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Full Length Article

Active corrosion protection performance of an epoxy coating applied on the mild steel modified with an eco-friendly sol-gel film impregnated with green corrosion inhibitor loaded nanocontainers

M. Izadi [a], T. Shahrabi [a,*], B. Ramezanzadeh [b,**]

[a] Department of Materials Science Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran
[b] Department of Surface Coatings and Corrosion, Institute for Color Science and Technology (ICST), P.O. Box 16765-654, Tehran, Iran

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ABSTRACT

In this study the corrosion resistance, active protection, and cathodic disbonding performance of an epoxy coating were improved through surface modification of steel by a hybrid sol-gel system filled with green corrosion inhibitors loaded nanocontainer as intermediate layer on mild steel substrate. The green inhibitor loaded nanocontainers (GIN) were used to induce active inhibition performance in the protective coating system. The corrosion protection performance of the coated panels was investigated by electrochemical impedance spectroscopy (EIS), salt spray, and cathodic disbonding tests. It was observed that the corrosion inhibition performance of the coated mild steel panels was significantly improved by utilization of active multilayer coating system. The inhibitor release from nanocontainers at the epoxy-silane film/steel interface resulted in the anodic and cathodic reactions restriction, leading to the lower coating delamination from the substrate and corrosion products progress. Also, the active inhibition performance of the coating system was approved by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and energy dispersive X-ray (EDS) analysis on the panels with artificial defects. The inhibitive agents were released to the scratch region and blocked the active sites on the metal surface.

1. Introduction

Epoxy resins are widely used as protective system on the metallic substrates due to different advantages, i.e. excellent chemical resistance, strong adhesion to the metal surface, high corrosion resistance, and good chemical, thermal and mechanical properties [1,2]. Despite the mentioned properties, the insufficient barrier performance against corrosive agents is one of the most disadvantages of the epoxy coatings [3]. Blistering and interfacial adhesion bond destruction in the coating/metal interface occur by corrosive moieties diffusion into the epoxy coating/metal interface [4,5]. Not only the coating deterioration but also the adhesion bonds destruction influence the barrier and inhibiting properties of the epoxy coatings at long exposure times. So, it is necessary to enhance the corrosion protection performance of the coating by various methods [6]. One of the commonly used procedures to induce the inhibitive protection in the epoxy coatings is the incorporation of nanoparticles, pigments, and capsules [7,8]. Chromate based pigments induce effective corrosion protection in the epoxy coatings [9]. However, high toxicity of chromate species guiding the researchers toward the development of new eco-friendly corrosion inhibitive systems [10,11]. Among the different protective agents, the inhibitive micro/nano containers are utilized by many researchers to replace the chromate pigments and induce active corrosion protection in the epoxy coatings. Ghazi et al. [12] used benzimidazole (BIA) and zinc cations intercalated montmorillonite (MMT) clay particles as an active agent in the epoxy-ester coating. They showed that the highest corrosion resistance was obtained by using the mixture of Zn-MMT + BIA-MMT clay particles. The complex formation between BIA^+ and Zn^{2+} cations was suggested as the cause of active performance of the epoxy-ester coating. $CaCO_3$ micro beads were modified with different corrosion inhibitors and utilized by Snihirova et al. [13] to induce an active performance in the water based epoxy coating. The better inhibition ability of the epoxy coating in the presence of cerium ions, and the active inhibition potential of coating system were confirmed by

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* Corresponding author.
** Corresponding author.

E-mail addresses: mazdak.izadi@modares.ac.ir (M. Izadi), tshahrabi34@modares.ac.ir (T. Shahrabi), ramezanzadeh-bh@icrc.ac.ir, ramezanzadeh@aut.ac.ir (B. Ramezanzadeh).

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electrochemical impedance spectroscopy (EIS) and local electrochemical impedance spectroscopy (LEIS) measurements, respectively. Montemor et al. [14] used layered double hydroxides and cerium molybdate hollow nanospheres as inhibitors (mercaptobenzothiazole) reservoirs to prepare active epoxy coating. The effective corrosion inhibition, active inhibition ability, and synergistic effect of the epoxy coating in the presence of both types of the nanocontainers were proved by EIS, scanning vibrating electrode technique (SVET), and scanning ion-selective electrode technique (SIET). The emeraldine base and salt forms of polyaniline (doped by hydrofluoric acid and camphorsulfonic acid) were added to the epoxy coating by Zhang et al. [15] to enhance the corrosion protection performance of coating. The EIS measurement results confirmed the better corrosion resistance of the camphorsulfonic acid-doped PANI coating.

The corrosion protection of mild steel was investigated by a large number of researchers. Refait et al. [16] investigated the corrosion of mild steel coupons at the seawater/sediments interface. The corrosion protection performance of mild steel sample was investigated by Kahyarian et al. [17] in the aqueous acetic acid solution. They showed that the electrochemical reactions rate was decreased in the presence of acetic acid. Dohare et al. [18] used expired Tramadol as a corrosion inhibitor for mild steel in 1 M HCl solution. The better corrosion protection in the presence of higher concentration of Tramadol was confirmed by electrochemical tests. In recent years, green organic compounds are investigated as corrosion inhibitors due to the many disadvantageous of synthetic inhibitors such as complicated synthesis process and toxicity [19,20]. So, the efforts for finding green organic compounds as cheap and non-toxic corrosion inhibitors have been performed in several researches [21,22]. So, it seems that utilization of green corrosion inhibitor loaded nanocontainers (GIN) in the epoxy coatings can be used as effective way to enhance the protection performance of the coatings. Nitrogen containing inhibitors are effective agents in corrosion protection of metal substrates [23]. The plant extracts containing polar functions with N, S, and O in the conjugated structure which are adsorbed on the metal surface with the polar groups, leading to the inhibitive surface film formation [24]. There is different heterocyclic compounds in the Nettle plant which can interact with steel surface and reduce the corrosion rate of metal [25]. Also, the Nettle constituents can chelate with transition metals such as Zn^{2+} and make complexes which absorb on the metal surface. Therefore, combination of the GIN and zinc acetate can be used as an efficient way to induce active inhibitive protection in the epoxy coating. However, there is several limitation in order to incorporate additives directly into the epoxy coatings such as blistering and lack of adhesion between the containers and epoxy matrix [26]. Also, the adhesion of epoxy coating to the metal surface can be improved by surface pretreatment, i.e. using surface modification or intermediate layers. Among various surface pretreatment methods the use of eco-friendly sol-gel coatings has attracted high consideration of the researchers in recent years. Alkoxy silanes are mediators with two alkoxy (X) and organofunctional (Y) groups in their structures which are written as $X_3Si(CH_2)_nY$. The alkoxy group (ex: methoxy, ethoxy, etc.) is hydrolysable agent which can attach to inorganic materials (such as metallic substrates) and the organofunctional groups (ex: amino, vinyl, hydroxyl, etc.) react with polymeric materials (such as primer organic coatings) [27]. This coupling action of silanes plays an important role in adhesion improvement of organic coatings on metallic substrates. Also, the silane films with dense and cross-linked network siloxane chains (Si-O-Si bonds) act as a good barrier against water, oxygen, and other aggressive agents which diffuse to the substrate/coating interface [28]. However, there is no inhibitive protection in the silane films. So, it is necessary to enhance the corrosion protection performance of this coating by incorporation of active agents into the silane films. The mesoporous silica nanoparticles encapsulated with p-coumaric acid (CA) were utilized by Wang et al. [29] to induce the active inhibition performance in the ZrO_2-SiO_2 sol-gel coating. They used two sol-gel layer with the smart nanocontainers and Ce(IV) salt to apply bi-layer coating on the AA2024 panels. They showed that the combination of CA and Ce(III) produce a synergistic inhibition effect, providing significant active inhibition functionality. Ding et al. [30] synthesized smart nanocontainers based on the installation of the supramolecular assemblies to load 8-hydroxyquinoline as corrosion inhibitor. They applied the hybrid organic-inorganic sol-gel coating on the AZ31B panels and showed the satisfactory anticorrosion performance of designed hybrid system. Ding et al. [31] used silica nanoparticles to entrap 2-hydroxy-4-methoxy-acetophenone as corrosion inhibitors. The active protection of sol-gel coating was proved by electrochemical analysis. Regarding to the proposed works, the bi-layer hybrid coating containing GIN and zinc acetate is considered as intermediate inhibitive layer to induce an active performance to the epoxy system coating. The active multilayer coating layout is illustrated in Fig. 1.

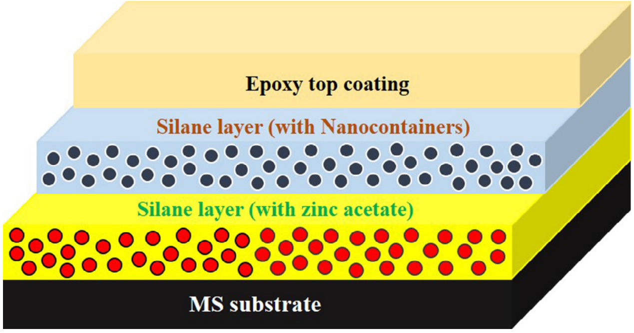

Fig. 1. Schematic illustration of GIN-EP coating on MS substrate.

In this work, a protective organic system based on GINs as a new reservoir was developed. Also, the zinc acetate was used to induce the synergistic effect with inhibitor molecules existing in the GIN structure. The active hybrid sol-gel film containing GINs was prepared and characterized by field-emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR), atomic force microscopy (AFM), and energy dispersive spectrometry (EDS) analysis. Electrochemical impedance spectroscopy (EIS) measurements, cathodic disbonding, and salt spray tests were employed to investigate the corrosion inhibition performance of the active coating. Also, scanning electron microscopy (SEM), EDS, and EIS measurements (on the coated samples with artificial defects) were used to study the active performance and active inhibition mechanism in the organic coating system.

2. Materials and methods

2.1. Materials

In this study the Nettle leaves, commonly known as Urtica Dioica, is used as a green source of corrosion inhibitors. For many years the Nettle leaves, which is an herbaceous perennial flowering plant, has been used as a source of medicine, food, and fiber. Flavonal glycosides such as quercitin, as well as carotenoids, chlorophyll, vitamins (C, B and K), histamine, serotonin, acids (e.g. carbonic and formic acid), and minerals (e.g. calcium, magnesium, and potassium) have been considered as the main components existed in the Nettle leaves structure [32]. According to literature, histamine, serotonin and quercitin are some of the most important and potent inhibitors existed in the Nettle leaves extract. The