



ELSEVIER

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

A self-curing, thermosetting resin based on epoxy and organic titanium chelate as an anticorrosive coating matrix for heat exchangers: Preparation and properties

Gongwen Tang, Kaiqiang Zhang, Zhishan Yan, Linrong Ma, Xin Huang*

The Institute of Seawater Desalination and Multipurpose Utilization, SOA, Tianjin, China

ARTICLE INFO

Article history:

Received 26 July 2016

Received in revised form 13 October 2016

Accepted 15 October 2016

Available online xxx

Keywords:

Self-curing

Coating

Heat exchanger

Epoxy resin

Organic titanium

ABSTRACT

A self-curing, thermosetting resin containing epoxy groups and organic titanium chelate bonds was synthesized by varying the concentrations of bisphenol A epoxy resin (EP) and diisopropoxy-bis ethylacetato titanate (SG). The structural characterizations via Fourier transform infrared spectroscopy and ^{13}C nuclear magnetic resonance confirmed the successful preparation of the self-curing, thermosetting EP-SG resin. The storage stability of the EP-SG resin was determined by measuring the change in viscosity at 50 °C. The curing behavior and thermal stability were assessed via differential scanning calorimetry and thermo-gravimetric analysis. The mechanical properties of the cured coatings were discussed in the context of the corresponding standards. The chemical resistance was tested using an immersion test. Our study revealed that the EP-SG resin has very good storage stability and can be cured via heating without the use of any curing agents. This advantage avoids the issues of non-uniformity, bubbles, and incomplete solubility of the curing agents in the epoxy resins. The resin possesses good thermal resistance, excellent physical and mechanical properties, and good chemical resistance, which makes it suitable for use as a heavy-duty coating for heat exchangers.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Heat exchangers play a very important role in petrochemical refineries. They are used in various processes including conversion, utilization, and recovery of thermal energy [1]. Corrosion protection is critical for heat exchangers since they are frequently exposed to severe conditions and are costly to maintain [2–4]. Thus, there is a commercial interest in reducing or avoiding corrosion of heat exchangers. Heat exchangers used in the petroleum industry are typically made of low-carbon steel, which is prone to corrosion and requires periodic replacement. To reduce replacement costs, high-nickel alloys and stainless steels are commonly used in place of carbon steel. However, they are much more expensive than low-carbon steel, which limits their range of application [5]. Once inexpensive carbon steel tubes are coated with a low-cost, thermally conductive coating that provides corrosion resistance equal to that of high-grade alloy steels, the capital cost of geothermal heat exchangers can be reduced considerably [6]. Naturally, some attention has been paid to the development of corrosion-resistant

coatings for carbon steel exchangers. For example, Holberg et al. [7] prepared urea-siloxane hybrid coatings from a dipodal diurea silane and methyltriethoxysilane via the sol-gel method. These coatings combine corrosion protection with scratch and solvent resistance in a single layer. They also enable the incorporation of polydimethylsiloxane (PDMS) to achieve repellent properties. The coating was applied to plate heat exchangers mounted on North Sea oil platforms in order to prevent crude oil-derived fouling. Sugama et al. [8,9] designed and developed several poly(phenylenesulfide)-based coating systems aimed at extending the useful lifetimes of the carbon steel heat exchanger tubes used in geothermal binary-cycle power plants operating at temperatures up to 160 °C. In addition, a fluoropolymer and a hybrid epoxy/fluoropolymer resin were studied for their potential use in preventing corrosion of the carbon steel pipelines used in the petroleum industry [5]. However, to the best of our knowledge, nearly all of the anticorrosion coatings for heat exchangers are multi-component systems, which require a curing agent for crosslinking. Thus far, no single-component, self-curing coating for heat exchanger anticorrosion protection has been reported.

Epoxy resins, a very important class of thermosetting polymers, are widely used as protective coatings and adhesives due to their outstanding performance in terms of corrosion protec-

* Corresponding author.

E-mail address: 13752134728@163.com (X. Huang).

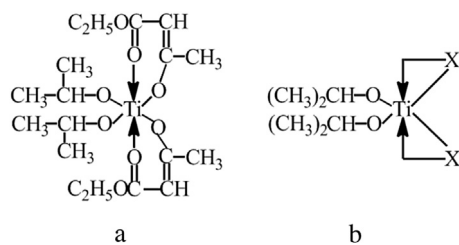


Fig. 1. (a) Molecular structure and (b) skeleton symbol of SG.

tion, chemical resistance, and adhesion [10,11]. Synthetic resins typically require curing agents with functional groups such as hydroxy groups, carboxyl groups, or amino groups for crosslinking. Unfortunately, non-uniformity and insolubility, which cause coating defects, are unavoidable in two-component systems because of differences in the solubility parameters of the epoxy resin and curing agents [12]. The importance of avoiding coating defects is clear: non-defective anticorrosive coatings may have lifetimes of up to 20 years. In contrast, the lifetime of a coating that contains physical damage is much shorter. In addition, the properties and quantities of the curing agents also affect the final properties of the crosslinked resin [13]. Single-component, self-curing epoxy resin coatings have gained attention because of their long pot life, convenience, and ability to cure without an agent. Chen et al. [14] designed a self-curing system of amino-terminated and carboxyl-containing polyurethane and a carboxyl-containing epoxy resin with a latent curing agent in the water phase. However, this self-curing system requires two components and a latent curing agent. Mikroyannidis [15] synthesized a new series of resins, including eight structurally different, self-curing epoxy compounds with azomethine linkages. Free carboxy, amino, and phenolic hydroxy groups can be found in glycidyl ethers and esters, and can thermally crosslink without the presence of a curing agent. Huang et al. [12] synthesized a self-crosslinking compound with both epoxy groups and anhydride groups from tung oil fatty acids. However, trace amounts of a tertiary amine were needed for self-crosslinking. Without using any external crosslinking agents, Patel et al. [16] developed novel, self-curable, cathodically depositable coatings from glycidyl functional epoxy ester-acrylic graft co-polymers. The coatings showed good overall performance, which supports their use in the coating industry.

Over the past thirty years, extensive research on the use of metals and their salts in the formulation of epoxy resin systems has been carried out. This has included the use of organo-transition metal complexes as catalysts for epoxy resins when co-cured with amines, anhydrides, and phenolics [17]. Organo-transition metal complexes have also been added to improve physical properties such as adhesion, flexural strength, fracture toughness, water adsorption, and heat resistance [17]. Titanium alkoxides are superb catalysts for crosslinking of epoxides [18]. Diisopropoxy-bis ethylacetoacetato titanate (SG) has two isopropoxy groups and two ethylacetoacetato ligands. SG is primarily used to improve the heat, chemical, and water resistances of printing inks, paints, coatings, and other products.

Our goal is to prepare a thermally self-curing paint with a long storage life for the prevention of heat exchanger corrosion in petrochemical refineries. In the present study, a self-curing bisphenol A epoxy resin, EP-SG, was synthesized using different molar concentrations of EP and SG. This EP-SG resin contains free hydroxy, epoxy, and titanium chelate groups, which can be thermally crosslinked without the addition of a curing agent or catalyst. The polymerization mechanism and curing behavior of the EP-SG resin were investigated via Fourier transform infrared spectroscopy (FTIR), ¹³C nuclear magnetic resonance (NMR), and gel permeation chro-

matography (GPC). The storage stability of the EP-SG resin was studied by detecting changes in the kinematic viscosity of the solution. Moreover, the thermal, physical, and chemical properties of the cured EP-SG coatings were also evaluated via various techniques.

2. Materials and methods

2.1. Materials

Bisphenol A epoxy resin (EP) was supplied by Jiangsu Sanmu Co., Ltd., China. Diisopropoxy-bis ethylacetoacetato titanate (SG) was purchased from the E.I. Du Pont Company, USA. Xylene, isopropanol and other chemicals were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China and used as received.

2.2. Preparation of the self-curing EP-SG resin

First, a certain amount of EP was dissolved in a xylene/isopropanol solvent mixture to obtain a 55 wt% solution. A quantity of the above EP solution was added to a three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer, and circulating water condenser. Then, the required SG was added to the round-bottomed flask. Finally, the above mixture was stirred vigorously for two hours at either room temperature or 80 °C. The resulting EP-SG resins prepared at room temperature or 80 °C were marked as EP-SG (R) and EP-SG (H) respectively, to study the effect of the reaction temperature on the resins and their coating properties. EP-SG resins with SG concentrations of 5%, 15%, 30%, and 50% with respect to EP were marked as EP-SG (5% SG), EP-SG (15% SG), EP-SG (30% SG), and EP-SG (50% SG), respectively.

2.3. Preparation of cured EP-SG coatings

For preparation of cured EP-SG coatings, a certain amount of the xylene/isopropanol solvent mixture was added to the EP-SG resin and stirred until the viscosity of the mixture was suitable for casting. Galvanized iron sheets were polished with successively fine grades of sandpaper and then washed thoroughly with acetone before further use. The above EP-SG resin solution was coated onto the treated galvanized iron sheets and dried at room temperature for 1–3 h, until the surfaces of the coatings were dry. Then, all coated samples were cured at 160 °C for 2 h in an air-circulating oven. Dried, uncured EP-SG coatings were marked as EP-SG (uncured) and cured EP-SG coatings were marked as EP-SG (cured).

2.4. Characterization

FTIR spectra were recorded in a Spectrum 100 FTIR spectrometer (FTS3000, BIORAD, USA), in the range of 4000 cm⁻¹–400 cm⁻¹. The solid-state ¹³C NMR spectra were recorded on a JNM-ECA400 (JEOL Co. Ltd., 100 MHz). The EP-SG (uncured) and EP-SG (cured) resins were pulverized into powder and put into zirconium sample tubes. The ¹³C NMR spectra were characterized using the CP/MAS method.

The weight average (*M_w*) molecular weights and molecular weight distributions (PDI) of EP and the EP-SG resins were determined via gel permeation chromatography (GPC). Samples were dissolved in tetrahydrofuran and filtered with a 0.22 μm filter. GPC measurements were carried out at a flow rate of 1 mL min⁻¹ and a temperature of 35 °C using polystyrene standards for calibration.

A Tu-4 cup was used to measure the viscosity of the EP-SG resin solution under isothermal conditions. The EP-SG resin solution was placed in a water bath at 25 °C for 2 h and its original viscosity was measured. Then, the resin was placed into an air-circulating oven at 50 °C. At preset time points, the sample was removed and cooled to 25 °C so that its viscosity could be measured. The storage stability

Download English Version:

<https://daneshyari.com/en/article/4999380>

Download Persian Version:

<https://daneshyari.com/article/4999380>

[Daneshyari.com](https://daneshyari.com)