Progress in Organic Coatings 114 (2018) 33–39

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Anticorrosive performance of super-hydrophobic imidazole encapsulated hollow zinc phosphate nanoparticles on mild steel

Ananda J. Jadhav, Chandrakant R. Holkar, Dipak V. Pinjari*

Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai, 400019, India

ARTICLE INFO

Keywords:
Anticorrosion
Encapsulation
Hollow zinc phosphate
Super-hydrophobic
Imidazole
Octanol

ABSTRACT

Superhydrophobic imidazole encapsulated hollow zinc phosphate nanoparticles were synthesized and used in an epoxy coating as a corrosion inhibitor for protecting the mild steel. The surfactant assisted facile sonochemical route has been used for the synthesis of hollow zinc phosphate nanoparticles. The nanoparticles were characterized by X-ray diffraction, Brunnauer–Emmett–Teller nitrogen adsorption/desorption isotherms, field emission scanning electron microscopy and transmission electron microscopy analysis to confirm the successive formation of a hollow assembly of the zinc phosphate. The encapsulation and the release (under acidic and basic pH conditions) of imidazole from the hollow lumen of the zinc phosphate were determined by UV–vis spectrophotometric analysis. The surface of the imidazole encapsulated hollow zinc phosphate nanoparticle was successfully grafted with octanol to achieve superhydrophobicity. The contact angle of the octanol-grafted nanoparticles was found to be 154° as their surface was modified by $-(CH_2)_6-CH_3$ groups. The anticorrosive performance of the prepared epoxy material has been checked by incorporating it into the epoxy resin and were coated over the mild steel panels. The results have been compared with the neat epoxy and normal zinc phosphate incorporated epoxy coatings for their corrosion inhibition performance. The electrochemical impedance spectroscopy and salt spray analysis have been used to evaluate the anticorrosion performance of all the three coatings. The anticorrosive performance of the epoxy coating incorporated with superhydrophobic imidazole loaded hollow zinc phosphate was found to be far superior compared to the neat epoxy and normal zinc phosphate incorporated epoxy coating.

1. Introduction

Mild steel is a commonly used fabrication material that is extensively used in many industries and day to day life [1]. Metal corrosion is a serious problem faced by many industries due to huge costs associated with their degradation [2]. The corrosion of plant metal can result into a loss of valuable materials, and can lead to a contamination of the synthesized product, reducing the efficiency of the plant and can also increase the maintenance cost resulting in frequent plant shutdowns [3]. The common method to avoid the metal corrosion is to cover the surface with a polymeric coating, to avoid the direct contact of the destructive reactive species with the metal surface [4]. The efficiency of the polymeric coating systems depend on its extent of blocking the properties for the diffusion of the H_2O, O_2, and possible electrolytes [5].

Thermosetting resins are mainly used in polymeric organic coating for the protection of metals, most of the coating ingredients such as solvent, organic corrosion inhibitors, and curing agents get leached out or desegregate from the protective film during the curing stage, which leads to faults in the film(microcracks, holes etc.) [6,7]. These defects are the source for the penetration of corrosive ions, leading to a reduction in corrosive resistance of the film [1].

Organic/inorganic inhibitor embedded coatings are being developed to overcome the issues related to the conventional coating system [3,8–12]. Imidazole is an outstanding corrosion inhibitor as it is cost-effective and is an environmentally friendly chemical [13–16]. Due to its high solubility in water, it can easily leach out from the coating which causes micropores and disrupts the integrity of the coating and can result in a reduction in the corrosion inhibition performance of the coating. To overcome this problem, an encapsulated or entrapment of highly water-soluble inhibitors inside the hollow lumen of the micro or nano water-insoluble inorganic particles have been extensively studied. Chenan and coworkers reported anticorrosive agent encapsulation in the hollow mesoporous zirconia nanospheres [17]. Chen and Fu prepared spherical shape mesoporous hollow silica for the loading of benzotriazole as a corrosion inhibitor [18]. Zhao and coworkers

* Corresponding author.
E-mail addresses: dv.pinjari@ictmumbai.edu.in, dpinjari@gmail.com (D.V. Pinjari).

http://dx.doi.org/10.1016/j.porgcoat.2017.09.017
Received 12 April 2017; Received in revised form 28 September 2017; Accepted 28 September 2017

prepared micron size hollow raspberry shaped polymeric particles for loading of benzotriazole [10]. Choi and co-workers formulated the Triethanolamine loaded hollow polystyrene nanoparticles for the protection of mild steel from corrosion [19]. Yi et al. [1], as well as Fix et al. [20], used halloysite nanotubes for the loading of anticorrosive agents. These nanocontainers loaded with corrosion inhibitors dispersed in the coating can release inhibitor on demand during the corrosion process and protect the underlying metal. This advanced technology helps in storing the inhibitor and thereby avoiding any adverse interaction of the inhibitor with the coating. Nanocontainers are capable of loading high amount of inhibitor, avoid detrimental untimely leaching of inhibitor and can ensure a sustained and stimuli-responsive release of the encapsulated inhibitor through the hollow lumen on demand. The release of the loaded anticorrosive materials is released by stimuli (i.e. change in temperature, pressure, variation in local pH, change in ionic concentration and/or the presence of aggressive ions) at the damaged area of the coating [21].

The concept of superhydrophobic coating for the protection of metals has a great potential. The superhydrophobicity of the anticorrosive nanomaterials has an excellent property to reduce the dissolution of the protective oxide layer formed between the coating and the metal surface as well as it can efficiently block the invasion of destructive species like H_2O and Cl^- thus, preventing the metal surface underneath the coating from further corrosion [22]. Recently, a lot of work has been reported on the development of superhydrophobic coatings based on ZnO [23], Al_2O_3 [24], SiO_2 [24–27], TiO_2 [9,28] and CuO [29]. All these materials never take part in the actual corrosion inhibition process. They are used as a carrier as well as provide the surface for the development superhydrophobicity.

No work has been reported on the synthesis of superhydrophobic zinc phosphate (ZP) nanoparticle. This work defines a new input to the strategy of superhydrophobic imidazole encapsulation into the lumen of hollow zinc phosphate nanoparticles (Su-Im-HZPn) for the smart corrosion inhibition onto the mild steel. Hollow zinc phosphate Nanoparticle (HZPn) with a hollow core/porous shell structure was synthesized through a combined action of ultrasonic radiation and a suitable surfactant [30]. Here, we have used zinc phosphate which is also an eco-friendly corrosion inhibition pigment for the loading of organic corrosion inhibitor. The anticorrosive property of the prepared materials was checked by incorporating it into the epoxy resin which was coated onto the mild steel. An accelerated salt spray exposure test (SST) was used to find the extent of corrosion under the coated film on the mild steel substrates. Electrochemical impedance spectroscopy (EIS) was employed to get significant mechanistic evidence regarding the corrosion inhibition mechanism. For the sake of comparison, a similar analysis was performed on neat epoxy (Epo) alone and industrially available zinc phosphate incorporated epoxy coating (ZP-Epo) coating on the mild steel panels.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (Zn $(NO_3)_2$ $6H_2O$), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), hexane, octanol, sodium lauryl sulfate (SDS), ammonia solution (25%), imidazole, and acetone were purchased from S. D. Fine Chemicals Ltd., Mumbai, India. Epoxy resin was requested from Nippon Paint Pvt. Ltd. Mumbai India. Absolute ethanol was obtained from Changshu Yangyuan Chemicals, China. Distilled water prepared using Millipore apparatus was used during all the experimental runs.

2.2. Preparation hollow zinc phosphate nanoparticle (HZPn)

The detailed experimental procedure for the preparation of HZPn, loading, and release of imidazole into the hollow lumen of the nanoparticles and its detailed characterization has been reported in our previous work [30].

In a typical procedure, a 100 mL of 33.4 mM of Zn $(NO_3)_2{\cdot}6H_2O$ and 100 mL of 20 mM of $(NH_4)2HPO_4$ solutions were prepared separately. The pH of the reaction was maintained to about 8.5 using ammonia solution (25–28%). SDS (1.0 wt.%), which was used as a surfactant, was added into the Zn $(NO_3)_2{\cdot}6H_2O$ solution before the reaction. The prepared aqueous solution of $(NH_4)_2HPO_4$ thus prepared was then added dropwise to the already prepared aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ in the presence ultrasonic irradiation (ACE horn, 22 kHz frequency at 40% amplitude) while maintaining the temperature of 5–10 °C over 30 min period. After complete addition of $(NH_4)_2$ HPO_4, the irradiation was continued for a further 30 min, which results in a formation of a dense white precipitate of HZPn. The precipitate was collected by centrifugation and washed repeatedly with water and ethanol. After complete washing, the product was dried at 40 °C for 12 h in a suitable oven. The imidazole loading in to the hollow lumen were carried in phosphate buffered saline (PBS) at pH 6 and 10 separately. The process involved, the addition of 50 mg of HZPn in 50 mL of PBS (pH were 6 and 10) containing 50 mg of imidazole. The resulting solution was stirred for 50 h at 37 °C. The imidazole that remained in the solution was determined using a UV–vis spectrophotometer (UV–vis spectrophotometer Hitachi U-2800), the absorbance value was measured at a characteristic wavelength (λ_{max} = 206 nm) of the imidazole. The percentage of imidazole loaded into the HZPn was determined by subtracting the initial amount of imidazole (1000 ppm) in the solution to the amount of imidazole remain in the solution.

2.3. Preparation of superhydrophobic nanoparticles

The imidazole encapsulated hollow zinc phosphate (Im-HZPn) were stirred in hexane containing octanol at room temperature (≈30 °C) for 4 h to impart Octyl groups on the nanoparticle surfaces, then the superhydrophobic imidazole loaded hollow zinc phosphate nanoparticles (Su-Im-HZPn) were obtained after washing the particle with ethanol which were then dried at 40 °C for 24 h.

2.4. Preparation of Su-Im-HZPn/epoxy coatings

Su-Im-HZPn was dispersed in epoxy resin using pigment Muller and acetone were used as a solvent. The anticorrosive performance of Su-Im-HZPn incorporated epoxy resin (Su-Im-HZPn-Epo) was checked on 70 mm × 50 mm × 1 mm, mild steel panel. Before the application of Epo, ZP-Epo and Su-Im-HZPn-Epo onto the mild steel panel, the panel surface was degreased using acetone and roughened using emery paper (grade 240, 360, 800) then washed with ethanol and dried. Then, the mild steel specimens were coated with Epo, ZP-Epo and Su-Im-HZPn-Epo with a thickness of 30–35 μm.

2.5. Characterization

To estimate the surface morphology and size of the HZPn and Su-Im-HZPn, the FE-SEM was carried out. In order to confirm the hollow structure, thickness of the shell and to confirm the imidazole loading visually into the hollow lumen of the zinc phosphate nanoparticles, TEM analysis was also carried out. The water contact angle was found out with the help of contact angle Goniometer (CA Goniometer 190-F2, Rame hart, USA) under ambient laboratory conditions. The anticorrosive performance of the coating was checked using electrochemical measurements (Autolab Instruments, Netherlands) and salt spray analysis (using Weiss Technik SC450) according to ASTM B117 (at 35 °C using 5 wt.% NaCl solution) in approximately 480 L chamber.

2.6. Corrosion inhibition tests

Corrosion inhibition property of the prepared Su-Im-HZPn was