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Corrosion protection of waterborne epoxy coatings containing mussel-inspired adhesive polymers based on polyaspartamide derivatives on carbon steel

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ABSTRACT

A novel mussel-inspired adhesive polymer (PHEA-DOPA) containing the 3,4-dihydroxyphenylalanine (DOPA) functional group based on polyaspartamide derivatives was synthesized. The corrosion protection of the waterborne epoxy coatings containing the adhesive polymers was investigated by electrochemical impedance spectroscopy (EIS). The results indicated that the PHEA-DOPA could improve the corrosion resistance of the waterborne epoxy coating. The corrosion products were also analyzed by Raman microspectroscopy (RM), indicating the formation of the insoluble DOPA-Fe complexes on the carbon steel surface. These complexes simultaneously acting as a passivating layer, can inhibit the process of corrosion at the metal-solution interface. The differential scanning calorimeter (DSC) measurement indicated that PHEA-DOPA can increase the crosslinking density of coating. The effect of O_2 on the protective mechanism of the PHEA-DOPA coating in a 3.5% NaCl solution was also evaluated by EIS. The results indicated that the barrier effect was significantly improved under aerated conditions because DOPA was oxidized to DOPA–quinone (Dq) by O_2, which triggered the reaction with Fe ions that were released from the surface of the carbon steel. This led to more compact coatings.

1. Introduction

Carbon steel is an excellent material and is widely used in ships, platforms, buildings, bridges, etc. However, it suffers from corrosion in inland and marine environments. Corrosion is the degradation of metal materials due to their interaction with corrosive ions in the environment. It not only results in a huge economic loss but can also have serious impacts on the environment and human health/safety [1–4]. Corrosion control is very important for reducing the societal costs by extending the lifetime of metallic materials. Coating protection is an economic and effective method of corrosion control. Epoxy coatings have good chemical resistance and good adherence. They are widely used on carbon steel substrates to control corrosion. Recently, waterborne epoxy coatings have attracted great interest due to the environmental concerns. However, the application of waterborne epoxy coatings is limited by their poor protective properties. These poor properties can be improved by adding corrosion inhibitors that cover the corrosion-sensitive site and form dense films via a crosslinking reaction [5].

Traditional corrosion inhibitors exhibit negative impacts on the environment and human health [6]. Over time, numerous traditional inhibitors have been restricted due to increasingly strict environmental regulations and increased awareness of environmental and health issues. Thus, there is an urgent need for new environmental corrosion inhibitors [7].

Mussel adhesive proteins (MAP) extracted from *Mytilus edulis* are non-toxic materials that have attracted considerable attention for their strong adhesive interactions over a range of substrates. Mefp-1 was the first to be isolated and purified from blue mussels. It can protect against the corrosion of carbon steel by forming a complex with the substrate [8–10]. However, it cannot adapt to the market due to its complex extraction method, low yield, and high cost [11]. The 3,4-dihydroxyphenylalanine (DOPA) molecule is responsible for the MAP mechanism, and catechol is the critical functional group of DOPA [12]. Hence, catechol plays a key role in the special properties of MAP [13]. As an alternative to MAP, adhesive polymer materials containing the catechol functional group

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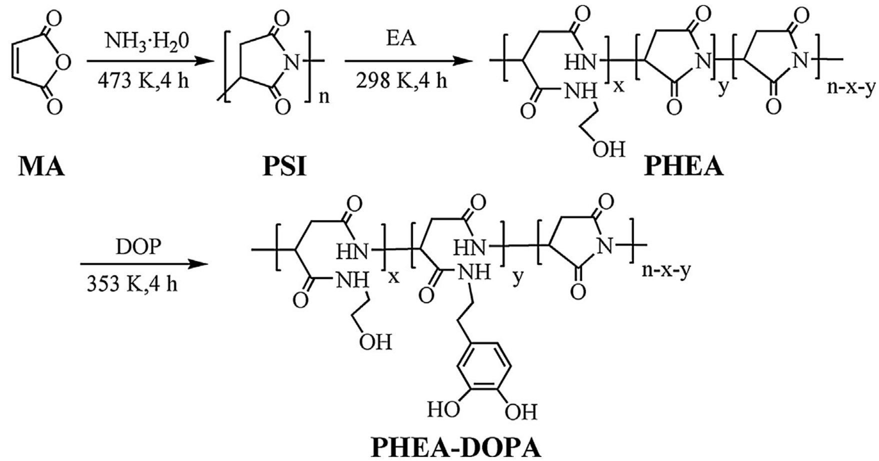

Fig. 1. Reaction scheme for the PHEA-DOPA synthesis.

can be obtained synthetically. This synthetic process is simple with common raw starting materials, which is beneficial to industrial applications.

Here, catechols were introduced to the side chain of polyaspartamide derivatives (PHEA-DOPA) as non-toxic corrosion inhibitors to provide inhibiting properties that mimic the MAP structure and prevent carbon steel corrosion. To the best of our knowledge, no reports on the corrosion performance of this polymer incorporating waterborne epoxy coatings on carbon steel has yet been reported.

First, we synthetized a novel inhibitor based on polyaspartamide derivatives. Then, the protective ability of this inhibitor incorporated with waterborne epoxy coatings on carbon steel was investigated. The protective mechanism of the PHEA-DOPA coating was also discussed.

2. Experimental

2.1. Materials

Maleic anhydride (MA), ammonium hydroxide, *N*,*N*-dimethylformamide (DMF), and dopamine hydrochloride (DOP) were synthesized by Xiya Chemical Reagent Co., Ltd. Ethanolamine (EA), acetone, and sodium sulfite were purchased from Xilong Chemical Co., Ltd. Waterborne epoxy resin (6520) and polyamide (8537) were obtained from Momentive Co. (USA). Q235A carbon steel (composition wt%: C: 0.22, P:0.01, Si: 0.25, Cr: 0.01, Mn: 0.32, S: 0.05 and Fe balance) was used as the matrix. Waterborne epoxy resin, polyamide, and carbon steel were all industrial grade. All the other reagents were analytical grade, and used without further purification.

2.2. Synthesis of adhesive polymers modified by catechol group based on polyaspartamide derivatives

The reaction scheme for the PHEA-DOPA synthesis is shown in Fig. 1. MA (1 mol) was dissolved in 300 mL H_2O with constant stirring for 1 h. Then, 2 mol $NH_3 \cdot H_2O$ was added to the solution at 263 °C for 1 h. The mixture was subsequently cooled down to 200 °C under vacuum for about 4 h to obtain the polysuccinimide (PSI) product.

Next, 1 g of PSI was dissolved in 30 mL DMF in a three-neck flask and the ethanolamine (0.34 g) was added slowly at room temperature with constant stirring for 4 h. The reaction proceeded under a nitrogen atmosphere, and 0.06 g sodium sulfite was added at room temperature with stirring for 10 min. Subsequently, the DOP (0.38 g) was added at 90 °C in an oil bath and reacted for 4 h. The product was precipitated in 400 mL of cold acetone. The filtered product (PHEA-DOPA) was then dissolved in 5.5 g distilled water as the final addition inhibitor.

2.3. Coating preparation

The carbon steel samples were cut into cylinder shapes ($1\ cm^2 \times 5\ mm$), and the sides of the steel sample were sealed with an epoxy leaving a working surface area of $1\ cm^2$. The working surface of the specimen was ground by SiC paper over several steps down to 1200 grit finish. Then, the samples were cleaned in ethanol ultrasonically and dried under nitrogen flow before use.

The two-component water-based coatings were prepared using a waterborne epoxy resin and polyamide hardener from Momentive Co. To assess the anti-corrosive effects of the new inhibitors, the solution for coating preparation was loaded with 5 wt% (relative to the weight of the coating solution) of PHEA or PHEA-DOPA, and stirred for 10 min. A coating solution without any additives was also prepared as control. Three epoxy coatings were prepared: a blank coating (without additives, labeled EP coating), coatings loaded with PHEA (labeled PHEA coating), and a coating loaded with PHEA-DOPA (labeled PHEA-DOPA coating). The coatings were prepared by spraying method and cured at room temperature for 7 d. The dry film thickness was determined via a MiniTest 600 Coating Thickness Gage (Elektrophysik Corporation, USA); the thickness of the dry coatings were $60 \pm 5\ \mu m$ in this experiment.

2.4. Electrochemical studies

Electrochemical impedance spectroscopy (EIS) measurements were carried out on Metroum Autolab PGSTAT302N potentiostat (Netherlands). All the spectra were recorded at open circuit potential. A standard three-electrode cell was used including the coated carbon steel sample as a working electrode with an exposed working area of $1\ cm^2$ in 3.5 wt% NaCl solution, a Pt plate as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. The cell was placed in a Faraday cage to avoid interferences with external electromagnetic fields and stray currents. The frequency ranged from 100 kHz to 10 mHz. All the measurements were performed at room temperature. The software ZsimpWin (Princeton Applied Research, TN, USA) was used to analyze the data.

2.5. Physical and chemical characterization

2.5.1. Characterization of synthesized polymers

Fourier transform infrared spectroscopy (FT-IR) measurements of the polymer were carried out with a Nicolet IR10 (USA). The samples were tested via the FTIR-ATR method.