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Chitosan-based self-healing protective coatings doped with cerium nitrate for corrosion protection of aluminum alloy 2024

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ABSTRACT

The good film forming ability, specific solubility and versatile chemical functionalization of chitosan make it a promising candidate for "green" protective coatings. In the present work, these features are exploited together with chitosan high complexing ability to obtain inhibitor-containing anticorrosion coatings for active protection of aluminum alloys. The functionalization of chitosan with fluorinated substituents was also evaluated as a possible route to improve barrier and surface properties of the coating matrix. It was observed that the chitosan layer worked as a reservoir for cationic Ce^{3+} corrosion inhibitor due to the complexation of Ce^{3+} with chitosan amino groups, which prevents its uncontrollable and fast leaching. These Ce-containing coatings were found to confer active corrosion protection toward aluminum alloy 2024 as shown by electrochemical impedance spectroscopy. Moreover, the corrosion tests evidence the self-healing ability of prepared chitosan-based "green" protective coatings. The interaction between Ce^{3+} and chitosan and the concentration effect of the former on the performance of the latter from a corrosion standpoint is also discussed.

1. Introduction

In the last decade, studies involving the use of environmentally friendly materials obtained from renewable resources have registered a significant increase. In particular, polysaccharides such as, chitin, cellulose and starch, have gained considerable attention because of their specific properties and high availability [1,2]. Chitin is the second most abundant polysaccharide on Earth, after cellulose, being an important structural element present in crustaceans exoskeletons [3,4], squid stilettos [4–6], fungi and also in insects, arachnids, mollusks and some species of algae [7]. Chitin is insoluble in almost all known solvents, which limits significantly its processability and application. However, its deacetylated derivative, chitosan, presents more interesting features, including solubility in aqueous acidic media. From a chemical point of view chitosan is a linear copolymer of β-(1-4)-2-amido-2-deoxy-D-glucan (glucosamine) and β-(1-4)-2-acetamido-deoxy-D-glucan (*N*-acetylglucosamine) that can be produced from chitin by means of a partial alkaline deacetylation.

Chitosan is one of the most promising polysaccharides due to its unique physicochemical properties namely biocompatibility, antimicrobial activity, biodegradability and excellent film-forming ability, which have attracted scientific and industrial interest [8]. When chitosan is dissolved in a dilute acidic medium, the amine groups are protonated and the ensuing positive charges confer polyelectrolyte-like behavior to the macromolecule. Chitosan has been successfully used in several fields such as biotechnology, pharmaceutics, biomedicine, packaging, wastewater treatment, cosmetics and food science. It is also used in many applications involving the controlled release of active agents, and also as constituent of functional coatings [9–11]. For example, several recent reports suggest the use of chitosan and its derivatives as environmentally friendly protective coatings, as in the case of metal implants aiming to control the rate of dissolution of active components and to increase their biocompatibility [12] and corrosion resistance [13,14].

The application of organic polymeric coatings is currently the main method of passive corrosion protection of metallic structures. Nevertheless, solvent-based coating formulations often used lead to significant VOC emissions. In fact, paint industry is still one of the main contributors to VOC production worldwide. However, limits on VOC emissions from paints and varnishes have been enforced in Europe [15], as well as in the United States and Canada. These new regulations have been fostering the development of alternative environmentally friendly protective coatings. Chitosan has been considered among the most promising candidates in this context because of its specific properties such as good film-forming ability,

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superior adhesion to metallic surfaces and versatility associated with the easiness of chemical functionalization.

In a recent report by Lundvall et al., a smooth and homogeneous chitosan layer was deposited on anodized aluminum alloy 2024, but its high water permeability resulted in reduced (barrier) protective properties [16]. When the polymer provides little barrier effect, additional *active* corrosion protection is required to ensure an effective suppression of the corrosion processes on the metal surface. Moreover, the degradation of the coatings under service life conditions is inevitable (e.g. high temperature gradients, UV radiation, mechanical impacts), and when micro-defects appear during exposure of the coated metallic structures, the active protection mechanism will work inhibiting the corrosion processes at the unprotected sites.

The self-healing effect is generally defined as the recovery of coating integrity after some kind of damage occurs, and it was already reported for chitosan-derived systems. In a recent work by Gosch and Urban, a self-healing polyurethane-based coating with oxetane-substituted chitosan precursor was prepared [17]. Accordingly, the four-member oxetane rings open creating two reactive ends upon mechanical damage of the polymer network. The chitosan chain scission occurs, forming crosslinks with the reactive oxetane end, thus repairing the network, when exposed to ultraviolet light.

In the case of anticorrosive coatings the recovery of coating integrity is not obligatory, as long as the metallic substrate is kept under protection. The self-healing of anticorrosion protective coatings can be achieved through active corrosion protection, based on the incorporation of corrosion inhibitors into the coating system [18].

The first results on active chitosan-based coatings loaded with corrosion inhibitors were reported recently by our group [19]. The chitosan film was used as a corrosion inhibitor reservoir pre-layer before deposition of a barrier hybrid coating. The chitosan pre-layer worked as a reservoir layer of corrosion inhibitor whereas the hybrid coating conferred the barrier effect delaying the ingress of electrolyte species.

In this work the hybrid coating was deliberately not used. The main aim is to use a completely green approach, based on chitosan systems. In addition to chitosan being used as a reservoir for corrosion inhibitors, an attempt to improve surface and barrier properties of chitosan was tried by means of chemical functionalization. The use of a fluorinated chitosan derivative could give rise to matrices with different characteristics from the corrosion protection standpoint. Herein, aluminum alloy 2024-T3 (AA2024) coated with chitosan-based films (unmodified and functionalized with fluorine groups) was investigated in the presence and absence of a well-known corrosion inhibitor (cerium nitrate). AA2024 was chosen because it is widely used in the aeronautical industry, which represents one of the most challenging cases due to the strict safety and reliability requirements. Cerium (III) nitrate ($CeNO_3$) was selected as corrosion inhibitors due to its known inhibiting properties for copper-rich aluminum alloys and low toxicity. Chitosan and its derivatives were characterized by ^1H NMR and ATR-FTIR while anticorrosion performance of coated substrates was assessed by electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

The commercially available reagents and solvents were employed as received. Chitosan, with a relative molecular weight of 543,000 and a deacetylation degree (DDA) of 95%, was kindly provided by Mahtani Chitosan Pvt. Ltd. (India), was purified by re-precipitation from a 1% acetic acid aqueous solution using 0.5 M NaOH in water. The ensuing precipitate was filtered and thoroughly washed with distilled water until neutrality and subsequently freeze-dried and finally characterized [20].

A commercial aluminum alloy 2024-T3 with a nominal composition of 4.4% Cu, 1.5% Mg, 0.6% Mn, and lower amounts of Fe, Si and impurities was used as the metallic substrate. All the alloy panels were chemically etched prior to coating applications by means of a typical three-step industrial cleaning procedure consisting of: (i) alkaline cleaning in a Metaclean T2001 at 60–70 °C for 15–25 min, followed by (ii) alkaline etching in a Turco Liquid Aluminetch N2 at 60 ± 5 °C for 30–60 s and, finally, (iii) acid etching in a Turco Liquid Smutgo NC at 30 ± 5 °C for 5–10 min. After the chemical etching, all the metallic panels were thoroughly washed with distilled water.

2.2. Functionalization of chitosan with glycidyl 2,2,3,3-tetrafluoropropyl ether (GTFE)

A 2 wt.% purified chitosan (CTS) solution was prepared by dissolving CTS in a 1% acetic acid aqueous solution. Subsequently, 2 equiv. (relative to the NH_2 groups of CTS) of GTFE was added under stirring, and the reaction was then carried out at 65 °C for 24 h. At the end, the GTFE-modified CTS was precipitated into an excess of absolute ethanol, washed three times with the same solvent, and then dried to constant weight in a ventilated oven at 60 °C.

2.3. Coating of the aluminum alloy panels

The chitosan-based formulations were applied by dip-coating, using a multilayer process in which the samples were immersed into and withdrawn from the CTS solutions at constant speed of 9 cm/min, and immediately dried before the deposition of the subsequent layer, until ten layers were accumulated.

2.4. Film preparation

Free-standing films were obtained by casting using 0.5 wt.% solutions of the purified chitosan samples in 1% (v/v) aqueous acetic acid. Two different inhibitor concentrations were added (1 and 10 wt.% to CTS solution), the initial dispersions were stirred for 12 h to achieve total dissolution, before spreading them onto an acrylic plate and drying them at 30 °C in a ventilated oven for 24 h.

2.5. Material characterization

The ATR-FTIR spectra were recorded with a Bruker IFS55 spectrometer equipped with a single horizontal Golden Gate ATR cell.

The ^1H NMR spectra were acquired with a Brucker Avance AMX300 spectrometer working at 300.13 MHz. For this purpose, CTS and its derivatives were diluted in a 1% deuterated acetic acid solution and the measurements were carried out at 50 °C.

Electrochemical impedance spectroscopy (EIS) technique was employed to evaluate the protective performance of the chitosan-based coatings against corrosion of the aluminum alloy during immersion in a 0.05 M NaCl aqueous solution. The measurements were carried out with a Gamry FAS2 Femtostat coupled with a PCI4 controller at an open circuit potential with applied 10 mV sinusoidal perturbations in the 100 kHz to 3 mHz frequency range, taking 7 steps per decade. For this purpose, a conventional three-electrode cell was used, composed of a saturated calomel reference electrode, a platinum foil as the counter electrode, and the chitosan-coated AA2024 substrates as the working electrodes, which had a surface area of 3.3 cm^2. All the measurements were done in a Faraday cage in order to avoid electromagnetic interference and the impedance plots were fitted using ZView 2 software.