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Epoxy coating based on montmorillonite-polypyrrole: Electrical properties and prospective application on corrosion protection of steel

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ABSTRACT

In this study, nanostructured composite based on Montmorillonite-Polypyrrole (Mt-PPy) was prepared via in situ chemical polymerization of Pyrrole in presence of Mt and dodecyl benzene sulfonic acid (DBSA). Subsequently, the as-prepared Mt-PPy additive as well as pure Mt and PPy were incorporated into an epoxy coating as anticorrosive protection additives for low carbon steel. The electrical conductivity, chemical changes and microstructure of the as-prepared electrically conductive additives were investigated. Steel coated specimens were prepared via solvent cast method and the anticorrosion protection ability of the coatings was evaluated by means of electrochemical impedance spectroscopy (EIS). Likewise, surface features of the coatings such as contact angle and roughness were examined. Due to the higher aspect ratio and ease of dispersion of Mt-PPy epoxy coatings loaded with Mt-PPy additives exhibited higher electrical conductivity values with respect to those containing merely PPy. Besides, contact angle (CA) between deionized water and Epoxy/Mt-PPy coated carbon steel was higher than CA for neat epoxy whereas CA of Epoxy/PPy and Epoxy/Mt were significantly reduced. EIS measurements revealed higher impedance values for Epoxy/Mt-PPy coating; the outputs of EIS suggested enhanced barrier property of epoxy coating when Mt-PPy additive was added. The results observed in this study are pointing towards the prospective use of the Epoxy/Mt-PPy with 5 wt% content as a corrosion protective coating for carbon steel.

1. Introduction

Interest in developing composites based on intrinsically conducting polymers (ICPs) has increased over the last three decades due to their functional property, i.e. redox reactions ability, which make the ICPs excellent for various technological applications such as mechanical sensors [1,2], scaffolds for tissue engineering [3], electronic devices [4], electromagnetic shielding [5,6], etc. In addition, the ICPs have been widely investigated in the field of corrosion protection of metal surfaces [7–10] and the advances made on this topic have led to commercial coatings based on ICPs with enhanced anticorrosion protection ability [11]. Furthermore, this class of polymers is attributed a non-toxic behavior which make the ICPs possible substitutes to the hazardous chromium hexavalent compounds [12]. Amongst ICPs used as protective corrosion additive, polypyrrole (PPy) has received considerable attention due to its straightforward polymerization, environmental and thermal stability as well as its electrical properties, which can be reversibly controlled by changing the oxidation state [13].

PPy for anticorrosion protection purposes can be either coated on metal surfaces via electrodeposition [14–16] or blended with conventional polymers resulting in a composite coating to be subsequently deposited onto metal surface [17,18]. For instance, PPy was electrodeposited onto iron and aluminum substrates from diverse precursor's solutions. Besides the good corrosion protection exhibited by PPy film, it was highlighted the importance of the dopant ion upon the anticorrosion protection ability displayed by the film [19]. In alternative to the electrodeposition of PPy layers, particle form of PPy can be obtained via the chemical polymerization wherein the polymer is doped with suitable counter-ion improving the dispersion of PPy in a wide range of organic solvents [13]. In this case, simultaneous solvent soluble and electrically conductive PPy particles are possible to be blended with conventional polymer coatings. The resulting formulation can be processed via traditional paints deposition methods such as solvent cast technique which is suitable for developments in laboratory scale and when a quick response of the coatings is desired.

Epoxy based binders loaded with PPy are amongst the polymer coatings formulations investigated for corrosion protection of steel and aluminum alloys. They are attributed the advantages of good adhesion

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on metal surface and mechanical properties from epoxy matrix alongside electrochemical properties and non-toxic behavior of PPy. For instance, it was observed that PPy-filled-epoxy systems are effective organic coatings to prevent corrosion on steel surface [17]. Besides the enhanced anticorrosion protection property observed, it was highlighted that the organic coatings containing conductive polymers are promising candidates to replace hexavalent chromates once those coatings presented electrochemical properties similar to those found for chromates. In another study, "smart" corrosion protective PPy/Epoxy coatings for mild steel [20] were formulated; in there the role of the secondary dopant used during PPy preparation on the corrosion protection mechanism was emphasized.

In spite of these advantages, a major restriction to formulate Epoxy/PPy coatings is how to disperse the electrically conductive additive across the polymer matrix. One of the most efficient alternatives to overcome this issue is to prepare a nanostructured functional organic-inorganic hybrid additive based on montmorillonite (Mt) and ICPs like Polyaniline (PAni) or PPy. In one investigation for instance, the incorporation of PAni-Mt and PPy-Mt nanostructured additives into epoxy coatings increased the corrosion protection on metal surface due to the good dispersion of PAni-Mt or PPy-Mt in the polymer matrix. It was proposed higher barrier property for the coatings loaded with PAni-Mt or PPy-Mt with respect to the neat epoxy, these additives reduced the coating permeability offering higher resistances for the ingress of oxygen and water from the electrolyte [21]. In another study, epoxy based polymer coating loaded with hybrid PPy-montmorillonite has been investigated on the corrosion protection of aluminum 5000 series, EIS measurements demonstrated higher corrosion protection epoxy coating in the order of Mt-PPy > PPy > Mt [18].

Nanostructured PPy-Mt additives can be prepared through the in situ polymerization of pyrrole in presence of sodic or organophilic Mt [22–27]. In our previous report, it was observed that the nature and size of counter ions, such as dodecyl benzene sulfonic acid (DBSA), sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) in conducting polypyrrole have significant influence on the site-specific interactions between insulating polymer matrix and conducting phase [28]. Moreover, due to the ease of dispersion and enhanced distribution of this nanostructured electrically conductive additive, coatings containing Mt-PPy exhibit higher electrical conductivity values and lower percolation threshold with respect to those based merely on PPy [29,30]

Even though many studies have dealt with the preparation of either thermoplastics or thermosetting polymer coatings based on Mt-PPy, to the best of our knowledge epoxy based coatings containing Mt-PPy as electrically conductive additive focused on the protection of carbon steel against corrosion remains a subject to be investigated. Based on this context, the purpose of this study is the preparation of electrically conductive polymer composites coatings containing montmorillonite (Mt), polypyrrole (PPy) and montmorillonite-polypyrrole (Mt-PPy). Special attention is given to the preparation and characterization of Mt.PPy nanostructured hybrid as electrically conducting additive. Mt.PPy has been obtained through the chemical polymerization of pyrrole in presence of montmorillonite and both, electrical conductivity as well as chemical structure have been assessed and confronted to pure Mt and pure PPy before being added into epoxy binder to form the steel coated samples. Owing to optimize the time comprised between the coatings preparation up to the evaluation of their properties, solvent cast method has been selected on the preparation of steel coated specimens. As far as this method is concerned, quick responses can be obtained while new formulations of polymer coatings are under development.

2. Experimental

2.1. Materials

Sodium bentonite (Vulgel CN 45) was supplied from *Aliança Latina Indústrias e Comércio Ltda*, Brazil. Pyrrole, 98%, (Sigma Aldrich) was purified by distillation under reduced pressure and stored in the refrigerator before use. Iron (III) chloride hexahydrate $FeCl_3{\cdot}6H_2O$ analytical grade (Vetec Quìmica Fina, Brazil) and dodecyl benzene sulfonic acid (DBSA) (Sigma Aldrich) were used as received. The Epoxy resin used on the coatings preparation was the diglycidyl ether of bisphenol-A (DGEBA) under the trade name TCR 550 (Triepox, Brazil). Toluene analytical grade (Vetec Quìmica Fina, Brazil) was used as dispersive medium and XR – 435 (Triepox, Brazil) as curing agent.

2.1.1. Synthesis of electrically conducting additives (Mt-PPy)

The preparation of both Polypyrrole (PPy) and nanocomposite montmorillonite-Polypyrrole (Mt-PPy) as the electrically conductive additives was based on the method described elsewhere [28]. In a typical preparation route to obtain Mt-PPy, 2.5 g of montmorillonite (Mt) and dodecyl benzene sulfonic acid (DBSA) were dispersed into 250 mL of distilled water (ionic conductivity near 1.0 μS/cm) under vigorous stirring for 2 h at room temperature. An extra solution was prepared using 0.25 mol of $FeCl_3{\cdot}6H_2O$ in distilled water. Both solutions were mixed together and the resulting reaction media sonicated for 20 min to improve dispersion of montmorillonite particles. Next, 50 mL of aqueous dispersion of Py (0.11 M), the molar ratio between DBSA/Py used in the polymerization was 1:5, were added dropwise to the reaction media to initiate polymerization. The reaction proceeded for 1 h under stirring at room temperature and continued all through the succeeding 24 h in a steady state for finishing the polymerization reactions. After, the conducting additives were filtered and washed with distilled water and dried at 60 °C. For the preparation of pure PPy, similar procedure has been adopted apart from the presence of Mt at the initial solution.

2.1.2. Coatings preparation

The coatings investigated in this study consisted in the epoxy based without the addition of additives as well as loaded with PPy, Mt and Mt-PPy as the electrically conductive additives at three corresponding contents 5, 10 and 15 wt%. The preparation of the coatings consisted in mixing 1.7 g of epoxy resin with 1.0 g of toluene. Next, each of the additives was incorporated into the dispersive media to form the corresponding coatings systems: Epoxy/PPy, Epoxy/Mt and Epoxy/Mt-PPy. The mixtures were therefore sonicated for 20 min using an ultrasonic processor (VCX 750 from Sonics & Materials Inc., USA). Finally, 0.83 g of curing agent was added into the dispersive media and the mixtures were deposited onto mild steel (AISI 1010). Before coatings deposition, steel specimens were degreased with ultra-sonication in presence of acetone and subsequently finished with emery paper in the order of 120, 400, 600, 800, 1200 and 4000. The resulting coatings were obtained after curing at room temperature for 24 h and the dry film thicknesses (d.f.t) were found near 0.25 ± 0.04 mm.

2.2. Characterization

Electrical conductivity of Mt as well as-prepared additives PPy, Mt-PPy and for the low-resistivity coatings were measured using the four probe standard method with a Keithley 6220 (USA) current source to apply the current and a Keithley Model 6517A (USA) electrometer to measure the potential difference. For neat Epoxy resin and high-resistivity composites, the measurements were performed using the two probe standard method with a Keithley 6517A (USA) electrometer connected to Keithley 8009 (USA) test fixture. All measurements were performed at room temperature and reported values are representative of an average of five measurements for each sample.

The dispersions and distribution of the additives into the epoxy