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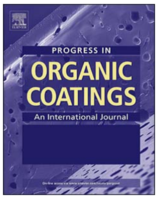

Comparative study of the effect of halloysite nanocontainers on autonomic corrosion protection of polyepoxy coatings on steel by salt-spray tests

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ABSTRACT

The comparative study was carried out to show the effect of the halloysite nanotubes loaded with three inhibitors with different properties (Korantin SMK, Halox 520 and $(NH_4)_2TiF_6$) as an additive for autonomic corrosion protection of polyepoxy coating on steel substrate. The comparison was carried out employing neutral salt-spray test (5% NaCl, 35 °C, different time). Commercial polyepoxy coating containing 20 wt% of zinc phosphate was used as a benchmark during testing. We demonstrated that inhibitor-loaded halloysites at 5 wt% concentration are able to successfully substitute 20 wt% zinc phosphate in the commercial polyepoxy coating even improving its corrosion protection performance, which depends in a large extend on the release profiles of the inhibitors loaded into halloysite nanotubes. On the contrary, addition of the free inhibitors into the coating showed complete deterioration of the corrosion protection properties for all inhibitors.

1. Introduction

Recent achievements in nanocontainer-based autonomic corrosion protection coatings demonstrated high potential of inhibitor-loaded containers to attain autonomous effect to the standard coating formulations [1]. In general, nanocontainers' formation and loading in the size range of 20 nm to 50 μm require the ability to form a nanocontainer shell which should be stable, permeable to release/upload of the materials and possess other desired functionalities (magnetic, catalytic, conductive, targeting, etc.). In order to develop functionalized micro- and nanocontainers, one has to combine different properties in the shell structure and composition. There are several approaches demonstrated so far for the design of nanocontainer depot systems: (i) polymer containers [2], (ii) halloysites [3], (iii) nanocontainers with polyelectrolyte shell [4], (iv) layered double hydroxides [5] and, finally, (v) mesoporous inorganic materials [6]. Paper of Jadhav et al. [7] describing the use of the encapsulated linseed oil for self-healing coatings made this inhibitor as an environmentally friendly active cargo. Core–shell microcapsules of urea-resorcinol-formaldehyde shell and linseed oil core material were prepared for self-healing coatings [8]. The capsules contained linseed oil as an active material where Co-octoate as drier material and/or octadecylamine as corrosion inhibitor can be dissolved as additional function component. Other authors showed similar effects for polyurethane capsules with linseed oil core containing second corrosion inhibitor mercaptobenzothiazole [9]. Smart dual inhibiting effect was also observed for microcapsules containing Tung oil as a core and poly(styrene sulfonate)/poly(ethylene imine) multilayer shell with corrosion inhibitor benzotriazole intercalated within the shell [10]. Corrosion process changes pH in the local area releasing entrapped inhibitors and passivating corrosion area. Example of the Layer-by-Layer assembly (LbL) technology applied for formation of the inhibitor-loaded capsules is the encapsulation of 2-methylbenzothiazole and 2-mercaptobenzothiazole inside poly(styrene sulfonate)/poly (diallyldimethylammonium chloride) shell sensitive to the local pH changes [11]. These nanocapsules are compatible with epoxy coatings and stable during the mixing, application and curing processes. Carneiro et al. [12] showed double-loaded nanocontainers based not on the organic core – polyelectrolyte shell combination but on inorganic core (layered double hydroxides) containing 2-mercaptobenzothiazole inhibitor and poly(styrene sulfonate)/poly(allylamine hydrochloride) polyelectrolyte shell loaded with Ce^{3+}. Release of the 2-mercaptobenzothiazole is based on the intrinsic properties of layered double hydroxides to intercalate ion-exchange species between layers while Ce^{3+} is electrostatically released by changing pH of polyelectrolyte shell.

Changes in the local environment of a coating during corrosion are

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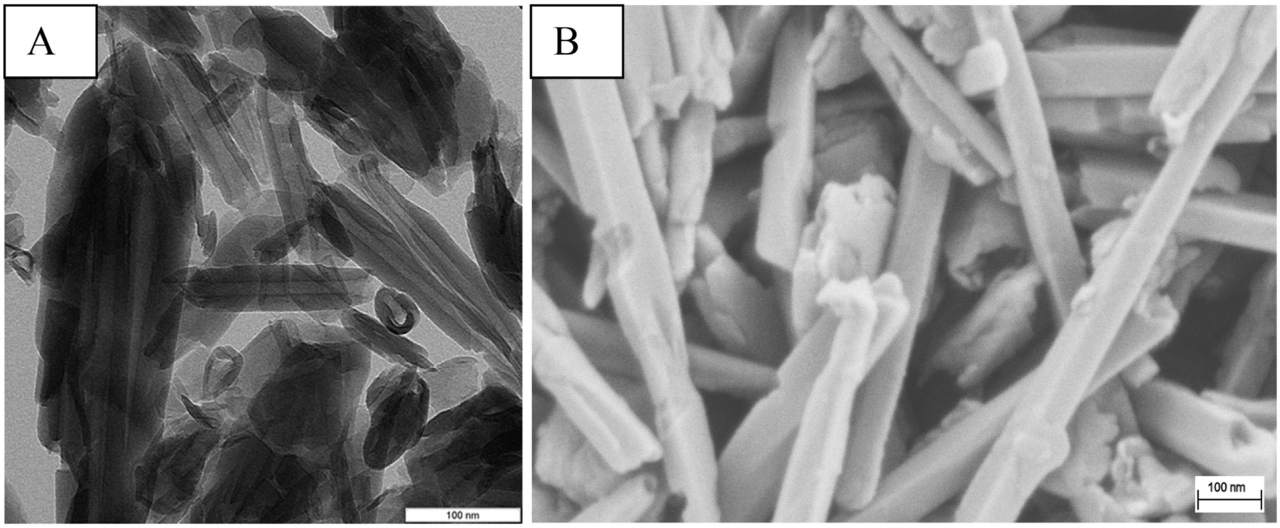

Fig. 1. TEM (A) and SEM (B) of the halloysite nanotubes used as host containers for corrosion inhibitors. Scale bar is 100 nm.

mostly of chemical nature (*e.g.*, electrochemical potential, pH, ionic strength or humidity) which can trigger swelling/shrinkage of the nanocontainers or change permeability of the nanocontainer shells [13–15]. Utilizing pH shift as stimulus for corrosion inhibitor release is the most promising way to design autonomic coatings due to the local pH decrease in anodic areas and local pH increase in the cathodic ones [16]. There are several comprehensive reviews published so far describing various combinations of nanocontainers and inhibitors, nature of nanocontainers, release profiles and electrochemical studies of corrosion protection performance. Wei et al., Zheludkevich et al. [17,18] surveyed anticorrosion performance of inhibitor-filled polymeric nano and microcontainers, halloysites, ion exchange clays and mesoporous silica capsules. Very detailed review by M.F. Montemor [19] summarized information about nano and microcontainers performance in the coatings acquired by localized techniques (scanning vibration electrode technique, SVET and scanning ion-selective electrode technique, SIET). Lvov et al. [20–22] demonstrated halloysite nanotubes loaded with corrosion inhibitors benzotriazole, 2-mercaptobenzimidazole and 2-mercaptobenzothiazole as effective additives for autonomic protection coatings for copper protection. The authors used optical and SEM visualisation to confirm autonomic action of the halloysite additives after exposure to 0.5 M aqueous NaCl. Another paper of these authors [23] employed SVET to demonstrate protection properties on the micron scale on the artificial cracks in NaCl solution. SVET and electrochemical impedance spectroscopy (EIS) were also used by us for demonstration of the self-controlled inhibitor release properties of benzotriazole-loaded halloysites in sol-gel coatings for aluminium protection [3,24].

Despite large number of the papers devoted to the nanocontainer-based autonomic protection coatings, most of them use lab-scale analytical methods for characterisation of their performance: EIS, polarisation, SVET and various adapted electrochemical techniques. Only paper of Zheludkevich et al. [25] analysed the efficiency of the nanocontainer-based autonomic coatings using industrial methods. However, the current numbers of the reported successful laboratory studies call for the transfer of the results to the industry for further commercialisation.

Here, we present comparative analysis of the halloysite nanocontainers loaded with three different inhibitors (Halox 520, Korantin SMK and $(NH_4)_2TiF_6$) as active ingredients for polyepoxy-based autonomic corrosion protection coatings. Anticorrosion performance was tested by neutral salt-spray test (ISO 9227, 5 wt% NaCl, 35 °C, different time) and a standard commercial polyepoxy paint (Lankwitzer-Lackfabric GmbH) containing 20 wt% of zinc phosphate was taken as a benchmark. Coating adhesion properties and comparative EIS data for the coatings with and without inhibitor-loaded nanocontainers are presented in Supporting Information section of the paper.

2. Experimental

2.1. Materials

Corrosion inhibitors Korantin SMK (alkylphosphoric ester with the chain length of alkyls in the ester group ranging from C6 to C10) and Halox 520 (60 wt% solution of poly(3-ammoniumpropylethoxysiloxane)dodecanoate in ethanol) were provided by BASF company, Germany and C.H. Erbslöh GmbH & Co. KG, Germany, respectively. $(NH_4)_2TiF_6$ and sodium poly(methacrylate) (PMA) were purchased from Sigma-Aldrich and used without further purification. Halloysites were provided by Atlas Mining Company (Dragon Mine deposit, Utah, USA).

2.2. Preparation of nanocontainers

Halloysites are naturally occurring layered kaolin-like aluminosilicates with hollow tubular structure. The aluminum hydroxide and the silicon oxide layers are bond covalently with each other. The bilayer rolls up to a tube, i.e. a hollow cylinder with aluminum inside and silicon outside. Halloysite nanotubes used in the paper have inner lumen with diameter 15–20 nm with outer diameter around 50 nm (Fig. 1a and b) and a specific surface area of 60 m^2/g with pore volume of 0.2 cm^3/g. Loading of the halloysite nanotubes with inhibitors was performed from the corresponding solutions under reduced pressure. 50 ml of 20 wt% ethanolic (Halox 520, Korantin SMK) or aqueous inhibitor solution ($(NH_4)_2TiF_6$) were mixed with 5 g of empty halloysites and then introduced into a desiccator with a reduced pressure. The air goes out from the halloysite inner volume, and is replaced by the solution containing corrosion inhibitor. The loading was performed three times followed by centrifugation in water at 5000 rpm. The inhibitor loading inside halloysite nanotubes was 20 ± 1 wt% for all inhibitors presented in this work (measured by TGA, Linseis STA PT1000 with a heating rate 5 K/min under air), which is the maximal loading capacity for the natural halloysites of this type. Outer PMA polyelectrolyte layer was deposited onto inhibitor-loaded halloysites by electrostatic adsorption from the 5 wt% aqueous solution. 5 g of loaded halloysite nanotubes were added to the polyelectrolyte solution and incubated for 20 min. Then, the separation of the nanocontainers from the rest of polyelectrolyte solution was done by filtration followed by