Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–11

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

The effect of surface morphology and treatment of Fe_3O_4 nanoparticles on the corrosion resistance of epoxy coating

A.A. Javidparvar[a], B. Ramezanzadeh[b,*], E. Ghasemi[c]

[a] Amirkabir University of Technology, Department of Maritime Engineering, Bandarabbas, P.O. Box 15875-4413, Tehran, Iran
[b] Department of Surface Coatings and Corrosion, Institute for Color Science and Technology (ICST), PO 16765-654, Tehran, Iran
[c] Department of Inorganic Pigment and Glazes, Institute for Color Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 2 August 2015
Revised 11 December 2015
Accepted 5 January 2016
Available online xxx

Keywords:
Nanopigment
Silane surface treatment
Surface morphology
Epoxy coating
Corrosion resistance
EIS

ABSTRACT

Magnetite iron oxide base nanopigments (Fe_3O_4) with two morphologies and different surface treatments were synthesized. Fe_3O_4 nanopigments were synthesized in the presence and absence of triethanolamine as surfactant and then were modified with 3-amino propyl trimethoxy silane (APTMS). Nanopigments were characterized by X-ray diffraction (XRD) analysis, field-emission scanning electron microscope (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy and thermal gravimetric analysis (TGA). Electrochemical impedance spectroscopy (EIS) was utilized to investigate the corrosion inhibition properties of the epoxy composites. It was found that both surface morphology and surface chemistry of the nanopigments significantly affected the corrosion resistance of the epoxy coating.

1. Introduction

Nowadays, corrosion protection of steel structures by organic coatings has been widely considered by many researches [1,2]. They can provide a physical barrier between the metal surface and the corrosive environment restricting the access of aggressive ions to the active sites of metal surface. However, most of the organic coatings cannot provide long term corrosion protection performance as the corrosive species such as oxygen, water and chloride ions can diffuse to the metal/coating interface through permeation into the coating porosities. Various kinds of anti-corrosive pigments have been used to improve the corrosion resistance of polymer coatings [3,4]. They are categorized in three main groups of barrier [5], sacrificial [6] and inhibitive pigments [7]. Among various kinds of pigments the chromate based pigments have been widely used for improving the corrosion protection properties of the organic coatings. However, the use of such pigments has been strictly restricted in recent years because of their high toxicity and environmental problems [8–10].

Recently, the researchers' attentions have been directed toward using different types of nanomaterials in the organic coatings to obtain a higher degree of protection than conventional pigments [11]. Owing small particle size and high surface area, they are able to produce proper barrier against corrosive electrolyte diffusion into the coating matrix. It has been shown that nanopigments can fill the porosities, cavities and free volumes existed in the coating matrix and increase the electrolyte pathway length. Ramezanzadeh et al. [12] investigated the anticorrosion properties of the epoxy coating filled with ZnO particles in nano and micro sizes. Their results showed that the coating reinforced with nano sized pigment had better barrier properties than the coating containing micro size one. We have showed in our previous researches that inclusion of SiO_2 [13], Al_2O_3 [14], clay [15], Al [16] and graphene oxide [17,18] nanoparticles into the organic coatings resulted significant improvement of the coating corrosion protection performance.

Due to the low toxicity and cost, and availability of the iron oxide based nanopigments, the researchers' attentions have been directed to investigate theirs properties [19–23]. Iron oxide nanoparticles have been used in various applications in different industries *i.e.* Magnetic Resonance Imaging (MRI), Drug Delivery System (DDS), catalysts, sensors, magnetic receivers, removing heavy metals from aqueous solutions, magnetic fluids, data storages, etc. There are different studies on the synthesis and characterization of the structural, and morphological properties of the iron oxide nanopigments. These nanoparticles have been synthesized by various methods *i.e.* thermal decomposition [24,25], hydrothermal method [26,27], sol–gel [28], microemulsion [29,30], chemical co-precipitation [31,32] etc. In a hydrothermal method,

* Corresponding author. Tel.: +98 2122969771; fax: +98 2122947537.
E-mail address: ramezanzadeh@aut.ac.ir, ramezanzadeh-bh@icrc.ac.ir (B. Ramezanzadeh).

http://dx.doi.org/10.1016/j.jtice.2016.01.001
1876-1070/

Table 1
Composition of the steel substrate.

Element	Fe	C	Si	Mn	P	S	Cr	Mo	Co	Cu
Wt.%	97.7	0.19	0.415	1.39	<0.005	<0.005	0.026	0.018	0.0429	0.0481

Table 2
Sample coding.

Sample coding	Description
Fe_3O_4	Nano magnetite synthesized in the absence of surfactant
APTMS-Fe_3O_4	Nano magnetite treated by APTMS
Fe_3O_4/TEA	Nano magnetite modified by triethanolamine as surfactant
APTMS-Fe_3O_4/TEA	Nano magnetite modified by both surfactant and APTMS silane agent

the nanopigments can be synthesized in a sealed container at high-temperature (130–250 °C) and vapor pressures (0.3–4 MPa) [33]. In this method, the nanoparticles can be synthesized with a controllable morphology and narrower particle size distribution [33].

Surfactants are used to overcome the Van der Waals forces between the particles and in this way the morphology and size of the nanoparticles can be effectively controlled. Both the size and morphology of the nanopigment can affect the magnetic and corrosion inhibition properties of the pigment [34–38]. Li et al. [39] reported the effects of different capping functional groups on the morphology of the magnetite nanoparticles. They found that addition of 3-amino propanol with NH_2 groups decreased the growth of nanoparticles and reduced the nanocrystals size. Guardia et al. [40] studied the effect of two capping agents *i.e.* oleic acid and dodecanoic on the size and morphology of the magnetite nanoparticles. Results showed that the particles synthesized in the presence of oleic acid were smaller and had a narrow size distribution with pseudo-spherical shape.

It has been shown that most of the nanoparticles are not compatible with the polymer coatings due to their polarity difference. Therefore, the surface chemistry of the nanopigments significantly influences theirs disperse-ability in the coating as well as the interactions between the pigment/polymer [41]. Surface treatment of the nanoparticles is an effective way to enhance the compatibility between the particles and coating resulting in the creation of stronger interactions. Silanization of nanoparticle is a popular method of changing the polarity of the particles and improving their stability in the polymeric coatings [42,43]. Behzadnasab et al. [44] investigated the corrosion performance of the epoxy coating reinforced with silane treated ZrO_2 nanoparticles. They used an amino propyl trimethoxy silane (APS) as silane coupling agent and showed that the corrosion protection properties of the coating was significantly improved by using 2–3 wt.% modified ZrO_2 nanopigments. They showed that surface modification of particles enhanced their stability in the epoxy resin in comparison with the unmodified nanopigment. Palimi et al. [45] studied the effect of silane treatment of Fe_2O_3 nanoparticles with 3-amino propyl trimethoxy silane (APTMS) on the corrosion protection properties of the polyurethane coating. They showed that surface modification of Fe_2O_3 nanoparticle with APTMS enhanced the particles dispersion in the polyurethane matrix, resulting in higher degree of corrosion resistance enhancement. Considering specific effects of both silane coupling agent and surfactant on the surface properties of the nanoparticles, studying the synergistic effect of these two factors on the protective properties of the coating containing these nanopigments can be great of interest.

This work aims at characterization of the morphology, phase structure and corrosion inhibition properties of a magnetite nanopigment synthesized via hydrothermal method. The composition and morphology of the pigments were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscope (FE-SEM). The effects of triethanolamin as surfactant and 3-amino propyl trimethoxy silane (APTMS) as silane coupling agent on the nanopigment properties were studied. Also, the epoxy nanocomposites reinforced with 1 wt.% of nanopigments were prepared and applied on the steel substrate. The protective properties of the composite coatings filled with unmodified and surface modified pigments were investigated by EIS and salt spray tests.

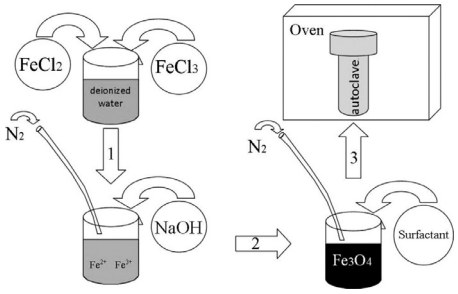

Fig. 1. A schematic of the synthesis process.

2. Experimental

2.1. Materials

$FeCl_3$, $FeCl_2$, NaOH, triethanolamine, 3-amino propyl trimethoxy silane, ethanol, HCl (50%), NaOH, butyl acetate, and NaCl were purchased from Merck Co. All of these reagents were used without further purification in all experiments. Epoxy resin (Araldite GZ7 7071 × 75) with epoxide value, solid content and density of 0.1492–0.1666 Eq/100 g, 75 wt.% and 1.08 g/cm^3, respectively was prepared from Saman Co. The polyamide hardener (CRAYAMID 115) with solid content of 50 wt.% was prepared from Arkema Co. Mild steel panels (10 cm × 8 cm × 0.2 cm) with the composition given in Table 1 were obtained from Foolad Mobarakeh (Iran). Sample coding used in this study is presented in Table 2.

2.2. Synthesis of Fe_3O_4 nanoparticles

In a typical synthesis procedure, solutions of ferric chloride and ferrous chloride in 50 mL deionized water with Fe^{3+}/Fe^{2+} ratio of 1.8:1 (mol/mol) were prepared as precursor solutions. The iron cations concentration was 0.1 mol/L. Then, 0.4 mol/L of surfactant was added into the solution (Table 3). The composition and reaction condition are presented in Table 3. A schematic procedure of the nanopigment synthesis is displayed in Fig. 1.

At First, the mentioned amounts of iron chlorides were dissolved in deionized water, and then sodium hydroxide solution was added to the solution in the presence of blowing nitrogen