Progress in Organic Coatings 77 (2014) 1935–1945

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Application of EIS and salt spray tests for investigation of the anticorrosion properties of polyurethane-based nanocomposites containing Cr_2O_3 nanoparticles modified with 3-amino propyl trimethoxy silane

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ARTICLE INFO

Article history:
Received 23 March 2014
Received in revised form 20 June 2014
Accepted 30 June 2014
Available online 23 July 2014

Keywords:
Surface modification
Cr_2O_3 nanoparticles
3-Amino propyl trimethoxy silane
EIS
Salt spray

ABSTRACT

The Cr_2O_3 nanoparticles were modified with 3-amino propyl trimethoxy silane in order to obtain proper dispersion and increment compatibility with the polyurethane coating matrix. The nanocomposites prepared were applied on the St-37 steel substrates. The existence of 3-amino propyl trimethoxy silane on the surface of the nanoparticles was investigated by Fourier transform infrared (FTIR) spectroscopy and thermal gravimetric analysis (TGA). Dispersion of the surface modified particles in the polyurethane coating matrix was studied by a field emission-scanning electron microscope (FE-SEM). The electrochemical impedance spectroscopy (EIS) and salt spray tests were employed in order to evaluate the corrosion resistance of the polyurethane coatings. Polarization test was done in order to investigate the corrosion inhibition properties of the Cr_2O_3 nanoparticle on the steel surface in 3.5 wt.% NaCl solution. The adhesion strengths of the coatings were evaluated by pull-off adhesion tester before and after 120 days immersion in 3.5 wt.% NaCl solution. FT-IR and TGA analyses revealed that surface modification of the nanoparticles with 0.43 silane/5 g pigment resulted in the greatest amount of silane grafting on the surface of particles. Results obtained from FE-SEM analysis showed that the surface modified nanoparticles dispersed in the coating matrix properly. Results obtained from EIS and salt spray analyses revealed that the surface modified particles enhanced the corrosion protection performance of the polyurethane coating considerably. The improvement was more pronounced for the coating reinforced with 0.43 g silane/5 g pigment. Moreover, the adhesion loss decreased in the presence of surface modified nanoparticles with 0.43 silane/5 g pigment.

1. Introduction

One of the most important and applicable methods of the corrosion control of metals in many industries is the use of organic coating systems. The organic coatings play as a physical barrier between the metal surface and the corrosive environment [1,2]. In this way, they could reduce the electrolyte diffusion rate into the metal surface. The organic/inorganic anticorrosive pigments are largely used in the organic coatings formulations to enhance its corrosion protection properties. Depending on the corrosion protection mechanism, they can be divided into three categories of barrier, sacrificial and inhibitive pigments [3]. Many different types of micro-sized anticorrosive pigments are used in the organic coating systems and their effects on the corrosion resistance have been extensively studied. However, the use of such pigments causes some undesired defects like decrease in transparency, flexibility, adhesion and scratch resistance of the coating [4]. One approach to overcome these problems is the use of nano sized anticorrosive pigments instead of micro sized one [5].

In recent years, the nanomaterials are introduced as a new branch of chemicals which resulted in many benefits in different industries i.e. chemical [6], medical, pharmaceuticals [7,8], optical and electronic [9]. The importance of nanomaterials compared to conventional micro sized pigments is mainly due to their small size and large specific surface area. The decrease in size of the particles causes mechanical properties enhancement of the coating [10–12].

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http://dx.doi.org/10.1016/j.porgcoat.2014.06.025
0300-9440/

There is a large number of reports indicating that the anticorrosion properties of the polyurethane coatings can be markedly improved in the presence of nanoparticles [13–16].

However, the nanoparticles have strong tendency to aggregation when incorporated into the organic coating matrix. The large size agglomerated nanoparticles act as defect and reduce corrosion protection properties of the polymeric matrix [17,18]. To avoid these drawbacks, the surface treatment of nanoparticles has been proposed [19,20]. Surface treatment of nanoparticles with silane coupling agents has been done as one of the most efficient approaches to enhance their compatibility with the organic coating and prevent their agglomeration. Silane coupling agents can form covalent interactions with the particles surface through sol–gel process. Surface treatment of nanoparticles changes the nature of the nanoparticle surface [21,22]. Replacement of the polar groups presented on the nanoparticles surface with the organic groups of silane causes better compatibility and dispersion in the organic coating [23–29].

There are different reports showing that the surface treatment of the nanoparticles led to an improvement in the corrosion resistance of the organic coatings. Dolatzadeh et al. [21] studied the anticorrosion performance of the polyurethane coating containing SiO_2 nanoparticles modified with organosilane. They found that surface modification f silica nanoparticles by hydrophobic chains caused the improvement of the interfacial interactions at the polyurethane/silica nanoparticle interface, resulting in a better corrosion performance. Behzadnasab et al. [30] reported that surface treatment of the ZrO_2 nanoparticles with amino propyl trimethoxy saline caused a remarkable increment in the corrosion protection performance of the epoxy coating. Kathalewar et al. [31] investigated the effects of ZnO nanoparticles treated with 3-Glycidoxy propyl trimethoxy silane on the anticorrosion properties of the polyurethane coating. They showed that surface treated ZnO nanoparticles increased the corrosion resistance of the polymeric matrix significantly.

The aim of this research is to study the corrosion protection performance of the polyurethane coatings reinforced with Cr_2O_3 nanoparticles modified with 3-amino propyl trimethoxy silane. TGA and FT-IR analyses are utilized in order to evaluate the amount of silane grafting on the surface of nanoparticles. Anticorrosion properties of the coatings are studied by EIS and salt spray tests.

2. Experimental

2.1. Materials

Nano-sized Cr_2O_3 (60 nm in size) nanoparticles were prepared from Alpha Nano Powder Co. The nanoparticles were modified with 3-amino propyl trimethoxy silane (APTMS) supplied from Merck Co. Polyurethane coatings were prepared using acrylic polyol 1780M (Merck Co.) and isocyanate desmodur N75 (Bayer Co.). Mild steel sheets (with dimension of 10 cm × 8 cm × 0.2 cm) were prepared from Foolad Mobarakeh Co. (Iran). The steel sheet has the following composition (wt.%): Fe (97.7), C (0.19), Si (0.415), Mn (1.39), P (<0.005), S (<0.005), Cr (0.026), Mo (0.018), Co (0.429) and Cu (0.0481).

2.2. Surface treatment of Cr_2O_3 nanoparticles

The Cr_2O_3 nanoparticles were treated by different amounts of 3-amino propyl trimethoxy silane. For this purpose, 5 g Cr_2O_3 nanoparticles were added to a three neck reactor containing mixture of ethanol and H_2O under reflux at 80 °C. The suspension was then dispersed by a homogenizer. Then, 0.43, 3 and 5 g 3-amino propyl trimethoxy silane was separately added to the mixture. The pH value in hydrolysis step was adjusted at around 1.5–3 by addition of hydrochloric acid. The hydrolysis reaction was continued up to 1 h. After that, 50 vol% sodium hydroxide solution was added to suspension and the pH value in condensation step was adjusted at around 8–10. The reason for doing surface treatment of nanoparticle at low and then high pHs is obtaining the maximum grafting of silane. The acidic condition causes the maximum hydrolysis of silane and the alkaline condition results in the highest condensation of hydrolyzed silanes on the surface of nanoparticles. The suspension was kept for 2 h at this condition. Finally, the resultant suspension was centrifuged and the residue washed for six times by mixture of water and ethanol to remove the physically adsorbed silanes. Then, the remained precipitate was dispersed in the mixture of ethanol and H_2O. Finally, the nanoparticles were obtained by spray dryer. The list of materials used and their amounts are given in Table 1.

Table 1
Surface modification bath components for the modification of 5 g of Cr_2O_3 nanoparticles with APTMS.

Silane (g)	Ethanol (g)	H_2O (g)	HCl (37%)[a] (cm^3)	NaOH (50 wt.%)[b] (cm^3)
0.43	19.44	0.77	0.4	0.5
3	121.5	4.86	1.4	0.8
5	218	8.90	3.5	1.8

2.3. Cr_2O_3/polyurethane nanocomposite preparation

Nanocomposites were prepared by addition of 1, 2 and 3 wt.% of unmodified and surface modified Cr_2O_3 nanoparticles to the acrylic polyol. Nanoparticles were dispersed in the polyol by the aide of zirconia pearls for 8 h. Then, the isocyanate hardener was mixed with polyol in which the ratio was 1:4. The coatings prepared were applied on the steel panels (10 cm × 15 cm) by a film applicator. Before coating, the steel panels were polished with emery papers of 600 and 800 grades followed by acetone degreasing. Finally, the coatings were cured at 70 °C for 4 h.

2.4. Characterization

2.4.1. Characterization of surface modified nanoparticles

TGA and FTIR analyses were carried out in order to evaluate the silane grafting on the surface of nanoparticles. For this purpose, the FTIR model Perkin-Elmer and TGA model SDTA 851 were utilized. TGA analysis was carried out at temperature region of 25 °C to 700 °C and heating rate of 5 °C/min in nitrogen atmosphere.

2.4.2. Nanocomposite properties characterization

The Cr_2O_3 nanoparticles dispersion in the polyurethane coating was studied by a field emission scanning electron microscopy (FE-SEM Mira).

Corrosion protection properties of the nanocomposites were studied by EIS and salt spray tests. Polarization test was also done by Ivium Compactstat on the steel sheets immersed in the 3.5 wt.% NaCl solutions without and with nano-Cr_2O_3 extract. The EIS was performed with an Ivium Compactstat with a perturbation and frequency range of ±10 mV and 10 kHz–10 mHz, respectively at open circuit potential (OCP). Polarization test was carried out at the sweep rate of 1 mV/s in the range of ±100 mV from OCP. The EIS and polarization measurements were performed in a three electrode cell containing auxiliary electrode (graphite), saturated reference electrode (Ag/AgCl/KCl (saturated)) and working electrode (mild steel). The surface area of the samples was 1 cm^2 and the EIS measurements were done in 3.5 wt.% NaCl solution at pH of 11. The salt spray test was carried according to ASTM B117. The coatings with and without nanoparticles was exposed to 5% NaCl fog for 624 h. The