



Self-curing poly (2, 6-dimethyl-1, 4-phenylene oxide)-organic titanium chelate resin for thin anticorrosive coatings



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

The Institute of Seawater Desalination and Multipurpose Utilization, State Oceanic Administration, Tianjin, China

ARTICLE INFO

Keywords:

Self-curing

Coating

Poly (2, 6-dimethyl-1, 4-phenylene oxide)

Organic titanium chelate

Anticorrosive

ABSTRACT

Poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) has been extensively investigated as an outstanding engineering plastic. Functionalized PPO with low molecular weight has been widely studied to expand its applications, while there are relatively few reports on PPO-containing coatings. In this work, a terminal phenolic hydroxyl group PPO (RPPO) with low molecular weight was synthesized by redistribution of high molecular weight commercial PPO with bisphenol A via benzoyl peroxide as an initiator. The self-curing, thermosetting RPPO-organic titanium chelate resins were first developed via the reaction between phenolic hydroxyl groups in RPPO and isopropoxy groups of diisopropoxy titanium bis (acetylacetonate). Thin coatings with 10 μm thickness could be obtained by heat curing without any curing agents. Characterization using Fourier transform infrared spectroscopy and ^{13}C nuclear magnetic resonance showed evidence of the successful preparation of the self-curing, thermosetting resins. The curing behavior and thermal stability were assessed via differential scanning calorimetry and thermogravimetric analysis. The mechanical properties of the cured coating were discussed and the chemical resistance was tested using accelerated immersion tests. Benefited by the self-curing mechanism, issues of non-uniformity, bubbles, and low storage stability caused by curing agents were avoided. It was found that the thin coating possessed good thermal and mechanical properties. Owing to the rigid aromatic chain structure and strong Ti-O bond in the crosslinked structure, the glass transition temperature was improved and the thermal degradation temperature could reach up to 402 $^{\circ}\text{C}$. No degradation was found after 72 h accelerated immersion tests in boiling water, boiling seawater and boiling butanone, which should be critical to the resin's potential application for anticorrosive coating.

1. Introduction

Poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) and its derivatives have been outstanding engineering plastics for more than 50 years [1–4]. Attributed to its low dielectric constant, PPO is one of the materials with the potential to satisfy the demand for copper clad laminate, especially for use as the basic material in high-frequency printed circuit boards [5–7]. Commercial physically modified PPO has been widely adopted ascribed to its high glass transition temperature (approximately 212 $^{\circ}\text{C}$), low water absorption, low flammability and high dimensional stability [8,9]. In addition, PPO has been used to improve the fracture toughness of thermosetting networks, which extends its performance in the automobile and machinery industries [10,11].

However, high molecular weight thermoplastic PPO possesses high melt viscosity and poor film-forming ability, which limits its processing and final application. Moreover, the low resistance to non-polar solvents and non-curable nature also discount its use [2,3]. Therefore, control of the molecular weight of PPO is an important issue for

modifying their properties. It is noteworthy that different from the traditional physical modification, low molecular weight PPO with functionalized groups can be obtained by chemical modification.

The redistribution of high molecular weight commercial PPO to increase reactive functional groups in per chain is an elegant chemical modification method [12–15]. Well-studied by White and others, many redistribution processes for producing low molecular weight PPO with phenolic, epoxide or vinyl-terminated groups have been developed [12,15]. In addition, low molecular weight PPO can also be prepared by the oxidative polymerization of 2, 6-dimethyl phenol in the presence of a copper-amine-complex catalyst under oxygen. By introducing bromo, vinyl, and epoxide groups into PPO sequentially, a new class of thermosetting polymers with PPO as the backbone were synthesized [16–22]. Interestingly, attributed to the absence of polar groups in the polymer backbone, PPO possesses excellent separation properties that make them suitable candidates for gas separation [18,19]. Through further reactions such as quaternization and functionalization with hindered fluorene side chains, PPO can be employed to prepare proton

* Corresponding author at: The Institute of Seawater Desalination and Multipurpose Utilization, State Oceanic Administration, Tianjin, 300192, China.
E-mail address: 15822982856@163.com (X. Huang).

and anion exchange membranes [20–22]. However, to the best of our knowledge, no PPO-containing coating for anticorrosion protection has been reported.

Titanium chelates are formed from tetraalkyl titanates or halides and bi- or polydentate ligands. They are known to react easily with active groups to form complexes with significantly different properties from the starting materials [23–26]. Titanates are often used in epoxy-based paint, because they can promote hardening of epoxy resins and improve adhesion of metals to epoxies [23,24]. The phenolic compounds can react with the organic titanate to form a highly colored titanium phenolate and can be crosslinked by heating. The acetylacetonate complexes of titanium function as adhesion promoters for the ink binder while also improving the cold-storage stability of the products [23,25]. Due to titanium's high affinity for oxygen atoms, titanium chelates can bond to oxide surfaces, to yield a scratch-resistant oxide coating [26].

Recently, single-component, self-curing coatings have gained attention because of their long pot life, reducing the probability of coating defects, convenience, and ability to cure without an agent [27–29]. For example, novel self-curable cathodically depositable coatings were developed from glycidyl functional epoxy ester-acrylic graft co-polymer without using any external crosslinking agents [27]. In our previous work, a self-curing, thermosetting resin (EP-SG resin) based on epoxy and organic titanium chelate were prepared as an anticorrosive coating matrix for heat exchangers [29]. Benefited by the self-curing mechanism, the resin has good storage stability and can be stored for more than one year without gelation.

Given the diversity and wide usage of PPO in blending modification, high-frequency printed circuit boards and exchange membranes, there are few studies about PPO-containing anti-corrosion coatings. The goal of our present work is to fill that gap. In this research, a self-curing PPO-organic titanium chelate resin with a long pot life, was synthesized using redistributed PPO (RPPO) and diisopropoxy titanium bis (acetylacetonate) (GBA). Without the addition of a curing agent or catalyst, thin coatings with potential for use in corrosion prevention can be obtained by thermal crosslinking. The reaction mechanism of the PPO-GBA resin was investigated via Fourier transform infrared spectroscopy, ^{13}C nuclear magnetic resonance. The curing behavior and thermal stability were assessed via differential scanning calorimetry and thermo-gravimetric analysis. Moreover, the mechanical properties as well as the effect of the RPPO and GBA on chemical resistance performance were investigated.

2. Experimental methods

2.1. Materials

PPO ($M_n = 28500$, polydispersity index (PDI) = 2.5) was supplied by Nantong Xingchen Synthetic Material. Co. Ltd, Ruicheng Branch. Bisphenol A (BPA) and benzoyl peroxide (BPO) were purchased from J & K Scientific, China, and used as received. Diisopropoxy titanium bis (acetylacetonate) ($\text{Ti}(\text{CH}_3\text{COCHCOCH}_3)_2(\text{C}_3\text{H}_7\text{O})_2$) solution (75 wt.% in isopropanol) was purchased from the E.I. Du Pont Company, USA. Tinplate sheets and carbon steel bars were purchased from Dongguan Dalai Instrument Co., Ltd. Toluene, xylene, tetrahydrofuran (THF) and methanol were obtained from Tianjin Heowns Biochem Technologies LLC, Tianjin, China. All other reagents were supplied by Tianjin Kernel Reagent Co., Ltd, China, and used without further purification.

2.2. Synthesis of redistributed PPO (RPPO)

The redistributed PPO (RPPO) was prepared according to the literature method [12,13]. Briefly, PPO (20 g, 0.7 mmol) and BPA (1.84 g, 7 mmol) were dissolved in 100 mL toluene at 90 °C under argon atmosphere. Subsequently, BPO (0.58 g, 2.1 mmol) was added dropwise over 1 h. After maintaining the reaction at 90 °C under an argon

atmosphere for another 6 h, the mixture was allowed to cool to room temperature and then added to methanol to precipitate the product. The resulting product was collected by filtration and then dried in a vacuum oven at 80 °C. The dried product was ground to powder, washed with methanol several times, and finally obtained.

2.3. Preparation of the RPPO-GBA resin

RPPO-GBA resin was prepared by weighing the desired ratio of RPPO and GBA (20 wt.% GBA with respect to RPPO) into a glass jar. Then, the blend ingredients were dispersed in xylene (4:1 w/w solvent/blends) using an ultrasonic vibrator (100 W, 40 kHz) for 30 min. Finally, the obtained resins were sealed for further use.

2.4. Preparation of the RPPO-GBA coating

The tinplate sheets with dimensions of 120 mm × 35 mm × 0.2 mm were used as substrates for the physical and mechanical tests. The sheets were prepared using sandpaper with grit sizes of 800, rinsed thoroughly with acetone and ethanol, and then air-dried prior to use. For the immersion tests, carbon steel bars with 100 mm long and 10 mm in diameter were also treated similarly. According to the GB/T1727-1992 standard, the above RPPO-GBA resin solution was dip-coated onto the treated iron sheets or carbon steel bars, then dried at room temperature for 1 h. All coated samples were cured at 200 °C for 2 h in an air-circulating oven. Attributed to the low solution concentration (20 wt.%), the dry film thickness of all samples was measured to be $10 \pm 2 \mu\text{m}$. The thickness of the coating was measured by means of an electromagnetic thickness gauge according to ISO 2808.

2.5. Characterization

The relative molar mass and PDI of the prepared RPPO were determined using gel permeation chromatography (GPC, Waters 1515–2414). The flow rate was 1 mL/min of THF at 40 °C. The structure analyses of the RPPO-GBA resins upon curing were conducted using Attenuated Total Reflectance FTIR (ATR-FTIR) and ^{13}C solid-state nuclear magnetic resonance (NMR) spectra. ATR-FTIR spectra were recorded using a spectrum 100 FTIR spectrometer (FTS3000, BIORAD, USA) in the range from 4000 cm^{-1} to 400 cm^{-1} . The RPPO-GBA coating was cured at 200 °C for 2 h and then used as the IR sample. The solid-state ^{13}C NMR spectra were recorded on a JNM-ECA400 (JEOL Co. Ltd., 100 MHz). The RPPO-GBA resins and cured coatings were pulverized and put into zirconium sample tubes. The ^{13}C NMR spectra were characterized with the CP/MAS method.

In order to determine the reaction process, research the thermal stability of the coating and find an ideal curing temperature, the curing behavior and thermal stability of RPPO-GBA resin was assessed with differential scanning calorimetry (DSC) and thermo gravimetry analysis (TGA). TGA was performed with a simultaneous thermal analysis (DSC/DTA-TG, NETZSCH, STA 409 PC Luxx[®], Germany) under a nitrogen atmosphere at a heating rate of 10 °C/min from 30 °C to 500 °C. DSC was performed with a diamond differential scanning calorimeter (NETZSCH DSC 200 F3, Germany) under a N_2 atmosphere. The samples were first heated at 10 °C/min from 50 °C to 280 °C and held for 5 min, and then cooled to 50 °C at 10 °C/min. They were maintained at 50 °C for 5 min and then heated to 280 °C at 10 °C/min again. The glass transition temperature (T_g) of each cured sample was determined by the second heating scan.

The pencil hardness of the RPPO-GBA coatings was determined using standard pencils according to ASTM D3363-74. Flexibility was tested using the QTX-Paint Film Flexibility Tester (Dongguan Dalai Instrument Co., Ltd) according to GB/T 1731–1993 standard. The flexibility is presented by the smallest diameter of mandrel bar in which cracking was not observed. Impact strength was measured by an impact testing machine (Tianjin Weida Testing Machine Manufacturer) with a

Download English Version:

<https://daneshyari.com/en/article/4999086>

Download Persian Version:

<https://daneshyari.com/article/4999086>

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