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Water and corrosion resistance of epoxy–acrylic–amine waterborne coatings: Effects of resin molecular weight, polar group and hydrophobic segment

Min Liu [a], Xuhui Mao [a], Hua Zhu [a], An Lin [a], Dihua Wang [a,b,*]

[a] School of Resource and Environmental Science, Wuhan University, Wuhan 430072, PR China
[b] State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China

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ABSTRACT

A two-step esterification process is developed for the synthesis of epoxy–acrylic-grafted-copolymer waterborne resins. The effect of synthesis parameters on water and corrosion resistance of the waterborne coatings is investigated. The results reveal that moderate increasing of the resin molecular weight (<8000 Da) and carboxyl content (<27 wt.%) increased the crosslinking property, thereby improved the anticorrosion performance of the coatings. Longer epoxy-octanoic hydrophobic chains can provide stronger shielding effect on the hydrophilic portion of the polymer matrixes. The polar group content in a waterborne resin can be optimized for better anticorrosion performance, whereas the optimal value is coating-specific.

1. Introduction

Increasing environmental pressures are forcing the coating industry to minimize the release of volatile organic compounds (VOCs) and result in a continuous shift from solvent-borne coating to waterborne coating [1,2]. At present, waterborne organic coatings have been wildly employed as building coatings and wood paints, while their application as anticorrosive coatings for metal is still limited [3–6]. As is well known, hydrophilic components with polar groups or ionic groups are necessary for water-soluble or hydrosol resins. However, these polar groups are believed to form water penetration channels in the polymer matrixes of waterborne coatings [7,8]. The formation of a waterborne film is a complicated process consisting of three stages [8–15]: particle packing; particle deformation and compression; and particle coalescence. In the particle coalescence stage, molecular rearrangement occurred and polymer particles with the groups of similar polarity tended to aggregate [7,16]. As a result, the polar groups in the particles form polar channels for water permeation, accelerating the water uptake in waterborne coatings and deteriorating the corrosion resistance. Perez et al. [5] reported that the water apparent diffusion coefficient (D_{app}) for waterborne acrylic paint was 10 times higher than that of organic-solvent paints. Mikols et al. [17–19] found that water existed in the polymer matrix in two distinct forms: free water filling the microcavities and bound water combined with polar groups of the polymer network. Viktor et al. [20–22] investigated that absorbed water mostly located in the hydrophilic part of the polymer matrixes and caused irreversible swelling of polymers. Vanderwel et al. [23–26] found that the water absorption caused by the hydrogen bonding between water and polar groups was common in hydrophilic coatings, and the absorbed water induced the swelling of the crosslinked polymers and weakened the mechanical property of the coatings.

Many efforts have been made to improve the anticorrosive property of waterborne coatings. An optional method is to improve the crosslinking property [1,27–31]. Chemical reactions between different polar groups not only facilitate crosslinks and thus enhance the physical and chemical integrity of the coalesced film, but also reduce the number of polar groups and thereby lower the water sensitivity of the coatings [15,27,31]. Reactive polar groups for coating systems usually include epoxy groups, hydroxyl groups, carboxyl groups, amino groups, *N*-methylolacrylamide groups, blocked isocyanates and acetoacetate groups, etc. [7,15,27–31]. Crosslinking property of a coating is known to be impacted by the number density of these reactive polar groups. However, it remains controversial regarding the exact relation between them. Many studies suggested that more crosslinked units were needed in each polymer chain to obtain better crosslinking property [7,15]. Others reported that an increase in density of reactive polar groups resulted in poor crosslinking property and reduced tensile strength of the cured films [32–34]. High reactive group content

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* Corresponding author at: School of Resource and Environmental Sciences, Wuhan University, Wuhan 430072, PR China. Tel./fax: +86 27 68775799.

E-mail addresses: liumhb@126.com (M. Liu), clab@whu.edu.cn (X. Mao), zhuhua333@126.com (H. Zhu), linanwd@126.com (A. Lin), wangdh@whu.edu.cn (D. Wang).

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caused fast crosslinking reactions, thereby suppressed further polymer interdiffusion and lowered the gel content of the film [35].

Besides, the molecular weight of the polymer particles has been considered as another important parameter for crosslinked films [7,14,36–38]. It is well known that coatings with high resin molecular weight are superior in barrier performance, because more interdiffusion of polymer chains occurred between large resin molecules and led to a better crosslinking property [7]. However, some studies also reported that higher resin molecular weight may exert negative influences on the properties of the coatings. With high molecular weight resins, the waterborne coatings showed lower dispersibility and compatibility, hence poor film smoothness and protective property [14,36].

In order to elucidate the effect of resin molecular weight and polar group content on the barrier performance of waterborne coatings, a two-step esterification process is developed in this study to prepare various epoxy–acrylic-grafted-copolymer waterborne resins (EA resins), and the water and corrosion resistance of their unpigmented waterborne coatings were evaluated. Unlike the previously reported methods, the two-step esterification process was designed to accurately control the molecular weight and carboxyl content of the EA resins. Hence the prepared coatings allow us to evaluate the effect of polar groups on the water and corrosion resistance. The scientific hypothesis of this study is that optimum resin molecular weight and carboxyl content of the EA resins not only ensure good water dispersibility, but also promise favorable crosslinking property and anticorrosion performance for the coatings.

2. Materials and experimental

2.1. Chemical materials

Two types of bisphenol-A epoxy resins (E-12 and E-20), the typical structure of which was depicted in Fig. 1, were purchased from Sinopec company (China) and were used as received. E-12 and E-20 hold a number-average molecular weight (M_n) of ~2000 and ~1000, respectively. The curing agent was methylated amino resin at 80 wt.% solid content (Type SM5717, Sanmu Group Co., China). All the other chemical reagents were provided by Sinopharm Chemical Reagent Co. (China).

2.2. Preparation of epoxy–acrylic waterborne coatings

EA resins were synthesized by a two-step esterification process, as depicted in Fig. 2. The first esterification is to decrease the functionality of the epoxy resin. Epoxy monomers reacted with equal mole ratio *n*-octanoic acid at 105 °C for 100 min to produce the epoxy-octanoic ester (EP), and a certain amount of *N*,*N*-dimethylethanolamine (DMEA) was used as the catalyst. The mixed organic solvents for the reaction include 50 wt.% propylene glycol methyl ether and 50 wt.% *n*-butyl alcohol. PA prepolymer was prepared via a free radical polymerization of several acrylic monomers (see the recipe described in Table 1). At the beginning of reaction, one-third of portion I was added into a three-neck flask equipped with a constant temperature magnetic blender. When the temperature rose to 75 °C, portion I, portion II and the remaining two-third of portion III were instilled into the flask by a constant flow pump. After 60 min of reaction, the temperature was elevated to 85 °C and maintained till to the end of the dropwise addition (~90 min). Afterwards, the reaction system was kept at 85 °C for additional 120 min. The second esterification step was the reaction between the prepared EP and PA prepolymers. Based on solid contents of the resultant solutions, the mass ratio of EP to PA was 3:7, and the reaction condition was the same as that of the first esterification. Finally, the obtained epoxy–acrylic graft copolymer (EA resin) was prepared.

For the preparation of an unpigmented epoxy–acrylic coating (EA coating), the EA resin was neutralized by DMEA and mixed with amino resin (curing agent). Then the mixture of the two resins was diluted to 45 wt.% solid content with distilled water prior to use. The addition amount of amino resin was determined by the reactive group contents of the EA resin.

2.3. Preparation of samples

Commercial aluminum foil and galvanized steel sheet, with the compositions given in Table 2, were used as substrates for EA coatings. Samples on aluminum foils (150 mm × 150 mm × 0.01 mm) were used for water absorption test. Galvanized steel sheets (100 mm × 50 mm × 2 mm) were used as the substrates for electrochemical impedance spectroscopy (EIS) test and neutral salt spray (NSS) test. The metal substrates were degreased using acetone solvent and dried in air before the experiments. The coatings were painted by roll coating method at ambient temperature (~25 °C), and were cured at 150 °C temperature for 30 min. After the curing process, the samples were kept in desiccators for 30 days before measured. The thicknesses of the obtained coatings are 10 ± 2 μm, as measured by a coating thickness gauge (TT260, Beijing TIME Corp., China).

2.4. Measurements

Molecular weights of the PA and EA resins were determined by gel permeation chromatography (GPC) (2690D, Waters Corp., USA), using tetrahydrofuran (THF) as an eluent. Glass transition temperature (T_g) of the cured films was measured by differential scanning calorimetry (DSC) (Q20, TA instruments, USA). The measurements were carried out under the protection of nitrogen atmosphere with a scanning rate of 10 °C min^{-1} in the temperature range from −50 °C to 300 °C. The whole measuring process was operated according to ASTM/D3418-82. Gel content, representing the insoluble fraction of a cured film in a good solvent [7], was tested by extracting the cured film with refluxing 2-butanone in a Soxhlet extractor for 10 h. Water absorption of the films was evaluated following a standard method (HG2-1612-1985). Viscosity of the coatings was determined by a digital viscometer (DV-79, Shanghai Nirun Intelligent Technology Co., Ltd., China), at a constant temperature of 25 °C. Thermal decomposition behavior of the films was examined with a thermo-gravimetric analysis (TGA) (Diamond TG/DTA, PerkinElmer instruments, USA) under nitrogen flow. The TGA spectra were acquired in the temperature range from 30 °C to 650 °C at a heating rate of 5 °C min^{-1}. NSS tests were conducted in a salt spray cabinet (Wuxi Tainuo Testing Equipments Co., Ltd., China), with spraying NaCl solution (50 ± 5 g dm^{-3}, pH = 6.5–7) at 35 ± 0.5 °C, lasting for 600 h.

EIS was performed with an electrochemical workstation (PARSTAT 2273, Princeton Applied Research, USA) at room temperature

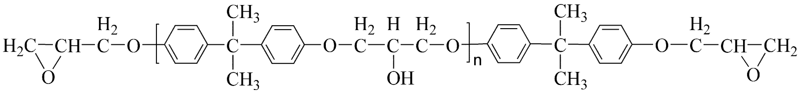

Fig. 1. General molecular structure of bisphenol-A epoxy resin (n = ~5.5–6 for the E-12, n = ~2–2.5 for the E-20).