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Liquid flame spray fabrication of polyimide-copper coatings for antifouling applications

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ABSTRACT

Liquid flame sprayed polyimide-copper coatings were developed for marine antifouling applications. Mixture of polyimide precursor and copper particles was prepared as the starting feedstock for making the composite coatings. Synthesis of polyimide was achieved during the spraying and polyimide acts as binder to fix copper particles. Copper particles were enwrapped by polyimide matrix and distribute evenly in the coatings. Further electrochemical testing revealed excellent corrosion resistance of the coatings in artificial seawater. The coatings resist effectively colonization of *E. coli* and *Bacillus* sp. bacteria on their surfaces, suggesting their remarkable antifouling performances. The results shed light on construction of polymer-based antifouling layers for widespread marine applications.

1. Introduction

Biofouling and corrosion have long been worldwide concerns for marine artificial infrastructures and caused massive economic losses. Biofouling occurred in the marine environment is usually initiated by adsorption of marine macromolecules and subsequent biofilm formation developed from adherence of bacteria/diatoms [1]. The strategy to prevent or alleviate the occurrence of biofouling usually involves physical, chemical and biological ways for resisted attachment or killing of marine microorganisms [2]. Compared to the conventional concept of sterilization, surface modification by antimicrobial layers, for example copper-containing thin films, nanosilver films and titania coatings, already showed encouraging promises for pronounced antifouling performances [1,3]. Among the antifouling layers developed so far, use of the antifoulants comprising silicon or fluoride has been seen effective owing to their non-toxic, broad spectrum and environment-friendly nature. But insufficiency in antifouling performances persists challenging for these coatings. And few materials that have been considered for protective coatings satisfy the requirement for both favorable antifouling capability and sufficient corrosion resistance [4]. Novel antifouling materials that can be processed to the form of surface coatings are yet to be developed extensively. A variety of functional polymers have been attempted for combating marine biofouling and biocorrosion with constrained environmental impact. As an alternative polymer, polyimide has been attracting intense attentions due to its unique mechanical properties, chemical stability and exceptional biocompatibility [5,6]. However, due to the difficulties in controlling chemical imidization and thermal imidization for synthesis of polyimide, recent research efforts have been devoted to exploring the techniques for large-scale coating fabrication of polyimide. In addition, polyimide alone does not offer antifouling properties, addition of antifouling materials is essential to achieve the desired performances. In this letter, polyimide precursor was prepared and copper particles were incorporated for coating fabrication by liquid flame spray. The coatings with unique dispersion of copper have been made and a wrapping structure by polyimide surrounding copper particles ensured controlled release of copper for long-term antifouling performances of the coatings.

2. Experimental

Polyimide precursor was prepared for flame spray synthesis of polyimide by the reaction between 4,4′-oxybisbenzenamine (ODA, D104463, Aladdin, China) and pyromellitic dianhydride (PMDA, P109616, Aladdin, China). For the polyimide-Cu (10 wt.% Cu and 30 wt.% Cu) coating fabrication, prior to the spraying, commercially available copper powder ($-20+5$ μm, Changsha Tianjiu

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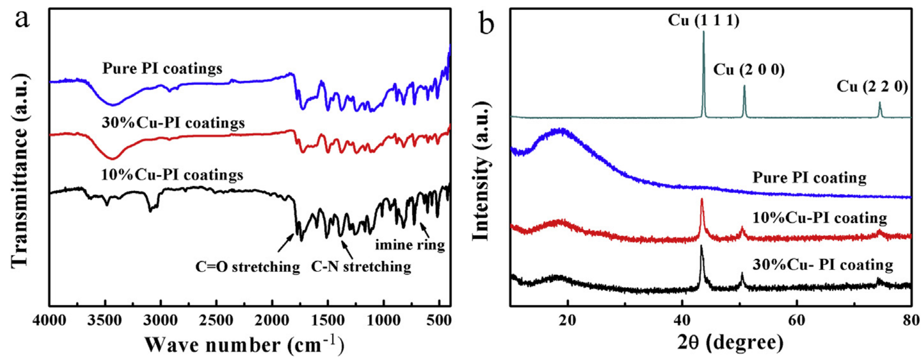

Fig. 1. IR spectra (a) and XRD patterns (b) of the samples.

Materials Co., China) was added into the solution and complete mixing was made. The coatings were deposited by flame spray (CDS 8000, Castolin, Germany) on 316L stainless steel plates with the dimension of $30 \times 20 \times 1.5$ mm. Oxygen and acetylene were used as the combustion-supporting and fuel gas with the pressure of 0.7 MPa and 0.1 MPa, respectively.

The coatings were characterized by Fourier transform infrared spectroscopy (Nicolet 6700, Thermo Fisher Scientific, USA) with the resolution of 4 cm^{-1} and a scan range of 4000–400 cm^{-1} and X-ray diffraction (XRD, D8 Advance, Bruker AXS, Germany) using Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV. Morphology of the samples was characterized by field emission scanning electron microscope (FESEM, FEI Quanta FEG250, the Netherlands) and laser confocal microscope (CLSM, ZEISS, LSM700, Germany). For the corrosion testing of the coatings, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) spectra were acquired using a Solartron Modulab system (2100A, UK). All tests were conducted at room temperature as per the testing procedures reported in another paper [7] in artificial seawater (ASW) prepared according to the ASTM D1141-98 (2003). Gram-positive *Bacillus* sp. (MCCC 1A00791) and gram-negative *E. Coli* (ATCC 25922) bacteria were chosen for the antifouling testing following the protocol reported previously [8]. For FESEM observation of the bacteria attaching on the surfaces of the samples, the bacteria were fixed by 2.5% glutaraldehyde for 24 h, dehydrated gradually and coated with Pt.

3. Results and discussion

The polyimide-Cu coatings with tunable thickness ranging from tens of microns to tens of millimeters have been fabricated by the one-step liquid flame spray. IR and XRD spectra of the coatings suggest complete synthesis of polyimide and well-retained copper during the coating deposition (Fig. 1). The vibrational IR bands at 726, 1122 and 1390 cm^{-1} refer to the out-of-plane bending mode, the transverse stretching mode, and the axial stretching mode of imide CNC, respectively [9]. Cyclic anhydrides have carbonyl absorptions at 1775 cm^{-1}, which is attributed to an asymmetric stretching mode [10]. The extra absorption peaks located at 833 to 873 cm^{-1} region are assigned to absorption of two adjacent hydrogen of benzene ring and an isolated hydrogen atom of another adjacent benzene ring [10,11]. XRD curve of the pure polyimide coating shows a broad peak at the 2θ of 18.3°, indicating amorphous nature of polyimide [12]. It is clear that the incorporation of copper did not trigger structural changes of polyimide, in turn suggesting the feasibility of making polyimide-Cu coatings by the liquid flame spray route. In addition, there are no obvious peaks of copper oxide for the as-sprayed coatings. This indicates minor or negligible oxidation of copper during the deposition.

FESEM characterization together with EDX analyses suggest homogeneous dispersion of Cu particles in the coatings (Fig. 2). Synthesis of polyimide during the spraying is associated with evaporation of solvent and imidization reaction. Copper particles retain their contours in the coatings, indicating unmolten state during the spraying and they are coated with a thin layer of polyimide (Fig. 2 b). Areal surface roughness RSa of the coatings exhibits the average value of 7.589 μm, 10.716 μm, and 14.653 μm for the pure polyimide coating, the polyimide-10% Cu coating, and the polyimide-30% Cu coating, respectively. It is interesting to note that polyimide acts as binder entrapping copper particles, which is promising since this structural feature would facilitate constrained release of copper into physiological media for long-term functional services.

The electrochemical testing reveals significantly enhanced anti-corrosion performances of the polyimide-based coating (Fig. 3 a). Corrosion potential exhibits the value of −0.2843 V and −0.2085 V for the 316L plate and the pure polyimide coating, respectively. The value changes remarkably to 0.0212 V for the

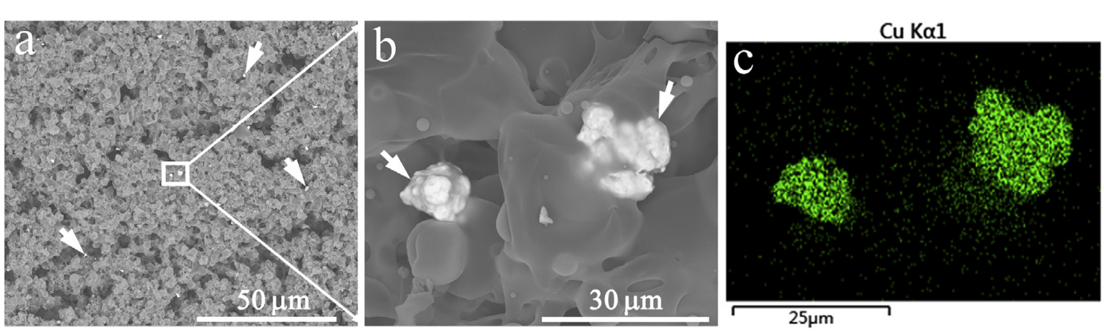

Fig. 2. FESEM pictures and EDX analyses of the as-sprayed polyimide-Cu coatings showing even distribution of copper particles in polyimide matrix and enwrapping state of the particles by polyimide. The white arrows point to typical copper particles seen on the top surfaces of the coatings.

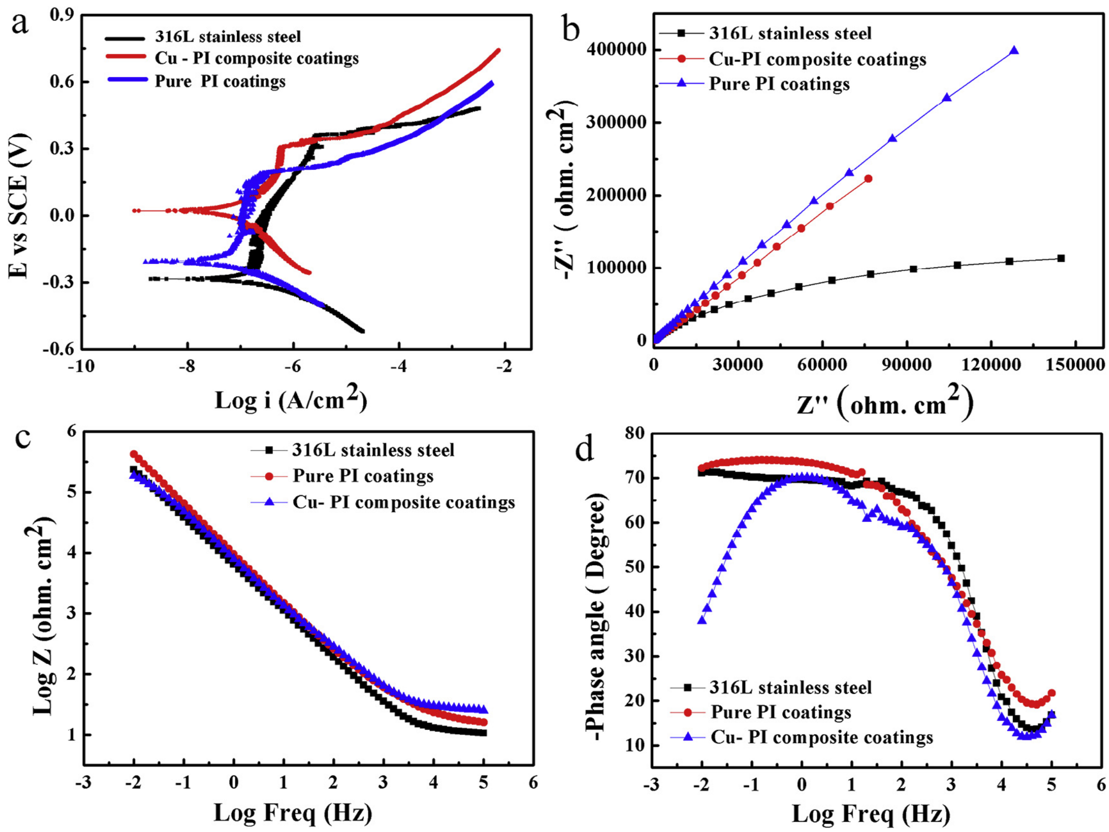

Fig. 3. Electrochemical testing results for the samples tested in synthetic seawater, (a) polarization curves, (b) Nyquist plots, and (c, d) Bode plots.

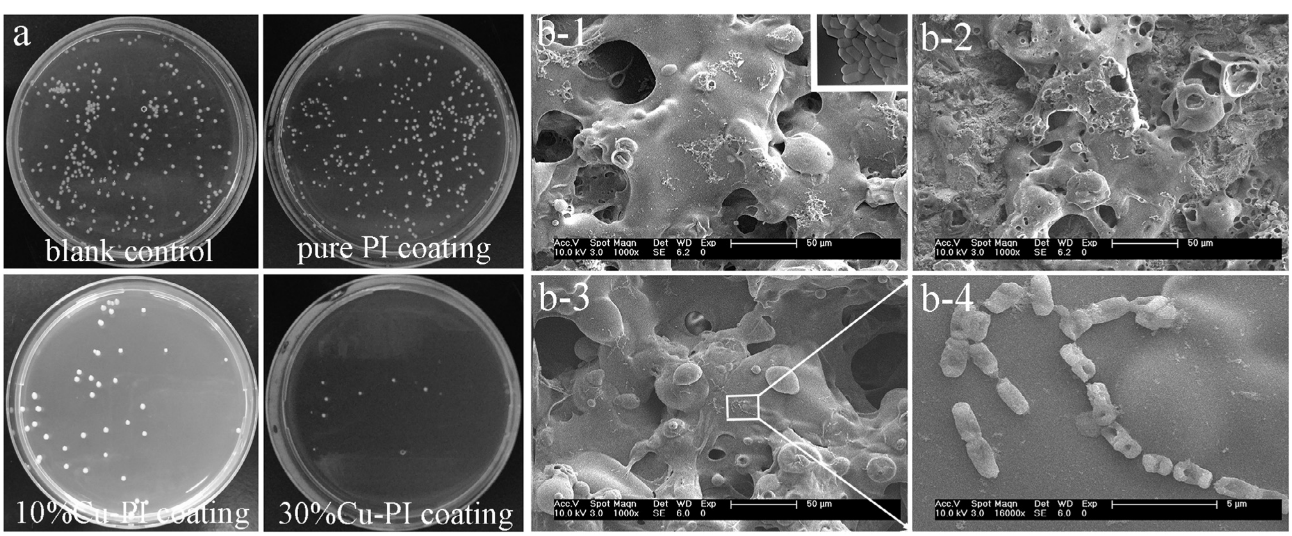

Fig. 4. Antibacterial testing results of the samples, (a) digital photos of *E. coli* colonies in the Petri dish containing nutrient agar after 6 h incubation, and (b) SEM images showing adhesion of *Bacillus* sp. on the samples and obvious killing of the bacteria is seen on the surfaces of the polyimide-Cu coatings (b-1: the pure polyimide coating, the inset is enlarged view of the healthy bacteria colonized on the coating surface; b-2: the 10% Cu-polyimide coating; and b-3, b-4: the 30% Cu-polyimide coating, b-4 exhibits the dead bacteria showing ruptured membrane).

30% Cu-polyimide coating, suggesting enhanced tendency of corrosion resistance. In addition, corrosion current density of the polyimide coating, 0.5772×10^{-7} A/cm^2, is much lower than that of the 316L plate, 1.0859×10^{-7} A/cm^2, indicating the protecting efficiency of polyimide layer. It is not surprising that addition of the easily-eroded copper increased slightly the corrosion current density (0.6193×10^{-7} A/cm^2 versus 0.5772×10^{-7} A/cm^2). Similar tendencies were also revealed for the electrochemical impedance values (Fig. 3b). The highest resistance value was obtained for the pure polyimide coating while the lowest resistance value was exhibited by the uncoated 316L plates. It is obvious that the passive layer of the polymer-based materials is capable of inhibiting diffusion of aggressive electrolyte species toward metal substrate [13,14]. The Bode plots were provided to represent the impedance spectra (Fig. 3 c, d), since the high-frequency impedance features are difficult to discern in Nyquist plots. The slightly increased impedance value of the coating samples further suggests their enhanced corrosion resistance. Nevertheless, the copper-containing polyimide coatings show excellent corrosion resistance.

Extinguishing efficiency of *E. coli* bacteria was determined by the standard plate counting approach through triplicate experiments. The antifouling testing against attachment and colonization of *E. coli* shows encouraging antibacterial properties of the copper-containing coatings (Fig. 4). The 316L plates and the pure polyimide coatings do not show antimicrobial activity. In comparison, addition of copper (10 wt.% and 30 wt.%) in polyimide gives rise to noteworthy sterilization effect (Fig. 4a). Adhesion testing of *Bacillus* sp. further evidences the excellent antifouling performances of the Cu-containing coatings (Fig. 4b). Killing of the bacteria is clearly seen and higher dosage of copper gives rise to more pronounced constrained adhesion of the bacteria. There have been extensive reports on copper-associated bacteria-killing and related mechanisms were well established [15,16]. It seems clear that contact of the bacteria with the Cu-containing surface ruptures the membrane of the bacteria by contact killing (Fig. 4b-4). It is virtually known that marine biofouling is usually initiated by adsorption of organic molecules and subsequent microbial colonization for biofilm formation. The prohibited adhesion of bacteria obviously impedes formation and development of bacterial biofilm. It is therefore anticipated that the newly constructed copper-containing polyimide coatings possess promising antifouling performances. Yet, further extensive research efforts are needed to examine the continuous releasing behaviors of copper ions from the coatings and adhesion of the coatings after long-term exposure to aqueous solutions.

4. Conclusions

Novel polyimide-copper coatings were constructed by liquid flame spray route and the coatings exhibit excellent antifouling and anti-corrosion performances. Polyimide acts as binder matrix fixing copper particles and constrains release of copper into surrounding physiological media for long-term antifouling functions. The enwrapped structure offers the coatings intrinsic advantages of polyimide and antibacterial performances of copper. The cost-effective large-scale fabrication route for making the polymer-based antifouling layers sheds light on constructing marine antifouling coatings and fabrication of polymer-based composites for various applications.

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