



Synthesis of waterborne epoxy/polyacrylate composites *via* miniemulsion polymerization and corrosion resistance of coatings



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ARTICLE INFO

Keywords:

Epoxy resin
Polyacrylate
Corrosion protection
Miniemulsion polymerization

ABSTRACT

To improve the corrosion resistance of waterborne polyacrylate latexes coatings, an epoxy/polyacrylate (EP/PA) composite latex with high EP content was developed *via* miniemulsion polymerization as the matrix of anticorrosion coatings. Transmission electron microscopy illustrated that the EP/PA composite had spherical shapes with the diameter of 130–199 nm. In addition, differential scanning calorimeter and thermal gravity analysis thermograms suggested that the EP/PA composites showed good compatibility and thermal stability. The barrier properties of the EP/PA composite coatings were also remarkably enhanced by the crosslinking between EP groups and primary amines during film formation. Moreover, the use of phosphate emulsifier could act as an adhesion promoter to form a passive layer to prevent metals from further corrosion. The corrosion resistance of EP/PA composite coatings on cold-rolled steel was fully investigated by the Tafel polarization test, salt spray test, and scanning electron microscope. The Tafel polarization test results show that the EP/PA composite coatings exhibited a low corrosion rate of 1.2 μm per year, which was better than the PA coatings by a factor of 24. Therefore, the obtained EP/PA composites could significantly improve the corrosion resistance of waterborne polyacrylate latexes, and showed a great potential application in the aqueous metal coatings.

1. Introduction

The protection of metal from corrosion has always been a challenge. Metals and their alloys are the backbone of human civilizations; consequently, their protection from corrosion remains an area of high interest to materials scientists [1,2]. Corrosion of metals causes large economic losses annually in both developed and developing countries. Organic coatings are the most widely used method for corrosion control [3–5]. Among the binders of organic coatings, polyacrylate (PA) is one of the most significant adhesive materials because of its adhesive property, flexibility and weather resistance [6,7]. Currently, due to the increasing strict law of environmental protection, waterborne PA coatings have attracted increasing attentions in both academic and industrial fields [8–10]. However, waterborne PA coatings are still permeable to corroding agents such as water, oxygen and destructive ions Cl^{-1} , H^{+} to the substrates, which restricts its application in the field of anticorrosion coatings [11]. Epoxy (EP) resin is widely used in adhesives, coatings and electrical insulation materials due to its excellent adhesive properties, corrosion resistance, water resistance, impermeability and chemical resistance [12,13]. Consequently, PA modified by EP may combine advantages from EP and PA to create a hybrid

anticorrosion coating [14,15].

Several methods have been utilized to prepare EP/PA composites. Although directly blending the aqueous EP dispersion with acrylic latex is a popular approach, it cannot normally obtain the desirable results due to the limited compatibility between EP resin and PA [16–18]. Therefore, different strategies for preparing EP/PA composites other than by direct blending have been described in previous literature [18]. For instance, EP resin can be esterified with the carboxyl groups of an acrylic polymer in the presence of a tertiary amine. The adduct is then treated with a base to obtain the EP/acrylic waterborne resins [19,20]. Nevertheless, based on the gelation theory, this strategy often means that the ester bond of the esterified product will be hydrolyzed over time [21]. At present, the waterborne EP/PA composites are mainly prepared by emulsion polymerization. More recently, Chen et al. [22] demonstrated the synthesis of EP/acrylic hybrid latexes with core-shell structure by emulsion polymerization processes. Similarly, a damping material based on EP/PA composites with core-shell structure was synthesized by two-stage emulsion polymerization in our previous work [23]. However, in conventional emulsion polymerization, mass transfer of these monomers from monomer droplets to polymer particles through the aqueous phase is diffusionally controlled. Hence, high EP

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content cannot be readily incorporated into the polymer due to its hydrophobicity [24–26]. To solve these problems, miniemulsion polymerization has been recently used to incorporate or graft resin into acrylate latex to obtain more stable composite latexes [27–29].

Miniemulsions have droplet sizes between 50 and 500 nm, which involves the use of an effective surfactant/costabilizer system to produce small monomer droplets. The droplet surface area in this system is exceedingly large, and most of the surfactant is adsorbed at the droplet surface [30]. Hence, the droplet nucleation is dominant because of the absence of micelles, which aids in the preparation of EP/PA composites by generating monomer droplets that contain EP prior to polymerization. [31]. In the early work of Kawahara et al. [32,33], an EP/acrylic composite latex was prepared by the miniemulsion polymerization. Their studies found that almost all EP groups were remained even after miniemulsion polymerization, and the EP groups were gradually lost at 50 °C by crosslinking with carboxyl groups during storage. However, their reports did not focus on or give detailed information about the corrosion protective effect of composite latex.

In this study, an EP/PA composite latex with high EP content was developed via miniemulsion polymerization as the matrix of anticorrosion coatings. The barrier properties of the EP/PA composite coatings were remarkably enhanced by the crosslinking between EP groups and primary amines during film formation. Obviously, the high EP content was helpful in achieving the perfect corrosion resistance of EP/PA composites due to the dense crosslinking point obtained. Herein, we designed the different EP content in composite latex particles and studied their influence on the particle size, morphology and thermal behavior of EP/PA composite latex. To further improve the corrosion resistance of EP/PA composites, the use of phosphate emulsifier could act as an adhesion promoter to form a passive layer to prevent metals from further corrosion. Therefore, the corrosion resistance of the EP/PA composite coatings were remarkably enhanced by the synergistic effect of dense crosslinking coatings and passive layer.

2. Experimental

2.1. Materials

Bisphenol A EP resin E-51 (EP value of 0.48–0.54) was bought from Shanghai Resin Co., Ltd. (Shanghai, China). *n*-Hexadecane (HD) was purchased from Shanghai Aladdin reagent Co., Ltd. (Shanghai, China). The monomers butyl acrylic (BA; analytical pure), methyl methacrylate (MMA; analytical pure), and methacrylic acid (MAA; analytical pure) were obtained from Tianjin Damao Chemical Reagent Co., Ltd. (Tianjin, China) and purified by distillation before use. The phosphate surfactant (PS-630) was obtained from Shanghai Zhongcheng Chemical Co., Ltd. (Shanghai, China). Potassium peroxydisulfate (KPS) and sodium bisulfite (NaHSO₃) were the products of Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Modified amine curing agent (SM-211) was supplied from Jiangsu Sanmu Chemical Co., Ltd. (Yixing, China). All the reagents were used as received, and deionized water was used to prepare all the emulsions.

2.2. Preparation of EP/PA composite latex

The EP/PA composite latex was prepared through the miniemulsion polymerization process, and the details of the reaction recipe are listed in Table 1. First, the desired amount of EP resin was dissolved into the oil phase mixture of MAA, MMA, BA, and the costabilizer (HD). Then, the mixture was stirred at 360 rpm at room temperature for 10 min. Afterwards, an aqueous solution of the surfactant PS-630 was added into the oil solution under moderate stirring (500 rpm) for 0.5 h. Finally, the coarse emulsion was further homogenized by ultrasonication at 950 W, 20 Hz for 20 min. Batch polymerization was performed in a 500 mL four-necked round-bottom flask equipped with a mechanical stirrer, addition funnel, N₂ inlet, and thermometer. Potassium

Table 1

Typical recipe for the preparation of EP/PA composite latex. (10, 20, 30 and 40 represent the content of epoxy resin).

Components	EP/PA-10	EP/PA-20	EP/PA-30	EP/PA-40
E-51/g	15	30	45	60
MMA/g	82	73	64	54
BA/g	51	45	39	34
MAA/g	2	2	2	2
HD/g	0.5	1	1.5	2
PS-630/g	3	3	3	3
NaHSO ₃ g	0.75	0.75	0.75	0.75
K ₂ S ₂ O ₈ /g	0.75	0.75	0.75	0.75
H ₂ O/g	200	200	200	200

peroxydisulfate (KPS, 0.75 g) in 15 mL deionized water and sodium bisulfite (NaHSO₃, 0.75 g) in 15 mL deionized water was used as a redox initiator pair. When the reaction temperature was reached at 55 °C, the initiator solutions were added to the polymerization flask at rate of 0.15 mL/min for 2 h. Subsequently, the polymerization was carried out at 65 °C for 5 h under N₂ protection to obtain the composite latex particles.

2.3. Preparation of samples

The mass ratio of EP resin to curing agent was set at 1:1.2, and stirred for 30 min to obtain a uniform mixture. The latexes were cast on the steel substrates under ambient temperature, and the samples were then maintained at 120 °C for 2 h [34]. The thickness of the dried coating films was 50 ± 3 μm.

2.4. Characterization

The particle size distributions of EP/PA composites were measured using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK). Transmission electron microscopy (TEM) photographs of the latex particles were obtained using a JEM-2100 microscope (JEOL Co., Japan) at an accelerating voltage of 200 Kv. The ratio between the number of particles and the initial number of droplets (N_p/N_d), A_{surf} and surface tension were calculated according to the literature [45,46].

The Fourier transform infrared spectrum (FTIR) of samples in KBr pellets and of the composite latex film were recorded on a Nicolet 6700 spectrophotometer (Thermo Fisher, USA). Glass transition temperature (T_g) of the cured films was measured by differential scanning calorimeter (DSC) (Q20, TA instruments, USA) at a heating rate of 10 °C/min from –50 °C to 150 °C. The thermodynamic properties of specimens were investigated by a DTG-60H thermal gravity analysis (TGA) (Lacerta Technology Ltd., Japan) from 20 °C to 700 °C in N₂ atmosphere at a heating rate of 10 °C/min.

To evaluate the corrosion behavior of EP/PA composite coatings, potentiodynamic polarization was performed in 5 wt% NaCl solution with a PARSTAT MC 2000 multi-channel electrochemical testing system (AMETEK Inc., USA). The polarization resistance (R_p in Ω cm²) was measured by sweeping the applied potential from –1 V below to 1 V above the E_{corr} at a scan rate of 1 mV/s. To check the reproducibility of the Tafel polarization tests, each test was carried out using three replicates to ensure repeatability. The standard deviation of the three measurements are reported. The corrosion current density (I_{corr}) was determined through superimposing a straight line along the linear portion of the anodic or cathodic curve and extrapolating it through E_{corr} (Tafel extrapolating method). Also, Ivium Stat software was used to analyze the polarization test results, and the corrosion rate was calculated through the following equation [35,36]:

$$R_{corr} = \frac{0.0032 \times I_{corr} \times M}{n \times d}$$

where I_{corr} , M , n , and d represent corrosion current density (μA/cm²),

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