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Self-healing epoxy coatings loaded with inhibitor-containing polyelectrolyte nanocapsules

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ABSTRACT

The self-healing polymer coatings containing organic corrosion inhibitors are intensively investigated as an alternative for highly toxic Cr(VI)-based systems. Protective self-healing coatings are realized by embedding "smart" containers, able to release a corrosion inhibitor under some specific conditions occurring when the corrosion process starts (e.g. on pH change) or upon a mechanical damage. In this study a system with the corrosion inhibitors (2-methylbenzothiazole (BT) and 2-mercaptobenzothiazole (MBT)) encapsulated inside the polyelectrolyte nanocapsules embedded in the water-based epoxy coatings is tested for its self-healing performance. The nanocontainers were prepared by the electrostatic adsorption of polyelectrolytes directly on the oil phase drops containing the inhibiting agent. The results for BT emulsion droplets and the mixture of BT and MBT encapsulated by docusate sodium salt/poly(diallyldimethylammonium chloride) (AOT/PDADMAC) and docusate sodium salt/poly(diallyldimethylammonium chloride)/poly(styrene sulfonate) (AOT/PDADMAC/PSS) surface complexes are presented.

The X-ray Photoelectron Spectroscopy (XPS) was used to confirm the release of the inhibitor from the scratched coating. The influence of the nanocapsules on the barrier properties and self-healing performance of the epoxy coatings were tested by electrochemical impedance spectroscopy (EIS) in NaCl solution, the salt spray test (SST) according to ISO9227 and filiform corrosion test (FFT) according to EN ISO 3665. Potential blistering was rated according to EN ISO 4628-2.

1. Introduction

Polymer coatings are widely used for the protection of metal surfaces against corrosion. They form a barrier for the corrosive species providing the passive protection and simultaneously they may serve as a matrix for anticorrosive agents, which are responsible for an active anticorrosive action [1]. The aluminum alloys are commonly applied in the transportation and aerospace industry due to their excellent mechanical properties and low weight [2]. Triazole and thiazole derivatives are proposed as corrosion inhibitors for protection of the aluminum alloys instead of toxic hexavalent chromium-based anticorrosive agents [3,4]. One of the most promising inhibitors is 2-mercaptobenzothiazole (MBT), which adsorbs at the alloy surface and forms a thin film protecting the surface against corrosion [5]. Despite the fact that MBT dissolved in the corrosive solution is a very efficient inhibitor for aluminum alloys, the addition of MBT to the polymer coating does not improve its anticorrosive performance [6]. Moreover, a detrimental effect of MBT on the polymer matrix and a possible deactivation of the inhibitor were shown. That negative effect of directly introduced agents was observed also in the case of other corrosion inhibitors [7,8]. A possible solution to this problem may be the encapsulation of the inhibitor inside nano/micro-reservoirs [6,8,9] that prevents the interaction of the inhibitor with the polymer matrix and provides the self-healing properties. The self-healing in this case is defined as the ability to hinder the corrosion activity in the defect by the coating itself by employing any mechanism. Therefore, the corrosion protective system recovers its main function, the corrosion protection, after being damaged [10].

On the other hand, the addition of the containers may reduce the barrier properties of the coating due to their size and incompatibility with the matrix. Borisova et al. [6] compared the effect of mesoporous silica nanocontainers differing in size (80 and 700 nm) loaded with MBT, finding that the bigger containers introduced

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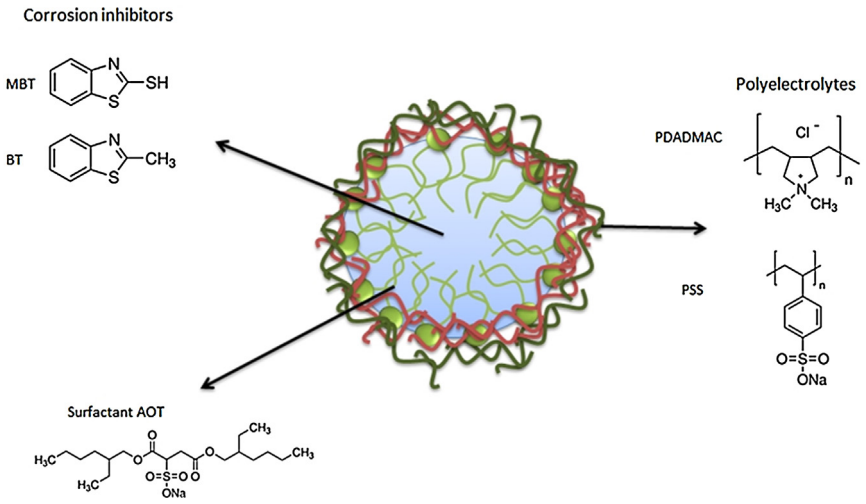

Fig. 1. The illustrative scheme of the inhibitor-containing nanocapsule.

more strain and defects to the matrix resulting in worsened barrier properties whereas the addition of smaller capsules did not influence the barrier properties of the coating.

Depending on the desired triggering mechanism, the type of inhibitor and a polymer matrix many different strategies of encapsulation, e.g., enclosing the inhibitor in the polymeric capsules formed by the interfacial polyaddition, filling the inorganic porous nanoparticles by the adsorption of the inhibiting species or fabrication of the $CaCO_3$ microbeads loaded with inhibitor in situ were reported [1,11–15]. The most common triggering mechanisms are: local pH changes caused by the corrosion process [8,11,16,17], mechanical rupture [12,18,19] and ion-exchange process [20–23]. The ion-exchange mechanism occurs, e.g. in the case of the layered double hydroxide (LDH)-based nanocontainers built of stacks of positively charged mixed-metal hydroxides, stabilized by anions and solvent molecules located in-between the stacks. The anionic corrosion inhibitors are released from the nanocontainers and simultaneously the aggressive anionic species such as chlorides are trapped [21,24]. Montemor et al. investigated the epoxy coating modified with a mixture of two different containers: LDH-based and cerium molybdate (CeMo) nanospheres loaded with the same corrosion inhibitor (MBT) [25]. Synergistic inhibition effect related to the different activation mechanisms was observed providing the early stage corrosion protection and long term corrosion inhibition. Recently, another interesting application of combination of CeMo nanospheres with water and chloride traps in the epoxy coating has been demonstrated [26].

Raps et al. reported the mechanical damage mechanism for healing the micro-scale defects of the epoxy primer doped with polyurea capsules. The active corrosion protection was accomplished by releasing the inhibitor solution in a water-displacing fluid upon the formation of micro-cracks on the coating surface [12]. One of the most common pH-sensitive systems comprises polyelectrolyte (PE)-based shells deposited on the inorganic cores by means of the layer-by-layer (LbL) self-assembly method. Various particles, such as ZnO, SiO_2 or natural halloysite nanotubes were studied as inorganic cores [8,27–29] on which PE shell can be built by the adsorption of oppositely charged polyelectrolytes. The inhibitor can be located inside the inorganic core or in-between the adjacent PE layers.

Plawecka et al. [30] reported a different approach to encapsulate the inhibitor in the PE shell using the method previously developed by Szczepanowicz et al. [31] which involves a direct adsorption of polyelectrolytes on liquid cores. PE capsules loaded with MBT were used for modification of epoxy coating for protection of AA5083 alloy and galvanneal substrates. The pH-based triggering mechanism was tested in that work and the inhibition of small defects by active species released from nanocapsules was shown.

In the present work a self-healing activity of two different water-based epoxy coatings (model system without additives and fully commercial paint) on AA2024 T3 alloy is investigated. The coatings were modified with the similar PE capsules as used in previous work [30], loaded with 2-methylbenzothiazole (BT) and MBT - both widely known corrosion inhibitors for aluminum alloys [6,18]. X-ray Photoelectron Spectroscopy (XPS) was used to confirm the release of the inhibitor from the scratched coating. The self-healing properties of water-based epoxy coatings with the addition of the capsules were investigated by electrochemical impedance spectroscopy (EIS), salt spray test (SST) and filiform corrosion test (FFT).

2. Experimental

2.1. Synthesis and characterization of the nanocapsules

The capsules were obtained by adsorption of the oppositely charged PEs directly on liquid cores using a previously reported procedure [30]. Three different types of cores were studied: BT, MBT+BT and chloroform, respectively. The schematic illustration of the inhibitor-loaded nanocapsule is presented in Fig. 1. Poly(diallyldimethylammonium chloride) (PDADMAC) (MW ~ 100,000–200,000) and poly(sodium 4-styrenesulfonate) (PSS) (MW ~ 70,000) were used as a polycation–polyanion pair. The encapsulation process was monitored by dynamic light scattering (DLS) and UV–vis measurements. In order to evaluate the colloidal stability of the nanocapsules the measurements were performed just after preparation and after 12 months of storage. The Zetasizer Nano Series apparatus from Malvern Instruments and UV-1800 spectrophotometer (Shimadzu) were used.

Four different aqueous suspensions of nanocapsules were tested: positively charged empty reference nanocapsules (PDADMAC/chloroform), positively charged nanocapsules loaded with 2-methylbenzothiazole (PDADMAC/BT), positively charged nanocapsules loaded with the mixture of the corrosion inhibitors (PDADMAC/BT+MBT) and negatively charged nanocapsules loaded with the mixture of the corrosion inhibitors (PSS/PDADMAC/BT+MBT).