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# Investigation of corrosion protection properties of an epoxy nanocomposite loaded with polysiloxane surface modified nanosilica particles on the steel substrate

E. Matin<sup>a</sup>, M.M. Attar<sup>a,\*</sup>, B. Ramezanzadeh<sup>b</sup><sup>a</sup> Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, P.O. Box 15875-4413 Tehran, Iran<sup>b</sup> Department of Surface Coating and Corrosion, Institute for Color Science and Technology, No. 59, Vafamanesh Street, Hosainabad Square, Lavizan, Tehran, Iran

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## ABSTRACT

In this study, it has been aimed to investigate the corrosion protection properties of an epoxy/polyamide coating loaded with different concentrations (ranged from 3 to 6% (w/w)) of the polysiloxane surface modified silica nanoparticles (nano-SiO<sub>2</sub>). The nanocomposites were applied on the steel substrates. Field emission scanning electron microscope (FE-SEM) and UV–vis techniques were utilized in order to investigate the nanoparticles dispersion in the coating matrix. The effects of addition of nanoparticles on the corrosion resistance of the coating were studied by an electrochemical impedance spectroscopy (EIS) and salt spray test. The coating surface degradation was studied by optical microscope and Fourier transform infrared radiation (FT-IR) spectroscopy. Results obtained from UV–vis and FE-SEM analyses revealed proper and uniform distribution of surface modified nanoparticles in the epoxy coating matrix. It was shown that the coating corrosion protection properties were significantly enhanced in the presence of 5 wt% silica nanoparticles. Less degradation occurred on the surface of the coatings loaded with 5 wt% nanoparticles.

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## 1. Introduction

Organic coatings are widely used to protect steel structures against corrosion due to their barrier properties which prolong diffusion of corrosive species into the coating/metal interface [1–6]. However, it is noteworthy that all of the organic coatings are permeable to potentially corrosive species such as oxygen, water and aggressive ions [7]. The barrier properties can be enhanced by incorporation of anticorrosive fillers into the coatings. It has been shown in many reports that using anticorrosive pigments, i.e. phosphate, chromate and metallic pigments, is a promising way to obtain coatings with reliable corrosion protection properties [8–10]. Many different kinds of conventional micro sized inorganic pigments like ZnO, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have been used to improve the mechanical properties of the organic coatings. It has been also shown that the corrosion resistance of the coatings can be also improved using such anticorrosive pigments [8–10]. These pigments can improve the corrosion resistance of the organic

coatings through different mechanisms [9–11]. In recent decades, the attention of the researchers has been directed to using nano size particles in the organic coatings in order to improve their corrosion protection properties. The nano sized pigments produce much better barrier properties than micro size additives even at low concentrations [12,13]. The high corrosion resistance of the coatings containing nanoparticles may be attributed to their high specific area resulting in great barrier properties [14–16]. There were various reports concerning improving corrosion resistance of the organic coatings using nanoparticles such as TiO<sub>2</sub> [17], ZnO [18], ZrO<sub>2</sub> [16] and organoclay [19]. However, very high surface energy and specific surface area of the nanoparticles are the reasons for their low compatibility with the coating matrix and strong tendency to form aggregates. The large size agglomerated nanoparticles act as defect in the coating matrix producing channels and pores for the corrosive electrolyte diffusion into the coating matrix. This would cause severe decrease in the coating corrosion resistance [20,21]. It has been attempted to find methods to overcome this problem. One successful approach is breaking the large size agglomerated nanoparticles through applying mechanical shear and/or ultrasonic irradiation [22,23]. However, strong physical/chemical interactions between the nanoparticles and the

\* Corresponding author. Tel.: +98 21 64542404; fax: +98 21 66468243.  
E-mail address: [attar@aut.ac.ir](mailto:attar@aut.ac.ir) (M.M. Attar).

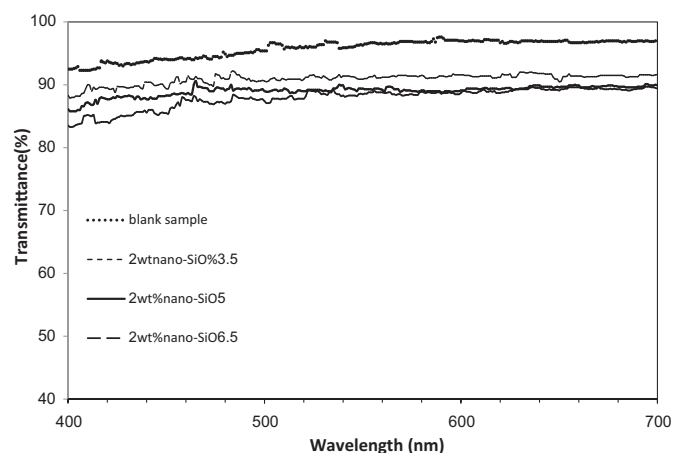


Fig. 1. Variations of transmission versus wavelength of the epoxy nanocomposites containing various loadings of silica nanoparticles.

polymeric matrix cannot be obtained in this way. Different types of coupling agents like silanes are utilized to modify the surface of nanoparticles in order to make them compatible with the polymer matrix. Surface modification of nanoparticles by silane coupling agents also causes the formation of chemical and physical interactions with the coating matrix [23–25]. Behzadnasab et al. [26] investigated corrosion performance of the epoxy coatings containing silane treated  $ZrO_2$  nanoparticles. They reported that the chemical interactions between the epoxy coating matrix and the surface treated nanoparticles caused high barrier properties and ionic resistances. Kathalewar et al. [27] studied the anticorrosion properties of the polyurethane coating loaded with ZnO nanoparticles treated with 3-glycidoxy propyl trimethoxy silane. They showed that surface modification of ZnO nanoparticles by 3-glycidoxy propyl trimethoxy silane enhanced the corrosion resistance of the coating matrix significantly. Silica nanoparticles are modified with organosilanes in order to make them compatible with non-polar or weakly polar coating matrixes. The organosilanes chains grafting on the surface of silica nanoparticles causes the increase of the miscibility of silica nanoparticles with the organic coating. Dolatzadeh et al. [28] reported the effects of surface modification of  $SiO_2$  nanoparticles with organosilane on the anticorrosion performance of the polyurethane coating. They found that modifying the surface of silica nanoparticles by hydrophobic chains caused the improvement of the interfacial interactions at the polyurethane/silica nanoparticle interface, resulting in a better corrosion performance. To the best of our knowledge, there is no systematic report on studying the effects of addition of polysiloxane surface modified nano- $SiO_2$  particles on the corrosion resistance of the epoxy coating.

In this study, the epoxy-polyamide based nanocomposites were prepared using polysiloxane surface modified  $SiO_2$  nanoparticles. UV-vis and FE-SEM techniques are employed in order to investigate the nanoparticle dispersion in the epoxy coating matrix. Optical microscope and FT-IR analysis were conducted to evaluate the epoxy nanocomposite degradation after 30 days immersion in 3.5 wt% NaCl solution. EIS and salt spray tests were performed in order to investigate the corrosion protection properties of the epoxy polyamide coating on the steel substrate.

## 2. Materials and methods

### 2.1. Preparation of epoxy nanocomposite coatings

Nanocomposite coatings were prepared using medium polar surface modified nanosilica. For this purpose, the nano- $SiO_2$

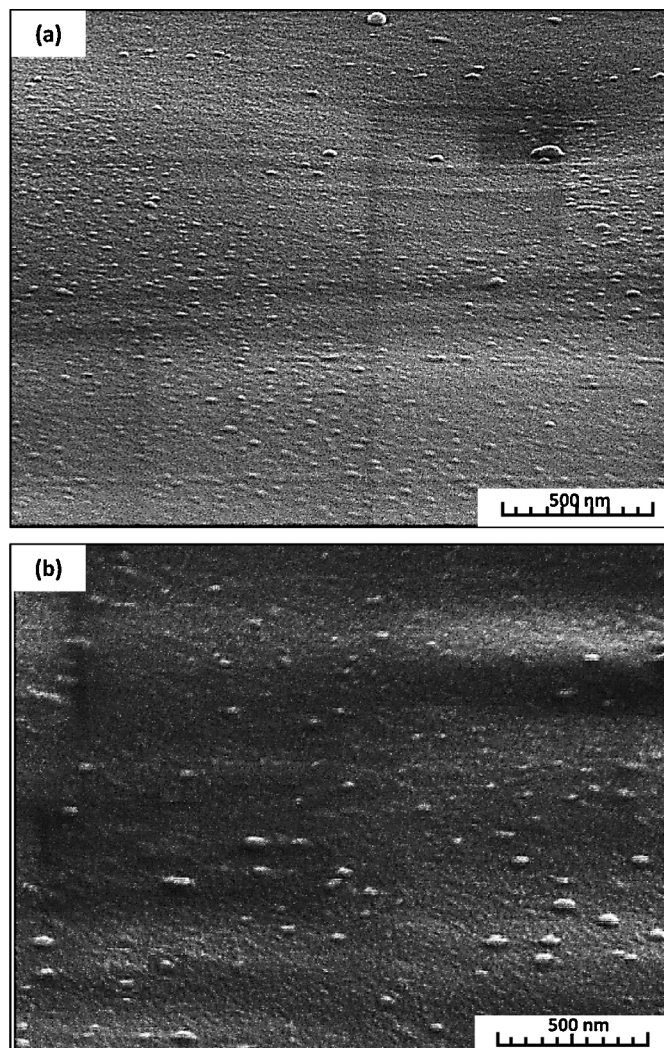


Fig. 2. FE-SEM micrographs at different magnifications of the coating containing 5 wt% nanoparticles: (a) 50,000 $\times$  and (b) 100,000 $\times$  magnifications.

particle was prepared from BYK Co. (BYK-3652). BYK-3652 is a silica nanoparticle modified with polysiloxane coupling agent. It was dispersed in the mixture of solvents: methoxypropylacetate/methoxypropanol 6/1. Therefore, dispersing this nanoparticle in the epoxy coating is not so difficult. The particle size and density of the nanoparticles are 20 nm and  $0.0017 \text{ g cm}^{-3}$ , respectively. Nanocomposites were prepared by addition of 3.5, 5 and 6.5 wt% of nano- $SiO_2$  to an Araldite G27 7071X75 epoxy resin. The epoxy resin used was based on bisphenol-A in a xylene solution having solid content, epoxy value and density of 74–76%, 0.14–0.16 equivalent per 100 g and  $1.08 \text{ g cm}^{-3}$ , respectively. To achieve proper dispersion of nanoparticles in the epoxy coating formulation, a mechanical mixing (shear rate of 2000 rpm) was performed to the nanocomposites for 20 min.

Stoichiometric values of polyamide curing agent was added to the composite formulation and another mixing was done. The nanocomposites were then applied on the surface of mild steel (St-37) panels and glass sheets using an applicator (with a wet film thickness of  $120 \mu\text{m}$ ). Before the coating application, the steel panels were abraded with magnetic polisher followed by acetone degreasing. Finally, samples were baked in an oven at  $120^\circ\text{C}$  for 30 min. The free films of the nanocomposites were prepared from the glass coated sheets. For this purpose, the coated samples were

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