Materials Research Bulletin 80 (2016) 7–22

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Electrochemical and anticorrosion behaviors of hybrid functionalized graphite nano-platelets/tripolyphosphate in epoxy-coated carbon steel

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ARTICLE INFO

Article history:
Received 14 October 2014
Received in revised form 23 May 2015
Accepted 15 June 2015
Available online 17 March 2016

Keywords:
A. Composites
A. Nano-structures
C. Impedance spectroscopy
D. Electrochemical properties

ABSTRACT

Functionalized graphite nano-platelets (FGNP) were combined with tripolyphosphate (TPP) to gain a hybrid nano-particle (FGNP-TPP) with homogenous dispersion in epoxy, resulting in an excellent anti-corrosion coating for carbon steel substrate. Characterization analyses of the hybrid nano-particle were performed by FT-IR, SEM, XRD and TEM. TPP was linked to FGNP nano-particles by hydrogen bondings. Different epoxy coatings formulated with 1 wt.% of FGNP, FGNP-TPP and TPP were evaluated. Electrochemical investigations, salt spray and pull-off tests showed that the hybrid nano-particle can provide long-term corrosion protection compared to FGNP and TPP due to synergistic effect between FGNP as an accelerator and TPP as a corrosion inhibitor to produce a uniform and stable iron-phosphate passive film with high surface coverage.

1. Introduction

In recent years, graphene and its derivatives such as graphene oxide (GO) and graphite nano-platelets (GNP) have gained considerable attention in nano-materials field [1]. Some properties, such as unique mechanical strength, electrical and thermal conductivity, thermal stability, chemical inertness, electromagnetic interference and impermeability to small ions and molecules make them as ideal candidates for various applications [1–5]. In comparison with carbon nano-tubes, graphene nano-materials are excellent reinforcing materials due to their lower cost, higher surface area and very good mechanical stiffness [6]. They were initially prepared from graphite that is naturally abundant and widely available [6]. Some studies have suggested the corrosion protection functionality of graphene and graphene oxide [7–10]. Electrochemical and anti-corrosion behaviors of functionalized graphite nano-platelets (FGNP) in epoxy coating were described in detail in our previous paper [11]. FGNP was used as a compatible nano-particle to develop a homogenous epoxy nano-coating with impressive anti-corrosion behavior for carbon steel [11]. The results showed that FGNP-epoxy coating had excellent adhesion to the metal substrate and protected it by physical barrier and passivation (iron oxide passive film) mechanisms [11]. As long as the integrity of this iron oxide passive film be guaranteed, the corrosion rate will be minimal [12].

In some literatures, the electrolyte pH, oxygen content, aggressive ions concentration and additives were regarded as factors contributing to the iron oxide passive film formation and its degradation [12,13]. The passive films damage can be prevented by adding corrosion inhibitors such as chromate, phosphate, nitrite, tungstate and molybdate into coatings [12]. Phosphate salts have some advantages compared to the other inhibiting agents such as lower cost, lower toxicity and ready availability that led to their wide use in practice [12]. Great deals of studies have been devoted to the corrosion inhibition effects of phosphate compounds [14–16].

During the recent decades, classical toxic anti-corrosive pigments like chromate and lead have been gradually replaced by zinc phosphate and related compounds [17]. The anti-corrosion performance studies of zinc phosphate had led to contradictory results that are not yet conclusive [18,19].

The low solubility of zinc phosphate in water and its extremely coarse crystalline precipitations, hinder the growth of effective protective films [20].

Reduction of particle size, chemical modification and changing orthophosphate anion to tripolyphosphate (TPP) enhance the corrosion inhibition properties due to its improved water solubility [18,20]. One key feature of the most polyphosphate grades is

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http://dx.doi.org/10.1016/j.materresbull.2015.06.052
0025-5408/

phosphate content increment which enables excellent long-term protective behavior [17,21].

Polyphosphates have shown efficient corrosion inhibition [17,20].

Moreover, inorganic tripolyphosphates constitute a promising novel group of non-toxic phosphate inhibitors for paints [17,20,22]. It is believed that TPP anions ($P_3O_{10}^{5-}$) react with iron ions at anodic sites of steel surface, which constitute an insoluble layer containing, mainly, ferric tripolyphosphate [20]. Also, TPP may partially amalgamate with the passive film appearing on the metal surface and improve its protective properties [23].

This iron phosphate film is very hard and exhibits great adhesion to the steel substrate [20]. However, since all of these anti-corrosive pigments are micro-sized, they should be used in high values (10–30% volume fraction or 40–60% wt) in organic coatings to be effective [17,24]. In addition, leveling and dispersing agents are needed for these pigments dispersion [17,18,24].

In this study, FGNP nano-particles were modified with TPP anions to achieve hybrid FGNP-TPP nano-particles. The hybrid nano-particles were capable of being thoroughly distributed in epoxy coating without requiring any dispersing and leveling agents.

They also exhibited more efficient anti-corrosion performance compared to FGNP and TPP pigments. Synergistic effect between FGNP and TPP inhibitor made FGNP-TPP as useful anti-corrosion nano-material for long-term corrosion protection. Moreover, since this hybrid nano-particle is used in lower amounts than micro-sized zinc phosphate and related compounds in paint formulations, it is preferred from economic point of view.

In fact, both surface passivation ability and barrier properties of the nano-coating can be optimized using this hybrid anti-corrosive nano-particle.

2. Experimental

2.1. Materials

The purchased graphite intercalated compounds (GIC), was an expandable sulfuric acid-intercalated graphite Spec: 9950250 (Boading Action Carbon Co., Ltd). Sodium tripolyphosphate (STPP) technical grade 85% was prepared from SIGMA-ALDRICH and ethanol 96% was prepared from Merck. Epoxy resin EPIRAN6 (EEW 185–196), H46 amine hardener (H active:100) and epoxy thinner T51 were prepared from Khuzestan petrochemical Co., Pars Gohar Co. and Rangin Zereh Co. respectively. Carbon steel (ST37) plates were used as base metals for the coatings. Sodium chloride was obtained from Merck company and aqueous solutions were prepared from double distilled water.

2.2. Preparation of hybrid FGNP-TPP

FGNP was fabricated as described in detail in our previous work [11]. In summary, expanded graphite (EG) was obtained by rapid thermal expansion of GIC at 900 °C under inert argon atmosphere. Then, EG was sonicated in water/ethanol (25/75 (% v/v)) solution in an ice bath for 8 h to obtain FGNP in the range of 20–40 nm [11].

For preparation of hybrid FGNP-TPP, STPP was added to the mixture and gently stirred at 300 r.p.m and 40 °C to achieve a viscous homogeneous paste, followed by drying in an oven at 40 °C for 48 h. The weight ratio between FGNP and STPP was 1:1.

2.3. Preparation of coating systems

FGNP, FGNP-TPP and STPP pigments at concentration of 1 wt.% were incorporated into epoxy coatings hereafter named as: FGNP-epoxy, FGNP-TPP epoxy and STPP-epoxy, respectively.

First, FGNP-TPP powder was dispersed in epoxy thinner (T51) by sonication for 30 min, subsequently added into the epoxy resin and mixed for 2 h to ensure a homogeneous dispersion. FGNP-epoxy was prepared by the same method.

For preparing STPP-epoxy, a mixture of the resin and STPP pigments were mixed by a Perl-mill mixer for 8 h in order to get homogenous distribution. To achieve the final coatings, amine hardener H46 curing agent was added to the mixtures.

The coatings were applied by air spraying over sand blasted carbon steel panels (SSPC-SP3) of 15 cm × 10 cm and were evaluated after 14 days of curing at room temperature. The thicknesses of the dry films after subtracting the sand blast profile (ASTM D4417) (20 μm) were obtained 60 ± 5 μm.

2.4. Analytical characterization

Surface morphologies of the carbon steel exposed to STPP inhibitor solution and the morphology of FGNP-TPP nano-particles were investigated using AIS-2100 SERON Co. scanning electron microscope (SEM). To examine the interactions between FGNP and TPP, fourier transform-infrared spectroscopy (FT-IR) was taken with KBr pellets using a Bruker alpha FT-IR spectrometer in the range of 4000–500 cm^{-1}. In order to investigate the composition of passive film formed on carbon steel, X-ray diffractions (XRD) analysis were carried out using a Philips Model PW1840 X-ray diffractometer employing Fe filtered Co Kα radiation (k = 1.789010 Å) with 30 mA flow intensity and voltage of 40 kV, in a range of 2–110°. Distribution homogeneity and the particle size of FGNP-TPP pigments in the nano-coating were investigated, using a CM 30, Philips Co. transmission electron microscope (TEM) instrument.

2.5. Electrochemical and anti-corrosion characterization

Electrochemical measurements for the investigation of corrosion protection performances of the coatings were performed on an Autolab potentiostat galvanostat 84165 with Nova 1.6 software.

A three-electrode cell was used employing the coated plate as working electrode with an exposed area of 12.56 cm^2, graphite as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

The tests were performed at room temperature in 3.5 wt.% NaCl solution in frequency range of 10 mHz–100 kHz with an a.c amplitude of 10 mV.

Initially, the open circuit potential (OCP) was monitored for 30 min to ensure its stability and then, the impedance measurements were carried out in OCP potential.

In order to minimize noise interference, all experiments were carried out in a faraday cage. The experimental data were analyzed using the commercial software ZsimpWin 3.22 developed by Princeton Applied Research, TN, USA.

The corrosion resistance of bare steel samples in the presence of STPP inhibitor was studied by a potentiodynamic polarization test after 4 h immersion in inhibitor solution in stable OCP. The test was carried out by an Ivium potentiostat in an electrochemical cell including bare steel specimen (working electrode), graphite (counter electrode) and saturated Ag/AgCl (reference electrode). The polarization curves were obtained at sweep rate of 1 mV/s in the range of ± 200 mV from OCP. The test was carried out on 1 cm^2 of the samples in inhibitor solutions.

The corrosion resistances of the coatings were studied in a salt spray test cabin ERICHSEN according to ASTM B117.

The coated samples were exposed to a direct spray (0.7 bar) of NaCl 5 wt.% solution at 35° C for 650 h. Coatings adhesions were measured using a direct pull-off adhesion test method in accordance with ASTM D4541 type III by a Posi Test-AT-N digital adhesion tester.