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Chitosan-based coatings for corrosion protection of copper-based alloys: A promising more sustainable approach for cultural heritage applications

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ABSTRACT

The attractive physicochemical properties of chitosan make its derived materials promising candidates for the reliable and sustainable corrosion protection of metallic substrates. In this work, chitosan-based coatings embedding different corrosion inhibitors, i.e. benzotriazole (BTA) and mercaptobenzothiazole (MBT), were investigated for the protection of copper-based alloys, with the aim to extend their application to the preservation of works of art exposed to indoor atmosphere. The composition of the formulations was optimized paying particular attention to their potential application in the field of cultural heritage. To assess the efficacy of the coatings, tailored accelerated corrosion tests were carried out on bare and coated bronze substrates. Coated and uncoated alloy disks were characterized before and after corrosion treatments by optical microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. Moreover, an image analysis protocol was defined to evaluate the extent of surface modifications after degradation treatments. The obtained results revealed that the chitosan-based coatings containing BTA and MBT fulfil the aesthetic criteria required in the field of cultural heritage and are able to inhibit the corrosion of bronze alloys. It is worth noting that a synergic effect between the chemical protection provided by the inhibitors and the physical one provided by the polymer matrix was observed. Our findings demonstrate that the developed systems are suitable for a reliable and more sustainable protection of indoor bronze artefacts, thus representing a promising alternative to commercial products and particularly taking advantage from the use of non-harmful solvents for their application and removal.

1. Introduction

The development of high-performance materials that satisfy requirements related to environmental sustainability and cost-effectiveness represents a serious challenge for the scientific community. Specifically, in the field of art conservation the research of effective and non-toxic corrosion protective treatments has recently registered a significant increase, due to new strict health and safety regulations related to the use of chemical products, as well as to the need of reducing the use of petroleum-derived materials [1].

A valid strategy for the protection of metal substrates is the use of “active” coatings consisting of a passive polymer matrix loaded with chemically active compounds, such as corrosion inhibitors.

Differently from the direct application of corrosion inhibitors on the metal surface, which is one of the currently used procedure [2], their incorporation into the polymer matrix may provide a twofold advantage: (i) it allows to use low amount of inhibitors; and (ii) it permits to immobilize them in the coating, thus possibly reducing their leaching in the environment and obtaining long-lasting protective films. Note that the most commonly used corrosion inhibitors for copper and copper-based alloys, such as benzotriazole (BTA) and its derivatives [3], are toxic (as pure inhibitor) and this aspect represents a critical issue for what concerns their handling and leaching in the environment [4,5].

In this scenario, the use of eco-friendly polymeric materials obtained from renewable sources, which act both as barrier layer and reservoir for corrosion inhibitors, is an attractive approach for the development of reliable, sustainable and active protective coatings [6–11]. The choice of natural polymers that are soluble in water-based solutions may avoid the use of harmful solvents (as toluene, acetone, white spirit and xylene) that are necessary for the application and removal of commonly used commercial protective coatings, consisting of

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BTA dispersed in acrylic resins (Paraloid B72™, 70 methylmethlacrylate/30 ethyl acrylate copolymer) or microcrystalline waxes [2]. Therefore the development of innovative water-soluble products is mandatory, especially for conservation interventions on unmovable works of art.

It is also worth noting that "ideal" protective coatings for cultural heritage applications, besides preventing substrate degradation by using safe procedures, have to fulfil demanding aesthetic requirements. In particular, they have to be transparent and colourless, avoiding any modification in the appearance of the works of art, and they have also to be easily applicable and removable.

In the field of polymer-based coatings, chitosan turned out to be a very interesting material and a good alternative to conventional coating systems due to its intrinsic properties, including biocompatibility, antimicrobial activity, biodegradability, superior adhesion to metallic surfaces and the ability to reversibly form complexes with potential corrosion inhibitors [12,13]. Moreover, chitosan is soluble in aqueous media and can be obtained from renewable sources. It derives from the partial deacetylation of chitin, which is the main constituent of the exoskeleton of crustaceans and insects and it is one of the most abundant biopolymer in nature. The structure of chitosan, consisting of β-(1–4)-2-acetamido-D-glucose and β-(1–4)-2-amino-D-glucose units, also gives to the polymer excellent film forming ability, which makes it suitable for applications in various fields [14–17]. The interest in chitosan as a coating for metallic substrates has increased in recent years, especially for magnesium [18–20] and steel alloys [21] used for biomedical applications. The development of chitosan coatings doped with Ce^{3+} metal cations or containing 2-mercaptobenzothiazole (MBT) as corrosion inhibitors have been previously reported in literature also for the protection of aluminium alloys [22,23]. Moreover, chitosan-based low-pH-sensitive hydrogels loaded with BTA were prepared by Li et al. [3]. They investigated BTA loading capacity and releasing ability of the hydrogels and their performance in the corrosion protection of copper. Little has been reported about chitosan as green inhibitor for copper corrosion in acidic medium [24] and studies reporting the use of chitosan for copper-based alloys in the field of cultural heritage are scarce.

In the present work, active coatings based on chitosan with two different corrosion inhibitors, BTA and MBT, as sustainable and water-soluble corrosion protective systems for the conservation of indoor bronze artefacts were investigated. A copper-based alloy, with chemical composition and metallurgical features similar to those commonly used in bronze objects of art, was used as the metallic substrate. The BTA was selected since it is the most commonly used corrosion inhibitor, whereas MBT is considered a promising low toxic alternative [23,25–28]. The effect of the type of acid used for chitosan dissolution, i.e. acetic acid (AcOH) and D-(+)-Gluconic δ-lactone (GDL), on the quality of the films deposited onto the bronze substrates and on the interaction of the polymer with the metal alloy was studied. The influence of glycerol addition, as plasticizer, on the morphological and protective properties of the coatings was also evaluated. Optical microscopy and scanning electron microscopy (SEM) were employed to evaluate the coating morphology and micro-structure. Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy (EDS) were used to investigate the coating/substrate interaction and to get information about the surface chemical composition. To assess the protective efficacy, tailored accelerated corrosion tests were optimized starting from a procedure previously reported in literature [29]. They consist of a mild heating of the bare and coated bronze substrates in the presence of acidic water vapours, which represent a more realistic environment with respect to the commonly used immersion in acidic solutions. The coated disks and the bare alloy used as reference were characterized by optical microscopy, SEM, EDS and FTIR before and after the accelerated corrosion treatments. An image analysis protocol was also defined to evaluate the extent of surface modifications after degradation tests. To the best of our knowledge, the active protection of bronze alloys by using chitosan-based coatings for the preservation of indoor works of art and their assessment with tailored procedures have not been reported so far.

2. Materials and methods

2.1. Materials

Chitosan (medium molecular weight, viscosity 200–800 cP, 75–85% deacetylated), D-(+)-gluconic δ-lactone (purity ≥99.9%), 2-mercaptobenzothiazole (purity 98%) and glycerol (analytical grade) were purchased from Sigma Aldrich. Benzotriazole (purity 99%) was purchased from Bresciani. Glacial acetic acid (purity 99.9%) was purchased from Carlo Erba, ethanol (EtOH, purity ≥99.8%) and water Cromasolv plus for HPLC were purchased from Sigma Aldrich. Before using, chitosan was washed in boiling water for 1 h, filtered, thoroughly washed with distilled water to remove impurities, and dried under vacuum for 12 h. A bronze alloy, with commonly used chemical composition [30,31] was purposely produced (labelled CNR 128, nominal composition of 92.8% Cu, 6.8% Sn, 0.2% Pb) and was used as the metallic substrate. The alloy disks have been polished by using SiC papers at 1200 grit and diamond pastes up to 1/4 µm in order to obtain a flat and smooth surface with a mirror-like finish. After polishing, the Cu-based alloys have been cleaned with ethanol.

2.2. Preparation of chitosan-based solutions and coatings

Chitosan solutions were prepared by dissolving 0.5 wt/vol% of purified chitosan in aqueous 0.1 M AcOH solution or in 0.05 M GDL solution. The concentrations of the two acids was selected in order to obtain a solution with a pH ~ 3.5. The initial dispersions were stirred for 24 h at 30 °C to achieve total dissolution of chitosan. The pH of the solutions was then adjusted to 6 by the addition of 1 M NaOH. The corrosion inhibitor, BTA or MBT (0.1 wt.% with respect to chitosan solution), was added to aqueous chitosan solutions with either AcOH or GDL. Glycerol (4 wt.% with respect to chitosan solution) was also used in some formulations. All the solutions were diluted with EtOH to obtain a mixture with a final water/ethanol (H_2O/EtOH) composition of 50/50 v%/v%. Therefore, the final inhibitor concentration in the water/ethanol formulation was 0.05 wt/vol%.

All the coatings were prepared by drop-casting 60 µL of the H_2O/EtOH chitosan-based solutions or 30 µL of only inhibitor solution (0.1 wt/vol% in ethanol) onto bronze disks with a diameter of 2.5 cm and by subsequent drying at room temperature. Removability tests were carried by using tissue paper soaked in water or ethanol.

2.3. Determination of the bronze disk wettability

Contact angle measurements were performed to determine the optimal composition of the liquid phase of the coating formulations and to quantitatively evaluate their wettability on the bronze substrates. The static contact angle (θ) was estimated with an automatic video-based measurement of contact angle performed at room temperature and humidity by using a Dataphysics OCA-20 Contact Angle System. Five microliters of liquid were placed on the bronze substrate and the Young/Laplace method has been used to calculate the static contact angle. Fifteen independent measurements were carried out for each type of liquid investigated to take into account the variability due to the surface roughness of the bronze disks. In addition, every five measurements the substrate was subjected to the polishing procedure. In such a way, the reproducibility of the polishing step was also verified.

2.4. Measurements of film thickness

The thickness of the deposited coatings was estimated by using a nanoindentation equipment (Nanotest Platform 2, Micromaterials) in