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Corrosion and fouling protection performance of biocide-embedded hybrid organosiloxane coatings on mild steel in a saline medium

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ABSTRACT

This work assessed the anticorrosion and antifouling properties of a novel sol-gel derived hybrid coating functionalized with 5 different organic and inorganic biocides. FTIR and NMR analysis of the newly synthesized polymeric base material confirmed the photo-induced organic polymerization of the allyl groups in the allyltrimethoxysilane precursor of the polymer and the inertness of the allyl groups in the allyl glycidyl ether precursor. The parent coating and biocide-embedded coatings were applied on mild steel sheets, cured with UV light, and subjected to thermal, morphological and electrochemical characterization. The cured coatings were thermally stable, and their hydrophobicity increased after immersion in a saline medium, owing to further polymer crosslinking. According to lab-based electrochemical and visual evaluations of the corrosion protection performance of the different formulations, the coating embedded with Irgarol and MOLY-white 101 had an improved performance, compared with the formulations with the other added biocides. Field testing results from the coated samples were consistent with the lab results; i.e., some biocides positively affected the anticorrosion and antifouling behavior of the hybrid coatings, whereas other biocides negatively affected the newly developed hybrid coating. The methodology reported here holds promise for the development of multifunctional hybrid sol-gel coatings for mild steel substrates with interesting anticorrosion and antifouling activities in saline.

1. Introduction

The corrosion and fouling of steel surfaces are major problems affecting the infrastructure of most industries, especially the oil and gas industries. One of the most widely used methods of mitigating these metal-loss processes is the application of barrier coatings [1–3]. In particular, chromate conversion coatings (CCC) are still the most effective and state-of-the-art technology for protecting various metal substrates. However, the effects of Cr(VI) on human health and the environment have prompted researchers to pursue alternative mitigation measures [4–6]. Therefore, the development of non-toxic and environmentally friendly coatings capable of providing the demanded corrosion protection is needed.

Hybrid organic-inorganic (HOI) sol-gel coatings are very promising replacements for CCC [7,8]. HOI materials combine the desirable properties of both inorganic (thermal stability, hardness, and durability) and polymeric (toughness and flexibility) components within a single network [9–11]. Moreover, the availability of precursors and high homogeneity of the coating matrix, combined with the many applicable deposition techniques, have made the sol-gel inhibition process for metal substrates, either as a simple inorganic silicon-based coating or an HOI coating, very attractive [12–14]. Researchers have become interested in using organotrialkoxysilane precursors bearing polymerizable vinyl or acryl groups for the production of highly protective UV-cured hybrid coatings [9,15–17]. UV curing has been widely used to improve the condensation and polymerization reactions of organic-inorganic hybrid materials [17,18]. However, the use of organosilane precursors with allyl groups in hybrid sol-gel materials has largely been unexplored in the literature [19,20].

In a recent application of sol-gel modification, modified silica coatings containing embedded biocides have been proposed as an approach for preparing sol-gel systems with interesting antimicrobial properties [21]. The appropriate choice of the precursor chemistry, reaction conditions, and biocide may produce functionalized hybrid sol-gels with high stability, reliable aging properties, extended shelf life, and microbiologically influenced corrosion (MIC) inhibition properties [22]. Babapour et al. [23] reported the synthesis of silica-based coatings containing biocide silver nanoparticles where they found that higher concentration of silver nanoparticles lead to longer time biocide activity. Biological active sol-gel coatings on Al and mild steel alloys were also developed by Akid and his group through the functionalization of novel base hybrid

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silica coatings with *Paenibacillus polymyxa* bacterial [24–26] or *Bacillus licheniformis* endospores [27]. The present work sought to investigate the synthesis of a novel hybrid sol-gel material from allyl precursors and functionalization of the resulting hybrid polymeric material with various organic and inorganic antibacterial agents (biocides). Both laboratory (spectral, thermal, morphological and electrochemical)-based studies and field trials were conducted to assess and compare the anticorrosion and antifouling properties of these bioactive UV-cured coatings for S-36 grade mild steel.

2. Experimental

2.1. Preparation of the coating

2.1.1. Materials

The following chemicals were purchased from Sigma-Aldrich (USA) and used as received: allyl glycidyl ether (AGET), (3-aminopropyl)trimethoxysilane (APTMS), Irgarol, 1,1-dimethylbiguanide hydrochloride, silver nanoparticle dispersion (40 nm in aqueous buffer), titanium nanosize powder (98.5% in mineral oil), 1-hydroxycyclohexyl phenyl ketone (photoinitiator, PI) and isopropyl alcohol (IPA). Allyltrimethoxysilane (ATMS) and polydimethylsiloxane, silanol terminated (PDMS), molecular weight 400–700, were obtained from Gelest Company (USA). The corrosion inhibitor used in this study was MOLY-white 101 (MOLY, 85% $ZnMoO_4$) and was obtained from Heucotech Ltd. Co. (USA). Nitric acid (HNO_3) and sodium chloride (NaCl) were purchased from Loba Chemie (India). Distilled water was used to prepare the acid and salt electrolyte solutions.

2.1.2. Preparation of the base hybrid material

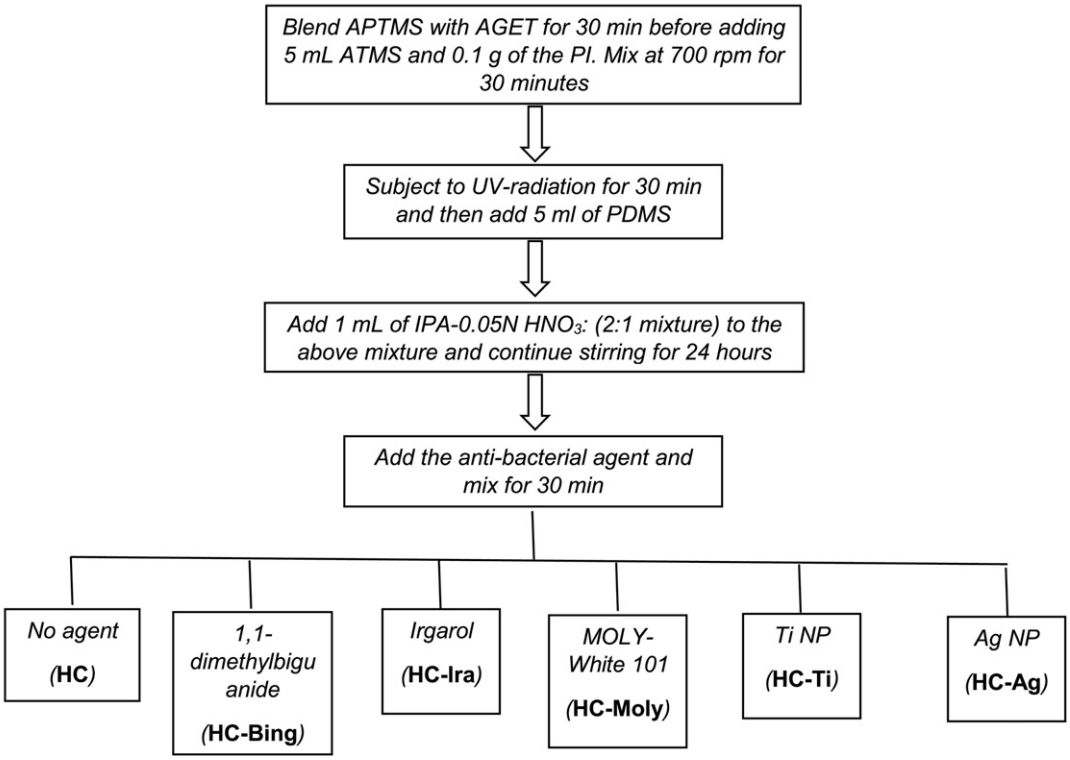
The inorganic-organic hybrid sol-gel material (hereafter denoted HC) was synthesized by blending 5 mL of APTMS (5.135 g, 0.0286 mol) with 5 mL of AGET (4.180 g, 0.0421 mol) in a 25-mL reactor at room temperature and under ambient atmosphere for 30 min. ATMS (5 mL, 4.815 g, 0.0297 mol) and PI (0.1 g, 0.489 mmol) were then added to the reaction mixture, which was stirred for another 30 min before being subjecting to continuous UV radiation (302 nm, energy equal to 100,000 mJ/cm^2) for 1 h. Next, 5 mL of PDMS solution was added to the reaction mixture, and the resultant colorless solution was stirred at 700 rpm for 2 h. Finally, the hydrolysis/condensation of the silanol groups of APTMS and ATMS was achieved by dropwise addition of 1 mL of a 2:1 mixture of isopropyl alcohol (IPA)-0.05 N HNO_3 to the reaction solution. This sol-gel mixture was stirred for 24 h at room temperature before further functionalization through the addition of antibacterial agents.

2.1.3. Preparation of functionalized polymeric materials

Colorless solutions (5 mL each) of the HC matrix were then embedded with 5% (w/v) antibacterial agents, i.e., 1,1-dimethylbiguanide hydrochloride (HC-Bing), Irgarol (HC-Ira), MOLY-white 101 (HC-Moly), Ti nanoparticles (HC-Ti) or silver nanoparticle dispersion (HC-Ag), and sonicated for 30 min, and the vials were labeled accordingly. MOLY-white 101 is also an inhibitive corrosion pigment that improves the corrosion protection performance of sol-gel coatings on mild steel [28,29]. The detailed stepwise procedure used to prepare these biocide-embedded coatings is presented in Scheme 1. Optimization of the reacting material ratios, reaction conditions and embedded biocide concentration as well as the testing of biocides stability and their releasing rate to the metal surface will be the subject of a future study for authors.

2.1.4. Deposition of coatings

S-36 mild steel Q-panels (Q-Lab Company, USA) with dimensions of 76 × 152 × 0.8 mm dimension (ASTM A1008, used as received) were sonicated (Vibra-Cell Sonics and Material INC., US) with absolute ethanol for and air-dried before the coatings were applied. A milliliter of each of the coating matrices was roller-coated (R K Print-Coat Instruments Ltd, UK) on each pre-treated steel panel. The thicknesses of the produced films (approximately 100 μm) were controlled using the blue metal bar attached to the instrument. The coated samples were allowed to dry for 1 h under ambient air and at room temperature and then cured under optimized conditions for 2 h in a CL-1000 UV crosslinker (UVP, LLC, USA) using a 302-nm lamp.



Scheme 1. Preparation of the biocide-embedded sol-gel coatings used in this study.