Biomimetic electroactive polyimide with *rose petal-like* surface structure for anticorrosive coating application

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Abstract. In this work, an electroactive polyimide (EPI) coating with biomimetic surface structure of *rose petal* used in anticorrosion application was first presented. First of all, amino-capped aniline trimer (ACAT) was synthesized by oxidative coupling reaction, followed by characterized through Fourier transform infrared spectroscopy (FTIR), liquid chromatography – mass spectrometry (LC-MS) and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. Subsequently, as-prepared ACAT was reacted with isopropylidenediphenoxy-bis(phthalic anhydride) (BPADA) to give electroactive poly(amic acid) (EPAA). Moreover, poly(dimethylsiloxane) (PDMS) was used to be the soft negative template for pattern transfer from the surface of *rose petal* to the surface of polymer coating. The EPI coating with biomimetic structure was obtained by programmed heating the EPAA slurry casting onto the negative PDMS template. The anticorrosive performance of as-prepared biomimetic EPI coating was demonstrated by performing a series of electrochemical measurements (Tafel, Nyquist, and Bode plots) upon cold-rolled steel (CRS) electrode in a NaCl aqueous solution. It should be noted that the biomimetic EPI coating with *rose petal-like* structure was found to exhibit better anticorrosion than that of EPI without biomimetic structure. Moreover, the surface contact angle of water droplets for biomimetic EPI coating was found to be ~150°, which is significantly higher than that of EPI coating with smooth structure (~87°), indicating that the EPI coating with biomimetic structure reveals better hydrophobicity.

The apparent mechanism for improved anticorrosive properties is twofold: (1) the biomimetic structure of EPI coating can repel water droplets. (2) electroactivity of EPI coating promotes the formation of densely passive layer of metal oxide on metallic surface.

Keywords: coatings, biomimetic, superhydrophobicity, electroactive polymer, corrosion

1. Introduction

Nature supplies inspiration for exploiting hierarchical structures to prepare biomimetic materials while focusing on environmental protection [1]. Due to multiplicity, abundance and renewability of natural resources different biological materials with unique geometries and internal structures can be used as templates and basic principles of organization assemblies,

and alternative routes for fabricating new structures can be explored [2, 3]. Scientists can synthesize a wide variety of materials inspired by biological species, such as bamboo [4], wood tattoo [5], seaweed [6], leaves [7–9], corn grains [10], peanut shells [11], sugar cane bagasse [12], cotton fibers [13], crab shells [14], butterfly wings [15], diatoms [16], egg shells [17], pollen grains [18], legumes [19], bacteria [20–22],

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viruses [23], cellulose [24–29], and DNA [30], with high reproducibility. Typically, these materials are often applied as uniform coatings with nanoscale or macroscale thicknesses. These practical examples have shown that biotemplates exhibit morphologically complex architectures, and promote an active site interaction between heterogeneous interfaces. In addition, they can be fabricated via the most common types of bottom-up fabrication procedures and are a means of creating useful three dimensional structures that may improve performance, particularly for anticorrosion applications.

For metal finish applications, corrosion control is always a concern and has therefore been a topic of extensive research. Currently, one of the standard industrial practices is to treat and/or coat metal surfaces with chromium-containing compounds. However, several adverse health and environmental effects of chromium compounds have been reported [31, 32]. Many organic and/or polymeric coatings are designed to protect a metal from in-service corrosion. In the past decades, the use of electroactive polymers, such as polyaniline, as corrosion protection coatings was explored for the potential replacements of chromium-containing materials [33]. In addition, aniline oligomer-based electroactive polymers (such as polyimides [34], epoxy resins [35], and polyurethanes [36]) have also been applied as the anticorrosion coatings.

Recently, polymeric coatings with biomimetic surface structures have been examined as anticorrosion coatings. For example, Weng *et al.* [8] reported on an electroactive thermally cured epoxy coating with biomimetic *Xanthosoma sagittifolium* leaf-like structure; this coating fabricated via a nanocasting technique was found to exhibit long-term corrosion protection, even in strongly acidic aqueous solutions. Moreover, corrosion protection was also evident when biomimetic structure natural leaves were fabricated using room temperature-cured epoxy [37], and UV-cured polyacrylate coatings [38]. However, the fabrication of biomimetic surface structure base on natural *rose petal* upon coating has not been investigated as a means for producing anticorrosion coatings.

In this work, an electroactive coating with *rose petal-like* surface structure is fabricated and evaluated for anticorrosion applications. First, amine-capped aniline trimer (ACAT) is synthesized by oxidative coupling, and then characterized by ¹H-NMR and FTIR spectroscopies and liquid chromatography (LC)-mass

spectrometry. Next, as-prepared ACAT is further reacted with 4,4'-(4,4-isopropylidenediphenoxy) bis(phthalic anhydride) (BPADA) in *N,N'*-dimethylacetamide (DMAc) solution to give electroactive poly(amic acid) (EPAA). A soft negative PDMS template was then prepared via nanocasting for pattern transfer with natural *rose petal* as the template. Finally, the biomimetic electroactive polyimide (EPI) coating was realized when the EPAA slurry was cast onto the negative PDMS template. Scanning electron microscopy (SEM) and atom force microscopy (AFM) are utilized to observe the surface topography with hierarchical structures of the biomimetic *rose petal-like* coatings. Superhydrophobicity and electroactivity of coatings with a *rose petal-like* surface structure are investigated on the basis of the static contact angle and electrochemical cyclic voltammetry, respectively. Standard electrochemical corrosion measurements are used to evaluate the biomimetic electroactive coating in NaCl solution. Moreover, electrochemical impedance spectroscopy (EIS) is employed to further confirm the enhanced corrosion protection of the coating with the *rose petal-like* surface.

2. Experimental sections

2.1. Materials and measurements

Aniline (Sigma-Aldrich) was distilled prior to use. The compounds 4,4-Diaminodiphenylamine sulfate, 4,4'-(4,4-isopropylidenediphenoxy) bis(phthalic anhydride) (BPADA, 97%) and sodium chloride were purchased from Sigma Aldrich, while *N,N'*-dimethylacetamide (DMAc) was purchased from Avantor. The liquid components (used for the soft template, Sylgard 184 and PDMS) were supplied by Dow Corning Corporation. All reagents were reagent grade unless otherwise stated.

Mass spectra were recorded on a Bruker Daltonics IT mass spectrometer model Esquire 2000 (Leipzig, Germany) with an Agilent ESI source (model G1607-6001). A Bruker 300 spectrometer, was used for measuring ¹H-NMR spectra, and was referenced to an internal standard of tetramethylsilane (TMS). The solvent was dimethyl sulfoxide (DMSO-*d*₆). Attenuated total reflectance FTIR spectra were obtained at a resolution of 4.0 cm⁻¹ and a range of 4000 to 650 cm⁻¹ with a spectrometer (FT/IR-4200) at room temperature. Surface morphologies were observed by SEM, (JOEL JSM-7600F). Three-dimensional surface was characterized by AFM, (Park systems XE-100). Contact angles of water droplets at various positions on

the sample surfaces were measured using a First Ten Angstroms FTA 125 goniometer at ambient temperature and the average contact angles from five measurements each position were calculated. Redox properties of as-prepared EPI coatings were investigated by cyclic voltammetry. Electrochemical corrosion measurements of sample-coated cold-rolled steel (CRS) electrodes were obtained by using VoltaLab 50 (PST050) potentiostat/galvanostat electrochemical analyzer. Electrochemical impedance spectroscopy (EIS) was performed using an AutoLab (PGSTAT302N) potentiostat/galvanostat electrochemical analyzer.

2.2. Synthesis of amine-capped aniline trimer (ACAT)

4,4'-diaminodiphenylamine sulfate (4.73 g, 0.016 mol) and aniline (1.48 g, 0.016 mol) were dissolved in a HCl aqueous solution (1.0 N, 150 mL) containing 15 g of NaCl. A solution of ammonium persulfate (3.6 g, 0.016 mol) in HCl aqueous solution (1.0 N, 25 mL) was added at a rate of approximately 60 drops/min to the previously described solution at 5 °C using a dropping funnel. The reaction mixture was stirred for 1 h at 5 °C. The resulting precipitate was collected by filtration, followed by washing with large amounts of HCl aqueous solution (1.0 N, 400 mL). Then, the filtrate was washed with NH₄OH solution (1.0 N, 100 mL) and followed by washing with distilled water. Thus, a blue powder was further dried in a vacuum oven at 50 °C for 24 h. The collected ACAT was a blue solid and the yield was approximately 40%.

2.3. Preparation of PDMS template

The PDMS template was prepared by using a 10:1 mixture (by weight) of the base and curing agent. After thoroughly mixing the base and curing agent, the pre-polymer was poured onto the template of fresh *rose petals* and then subjected to program heating at 60 °C for 2 h to ensure completion of the PDMS cross-linking process. Thus, a negative PDMS template was obtained.

2.4. Synthesis of polyimide

BPADA (0.52 g, 1 mmol) was added to 5.0 g of DMAc at room temperature with continuous stirring for 30 min. A solution containing 4,4'-Oxydianiline (ODA) (0.20 g, 1 mmol) in another 5 g of DMAc was prepared under magnetic stirring. After stirring

the ODA solution for 30 min, ODA solution was mixed with BPADA solution at room temperature to produce PAA. The curing at 150 °C was necessary to complete the imidization reaction from PAA to PI for 4 h. PI was also prepared for control experiment and all PI-coated CRS electrode was used as working electrode in electrochemical corrosion measurements.

2.5. Synthesis of electroactive polyimide (EPI)

BPADA (0.52 g, 1 mmol) was added to 5.0 g of DMAc at room temperature with continuous stirring for 30 min. A solution containing ACAT (0.288 g, 1 mmol) in another 5 g of DMAc was prepared under magnetic stirring. BPADA solution was added to the ACAT solution and stirring was continued for 3 h at room temperature to produce electroactive (polyamic acid) (EPAA). The EPAA was then coated onto the cold-rolled steel (CRS) substrate with and without the PDMS template, followed by curing at operational programmed temperature of 80 °C for 1 h. Another 4 h of curing at 150 °C was necessary to complete the imidization reaction from EPAA to EPI. Both EPI-coated CRS electrode with and without *rose petal-like* surface structures were used as working electrodes in electrochemical corrosion measurements.

2.6. Electrochemical corrosion studies

Coatings with ~30 μm thickness were obtained after drying in a fume hood for 24 h at room temperature. The edges of coupons were sealed with epoxy cement (SPAR[®]). The coated and uncoated coupons were connected to the working electrode of an electrochemical cell. For anticorrosion data, polarization curves were obtained by cyclic voltammetry (VoltaLab50 potentiostat/galvanostat) at a constant temperature. A 3.5% NaCl aqueous solution was used as the electrolyte, and the three-electrode configuration was employed in the circuit with the sample as the working electrode, a graphite rod as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The open circuit potential (OCP) at the equilibrium state of system was used as the corrosion potential E_{corr} [mV]. For the potentiodynamic polarization experiments, the potential was scanned from -500 to 500 mV at a scanning rate of 50 mV·s⁻¹. The corrosion current (I_{corr} , [μA·cm⁻²]) was determined by superimposing a straight line along the linear portion of cathodic or anodic curve and extrapolating it through E_{corr} .

Electrochemical impedance spectroscopy (EIS) measurements in the 3.5% NaCl aqueous solution were obtained by using an AutoLab (PGSTAT302N) potentiostat/galvanostat electrochemical analyzer. Impedance measurements were carried out in the frequency range of 10 Hz to 100 mHz with the working electrode embedded in epoxy, a carbon rod as the counter electrode, and the saturated calomel electrode (SCE) as the reference electrode. The working electrode was kept in the test environment for 40 min before measurement of impedance. All experiments were performed at 25 °C. Raw data were collected at least three times to ensure reproducibility and statistical significance.

3. Results and discussion

3.1. Characterization of ACAT

The representative $^1\text{H-NMR}$, Mass, and FTIR spectra for as-prepared ACAT were shown in Figure 1. From Figure 1a, the $^1\text{H-NMR}$ at $\delta = 5.45$ ppm and at $\delta = 7.25$ to 6.50 ppm could be assigned to the primary amine protons ($-\text{NH}_2$) and the splitting of the aromatic proton of ACAT, respectively. In the mass spectrum in Figure 1b, the molecular ion peak of ACAT appears at the position of 289, which is consistent with the theoretical molecular weight of ACAT. In Figure 1c, the FTIR spectrum of ACAT showed characteristic absorption bands at 3307 and 3210 cm^{-1} , which are due to the terminal NH_2 of ACAT. Moreover, the characteristic absorption bands appearing at 1598 and 1498 cm^{-1} can be assigned to the vibrational bands of the quinoid ring and the benzenoid ring of ACAT, respectively.

The as-prepared ACAT was reacted with dianhydride in DMAc to yield a solution of EPAA, which was used to prepare the biomimetic EPI coating. The process for preparing biomimetic EPI coatings via the nano-casting technique is illustrated in Figure 2.

3.2. Characterization of EPI derived from EPAA

Figure 3 illustrates the FTIR spectra of EPAA and EPI. In Figure 3a, the EPAA exhibits its characteristic peak at 3400–3600 cm^{-1} , which corresponds to the hydroxyl group from the carboxylic acid of EPAA. Moreover, the characteristic peak found at 3340 cm^{-1} can be attributed to the N–H stretching modes. In addition, the characteristic absorption peaks found at 1596 and 1503 cm^{-1} were assigned to the stretching modes of $\text{N}=\text{Q}=\text{N}$ and $\text{N}-\text{B}-\text{N}$, respectively, where

Figure 1. Characterization of as-prepared ACAT by (a) $^1\text{H-NMR}$, (b) mass and (c) FTIR spectroscopy

Q correspond to the quinoid ring and B signifies the benzene ring. The characteristic peak found at 1365 cm^{-1} was assigned to $\text{C}=\text{N}$ stretching. In Figure 3b, the FTIR spectrum of EPI revealed a characteristic absorption band at 742 cm^{-1} , which corresponds to the deformation of the imide group [39].

3.3. Surface morphological studies

Macroscopic and microscopic studies on the surface morphology of natural *rose petal* coatings and artificial biomimetic coatings were investigated using photography SEM, and AFM. Figure 4a shows a

Figure 2. Flow chart for the preparation of EPI coating with biomimetic *rose petal-like* surface structure

Figure 3. Representative FTIR spectra for (a) EPAA and (b) EPI

macroscopic photograph of the natural *rose petal*. Figures 4b and 4c show 1000× magnification SEM micrographs of the natural fresh *rose petal* and artificial biomimetic *rose petal-like* coating, respectively. In Figure 4b, the surface morphology of the natural *rose petal* exhibits a hierarchical surface with a microscale hemispherical-like morphology decorated

with many nanoscale wrinkles on the surface. The surface morphology of the biomimetic EPI coating appears to nearly identical to that of the natural *rose petal*, as shown in Figure 4c. Moreover, the three-dimensional morphological surface of the biomimetic EPI coating on the CRS electrode as shown in Figure 4d.

3.4. Contact angle (CA) measurements of as-prepared EPI coatings

The contact angle of water droplets (CAWD) on two different morphologies of coatings are illustrated in Figure 5. As shown in Figure 5a, the CAWD for natural *rose petal* was given to be 126° because of its natural micro/nano-structure. Additionally, the CAWD of PDMS template with negative micro/nano-structure was found to be 113°, as shown in Figure 5b. In Figure 5c, the CAWD for EPI with smooth surface was found to be 87°. After the nanocasting treatment was employed, the CAWD of EPI with biomimetic *rose petal-like* surface structure which was found to be 150° this structure could easily trap air within the valleys between hills, like lotus effect. As shown in

Figure 4. Macroscopic photography of the (a) natural *rose petal*. Microscopic SEM overlook image at magnification of $\times 1000$ for the (b) fresh natural *rose petal*, (c) EPI coating with biomimetic *rose petal*-like surface structure and (d) AFM image of EPI coating with biomimetic *rose petal*-like surface structure.

Figure 5. Contact angle of water droplets for (a) natural *rose petal* (b) negative PDMS template (c) CRS coated by EPI and (d) CRS coated by EPI with biomimetic *rose petal*-like surface structure

Figure 5d, EPI with biomimetic *rose petal*-like surface structure was found to show an increase of 63° over the standard EPI coating. Superhydrophobicity (i.e., CAWD $\sim 150^\circ$) of the biomimetic EPI implied that this biomimetic coating is a good candidate for corrosion protection.

3.5. Electoractivity investigation of EPI coating by cyclic voltammetry

Electroactivity of as-prepared EPI can be identified by electrochemical cyclic voltammetry. In Figure 6, these voltammetric studies of EPI demonstrate that the coating exhibits a single oxidation peak, which is similar to many longer oligomers that undergo a two-electron transfer [40]. The EPI coating exhibits an oxidation current (I_{ox}) of 0.372 mA/cm^2 and a reduction current (I_{red}) of 0.391 mA/cm^2 . The electroactivity of EPI coatings may lead to the formation of a dense,

Figure 6. Cyclic voltammetry for (a) PI and (b) EPI as measured in 1.0 M H₂SO₄ aqueous solution with scan rate of 50 mV/s

passive metal oxide layer, which would make EPI suitable for anticorrosion coating applications. In summary, both the superhydrophobicity and electroactivity results suggest that the biomimetic *rose petal-like* structures of EPI coatings make them promising as anticorrosion coatings. Standard electrochemical corrosion measurements of biomimetic coating will be discussed in the follow section.

3.6. Potentiodynamic measurement

In this study, a series of electrochemical corrosion measurements of as-prepared coatings were carried out on CRS electrodes with electrodes with various coatings. The coated CRS electrodes were immersed in an electrolyte of 3.5 wt% NaCl aqueous solution. Figure 7, shows the Tafel plots for the curve a) CRS coupon and curve b) CRS coated with PI, curve c)

Figure 7. Tafel plots for (a) neat CRS electrode, CRS coated with (b) PI, (c) EPI and (d) EPI with biomimetic *rose petal-like* surface structure, as measured in 3.5 wt% NaCl aqueous solution

Table 1. Contact angle and electrochemical corrosion measurements^a of CRS, CRS coated by PI, EPI and EPI with biomimetic *rose petal-like* surface

Sample code	E_{corr} [mV]	I_{corr} [$\mu\text{A}/\text{cm}^2$]	Thickness [μm]
CRS	-926	394.40	—
PI	-843	0.76	21 $\pm$ 1
EPI	-786	0.46	21 $\pm$ 1
REPI*	-540	0.05	21 $\pm$ 1

^aSaturated calomel electrode was employed as reference electrode.

*REPI is an abbreviation for EPI with biomimetic surface structure.

EPI and curve d) EPI with biomimetic *rose petal-like* structures. The corresponding data from Figure 7 are summarized in Table 1. Tafel plots of CRS electrodes coated with the three samples indicate that the corrosion potential (E_{corr}) is more positive for the coated CRS electrodes than for the uncoated CRS electrodes. It should be noted that the corrosion potential of CRS electrodes with the biomimetic EPI coating ($E_{\text{corr}} = -540$ mV) was found to be more positive than that of electrodes with EPI ($E_{\text{corr}} = -786$ mV) and PI coatings ($E_{\text{corr}} = -843$ mV). On the other hand, the corrosion current (I_{corr}) of all coated CRS electrode is lower than that of the uncoated CRS electrode. Moreover, the corrosion current of the biomimetic EPI-coated CRS electrode ($I_{\text{corr}} = 0.05 \mu\text{A}/\text{cm}^2$) was found to be lower than that of the electrodes with EPI ($I_{\text{corr}} = 0.46 \mu\text{A}/\text{cm}^2$) and PI coatings ($I_{\text{corr}} = 0.76 \mu\text{A}/\text{cm}^2$).

Based on the E_{corr} and I_{corr} data obtained from Tafel plots, the biomimetic EPI with *rose petal-like* surface structure was found to show better corrosion protection on the CRS electrode than PI, which may be attributed to two possible mechanisms. First, the biomimetic EPI coating with the *rose petal-like* surface structure has better hydrophobic characteristics than the PI coating. Secondly, the biomimetic EPI coating may form a dense, passive layer of metal oxide that protects the steel underneath [41], which is consistent with the redox electro-catalytic results of EPI. To further investigate anticorrosion properties of these materials, the electrochemical impedance spectroscopy (EIS) results of these materials will be discussed in the following section.

3.7. Electrochemical impedance measurements (EIS)

EIS was used to evaluate the difference in the activity between the surface of the bare CRS electrode and the sample-coated ones. Impedance is a totally

Figure 8. Nyquist plots for (a) neat CRS electrode and CRS coated with (b) PI, (c) EPI and (d) EPI with biomimetic *rose petal-like* surface structure as measured in 3.5 wt% NaCl aqueous solution

complex resistance when a current flows through a circuit consisting of capacitors, resistors, or insulators, and combination thereof. Figure 8 illustrates the Nyquist plots of the four measured samples: the curve a) CRS coupon and curve b) CRS coated with PI, curve c) EPI, and curve d) EPI with a biomimetic *rose petal-like* surface structure. Charge transfer resistances of all samples were determined by subtracting the intersection value of the high-frequency end from that of the low-frequency end of the semicircle arc with the real axis. Results were found to be 2.3, 200.1, 277.9 and 356.2 $\text{k}\Omega\cdot\text{cm}^2$ for Figure 8 curves a)–d), respectively. Moreover, Bode plots (impedance vs. frequency) of all samples are shown in Figure 9. The real impedance, or Z_{real} , is used to evaluate corrosion protection of the coatings. A low Z_{real} value could result from a very high capacitance

Figure 9. Bode plots for (a) neat CRS electrode and CRS coated with (b) PI, (c) EPI and (d) EPI with biomimetic *rose petal-like* surface structure as measured in 3.5 wt% NaCl aqueous solution

and/or very low resistance of the coating. In the case of Bode plots, the value of Z_{real} at the lowest frequency also represents corrosion protection. The Bode plots for bare CRS and CRS coated with PI, EPI, and EPI with biomimetic *rose petal-like* surface structures show Z_{real} values of 2.5, 3.7, 4.2 and 5.6 $\text{k}\Omega\cdot\text{cm}^2$, respectively, at the low frequency end. Note that the result obtained from the EIS (Nyquist plots and Bode plots) is consistent with the previous conclusion based on the Tafel plots.

4. Conclusions

EPI coatings with *rose petal-like* surface structures are prepared and investigated for their potential application as anticorrosion coatings. The EPI coatings with *rose petal-like* surface structures were compared to both EPI and PI without the biomimetic structure. To produce these EPI coatings, ACAT was successfully synthesized by an oxidative coupling reaction, and characterized with FTIR and $^1\text{H-NMR}$ spectroscopy and LC-Mass spectrometry. The characterized ACAT was reacted with BPADA in a DMAc solution to produce EPAA, which was eventually cured to form EPI. A nanocasting technique was used to produce a PDMS soft negative template suitable for pattern transfer by using natural *rose petals* as the template, leading to the formation of a biomimetic EPI coating. Investigation of the surface morphology of as-prepared biomimetic EPI via SEM and AFM revealed a natural *rose petal-like* hierarchical surface with a microscale hemispherical-like morphology decorated with many nanoscale wrinkles on the top surface. This morphology affects the hydrophobicity of the material. The surface contact angle of water droplets for the biomimetic EPI coating was found to be $\sim 150^\circ$, which was significantly higher than that of smooth EPI ($\sim 87^\circ$), indicating that the coating with the biomimetic structures effectively repels water droplets. Finally, the electroactivity of biomimetic EPI coatings was evaluated using electrochemical cyclic voltammetry, potentiodynamic measurement techniques, and electrochemical impedance measurements. Biomimetic EPI was compared to both EPI and PI without a biomimetic surface structure. In each measurement of the electroactivity of biomimetic EPI, the results indicated an improvement in corrosion resistance compared to EPI and PI without the biomimetic structures, as a result of the formation of a dense, passive layer of metal oxide on the surface of the metal.

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