Surface & Coatings Technology 216 (2013) 199–206

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

Evaluation of synergistic effect of nanozinc/nanoclay additives on the corrosion performance of zinc-rich polyurethane nanocomposite coatings using electrochemical properties and salt spray testing

N. Arianpouya [a,*], M. Shishesaz [a], M. Arianpouya [b], M. Nematollahi [b]

[a] Technical Inspection Engineering Department, Petroleum University of Technology, Abadan, Iran
[b] Electronic Engineering Department, Shariati University, Tehran, Iran

ARTICLE INFO

Article history:
Received 28 April 2012
Accepted in revised form 12 November 2012
Available online 23 November 2012

Keywords:
Nanocomposite coating
Zinc-rich coating
Clay
EIS

ABSTRACT

This research work focuses on the synthesis, characterization and processing of polyurethane/zinc/clay nanocomposites to improve the corrosion performance of zinc-rich coatings. Therefore different percentages of montmorillonite clay nanolayers were added to zinc-rich polyurethane nanocomposites. Ultrasonication process was used to prepare polyurethane/nanozinc/nanoclay composites. Then coatings were applied on steel panels with composition of 10 wt.% nanozinc and 0.5 wt.%, 1 wt.%, 1.5 wt.%, and 2 wt.% nanoclay. TEM was used to analyze the structural characteristics of the samples. The results of the structure analysis revealed the size of nanomaterials. The anticorrosive properties of the nanocomposites were investigated using DC polarization technique, electrochemical impedance spectroscopy (EIS), water absorption and salt spray test. The results of electrochemical tests showed that addition of clay nanolayers improves the corrosion resistance of coatings and the best corrosion performance obtained for the nanocomposite sample with 2 wt.% nanoclay. Also, according to the results of the salt spray test, the sample with 2 wt.% nanoclay showed the least H_2O penetration and exfoliation adjacent to the scratches.

1. Introduction

Hot-dip galvanized steel has been used for more than 100 years in a myriad of projects across the world [1]. It is specified not only for its superior corrosion protection and durability, but also for its low maintenance, economical benefits and low environmental impact [1,2]. But today, due to limitations of hot dip galvanized coatings applied to cover the large constructions, zinc-rich paints as a suitable alternative for these coatings have been used, and extensive research is being done to improve the properties of these coatings [2]. Zinc-rich paints are one of the most effective coatings used in order to protect steel from corrosion [3]. They are used in many aggressive media: sea water, marine and industrial environments [4]. For solvent-based zinc-rich paints, it seems to be established that, at least at the beginning of immersion, zinc particles provide a cathodic protection of the steel substrate [4,5]. In fact, zinc metal causes electrical conductivity of dry film by binding to the surface of the base metal and protects the substrate with sacrificial galvanic protection [5]. Then, a long term protection develops due to the formation of zinc corrosion products, reinforcing the barrier effect of the paint [6]. Physico-chemical properties and corrosion resistance of solvent-based zinc-rich paints strongly depend on pigment volume concentration (PVC), shape and size of zinc dust [7]. In common liquid zinc-rich paint, zinc is usually introduced as spherical pigments with a mean diameter ranging from 5 to 10 μm [8]. The more is the amount of zinc in dry film, the more similar are the film properties to hot dip galvanized coatings [8–10]. However, by increasing the amount of zinc in coating, the adhesion properties of the film become weaker [9,10]. To ensure good electrical contacts between zinc pigments and the steel substrate, a high pigment concentration is required and usually good results are obtained with 92 wt.% to 95 wt.% zinc in dry film [10]. Therefore, the problem is that high percentage of zinc pigments is needed to increase coating efficiency [10,11]. On the other hand, the pigment particle size is very effective on the required percentage of zinc pigment [12]. So, in this paper the nanoparticles were used to reduce the amount of required zinc. In addition, during production of zinc pigments, some parts of the molten zinc are in contact with oxygen and in fact there is a mixture of zinc and zinc oxide [12–14]. Jagtap et al. found that a specific amount of zinc oxide in zinc-rich coatings could improve the corrosion resistance of zinc-rich coating due to the barrier properties [15]. So it seems that addition of lamellar pigments (The primary particles of a pigment may be nodular, spherical, prismatic, platelet or lamellar.) to the coating has double protection effect on the efficiency of zinc-rich coating. Therefore, in this study in order to analyze the synergistic effect of the clay and zinc, zinc pigment was used in combination with different amounts of montmorillonite clay nanolayers.

* Corresponding author. Tel.: +98 9168386587; fax: +98 631 442 3520.
E-mail address: mohamadreza.shishesaz@gmail.com (N. Arianpouya).

0257-8972/$ – see front matter
http://dx.doi.org/10.1016/j.surfcoat.2012.11.036

Table 1
Closite 20A Nanoclay pigment properties.

Organic modifier	Structural formula	Modifier concentration	Moisture content
Dimethyl dihydrogenated tallow, quaternary ammonium (2M2HT)	$CH_3-N^+(CH_3)(HT)-HT$	95 meq/100 g clay	<%2
Particle size	Color	Density	Relative hydrophobicity
<13 μm	Off-white	1.17 mg/l	Strongly hydrophobic

Table 2
Nanozinc pigment properties.

Name of nanopowder	Powder shape	Average grain size	Apparent density
FZnN-20	Sphericity	20 nm	0.4 g/cm^3

Table 3
Sample properties.

Nanocomposite coatings	Nanozinc pigments %wt.	OMMT pigments %wt.
PNC1	10	0
PNC2	10	0.5
PNC3	10	1
PNC4	10	1.5
PNC5	10	2

PNC: polymer nanocomposite coating.

2. Experimental

2.1. The preparation of samples and materials

The steel panels with 6.5 × 6.5 × 0.4 cm^3 dimensions were used for EIS measurements and with 15 × 6.5 × 0.4 cm^3 dimensions for salt spray testing. The panels were sandblasted to Sa 21/2 according to ASTM D609 and used as metallic substrates. Nanozinc particles obtained from Sigma-Aldrich Company, and organically modified montmorillonite clay (OMMT, Closite 20A) obtained from Southern Clay Products Co., Gonzales, TX, USA, was dried at 80 °C for 24 h. The physical characteristics of these additives are shown in Tables 1 and 2. The polyurethane resin was obtained from reaction between two parts: polymeric methylone diphenylene diisosianate (polymeric-MDI; Suprasec 2496; NCO wt.% = 31.3, average functionality = 2.5; Huntsman Polyurethanes) and castor oil polyol (Albodur 912 VP, OH_v = 210 mg KOH/g, average functionality = 2.3, Albedingk Boely Company).

2.2. Preparation of nanocomposites

The castor oil was slowly heated to 60 °C in a water bath and then 10 wt.% zinc pigment was added and the mixture was stirred at 1000 rpm for 2 h followed by sonication for 2 h. By addition of various percentages of OMMT (organically modified montmorillonite), this process was repeated. Then the mixture was mixed with MDI in 4:1 ratio and degassed in vacuum chamber. The synthesized nanocomposites were applied by 60 μm applicator on steel panels (so the wet thickness is 60 μm for the coating) and cured at 60 °C for two weeks in oven. The final thickness (dry thickness) of coating on the panels was between 40 and 50 μm as measured by Elcometer 456[3] coating thickness meter. The prepared samples were mentioned with PNC1 to PNC5 (PNC is an abbreviation for polymer nanocomposite) corresponding to different percentages of nanopigments (Table 3).

2.3. TEM

Transmission electronic microscopy (TEM) is a powerful tool for material analysis [16]. It allows a qualitative understanding of the internal structure and can directly provide information in real space, in a localized area, on morphology and defect structures [16,17]. By using this, the size, dispersion and interaction of nanopigments with polyurethane can be concluded [18]. In this research the TEM was performed in Mashhad Laab Company and the samples were prepared first in IBB Company to the 70–80 nm in a cupper grid.

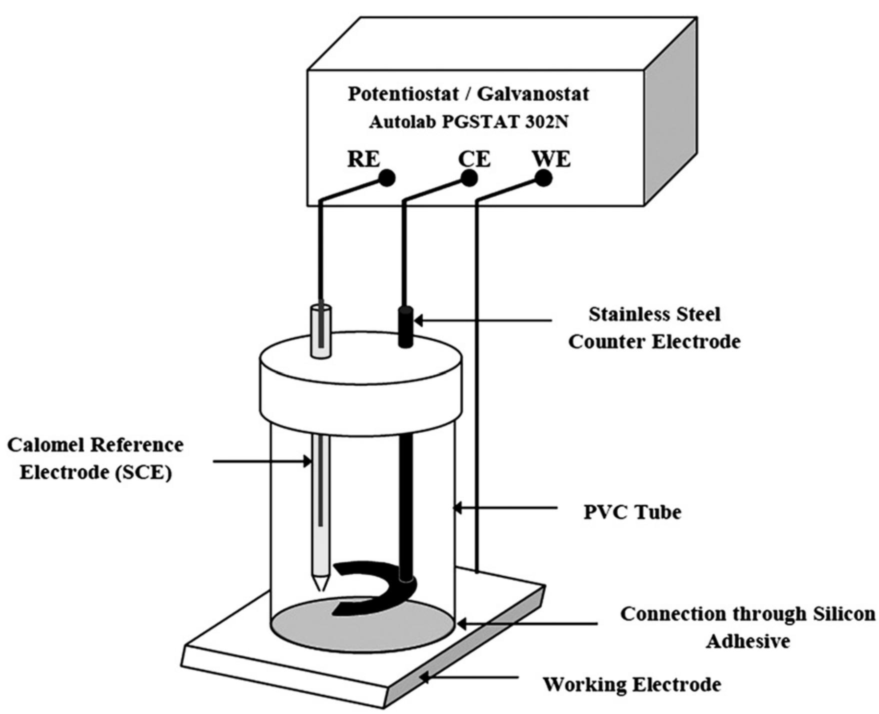

Fig. 1. A standard flat cell was used, employing the coated panels as working electrode, a horseshoe shaped stainless steel plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode and the setup was placed in a Faraday cage.