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Corrosion performance of waterborne epoxy coatings containing polyethylenimine treated mesoporous-TiO_2 nanoparticles on mild steel

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ABSTRACT

Waterborne epoxy coatings were modified by adding mesoporous-TiO_2 nanoparticles (meso-TiO_2). In order to achieve proper dispersion of meso-TiO_2 in the epoxy-based coating and make possible chemical interactions between meso-TiO_2 and polymeric coating, meso-TiO_2 was treated with polyethylenimine (PEI) of various molecular weights. Corrosion performance of mild steel coated specimens was investigated employing electrochemical impedance spectroscopy (EIS) and salt spray test. Coatings with meso-TiO_2/PEI (600 molecular weight) possessed the best corrosion performance among the coating specimens. The EIS results showed that the resistance value of coating with meso-TiO_2/PEI (600 molecular weight) was above $9.87 \times 10^7\ \Omega\,cm^2$ which was higher than neat epoxy coating. Possible chemical interactions between polymeric matrix and treated nanoparticles caused high barrier properties and high degree of cross-linking.

1. Introduction

Epoxy resins play a dominant role in protective coatings mostly due to their outstanding performance in terms of corrosion protection, chemical resistance and great adherence to many substrates [1]. Recently, more attentions have been paid to the waterborne epoxy resins due to the increased legislative restrictions on the emission of organic solvents to the atmosphere [2]. Nonetheless the successful application of waterborne epoxy coatings is often hampered by their disadvantages such as poor barrier properties [3]. The poor properties of waterborne epoxy coatings can be improved by inclusion of proper fillers. There are various reports concerning improving corrosion resistance of coatings using nanoparticles such as ZnO [4], SiO_2 [5], ZrO_2 [6] and organoclay [7].

In our previous work, we used mesoporous silica MCM-41 as a nanofiller to design nanocomposite and obtain excellent consequence [3]. We also have proved that polyaniline-mesoporous MCM-41 gave much better barrier properties at the same concentrations than MCM-41 [8]. Meso-TiO_2 has the larger pore size than MCM-41 which deemed to be one of the most promising mesoporous materials employed in anticorrosion coatings. However, because of their incompatibility with organic resin and aggregation, the advantages of meso-TiO_2 do not exhibit themselves to the full. Therefore, meso-TiO_2 need some modifications to turn their surface from hydrophilic to organophilic [9,10]. Besides organic surface of those fillers, their interaction with epoxy matrix largely decides the properties of coatings [11].

Polyethylenimine (PEI), which is composed of many amine groups on the line type macromolecular chains [12]. It not only can interact with hydroxyl groups on the surface and in the inner-channel of meso-TiO_2 to form hydrogen bonds, but also can react with the epoxy groups (Fig. 1) [13,14].

In this paper, to ensure appropriate dispersion in nano-sized scales and enhance possible chemical interactions between meso-TiO_2 powder and epoxy matrix, meso-TiO_2 was treated with polyethylenimine (PEI). The aims of this paper are (i) to achieve uniform dispersion of the meso-TiO_2 in the waterborne epoxy resins, (ii) to enhance the compatibility of meso-TiO_2 particles and waterborne epoxy resins by intermolecular force and the chemical crosslinking as displayed in Fig. 1, and (iii) to improve the corrosion resistant property of the epoxy coatings by adding meso-TiO_2/PEI.

2. Experimental

2.1. Materials

Polyethylenimine (PEI, 30 wt% soln. in water, M_W: 600, 70,000 and 700,000) was purchased from Alfa Aesar. Waterborne epoxy

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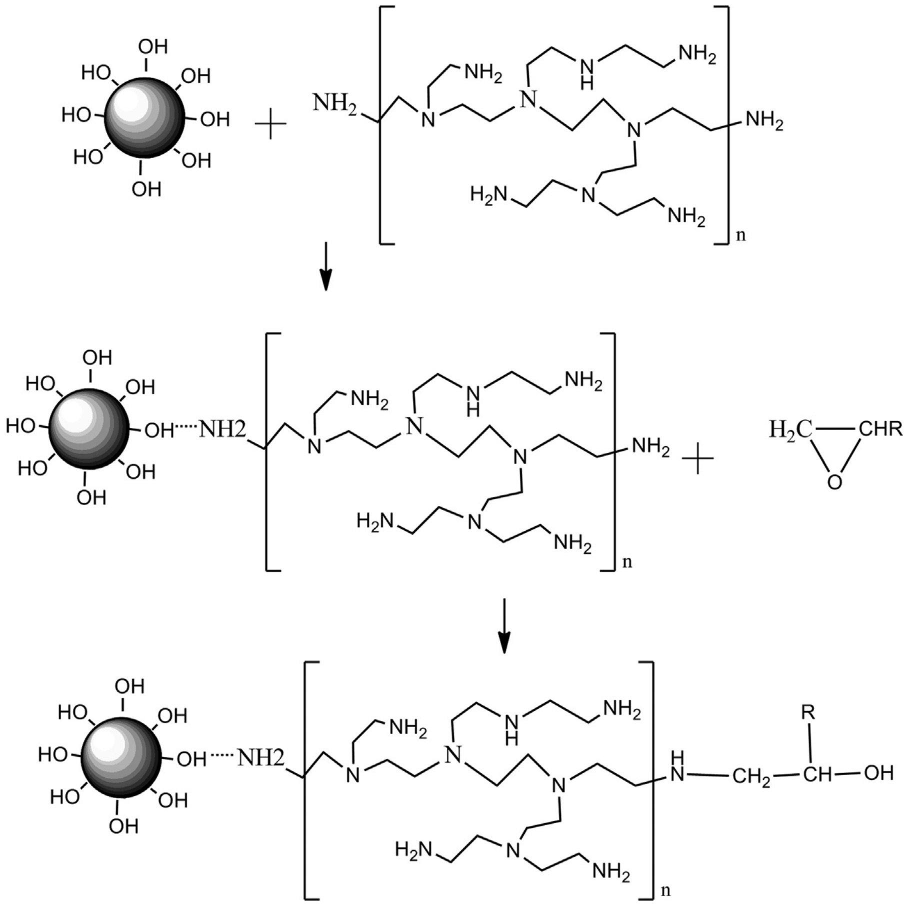

Fig. 1. Schematic depiction of chemical reaction of meso-TiO_2/PEI with epoxy.

resin (AR555) and curing agent (Anquamine419) were chosen as main components for the paint from APCI. Hexadecyl trimethyl ammonium bromide (CTAB) and tetrabutyl titanate (TBOT) were provided by Beijing Zhonglian Chemical Co. Ltd.

2.2. Preparation of meso-TiO_2

The procedures for preparing meso-TiO_2 were as follows. At first, 4 g of CTAB was dissolved in 16 ml of distilled water. Then 12 g of TBOT solution was slowly added into the CTAB solution, with stirring (300 rpm, 1 h). After being stirred for 1 h, a mixture containing 3 g of distilled water and 8 g of anhydrous ethanol was added dropwise to the flask and stirred for further 2 h at 100 °C. The chemical composition was washed three times. The synthesized product was subjected to calcinations in air at 350 °C for 8 h to remove the organic template on the surface and in the inner-channel of the particle, which was named meso-TiO_2.

2.3. Preparation of meso-TiO_2/PEI

Briefly, 2 g of meso-TiO_2 was firstly activated by anhydrous ethanol in ultrasonic machine for 20 min. The 1 g PEI was added into the mixture and stirred with magnetic stirrers for 6 h at ambient temperature. Finally, the products were separated using an LG10-2.4A centrifuge at 5000 rpm for 10 min in order to remove the residual of PEI.

2.4. Preparation of the anticorrosion coating

Coating preparation: Since this study is our continuous work on synthesis, characterization and application of mesoporous nanoparticle materials in organic coatings, optimum ratio of mesoporous nanoparticle to waterborne epoxy system was achieved based on the previous experimental researches [3,8,15]. In order to get smaller and better size distribution, a certain amount of nanoparticles dispersed in waterborne epoxy resin (AR555, APCI) were carried out by a pearl-mill, and then curing agent (Anquamine419, APCI) and distilled water added into the mixture stirred with magnetic stirrers for 20 min (Table 1).

Steel substrate preparation: Steel substrates with rounded corners and edges were polished by fine emery paper. They were washed with acetone and dried for further use. The liquid paints (neat waterborne epoxy and waterborne epoxy nano-composites) with 30 ± 3 μm were then applied by air spray and cured at room temperature. After the coated samples being solidificated, the thickness was measured by a Qnix4500 digital meter and kept in desiccator for a week before being tested.

2.5. Characterization

2.5.1. Testing of meso-TiO_2/PEI

N_2 adsorption–desorption isotherms at 77 K were conducted on micromeritics ASAP 2010 micro-pore analysis system. The samples were outgassed at 473 K for 4 h.

X-ray diffraction patterns were recorded on D/max-2500PC X-ray diffractometer, using Cu *K*a radiation at 50 kV and 200 mA with a scanning rate $1^\circ\ \mathrm{min}^{-1}$ by 0.01 steps.

For the sake of identifying the functional groups on the surface and in the inner-channel of modified meso-TiO_2, the infrared transmission spectra were performed on Nicolet MNGNA-IR560 with $4\ \mathrm{cm}^{-1}$ resolution.