 0.655 mol), glacial acetic acid (50 ml) and trioxane (7 g) were charged in reaction flask with stirring. Mixture of 0.5 ml concentrated sulfuric acid and 2.5 ml of glacial acetic acid was added slowly using drooping funnel and the mixture was stirred. The reaction temperature was increased up to 90–95 °C under nitrogen atmosphere. The temperature was maintained for 22 h with stirring. The reaction temperature was cooled and the mixture was poured into 3 l of ice water and allowed to stand overnight. The solid product was filtered and extracted twice with 100 ml of petroleum ether to remove water phase. The isolated solid was recrystalized from 150 ml acetone.

2.2.3. *Synthesis of polymer of Schiff base*

A three-necked flask (0.5 l capacity) equipped with a condenser, magnetic stirrer, thermometer and dropping funnel was charged with 5,5⁻-methylene-bis-salicylaldehyde (15 g), absolute ethanol (50 ml) and glacial acetic acid (200 ml). A solution of *o*-phenylenediamine (6.66 g) in glacial acetic acid (100 ml) was added slowly using dropping funnel. After 10 s a bright yellow precipitate was formed. Methanol (50 ml) was added with stirring. The solid product was isolated by filtration and washed with methanol.

2.2.4. *Synthesis of epoxy resins from Schiff Base monomers*

A three-necked flask (0.5 l capacity) equipped with a condenser, magnetic stirrer, thermometer and dropping funnel was charged with Schiff base monomer (31.6 g, 0.1 mol) and epichlorohydrine (92 g, 1 mol). The reaction mixture was stirred at temperature 40 °C under nitrogen atmosphere for 1 h. The reaction temperature was raised up to 90–100 °C. Sodium hydroxide (8 g, 0.2 mol in 16 g water) 50% concentrated solution was transferred to dropping funnel and added to the reaction flask within 2 h with stirring. The reaction temperature was raised up to reflux for 1 h at 90–100 °C. The obtained resins were isolated under pressure using rotary evaporator.

The same reaction condition was used to obtain epoxy binder based on Schiff base polymer.

2.2.5. *Curing of the prepared epoxy resins*

Pentaethylenehexamine (PEHA) and *p*-phenylene diamine (PDA) were used as curing agents for the curing of Schiff base monomer and polymer. Epoxy binders were mixed with (PDA) as curing agents in methyl ethyl ketone (MEK) as solvent to prepare 90% solution of the reaction mixture. After evaporation of the solvent at room temperature, the mixture was dried perfectly in vacuum oven and stored at −10 °C before use to prevent the curing reaction of the mixture. The weight ratios between epoxy binders were ranged between 4:1, 3:1, 2:1 and 1:1 as weight of epoxy:weight of curing agent. Cured network of epoxy binders was prepared after curing at 180 °C for 2 h and post-curing at 230 °C for 2 h.

2.2.6. *Measurements*

The epoxy content of resins is frequently expressed as weight per epoxide or epoxide equivalent weight (EEW) and epoxy functionalities were determined according pyridine/HCl method [12].

The nitrogen content was measured with a Tecator Kjeltech auto analyser. A Tecator 1007 digester was used for the initial digestion of the samples.

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

^{1}HNMR spectra of prepared resins were recorded on a 270 MHz spectrometer W-P-270 & Y Brulker using $CDCl_3$ solvent. Molecular weights of epoxy resins were determined by using a Muffi detector GPC Waters 600-E equipped with Styragel column.

Transition temperature of epoxy binders was measured with DuPont 2100 DSC 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.

Thermal stability of epoxy binders was determined by Perkin Elmer TGA 7 system under N_2 gas flow at heating rate of 10 °C/min. The start and final temperatures were 25 and 600 °C, respectively.

2.2.7. *Testing of the coatings*

It is common to use mild steel panels (15 cm × 10 cm) to evaluate the different properties of coatings. The other side of panels is coated and protected against corrosion environments by using coal tar epoxy primer. Then the panels are subjected to different testing procedure to evaluate their mechanical properties and their durability. Adhesion strength, mechanical properties (pencil hardness, impact, T-bend tests), chemical resistances (hot water, acid and alkali resistance, salt spray resistance and solvent resistance) were measured according to ASTM methods as reported in a previous study [13].

The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl and 5% of NaOH aqueous solutions using distilled water. The duration of the test was 90 days at 311 K. The degree of adhesion and visual inspection of blister and cracks were evaluated for the coated panels.

3. Results and discussions

The choice of inhibitors (paints, coats and corrosion inhibitors) against metal corrosion in many environments is