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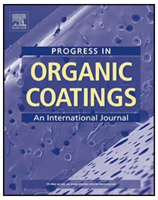

Preparation and failure behavior of fluorine-containing acrylic polyurethane coating

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ABSTRACT

A kind of fluorine-containing acrylic copolymer was synthesized via a two steps of fluorine modification route. A hydrophobic fluorine-containing acrylic polyurethane coating was prepared with the synthesized fluorine-containing acrylic copolymer and trimer of hexamethylene diisocyanate curing agent. The fluorine-containing acrylic polyurethane coating was employed as the topcoat, while a kind of epoxy coating was used as the primer. The failure behavior of the acrylic polyurethane and epoxy composite coatings in 3.5 wt.% NaCl aqueous solution and 5 wt.% salt spray environments were studied. Chemical structure of the copolymer was confirmed by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (^{19}F NMR). Glass-transition temperature (Tg) of the copolymer was determined with differential scanning calorimetry (DSC). The surface and cross-section morphologies of the coatings before and after failure test were explored via digital microscopy and field emission scanning electron microscopy (FESEM). The electrochemical impedance spectroscopy (EIS) was employed to analyze the coating corrosion resistance during the failure process. X-ray photoelectron spectroscopy (XPS) was used to provide insights into the chemical compositions of the coating surface. The results showed that the fluorine-containing copolymer and the corresponding coating were prepared as expected. The fluorine-containing acrylic polyurethane and epoxy composite coatings failed much faster in the salt spray environment than that in the NaCl aqueous solution. The different environment resulted in different surface chemical compositions.

1. Introduction

Organic coatings have been used for a long time to provide a barrier to prevent metal surface from being damaged in adverse environmental conditions [1,2]. Polyurethanes are used extensively in coating industries because of their excellent abrasion resistance, low temperature flexibility, excellent chemical, mechanical and physical properties [3,4]. Acrylic polyurethane coating was prepared by acrylic copolymers containing a certain amount of hydroxyl and isocyanate curing agents. Consequently, the coating combines the unique corrosion resistance of polyurethane with the weather-proofing ability of acrylic resins, which leads to outstanding mechanical, physical and chemical properties [3,5].

Fluoropolymers have been proved to be a typical low surface energy coating which behave outstanding hydrophobicity, oleophobicity, antifouling property and excellent resistance to environmental degradation [6–11]. Therefore, fluorine-containing acrylic polyurethane prepared with fluorine-containing acrylic resins and isocyanate curing agents possess better performance. Plenty of attention has been paid to the synthesis and properties of fluorine-containing acrylic copolymers [12–14]. Various fluorine-containing acrylic monomers have been employed to prepare fluorine-containing acrylic copolymers via radical polymerization [12,14–19]. In this case, the monomers were copolymerized with other normal hydrocarbon acrylates to prepare fluorine-containing acrylic copolymers. However, the molecular structure of the copolymer determines the migration behavior of the fluorinated segments, thus the surface energy of the copolymer film

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will decrease to a certain limit. Recently, we developed a novel kind of fluorinated monomer and a post-polymerization method to incorporate fluorinated moieties within the side chains of the copolymers [20]. Modified by the monomer, fluorine-containing copolymers with long side chains of perfluoroalkyl group and corresponding hydrophobic films were prepared.

The properties of the copolymer films were usually characterized when they were prepared before put into service environments. However, coatings will fail under the service conditions such as temperature, oxygen, water, pollutants, humidity and salt spray, etc., which can induce degradation of the coatings so as to cause the disappearance of the corrosion resistance. Wherein, water, oxygen and salt are critical service parameters for the coatings. Although there are a few studies have been paid on the durability of superhydrophobic and hydrophobic properties of some hydrophobic surfaces [21–23], the surfaces were generally prepared by chemical adsorption of monolayer owing low surface energy. Moreover, the test period was relatively short. Therefore, it is significant to study the failure behavior of the coatings under service condition.

In this paper, a kind of fluorine-containing acrylic copolymer was prepared via two steps of fluorine modification. At first, methyl methacrylate (MMA), butyl acrylate (BA), hydroxypropyl methylacrylate (HPMA) and acrylic acid (AA) were used as the normal acrylic monomers, while dodecafluoroheptyl methacrylate (DFHMA) was used as the fluorine-containing monomer. The monomers were copolymerized via a solution radical polymerization route. The synthesized copolymer was further modified by a kind of fluorinated monomer which was used for post-polymerization fluorine modification [20]. Fluorine-containing acrylic polyurethane was prepared with the synthesized fluorine-containing acrylic copolymer and trimer of hexamethylene diisocyanate (as a curing agent). The fluorine-containing acrylic polyurethane coating was employed as the topcoat, while a kind of epoxy coating was used as the primer. 3.5 wt.% NaCl aqueous solution soaking and 5 wt.% salt spray environments were employed to test the failure behavior of the coatings. Fourier transform infrared spectrum (FT-IR) and ^{19}F NMR were employed to characterize chemical structure of the copolymer. Differential scanning calorimetry (DSC) was used to test the glass transition temperature (Tg) of the copolymer. The surface features, electrochemical impedance spectroscopy (EIS), as well as the coating compositions were monitored during the failure process.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), hydroxypropyl methylacrylate (HPMA), and acrylic acid (AA) were purchased from Dongfang Yakeli Chemicals Limited Corporation (Beijing, China). Dodecafluoroheptyl methacrylate (DFHMA, mixture of $CH_2{=}C(CH_3)COOCH_2CF(CF_3)CFHCF(CF_3)CF_3$ and $CH_2{=}C(CH_3)COOCH_2CF(CF_2CF_3)CH(CF_3)CF_3$) was obtained from XEOGIA Fluorine-Silicon Chemical Corporation (Harbin, China). Butyl acetate and xylene were purchased from Beijing Chemical Works (Beijing, China) and used as solvents. Benzoyl peroxide (BPO) was used as initiator and obtained from Xilong Chemicals Limited Corporation (Shantou, China). 1H,1H,2H,2H-Perfluoro-1-decanol (FOH) was obtained from Guangzhou Liyuan Industrial Materials Co., Ltd (Guangzhou, China). Toluene diisocynate (TDI) was supplied by Tianjin Dengke Chemical Reagent Co., Ltd. (Tianjin, China). The hexamethylene diisocyanate trimer (N3375, Bayer) was used as curing agent. Epoxy coating (EP201) containing a filler of ferric oxide used as a primer was supplied by Marine Chemical Research Institute. All the reactants were used as received.

2.2. Synthesis of the fluorine-containing acrylic copolymer

The synthesis route was shown in Scheme 1. Firstly, a fluorinated acrylic copolymer was prepared via a solution radical polymerization route. The reaction was conducted in a four-neck round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, an addition funnel and a thermometer. A mixture of butyl acetate and xylene with a weight ratio of 2:3 was used as solvent. MMA, BA, HPMA, AA and DFHMA with a weight ration of 34:38.25:8.5:4.25:15 were used as the comonomers. The whole weight ratio of the solvent and the monomers was 3:2, and the initiator BPO accounted for 1 wt.% of the whole monomers. At first, 2/5 of the mixed solvent was added into the flask and heated to 100 °C under continuous stirring. Then a solution containing 1/2 of the solvent, all the monomers, as well as 9/10 of the BPO was added dropwise into the flask for about 3 h. The reaction was carried out at 100 °C for another 2 h after feeding. Next, a solution of the rest 1/10 of the solvent and 1/10 of the BPO were added dropwise into the flask. To promote the conversion of the residual monomers, the polymerization was continued for further 2 h. At last, the reaction mixture was cooled down to 70 °C and another fluorinated monomer was added into the flask to further modify the copolymer. The fluorinated monomer with a long perfluoroalkyl side chain and a reactive –NCO group was prepared by 1H,1H,2H,2H-Perfluoro-1-decanol (FOH) and TDI [20]. Consequently, the fluorine-containing acrylic copolymer was synthesized. The mole ratio of –NCO/–OH was 1:10, where–NCO was from the molecule of the fluorinated monomer, while –OH came from HPMA that was copolymerized within the acrylic copolymer. Titanium oxide was employed as the filler which was dispersed into the copolymer with a homogenizer. The concentration of the filler was about 11 wt.% based on the whole coating. The fluorine-containing acrylic polyurethane coating was prepared by mixing the fluorine-containing acrylic coating and stoichiometric isocyanate curing agent during the film formation process.

2.3. Coating preparation

Q235 steel was employed as the substrate. The size of the substrate was 60 mm × 40 mm × 10 mm. The substrates were polished with abrasive paper (No. 80) and washed with deionized water and absolute alcohol successively before painted. Epoxy coating (EP201) was used as the primer and the synthesized fluorine-containing acrylic polyurethane coating was used as the topcoat. The primer was spin-coated on the dried clean substrate with a desktop spin coater (KW-4A, Institute of Microelectronics, Beijing, China) at a speed of 600 rpm. The topcoat was then bladed on the primer via a wire rod coating apparatus after the primer was top-dried. Subsequently, the coated samples were moved to the experimental environments after complete curing at room temperature. The back and the edges of the samples were sealed with neoprene before test.

2.4. Environment accelerated corrosion test

The immersion experiment and neutral salt spray test were conducted to explore the failure behavior of the coating system. The immersion experiment was conducted at 40 °C, and the coated samples were immersed in 3.5 wt.% NaCl aqueous solution to simulate the soaking environment. The neutral salt spray test was conducted according to GB/T10125-2012. NaCl aqueous solution of 5.0 ± 0.5 wt.% with the pH value of 6.9 was sprayed over the samples at 35 °C. At least 5 panels were examined for each test. The surface