

Development of Multi-layered Self-healing Coating Systems for Corrosion Mitigation of Offshore Wind Turbines

Adamantini Loukodimou
School of Engineering
University of Leicester
University Road, Leicester, LE1 7RH
United Kingdom
and
NSIRC
Granta Park
Cambridge CB21 6AL
United Kingdom
al427@leicester.ac.uk

Vikas Kumar
School of Engineering
University of Leicester
University Road
Leicester LE1 7RH
United Kingdom

David Weston
School of Engineering
University of Leicester
University Road
Leicester LE1 7RH
United Kingdom

Shiladitya Paul
TWI
Granta Park
Cambridge CB21 6AL
United Kingdom
and

School of Engineering
University of Leicester
University Road, Leicester, LE1 7RH
United Kingdom
Shiladitya.Paul@twi.co.uk

Idalina Vieira Aoki
Polytechnic School University of São Paulo
Avenida Professor Luciano Gualberto, trav 3, nr
380
05508-000 Butantã - São Paulo - SP
Brazil
idavaoki@usp.br

ABSTRACT

The protection of offshore structures and more specifically of wind turbines from marine corrosion is crucial. In order to improve the operational efficiency and the overall lifetime, protection from this harsh environment is necessary. In this work, it is presented the formation of the polystyrene shell microcapsules using 3-octanoylthio-1-propyltriethoxysilane (NXT) as a corrosion inhibitor carrier that has self-healing properties when combined with a proper catalyst on the metallic substrates. Specifically, the synthesized inhibitor is applied on the Zn85/Al15 arc spray coating on S355 J2+AR metallic substrate. With different concentrations of the applied NXT inhibitor, the corrosion properties of the Zn85/Al15 coatings were measured using Electrochemical Impedance Spectroscopy (EIS), Open Circuit Potential

(OCP), Polarization Curve (PC) and Linear Polarization Resistance (LPR). Our results revealed that out of all the used concentrations, 300 ppm provides best protection. Surface morphological characterization exhibits that the coating is porous and corrodes readily, as expected to provide sacrificial protection to the underlying steel, so additional paint layer is necessary to fill the pores and provide a barrier layer. Hence, this work highlights the importance and applications of NXT based corrosion inhibitor with self-healing properties for metal structures in challenging environments.

Key words: Corrosion, offshore structures, self-healing systems, Zn85/Al15 sacrificial layer

INTRODUCTION

Offshore structures are subjected to harsh and challenging environments. The combined effect of UV radiation, seawater, temperature fluctuations and seaborne debris make this environment challenging for materials [1]. Therefore, installed structures such as wind turbines need extra corrosion protection for improved lifespan. The use of cathodic protection is the most common method [2] of mitigating the corrosion of offshore structures. However, in the splash and atmospheric zone, the cathodic protection systems are ineffective due to the lack of electrolytic contact (seawater) between the structure and the anode [3]. Therefore, the use of protective coatings becomes indispensable in the splash and atmospheric zone. The focus of this work is the conversion of commercially available conventional paint (epoxy) system to a novel autonomous external self-healing paint system by the addition of suitable encapsulated healing agents in the form of microcapsules. Dmitry G. Shchukin and Helmuth Möhwald has reported these new generation of coatings with improved efficiency [4]. The selection of the catalyst plays a crucial role, therefore, appropriate catalyst has been identified to polymerize and solidify the encapsulated corrosion inhibitor after the rupture of the microcapsules. The use of Zn coating for the protection of the steel structures exposed to corrosive environments is a well-known processing technique [5]. Here is reported a method to combine Zn alloy coating with the enriched paint layer to create a unique and novel self-healing system. Therefore, first part of the research is to optimize the concentrations of the corrosion inhibitor for the protection of Zn85/Al15 coating. These results are presented in this paper. The second part of this ongoing research is to prepare the microcapsules and load them with the corrosion inhibitor to mix with a marine paint and a catalyst for the application of the sacrificial layer. For any damage to the coated surface, the corrosion inhibitor will be released and the self-healing process (polymerization) will take place. Hence, the focus of this research is to develop a novel cost-effective two-layer system to prevent corrosion and related problems in the offshore sector.

EXPERIMENTAL PROCEDURE

Materials

All the materials and reagents were used as received. Carbon steel (S355 J2+AR) commonly used in the offshore industry was used as a substrate. 3-Octanoylthio-1-propyltriethoxysilane (NXT) (a transparent liquid) provided by Momentive Performance Mat. Inc., $\text{CH}_3\text{CH}_2\text{OH}$ (97%) purchased from Quimica Moderna, HNO_3 (65%), Polyvinyl alcohol (PVA) (small white beads) $(\text{C}_2\text{H}_4\text{O})_n$ from Vetec, Polystyrene-S70 (small white beads), Silwet (viscous transparent liquid) provided by Momentive Performance Mat. Inc. and NaCl purchased from Sigma Aldrich were used as reagents.

Substrate preparation

The carbon steel samples (S355 J2+AR) with dimensions 100x150x5 mm were blasted with alumina (size F24) as part of the surface preparation. Subsequently, zinc-aluminium alloy (Zn85/Al15) coating was prepared using the arc spray process (Zn/Al was a wire). Two passes were used for better coverage of the metallic substrate.

Synthesis of corrosion inhibitor

Ethanol/distilled water (50/50%) mixture was prepared in a beaker. To it, 3% by volume of NXT silane was added and the pH was adjusted to 4.0 by using dilute nitric acid. The solution consisted of 38.8 mL of ethanol/distilled water and 1.2 mL of NXT, which was stirred for 24h using a magnetic stirred in order to favor the hydrolysis of silane.

Synthesis of polystyrene microcapsules

Polystyrene microcapsules containing the corrosion inhibitor were synthesized using the solvent evaporation technique from an emulsion as described from Cavallaro and Vieira Aoki [6]. This technique is based on the water-in-oil-in-water (W1/O/W2) system, with W1 to be the microcapsule core (hydrolyzed silane), which emulsifies in a polymeric solution, O, forming an emulsion of water in oil (W1/O). When the emulsion is stabilized, this phase is dispersed in a continuous medium (W2) according to Martins et. al. [7]. More specifically, the emulsion consisted of the following parts; W1=water+corrosion inhibitor (NXT) as the core material, O=polystyrene+organic solvent (CH_2Cl_2)+hydrophobic surfactant (Silwet) as the shell of the microcapsules and W2=water+PVA (1% and 0.3%) as the continuous medium. For the synthesis, 2 ml of hydrolyzed silane, 38 ml of dichloromethane, 4 g of polystyrene and 2 ml of Silwet were added to a beaker. This mixture was put under ultrasonic stirring for 1 min to form a milky emulsion. Mixture was then transferred to another beaker and 200 ml of aqueous 1% PVA solution, as described from Cotting and Vieira Aoki [8], was slowly added into it under vigorous mechanical stirring (700 rpm). After the addition of the entire quantity of PVA, 800 ml of aqueous 0.3% PVA solution was added to the assembly. The final mixture was heated (about 40 °C) for 24h to complete the solvent evaporation. The microcapsules were filtered and washed with five aliquots of ethanol and they were placed in a tray in air to remove the excess humidity.

Experimental techniques

Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Detector (EDX) was used to study the surface morphology, the microstructure and the elemental analysis. Electrochemical techniques were used to test the performance of the corrosion inhibitor on the Zn85/Al15 coatings. To optimize the concentration of the hydrolyzed silane, six measurements with different concentrations (listed in Table 1) of the inhibitor were performed with a test electrolyte of 0.1 M NaCl (pH ~ 4.98). Test samples were prepared using glass cylinders on the metallic samples, glued with silicon to prevent any leakage of the test solution. A typical three electrode cell configuration was used with Zinc-Aluminium (Zn-Al), platinum (Pt) and silver/silver chloride (Ag/AgCl) as a working, counter, and reference electrode, respectively. The test area of the working and counter electrode was 5 cm² and 5.31 cm², respectively. The EIS experiments were performed in the frequency range of 40 kHz to 10 mHz with a potential disturbance of 10 mV rms and the estimated electrolyte resistance was at 100 Ohms.

Table 1
Summary of the used concentrations of the hydrolyzed NXT for the optimization of the test solution.

Concentration of silanol (ppm)	Volume of 0.1M NaCl (ml)	Volume of silanol (ml)
0	75.00	0.00
100	75.00	0.24
200	75.00	0.48
300	75.00	0.72
400	75.00	0.96
600	75.00	1.44

OCP was measured for 30 min and without the disturbance of the electrochemical cell. After the steady state was reached, EIS measurements were performed, then linear Polarization Resistance (R_p) was measured for ± 20 mV vs OCP with a scanning rate of 0.16 mV/s. Finally, polarization curves were measured for +500 mV vs OCP with scan rate of 0.5 mV/s.