Corrosion Inhibition and Antifouling Performance of Epoxy Coating Functionalized with PEDOT: PSS-Cerium Doped Zinc Oxide Hybrid Composites

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Abstract. Steel corrosion and biofouling have adverse impacts on various high-end engineering applications including, in biomedical and maritime industries. Smart functional polymer coatings have been developed to simultaneously control corrosion and prevent biofouling problems on steels. In this study, translucent epoxy coatings loaded with 1, 3, and 5 wt% of functional hybrid composite (HC) microparticles were formulated. The HC particles contained cerium doped ZnO encapsulated in conductive poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS) polymer at mixing ratio of 3:1. The effects of HC composition towards the corrosion inhibition and antifouling properties of the coating were evaluated. The anticorrosion performance of the coating films deposited on stainless steel (SS 316 L) substrates was evaluated by using the Potentiodynamic Polarization (PP) technique. The antifouling characteristics of the coatings were investigated by performing the antimicrobial susceptibility test and a series of photodegradation test in medium containing ~10⁸ CFU/ml of bacteria under UV light in 180 minutes. The findings revealed that the presence of PEDOT-PSS-Ce doped ZnO HC increased the barrier properties of the epoxy matrix on SS 316 L against corrosion. The corrosion inhibition properties increased with increasing HC composition. The formulated coatings also exhibited antifouling effects against bacteria. The Gram positive- S. aureus exhibited susceptibility against the coating whereas the Gram negative – S. aureus showed resistant. The coatings demonstrated photocatalytic properties under UV light irradiation and capable of inactivating <99% of bacteria in less than 180 min. The epoxy coating functionalized with 5wt% HC exhibited the highest corrosion inhibition performance (corrosion rate of 0.0001 mm/year) and excellent antifouling effects against selected bacteria.
1. Introduction

Steel corrosion and biofouling are two major concerns in high-end industries including the biomedical, automotive, chemical and maritime. They contribute to performance decline, deterioration of structure and increase the risk of product contamination. In the corrosion process, the iron in the steel oxidizes through contact with moisture, oxygen and electrolyte to produce rust. Meanwhile, the biofouling is caused by accumulation of microorganisms, algae, plants or small animals on steel surface exposed to a wet condition [1-3]. The cycle starts as microorganisms colonise on the steel surface and form biofilm [4-5]. Several types of steels including marine grade stainless steels [4], carbon steel [6-8] and galvanised steel [9-10], are prone to localized corrosions and exhibited biofouling tendency in biotic environment.

Controlling biofouling using oxidizing biocides such as chlorine, bromine and ozone are effective but they have no specific effects on corrosion [11-12]. Some corrosion protection coatings and paints are sometimes fail or delaminate over time due to biofouling attack [13-14]. For that reason, development of next-generation steel protection strategy should offer solution with synergistic action of corrosion inhibition and antifouling effects.

Smart functional coating is a special material with multiple functionalities and responsive to changing environment [15-16]. Presently developed functional coating materials for anticorrosion and antifouling applications have a few interesting features [17-19]. The coating matrix generally serves as barrier to isolate the substrate from the corrosive agents whereas the functional agents dispersed in it, enhances the corrosion resistance of the protected substrate. The coating also possesses hygienic features which can prevent bacteria attachment and disinfect the coating surface. Through this strategy, the deterioration due to corrosion and biofouling attacks can be minimized.

Conducting polymer (CP)-metal oxide hybrid composite (HC) is a new class of functional material that could be further explored as additive in the protection coating formulation. By using microencapsulation technology, micron or nano-sized metal oxide particles are encapsulated in a shell of conducting polymer to form a hybrid composite (HC) material. Small amount of HC particles are then dispersed in the coating matrix as the functional agent. This technique provides the opportunity of merging the properties of different types of material or creating novel materials with specific functionality. The polyaniline (PANI)–ZnO HC particles for instance have proven efficiency to boost anticorrosion performance of coatings and paints on steels [20-22]. The HC particles produce crack-free coating by filling in the pores during curing of coating while proper distribution of HC in coating matrix can improve cathodic protection of coating through enhancement of coating barrier properties against corrosion current [23]. The antimicrobial activity of CP-metal oxide HC particles and their effects on the overall antifouling properties of coating are still limited. However, combination of CP and metal oxide particles with known intrinsic antimicrobial properties is expected to produce HC with inherent antimicrobial and antifouling properties.

This work has therefore been conducted to formulate of new functional coating comprising epoxy matrix and PEDOT:PSS-Ce doped ZnO hybrid composite (HC) particles as the functional agent. Poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is $p$-type intrinsically conducting polymer with potential anticorrosion [24] and antimicrobial effects [25]. Ce doped ZnO is a modified $n$-type ZnO and its known for its photocatalytic properties under UV and visible light region [26,27]. The anticorrosive and antibacterial properties of this material has been previously reported in [28,29]. The effects of PEDOT:PSS-Ce doped ZnO HC composition on the anticorrosion and antifouling performance of the epoxy coating were evaluated.
2. Experimental

2.1. Hybrid Composite Preparation
Metal oxide particles containing 1 mol% CeO$_2$ and 99 mol% ZnO were prepared from ZnO nanoparticles (<50 nm) and Ce (III) nitrate hexahydrate precursors via wet chemical method. All precursor materials were mixed in citric acid (C$_6$H$_8$O$_7$) solution at the temperature of 70 – 80 °C for 3 hours. The precursor gel obtained after the process was dried at 110°C for 19 hours. The powder was calcined at 500 °C for 4 hours to remove moisture and excess organic compounds. High purity Ce doped ZnO particles were obtained after carrying sintering process at 1200°C for 5 hours. Size reduction procedure was performed obtain particles of less than 60 μm. The Ce doped ZnO particles were encapsulated with PEDOT:PSS. The weight ratio of PEDOT:PSS to Ce doped ZnO was set at 3:1 to sustain homogeneity of HC particles.

2.2. Preparation of Epoxy/PEDOT:PSS-Ce doped ZnO Hybrid Composite Coating
The coating solutions were prepared according to the formulations presented in table 1. A specific amount of HC particles was dispersed in a mixture of epoxy resin and diethylentriamide hardener. The mixing ratio of resin to harderner was set at the weight ratio of 10:1. The mixture was vigorously blended at 1000 rpm for 4 hours. The coating solution was coated on polished and cleaned stainless steel (SS 316 L) substrates (25 mm x 25 mm x 1.5 mm) using the drop-casting method for further analyses. Drying was performed in a convective oven at 60°C for 24 hours to completely cure the coating film.

| Sample    | PEDOT:PSS-Ce doped ZnO HC composition (wt%) | Epoxy matrix (wt%) |
|-----------|---------------------------------------------|--------------------|
| Coating SS 1 | 1                                           | 99                 |
| Coating SS 3 | 3                                           | 97                 |
| Coating SS 5 | 5                                           | 95                 |

2.3. Characterization and Performance Evaluation of Coating
The microstructure of HC particles and coatings were examined under SEM (JSM-6100). In addition, the elemental analyses were performed by using the energy dispersive X-ray (EDX) spectroscopy techniques.

The anticorrosion performance of the coating films deposited on SS 316 L substrate was evaluated by using the Potentiodynamic Polarization (PP) technique. In the polarisation current experiment, the potentials voltage was scanned from -1.0 to 0.3 V with the scanning rate of 0.01 mVs$^{-1}$ and the optimise current of 1 mA was applied through 3.5 % NaCl aqueous solution at room temperature.

A Tafel plot provides important electrochemical parameters such corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and corrosion rate (CR). Tafel plots were plotted over log(I) versus E. This plot consists of anodic and the cathodic curves and it is extrapolated to obtain $E_{corr}$. The intersection at the current density point is referred as the $I_{corr}$ value.

The antimicrobial susceptibility test was conducted according to Kirby-Bauer disc diffusion method with some modifications. Coating sample with 5 mm diameter was placed on agar plates streaked with Gram-negative, *Escherichia coli* (*E.coli*) and Gram-positive, *Staphylococcus aureus* (*S.aureus*). The plate was later incubated at 37°C for 18 hours. The width of inhibition zone created on the agar plate was measured. The strength of bactericidal effects is proportionate to the width of inhibition zone.

Photoresponsiveness and photocatalytic effects of coating under UV light were tested in a series of photodegradation tests in medium containing ~10$^8$ CFU/ml *E.coli* and *S.aureus* bacteria.
for 180 minutes. SS 316 L coupon was used as the coating support. The experimental set-up for performing the test is presented in figure 1. The antifouling effect of coating through photocatalytic mechanism could be deduced from the efficiency of the coating to inactivate bacteria in the treated solution.

Figure 1. Photodegradation test of epoxy/PEDOT:PSS Ce doped ZnO HC coatings in medium containing ~10⁸ CFU/ml of bacteria under UV light irradiation for 180 min.

3. Results and Discussions

3.1. Microstructure and Elemental Composition of Epoxy/PEDOT:PSS-Ce doped ZnO HC Coating

Figure 2 shows the SEM image and EDX spectrum of PEDOT:PSS-Ce doped ZnO HC. The HC particles appeared as dense globular cluster or granules with the approximate size of less than 10 μm. The finding reveals that the PEDOT:PSS polymer (which was represented by C, S and O) has covered the Ce doped ZnO particles (represented by Zn, Ce and O). Pt element detected in the spectrum was probably coming from the sputtered Pt during sample preparation.

Figure 3 shows the SEM surface images of the coating containing different HC compositions. The HC particles that appeared as bright spots could be seen randomly distributed on the coating. In agreement with [23], the coatings with HC were free of micro-cracks. Agglomeration of HC particles was noticed on the coating with 5 wt% HC causing the surface to become irregular compare to other coating formulations. Isolated and randomly distributed HC particles are required to produce functional coating with uniform properties [31].
3.2. Anticorrosion Performance of Epoxy/PEDOT:PSS-Ce doped ZnO HC Coating

Figure 4 shows the Tafel plots for uncoated SS 316 L and the SS 316L coated with epoxy/PEDOT:PSS-Ce doped ZnO HC coating and the results from Tafel extrapolation are listed in table 2. The corrosion performance is evaluated based on several important parameters such as the corrosion potential (E$_{\text{corr}}$), the corrosion current (I$_{\text{corr}}$) and the corrosion rate (CR). Excellent corrosion protection properties are indicated by the high E$_{\text{corr}}$ value, the low I$_{\text{corr}}$ value and the low CR value [32].

Figure 4. Tafel plot of epoxy/PEDOT:PSS-Ce doped ZnO coated on SS 316 L substrate.
Table 2. Electrochemical parameters of epoxy/PEDOT: PSS-Ce doped ZnO coated on SS 316 L substrate.

| Sample         | HC composition (wt%) | Corrosion potential, $E_{corr}$ (V) | Corrosion current density, $I_{corr}$ (A/cm²) | Corrosion rate, CR (mm/year) |
|----------------|----------------------|--------------------------------------|-----------------------------------------------|-----------------------------|
| Pristine SS    | -                    | -0.7613                              | $1.52 \times 10^{-6}$                         | 0.0176                      |
| Coated SS 1    | 1                    | -0.0515                              | $1.14 \times 10^{-7}$                         | 0.0013                      |
| Coated SS 3    | 3                    | -0.2010                              | $8.60 \times 10^{-8}$                         | 0.0010                      |
| Coated SS 5    | 5                    | -0.1391                              | $1.15 \times 10^{-8}$                         | 0.0001                      |

All coated SS 316 L exhibited 92.6-99.4 % lower CR values than that of unprotected SS 316 L. The value reduced from 0.176 mm/year in bare SS 316 L to as low as 0.0001 mm/year after coated with epoxy/PEDOT: PSS-Ce doped ZnO HC coating. The $I_{corr}$ value was suppressed from $1.52 \times 10^{-6}$ A/cm² to lower values ($0.115 - 1.14 \times 10^{-7}$ A/cm²) whereas the $E_{corr}$ values were increased as the SS 316 L were coated. The lower $I_{corr}$ value denotes that the coated sample has a lower impedance to current flow. The trend observed indicates that the epoxy/PEDOT: PSS-Ce doped ZnO HC coating has anticorrosive effects on SS 316 L substrate. The anticorrosive properties increased with increasing HC compositions.

The corrosion protection by epoxy/PEDOT: PSS-Ce doped ZnO HC coating on SS 316 L can be associated to several possible mechanisms. The coating layer may serve as a barrier that isolates the substrate from corrosion agents and thus, inhibits both anodic and cathodic reactions from occurring [23]. It is also believed that HC particles dispersed in the coating altered the anodic kinetics on the metal surface and keeps the metal in a more stable state [33,34]. This can be clarified with the increase in tortuosity of the diffusion pathway of O₂ and H₂O due to dispersion of HC in the epoxy coating [32]. Hence, the corrosion protection effects impart by HC addition is in agreement with a decline in CR value after coating was applied.

3.3. Antifouling Performance of Epoxy/PEDOT: PSS-Ce doped ZnO HC Coating

Figure 5 shows the zone of inhibition produced by different coating samples against S.aureus and E.coli strains. The Gram positive bacteria, S.aureus exhibited susceptibility against all tested coatings whereas the Gram negative bacteria, E.coli showed resistant except for coating with 3 wt% HC. The coating with 5 wt% HC formed the widest inhibition zone against S.aureus (10.0 ± 0.5 mm). The antibacterial activity increased with higher HC compositions. The findings suggest that HC particles functionalized the inert epoxy coating with essential antibacterial properties that can prevent fouling. It is believed that the Ce doped ZnO encapsulated in HC particles are responsible for the effect. In agreement with [35], ZnO exhibited more prominent cytotoxicity effects on the Gram-positive bacteria compared to the Gram-negative bacterial strains. The Gram negative bacteria has lipopolysaccharide (LPS) outer membranes that provide extra protection against the action by antibiotics [36].
Table 3 and 4 show the bacteria inactivation efficiency of epoxy/PEDOT:PSS-Ce doped ZnO HC coating against *E. coli* and *S. aureus*, respectively under UV light. All coatings efficiently inactivate almost between 99.100% of both *E. coli* and *S. aureus* in 180 min. Although similar result was also obtained by action of only UV light at the end of 180th min, it was noticed that the presence of coating with HC accelerated the complete bacterial inactivation process. More than 99% of the bacteria were inactivated within the first 30 minutes of the treatment.

**Table 3.** Photocatalytic inactivation of *E. Coli* bacteria by using epoxy/PEDOT:PSS/Ce doped ZnO coating under UV light for 180 minutes.

| Time / Sample | Control | 1 wt % HC | 3 wt % HC | 5 wt % HC |
|---------------|---------|-----------|-----------|-----------|
| Initial       | ![Initial](initial.png)   | ![Initial](initial.png)   | ![Initial](initial.png)   | ![Initial](initial.png)   |
| Final         | ![Final](final.png)       | ![Final](final.png)       | ![Final](final.png)       | ![Final](final.png)       |
| % bacterial inactivation after 30 min | 83.6 | 99.2 | 100.0 | 100.0 |
| % bacterial inactivation after 180 min | 99.9 | 100.0 | 100.0 | 100.0 |
Table 4. Photocatalytic inactivation of *S.aureus* bacteria by using epoxy/PEDOT:PSS/Ce doped ZnO coating under UV light for 180 minutes.

| Time / Sample | Control | 1 wt % HC | 3 wt % HC | 5 wt % HC |
|---------------|---------|-----------|-----------|-----------|
| Initial       | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| Final         | ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| % bacterial inactivation after 30 min | 75.3 | 90.3 | 98.7 | 99.2 |
| % bacterial inactivation after 180 min | 99.8 | 100.0 | 100.0 | 100.0 |

The bacteria inactivation mechanism by epoxy/PEDOT:PSS-Ce doped ZnO HC coating under UV light is associated to the dispersion of photoresponsive HC particles on the surface of the coating. It has been reported previously that Ce doped ZnO and PEDOT-ZnO possess photocatalytic behaviour under visible to UV light region [26,37]. The HC particles interacted with the illuminated UV light to photogenerate oxidizing reactive oxygen species (ROS) such as $\cdot$O$_2$ and $\cdot$OH radicals. These species are toxic substances which can oxidise the cell membranes resulting in damaging the bacteria cells [38]. This action inhibited the bacteria in planctonic phase from approaching the coating surface, thus providing the antifouling effect.

4. Conclusions

In conclusion, functional epoxy/PEDOT:PSS-Ce doped ZnO HC coatings containing 1, 3 and 5 wt% of HC have been successfully synthesized. The findings show that the dispersion of PEDOT:PSS-Ce doped ZnO HC particle functionalized the epoxy coating with anticorrosion and antifouling properties. The epoxy/PEDOT:PSS-Ce doped ZnO HC coatings enhanced corrosion performance of SS 316 L substrate by 92.6- 99.4%. The barrier properties and anticorrosion effect of the coating improved with increasing HC compositions. The coatings exhibited antibacterial properties against the Gram-positive bacteria, *S.aureus* with increasing HC compositions. In addition, the coatings demonstrated photocatalytic properties under UV light irradiation and capable of inactivating <99% of bacteria (*S.aureus* and *E.coli*) in less than 180 min. The epoxy coating functionalized with 5 wt% PEDOT:PSS-Ce doped ZnO HC exhibited the highest corrosion inhibition performance (corrosion rate of 0.0001 mm/year) and excellent antifouling effects against selected bacteria.

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