



Hydrophobic benzoxazine-cured epoxy coatings for corrosion protection

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ABSTRACT

A hydrophobic benzoxazine-cured epoxy coating (EPB) was prepared by a dip coating and thermal curing method using benzoxazine monomer (B-TMOS) as curing agent. Fourier transform infrared (FTIR) analyses confirmed the presence of thermal curing reactions and hydrogen-bonding interactions in the epoxy/polybenzoxazine system. The hydrophobicity of epoxy coatings induced by the incorporation of B-TMOS was enhanced significantly, and the water contact angles of resultant EPB coatings were higher than 98°. The corrosion protection ability of epoxy coatings was investigated by open-circuit potentials, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. The results showed that the charge transfer resistance (R_{ct}) of EPB coatings was increased by about three orders of magnitude compared with bare mild steel, and the protection efficiency values of all EPB samples were more than 98%. This increased corrosion protection property could be attributed to the high hydrophobic performance of EPB coatings.

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1. Introduction

Metallic corrosion causes considerable waste of natural resources. The annual cost of corrosion worldwide is estimated to exceed US\$ 1.8 trillion, which translates to 3–4% of the gross domestic product (GDP) of industrialized countries, even surpassing the loss caused by natural hazards [1]. Organic coatings have been employed to protect steel surfaces against versatile corrosion environments for a long time by introducing a barrier to prevent ionic transport and electrical conduction. The hydrophobic properties, water uptake and cross-linking density of the coating influence its ability for isolating the steel from corrosive electrolyte [2–6].

In the past decade, epoxy resins have been widely used as a coating material for corrosion protection, owing to its outstanding processability, excellent chemical resistance, high cross-linking density, and strong adhesion/affinity to substrates [7,8]. However, the high water uptake and hydrophilic nature of epoxy resins have hindered its application in humid conditions. Not only the absorbed water can deteriorate the thermal and mechanical properties of resin, but can also initiate corrosion reactions on the metallic substrates [9–11]. Hence, a lot of efforts have been made to improve the water resistance of epoxy coatings. Guo et al. [12] investigated nanostructured thermosets containing epoxy and poly(ϵ -caprolactone)-block-poly(dimethyl siloxane)-block-poly(ϵ -caprolactone) (PCL-PDMS-PCL) triblock copolymers.

This study showed that the water contact angle (CA) of ER/PCL-PDMS-PCL blends increased significantly with higher triblock copolymer concentrations, with CA > 80° at 60 wt% PCL-PDMS-PCL. Sordo et al. [13] incorporated PDMS additives into epoxy resins by a physical method, improving the surface properties of the cured materials without affecting the good adhesion properties of the epoxy films on polar substrates. Cui et al. [14] also reported that the synthesis of semi-interpenetrating fluorine-containing polyacrylate and epoxy resin with different fluorine content could improve the hydrophobic property of polymer networks. However, phase separation might occur due to the incompatibility of the incorporated additive along with the curing agent in these studies. Moreover, although fluoropolymers are favorable compounds for modifying the surface properties of coatings, the relatively high market price of such materials limit their applications. Therefore, it is of great interest to develop a kind of economic material to modify surface properties of epoxy coatings, which also has good compatibility with epoxy resins.

Recently, significant progress has been achieved on the cocrosslinking of benzoxazine with epoxy, whereby benzoxazine is used as a curing agent of epoxy due to the reaction between the phenolic –OH groups of the ring-opened benzoxazine and epoxide groups. It is believed that incorporation of polybenzoxazine into the epoxy network structure will result in excellent heat resistance, flame resistance, electrical insulation and mechanical performance [15–20]. Furthermore, polybenzoxazine is a class of thermoset resins with low surface energy, far lower than that of pure Teflon® [21,22]. In addition, non-fluorinated polybenzoxazine could remarkably reduce the production cost [23,24]. Above all, the

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hydrophobic properties of epoxy coatings can be improved by utilizing benzoxazine as a curing agent, and this benzoxazine-cured epoxy may have the potential to be applied as a low-cost hydrophobic coating material for corrosion protection.

The focus of the present work is to apply a polybenzoxazine precursor (B-TMOS) as epoxy curing agent. The B-TMOS cured epoxy (EPB) coatings were prepared by dip coating and thermal curing method. Fourier transform infrared (FTIR) spectroscopy was used to characterize the structure of the coatings. In particular, the changes in the surface properties of hydrophilic epoxy coatings upon the addition of hydrophobic B-TMOS were examined by contact angle measurement. Finally, the potential of EPB as a corrosion protective coating for Q235B mild steel (MS) electrodes is investigated by electrochemical measurements.

2. Experimental

2.1. Materials and reagents

The mild steel (MS) (Q235B, composition in wt%: C: 0.12, Mn: 0.32, Cr: 0.035, Si: 0.14, Ni: 0.040, S: 0.010, P: 0.012, Cu: 0.010, Fe: balance) was provided by Lanpec Technologies Co. Ltd, China. Bisphenol A and 4, 4'-diaminodiphenyl methane (DDM) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. 3-Aminopropyltrimethoxysilane (3-APTOS) was obtained from Diamond Advanced Material of Chemical Inc., China. Epoxy resins (type E-51, 0.53 eq/100 g) were purchased from Shanghai Resin Factory Co., Ltd, China. Paraformaldehyde, chloroform, xylene, n-butanol and other chemicals were from Shanghai Lingfeng Chemical Corp., China. All chemicals were of analytical pure reagent grade. Chloroform was purified by distillation over calcium hydride (CaH₂) prior to use; all other chemicals were used as received.

2.2. Synthesis of benzoxazine monomer

2,2-Bis (3-(trimethoxysilyl)-n-propyl-3,4-dihydro-2H-1, 3-benzoxazine)propane (B-TMOS) was synthesized by a method available in the literature (Scheme 1) [22,25]. The product was yellow liquid with a yield of 85.1%. FTIR (KBr): $\nu = 1498$ (tri-substituted phenyl group); 1231 (s; ν_{as} (C—O—C of benzoxazine ring)), 1016 (s; ν_s (C—O—C of benzoxazine ring)); 1085 (s; ν_{as} (Si—O—C)); 931 (oxazine ring). ¹H NMR (400 MHz, chloroform-d, δ): 6.75–7.26 (m, 6H, ArH), 4.82 (s, 4H, O—CH₂—N), 3.98 (s, 4H, Ph—CH₂—N), 3.58 (s, 18H, Si—O—CH₃), 2.73 (t, 4H, N—CH₂), 1.66 (m, 4H, —CH₂—CH₂Si), 0.67 (t, 4H, —CH₂—Si).

2.3. Sample preparation and coating method

Bare MS was used as substrate. The substrates were blasted to Sa 2 1/2 and then degreased with acetone. DDM-cured epoxy (EPD) was prepared by reacting of 30 wt% DDM with E-51. B-TMOS-cured epoxy (EPB) was prepared by reacting of different ratios of B-TMOS mixed with E-51. The structure of E-51 is shown in Scheme 2. MS plates were dip coated into the epoxy solution for uninterrupted six times with a withdraw speed of 320 mm min⁻¹. The substrates remained in the solution for 1 min every time. The EPD sample was polymerized at 80 and 150 °C, each for 2 h, respectively. The EPB samples were cured in one step at 230 °C for 2 h. Samples obtained by reacting 10 wt%, 20 wt%, 30 wt% and 40 wt% B-TMOS with E-51 were labeled EPB10, EPB20, EPB30 and EPB40, respectively. The thickness of the coatings was evaluated on the stainless steel surfaces before and after coating using a micrometer (Mitutoyo, Japan), resulting on thicknesses of ~5 μ m for all coatings.

2.4. Characterization

2.4.1. Fourier transforms infrared (FTIR) spectroscopy

FTIR measurements were carried out on a Nicolet iS10 FTIR spectrometer at room temperature (~25 °C) using the KBr pellet method. In all cases, 32 scans at a resolution of 1 cm⁻¹ were recorded. The samples were prepared by casting the mixture solution onto a KBr plate, and then the residual solvent was removed by drying in vacuum. Some of the samples were further cured at a given condition to form polymer films.

2.4.2. Surface properties

Static contact angles of the samples were determined by contact angle goniometry at 25 °C using a DataPhysicsOCA20 optical goniometer interfaced with image-capture software by injecting a 2 μ L liquid drop. Deionized water was used as the test liquid. In order to obtain reliable contact angle data, five droplets were dispensed at different regions of the films.

2.4.3. Adhesion measurement

A knife was used to make a cross-cut pattern (space the cuts 1 mm apart and make 11 cuts) at 90° angles throughout the coating. The coating was brushed lightly with a soft brush after each cut to remove debris from the surface. Scotch 600 tape was applied to the cut surface and rubbed with the eraser end of a pencil to ensure good attachment to the coating, and then the tape was removed after 90 s [4,26].

2.5. Corrosion evaluations

Electrochemical measurements were measured with a CH Instruments CHI660D (USA) workstation with a three-electrode system. The coated sample acted as the working electrode, a Ag/AgCl (saturated KCl) electrode was used as the reference electrode, and a stainless steel cylinder as the counter electrode. The electrodes working area was ~14 cm². Electrochemical corrosion measurements were investigated using a potentiodynamic polarization technique, open circuit potential (E_{ocp})-time curves and electrochemical impedance spectroscopy (EIS). All tests were performed in a corrosive medium (3.5 wt% NaCl aqueous solution) at ambient temperature. Samples were immersed for 30 min to ensure the steady-state prior to measurements; measurements were repeated at least three times. In the polarization current experiments, the potential was scanned from -100 mV below to +100 mV vs Ag/AgCl above the corrosion potential E_{corr} at a scan rate of 2 mV s⁻¹. The corrosion current I_{corr} and E_{corr} were obtained automatically from the Tafel plots using the CHI660D workstation analysis software. In the electrochemical impedance spectroscopy (EIS) measurements, a sinusoidal AC perturbation of 10 mV amplitude coupled with the open circuit potential was applied to the metal/coating system. The EIS test was managed in the frequency range from 100 kHz to 0.01 Hz. EIS analysis was performed by using Zview software.

3. Results and discussion

3.1. Structure characterization of EPB

In order to determine that both epoxy precursive and B-TMOS monomeric species were participating in the curing reaction, a qualitative infra-red analysis was undertaken for cured samples with different B-TMOS content compared with E-51 precursor and B-TMOS monomer, shown in Fig. 1. The benzoxazine ring is characterized by the absorption peak at 931 cm⁻¹, corresponding to out plane bending vibrations of C—H of the oxazine ring [22,27]. The disappearance of the oxazine band indicated that oxazine rings

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