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Novel properties of a conductive polymeric coating with an insulating nanoadditive

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ABSTRACT

Today, due to the limitations of hot dip galvanized coating, zinc-rich coating as a suitable alternative coating is used extensively, and the effectiveness of the mixture of a specific amount of zinc as a conductive and zinc oxide as a semiconductive additive to improve the corrosion resistance of these coatings has been illuminated. In this research, we obtained novel corrosion resistance properties for the conductive zinc-rich coating using clay layered silicate additive in spite of its insulating nature. So in this paper, zinc-rich polyurethane nanocomposite samples with addition of various concentrations of nanosilicate planes were prepared by ultrasonication method. Optical microscopy and X-ray diffraction for analysis of the structure and electrochemical impedance spectroscopy, water absorption and conductance for analysis the anticorrosive properties were done. Results showed improvement of corrosion resistance with increasing the value of clay in the coating up to 2 wt%. Since zinc-rich coating is a sacrificial coating dependent on conductivity, it seems insulating additives decreases its functionality, but it is interesting that the corrosion resistance is based on the interaction of two important parameters: barrier effect and conductance effect. Planar structure of clay silicate causes to reasonably increase the barrier effect of the coating. At the same time, sacrificial effect of conductive zinc particles gives unique properties to this new nanocomposite with considering the optimum percentage of clay additive to control the conductivity.

1. Introduction

Carbon steels are selected as constructed metals because of their mechanical properties and machinability at a low price, while at the same time they should be corrosion resistant. The most important and widely used metallic coating for corrosion protection of carbon steel is zinc and approximately half of the world's production of zinc is used to protect steel from rust [1–5].

Zinc can be applied on carbon steel by various processes. Hot-dip galvanizing is the most common process, and as the name implies, it consists of dipping the steel workpiece into a bath of molten zinc. It is specified for its low maintenance, economical benefits and low environmental impacts; however, it has some important practical limitations including interior or exterior items that cannot be galvanize coated due to size limitations or where on-site coating application (such as repair or touch-up) is required [6–8].

So today, due to limitations of hot dip galvanized coatings, zinc-rich paints as a suitable alternative to these coatings have been used increasingly popular in the construction and automotive industry, and extensive research is being done to improve the properties of these coatings [9–12].

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. 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. Then, a long term protection develops due to the formation of zinc corrosion products, reinforcing the barrier effect of the paint [13–17]. 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 [14–16]. In common zinc-rich paint, zinc is usually introduced as spherical pigments with a mean diameter ranging from 5 to 10 μm [17–20]. The more is the amount of zinc in dry film, the more similar are the film properties to hot dip galvanized coatings [21,22]. However, by increasing the amount of zinc in coating, the adhesion

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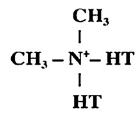
Table 1
Closite 20A Nanoclay pigment and Nanozinc pigment properties.

Closite 20A Nanoclay pigment properties			
Organic modifier	Structural formula	Modifier concentration	Moisture content
Dimethyl dihydrogenated tallow, quaternary ammonium (2M2HT)		95 meq/100 g clay	<%2
Closite 20A Nanoclay pigment properties			
Particle size	Color	Density	Relative hydrophobicity
<13 μm	Off-white	1.17 mg/l	Strongly hydrophobic
Nanozinc pigment properties			
Name of nano powder	Powder shape	Average grain size	Apparent density
FZnN-20	Sphericity	20 nm	0.4 g/cm^3

properties of the film become weaker. To ensure good electrical contacts between zinc pigments and the steel substrate, a high pigment concentration is required and good results are obtained with 92–95 wt% zinc in dry film [23,24]. Therefore, the problem is that high percentage of zinc pigments is needed to increase coating efficiency [16–26]. On the other hand, the pigment particle size is very effective on the required percentage of zinc pigment [26–30]. So, in this study 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 [31]. Jagtap and et al. [32] 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. So it seems that addition of lamellar pigments to the coating has double protection effect on the efficiency of zinc-rich coating. Among all the potential nanocomposite precursors, inorganic clay minerals consisting of layered silicates have been extensively used in the polymer industry, probably because they are natural, abundant and inexpensive and have a very large surface area [33–36]. Clay layered silicates can play an important role in terms of providing barrier properties and high impedance for the coating systems [35–38]. With respect to mentioned concepts, our idea for this study was selected as zinc-rich nanocomposite coating with addition of various concentrations of nanosilicate planes, and consequently synergistic effect of the clay and zinc pigments on the corrosion performance was analyzed.

2. Experimental procedure

2.1. Materials

The steel panels with 6.5 cm × 6.5 cm × 0.4 cm dimensions for EIS measurement were prepared [39]. 2-partial polyurethane including polymeric methylenediphenylenediisocyanate (polymeric-MDI; Suprasec 2496; NCO wt% = 31.3, average functionality = 2.5; Huntsman polyurethanes) and Albodur 912 VP (castor oil polyol; OH_v = 210 mg KOH/g, average functionality = 2.3) was purchased. Spherical nanozinc particles and organically modified montmorillonite clay with properties listed in Table 1 were used in this research. Nanozinc particles were obtained from Sigma–Aldrich Company, and organically modified montmorillonite clay (MMT, Cloisite 20A) was obtained from Southern Clay Products Co. Gonzales, TX, USA.

2.2. Synthesis 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 (ultrasonication process was performed at the frequency of 20 kHz with an inlet ultrasound power of around 1 W/mL, UIP 1000hd ultrasonic processor; titanium sonotrode with 18 mm tip diameter; Hielscher ultrasound technology). By addition of various percentages of OMMT (Organically Modified Montmorillonite), this process was repeated. Then a stoichiometric amount of MDI (in 4:1 ratio) was added to each sample and mechanically mixed again. The blends were then degassed under vacuum for 5 min and immediately poured into molds. By using this process, nanocomposites were prepared (Fig. 1).

2.3. Preparation of coated panels (samples)

The nanocomposites were applied on cold rolled steel substrates with a film applicator regulated for 50 μm wet-thickness and were allowed to be cured for two weeks at 60 °C [40]. The prepared samples were labeled as PNC1 to PNC5 (PNC: Polymer Nano Composite) corresponding to different percentages of nanopigments (Table 2).

2.4. Characterization

2.4.1. Structure

The optical homogeneity of the polyol/zinc/clay dispersions and effect of sonication process on de-agglomeration of clay and zinc pigment aggregates were examined using a BX-50 Olympus optical microscope. By incorporating a polarizer into the system, agglomerates of platelets and particles could be easily distinguished from the polyol matrix. The suspensions stability was analyzed by a sedimentation method. The blends were placed at 50 °C for two weeks [41,42] to observe the amounts of clay precipitates. The intercalation/exfoliation of nanoclay stacks and de-agglomeration of nanozinc colloids in the polymer matrix were measured by X-ray diffractometer (XRD, Bruker, D8ADVANCE, Filter Ni, X-Ray Tube Anode Cu, CuKα radiation, λ = 1.54 Å, at 40 kV and 40 mA). The diffraction patterns were collected for $2\theta = 0.5°–10°$ at the scanning rate of 0.5°/min for detecting clay layers and from 20° to 60° at the scanning rate of 0.5°/min for detecting zinc pigments.

The Transmission Electron Microscopy (TEM) was done for analysis of size, dispersion and the interaction of nano pigments with polyurethane, and was performed in Mashhad Laab Company. The samples were prepared first in IBB Company to 70–80 nm in a cupper grid. Also the conductance of synthesized nanocomposite coatings in this study was measured to analyze the value of connectivity of zinc particles at the presence of clay layers. The relative conductance of the PNC samples was measured with the help of a multimeter by bringing the pointers of the probes in contact with the coating on the surface between two points separated by 5 cm.