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Study on corrosion resistance of epoxy ester coating cross-linked by a new type of titanium ion curing agent

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ABSTRACT

With the environmental pollution caused by solvent-based coatings gets worse and worse, it is urgent to improve the anticorrosion property of waterborne coatings. As we all know, the coating showed better corrosion resistance because of the adding of curing agent. And tetra-*n*-butyl titanate is a coupling agent with excellent properties. But the waterborne epoxy coatings' feature of hydrolyzing easily limits its development. This study aimed to investigate the protection performance of the epoxy ester coatings with titanium ion curing agent (EC). To obtain excellent water resistant coatings, butyl titanate improved by ethylene glycol and triethanolamine is used as curing agent (ranged from 2 to 8 wt%) for epoxy ester resin. The chemical structures of the prepared coatings were analyzed by Fourier transform infrared spectroscopy (FTIR). And field emission scanning electron microscope (FESEM) was used to observe the coatings' surface morphologies. The corrosion resistance of the coatings was also examined by means of electrochemical impedance spectroscopy (EIS), surface topography and Copper-accelerated acetic acid-salt spray testing (CASS). From the FTIR spectra it was observed that demonstrated peak shift and changed in intensity with the adding of titanium ion curing agent. The corrosion resistance of the epoxy ester coating cured with titanium ion curing agent increased obviously. Its impedance reached 10^8 Ω cm^2, and it still remained as high as 10^7 Ω cm^2 even after immersion in 3.5 wt% NaCl solution for 40 days. Not only that, but the coating showed better corrosion resistance than other coatings when the curing agent's dosage increased to 5%. In addition, the observation of surface topography and CASS test confirmed with the results obtained from EIS.

1. Introduction

Coating is an effective approach to protect metal from rusting[1,2]. In recent years, the waterborne coatings have become an important development direction in the anti-corrosion coating industry as the global environmental pollution become more and more serious[3,4]. Virtually, the corrosion resistance of waterborne coatings is determined by the performance of waterborne coating textures and waterborne resin. In recent years, epoxy resin is widely used for anticorrosive coatings because of its excellent properties, such as strong adhesion, good chemical stability and remarkable mechanical capacity[5,6]. Although the waterborne technology of epoxy resin has been used for a long time, its drawbacks limit its application to a great extent, such as high brittleness, low impact resistance and poor corrosion resistance [7–10].

Hydrophobicity of coating, water absorption and cross-linking density influence its performance in isolating the steel from corrosive electrolyte[11–15]. There are mainly two ways to improve the anticorrosion performance of waterborne coatings. The most important way is to improve water resistance of the waterborne coatings because waterborne coatings are more hydrophilic than solvent-based coatings. They can absorb moisture from the air, and thus lose protection ability to metal[16]. Increasing the crosslink density of coating and adhesion to substrates is another good way to improve water resistance of the waterborne coatings[17]. Coatings with high cross-link density can effectively block corrosive mediums from reaching substrates, and a coating with high adhesion can prevent itself falling off from metal during service period. In fact, the curing process affects the both aspects deeply, and therefore most current studies have concentrated exclusively on the curing agent[18–22]. For instance, Lu et al. [20] studied the performances of epoxy coating cured by the triethylene tetramine (TETA) modified by silane, and he found that the cross-linking degree, hardness, adhesion and water resistance of coating were improved significantly. Mahendrasinh et al. obtained high-performance coatings using water compatible epoxies and water borne acrylamide, which was prepared from acrylamide, formalin and methanol[23]. Zhang et al. cured epoxy resin by a novel self-emulsifiable waterborne amine-terminated agent which displayed good thermal property,

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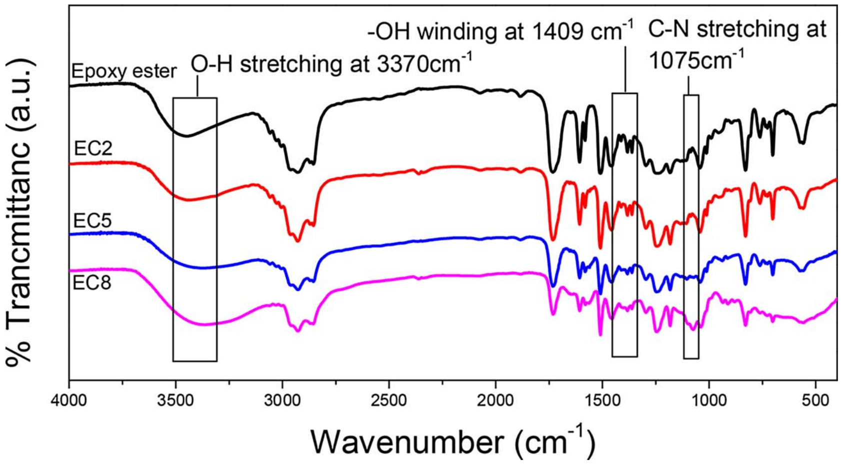

Fig. 1. FTIR spectra of epoxy ester EC2, EC5 and EC8 coatings.

hardness, toughness, adhesion, and corrosion resistance[24].

As mentioned before, the structure and curing process of the curing agent play an important role in the performance of epoxy resin coatings [25,26]. Tetra-*n*-butyl titanate has been widely used as a coupling agent in chemical industry due to its excellent cross-linking properties. However, its weakness of poor hydrolytic stability greatly limits its application in waterborne coatings and its use as epoxy resin curing agent has rarely been reported yet[27]. To address this problem, tetra-*n*-butyl titanate was improved with ethylene glycol and triethanol amine in this study to obtain the very structure of titanium ion cross-linker which can be stabilized in water. And then, it was used as a curing agent to solidify the waterborne epoxy ester resin to form a new type of waterborne coating. A series of characteristics of the corrosion resistant coatings were researched through electrochemical tests, immersion experiments, and CASS. Results showed that, epoxy resin cured by this modified titanium ion containing curing agent presented excellent corrosion resistance and hydrolytic stability.

2. Experiment

2.1. Materials

Tetra-*n*-butyl titanate and tris (2-hydroxyethyl) amine were provided by Sinopharm Group, ethylene glycol was purchased from Sigma-Aldrich (Shanghai) and waterborne epoxy ester was produced by Jiangsu Huaxia Paints Technology. All the materials were used without further purification. In addition, deionized water was made in a lab.

2.2. Methods

To prepare modified curing agent, 6.8 g of tetra-*n*-butyl titanate and 1.24 g of ethylene glycol were mixed at 70 °C for 30 mins at 1500 rpm. Then, 5.96 g of tris (2-hydroxyethyl) amine was added to the mixture and stirred at a high speed for 3 hrs at 85 °C. All the experiments were carried out in a distillation unit with nitrogen as protection gas.

Cold rolled mild steel sheets with dimensions of 120 mm × 70 mm × 5 mm were burnished using 400#, 800# and 1200# sandpaper, then cleaned with acetone and ethanol in an ultrasonic cleaning machine, and at last dried in the air. The surface profile of the specimens achieved grade Sa 2½ according to ASTM D4417-2003. 10 g of epoxy ester and curing agent mixtures that containing curing agent of 2%, 5% and 8 wt%., coded as EC2, EC5 and EC8 respectively, were prepared by constant stirring for 10 mins at 25 °C. After that, 30 g of water was added into the mixture and the stirring was conducted for another 10 mins. Finally, the steel samples were coated well by the prepared mixture via brushing and the thickness of the coating was monitored and controlled in the range of 65 ± 5 μm, which can be measured by Elcometer Kairda KD 5. Pure epoxy ester without curing agent was used as control. The coated samples be further tested later after drying oven at 80 °C for 3 h.

2.3. Testing and characterization

FTIR was carried out to perform qualitative analysis and trace the cross-linking process. ATR-Nicolet iS10 Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was used to record FTIR spectra in the transmittance mode. The data was collected in the wavenumber range of 400–4000 cm-1 at a resolution of 4.0 cm-1.

After sputtering with Pt alloy, scanning electron microscopy (SEM) was carried out using a ZEISS Merlin Compact (ZEISS, Germany) scanning electron microscope, operating at 15 keV. And the micro-topography of coating was measured. Electrochemical impedance spectroscopy(EIS) was conducted with a Solartron 2350 electrochemical interface and a Solartron 1260 impedance/gain-phase analyser. A standard three-electrode configuration consisting of the sample as a working electrode, a counter electrode (CE) and a saturated calomel electrode (SCE) were used to determine polarization behaviours. During the process and intervals of the electrochemical tests, the specimens were immersed in 3.5 wt% NaCl solution for up to 40 days. For each sample, the open circuit potential was first measured for a period of half an hour, and then, the impedance was measured and plotted via Zplot from the windows electrochemical impedance software at the sample's respective corrosion potential. A 10 mV (vs SCE) AC voltage was used as the imposed signal. In addition, the CASS was conducted according to the ISO 3770-1976 standards.

3. Results and discussion

3.1. Ftir

FTIR spectra of epoxy ester EC2, EC5 and EC8 coating are presented in Fig. 1. The absorption peak at 1409 cm^{-1} indicated bending vibrations of O—H in epoxy ester. With the increase of curing agent, it becomes weaker and weaker and even disappeared at last. This change is considered as an evidence that cross-linking can occur between epoxy ester and curing agent. The peak intensity of O—H stretching vibration at 3370 cm^{-1} increase, and at the same time, a stretching vibration peak of C—N appears at 1075 cm^{-1} when the dosage of the curing agent increased to 8%. It means that unnecessary curing agent remained in the coating and the initial dose was excessive. According to FTIR analysis, the proposed reaction between epoxy ester and the titanium ion curing agent was illustrated in Fig. 2. In general, the curing of epoxy ester coatings improved their barrier properties through forming a network of coating, which is beneficial to improve the corrosion