

Nanomechanical and Electrochemical Properties of Nano-composite Coatings for Maritime Applications

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ABSTRACT

The aggressive sea environment raises the need for synthesizing novel advanced coatings for maritime applications. Biofouling represents one of the most serious problems in modern maritime industries and its control is one of the biggest challenges for marine biotechnology. When a surface is submerged in seawater, a biofilm composed by microorganisms rapidly covers the surface which is subsequently colonized by algae and invertebrates, ultimately resulting to its corrosion. Antifouling paints based on colophony are proposed to degrade following an erosion mechanism, resulting in the degradation of the entire film (controlled depletion polymer - CDP). Unfortunately, CDP coatings based on colophony, display some disadvantages and the improvement of their efficiency is considered crucial. Thus, the improvement of marine paints for ships hulls constitutes a technological challenge. Carbon nanotubes (CNTs) are promising fillers in polymeric resins due to their extraordinary structural properties. It has been proven that the addition of CNTs in polymer based coatings could improve their mechanical and anticorrosion performance. However, it is crucial to achieve a stable and homogenous dispersion of CNTs in the coatings' matrix. For shipbuilding applications, a three layer coating system is used; an epoxy based primer, an anticorrosive barrier coat and a colophony based antifouling topcoat layer. In this study, we focused on the study of the influence of CNTs addition in both epoxy primer layer and antifouling topcoat. Firstly, we investigated the most suitable experimental procedure for the functionalization of CNTs surface, synthesized via chemical vapor deposition method. Our goal was to activate the CNTs surface, in order to create chemical bonds with the coatings resin. The produced nanocomposite coatings were applied through dip coating onto shipbuilding plate substrates and their mechanical and anticorrosion properties were evaluated through nanoindentation technique and electrochemical impedance spectroscopy, respectively. It was found, that the incorporation of carboxyl functionalized CNTs in the epoxy primer, leads to increased hardness values for the specimen with 0.2wt. % CNTs, but deteriorates its anticorrosion performance in all cases. Finally, it was shown that the incorporation of amino-functionalized CNTs in antifouling topcoat, improves significantly its mechanical performance without any effect on its anticorrosion behavior.

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INTRODUCTION

Engineered structures such as ships hulls and marine platforms are under constant attack from the aggressive marine environment (Chambers, et. al, 2006). The severe environment in combination with the problem of fouling contributes to the enhancement of corrosion phenomena (Lambourne, 1987). So, the need of multi-coat systems for the protection of these structures after manufacturing and during maintenance is essential (Stoye, et. al, 2006). Organic coatings are commonly used for the protection of metallic parts in maritime industry. For the protection of the ship's hull, a three layer coating system is needed; epoxy based primer, anticorrosive barrier coat and antifouling topcoat (Weismantel, 1981). Their efficiency can be improved by the addition of special nanostructures such as CNTs (Upadhyayula & Gadhamshetty, 2010).

The superior mechanical properties of CNTs render them ideal candidates for polymer reinforcement. Specifically, the introduction of CNTs into polymer matrices results in improvement of the mechanical and electrical properties of the produced nanocomposites (Spitalskya, et. al, 2010). A uniform dispersion of CNTs throughout the matrix is imperative in order to achieve efficient load transfer to the nanotube network. However, the dispersion of CNTs seems to be challenging since the strong attractive non-covalent forces developed between individual CNTs due to their huge aspect ratios causes them to aggregate into bundles and results in low interactions between CNTs and polymer matrices. In order to improve the dispersibility of CNTs into the polymeric matrices, surface functionalization of CNTs is required. By surface functionalization active groups are introduced in nanotubes sidewalls. A good interfacial bonding results in an efficient load transfer across the CNT–matrix interface, a necessary condition for improving the mechanical properties of the composite (Kim, et al., 2012).

In this work, multi-walled CNTs (MWCNTs) with different surface functionalization were synthesized and incorporated in both epoxy primer and antifouling topcoat paints, in various concentrations. Their nanomechanical and electrochemical properties were investigated via nanoindentation technique and electrochemical impedance spectroscopy (EIS), respectively. The main objective of this work was to propose the most efficient antifouling system in terms of both mechanical and anticorrosion response.

EXPERIMENTAL PROCEDURE

Materials and Synthesis

MWCNTs Synthesis & Functionalization. MWCNTs were produced via CVD method and purification procedure followed, in order to remove catalyst residues. The purified MWCNTs were firstly functionalized with –COOH groups using an acid solution mixture of 6M HNO₃:H₂SO₄ (1:3) (Zhiyuan, et. al, 2013). For the amino functionalization, MWCNTs-COOH were stirred in a 20:1 mixture of SOCl₂ and dimethylformamide (DMF) at 70°C (158 °F) for 1 day. After the acyl chlorination, they were centrifuged and washed with anhydrous tetrahydrofuran (THF) for five times. The remaining solid was dried under vacuum. The produced acyl-chlorinated MWCNTs were reacted with ethylenediamine solution at 100°C (212°F) for 2 days. After cooling to room temperature, the MWCNTs were washed with ethanol to remove excess diamine. Finally, the material was dried at room temperature overnight under vacuum (Soleimani, et. al, 2013).

Substrate preparation. As substrate, hot rolled steel shipbuilding plate Grade A was used. Its surface was treated according to the standard ASTM A 380-06, with mechanical abrasion and a combination of acids (ASTM, 2006).

Composite Coatings Synthesis. Epoxy Primer (EPOSIST HBS, Wilckens S.A.) and filler MWCNTs-COOH (0.05, 0.1, 0.2 and 0.4 wt. %) were thoroughly mixed with mechanical stirring (2200 RPM for 1800s). Respectively, antifouling paint (ECOMAR 70, Wilckens S.A) was mixed with pristine MWCNTs, MWCNTs-COOH and MWCNTs-Amino in a concentration of 0.1wt. %. This concentration was selected taking into account the literature (Nejhad, et. al, 2011) and preliminary tests. The coding of the produced samples is shown in Table 1.

Dip-coating. Coatings were applied to the shipbuilding plate using a single vessel dip-coater system (KSVNIMA) with a withdraw speed of $1.67 \cdot 10^{-3}$ m/s (5.47 ft/s).

Table 1. Description of the Tested Coatings Samples

Code	Primer	Tie coat	Top coat
EP _{Ref}	Epoxy	-	-
EP1	Epoxy + 0.05 wt. % MWCNTs-COOH	-	-
EP2	Epoxy + 0.1 wt. % MWCNTs-COOH	-	-
EP3	Epoxy + 0.2 wt. % MWCNTs-COOH	-	-
EP4	Epoxy + 0.4 wt. % MWCNTs-COOH	-	-
ARef	Epoxy	Anticorrosive	Antifouling
A1	Epoxy	Anticorrosive	Antifouling + 0.1 wt. % CNTs
A2	Epoxy	Anticorrosive	Antifouling + 0.1 wt. % MWCNTs-COOH
A3	Epoxy	Anticorrosive	Antifouling + 0.1 wt. % MWCNTs-amino

Characterization techniques

Scanning electron microscopy: The morphology of MWCNTs was determined by SEM using Nova NanoSEM 230 (FEI company) microscope with W (tungsten) filament.

Fourier transform infrared spectroscopy. FT-IR analysis was performed by using a ThermoScientific Nicolet 6700 Fourier Transform Infrared Spectrometer.

Nanoindentation testing. The nanoindentation tests were performed using a Hysitron TriboLab® Nanomechanical Test Instrument with a Berkovich diamond indenter (average radius 10^{-7} m) allowing the application of loads from 10^{-6} to 10^{-2} N ($2.25 \cdot 10^{-7}$ to $2.25 \cdot 10^{-3}$ lb_F). In all nanoindentation tests a total of 10 indents are averaged to determine reduced modulus (E_r) and hardness (H) values for statistical purposes, with a spacing of $15 \cdot 10^{-6}$ m ($5.91 \cdot 10^{-4}$ in). In order to operate under closed loop LC, feedback control option was used. Indentation tests were performed following a trapezoidal loading curve; loading and unloading segments were kept constant at 10s each, and hold time was set at 20s in all cases to avoid nose effect due to the viscoelastic properties of the tested samples. Our aim was to evaluate the bulk properties of each coating in order to avoid surface roughness (Skarmoutsou, Charitidis, Gnanappa, Tseripi, & Gogolides, 2012). Based on the half-space elastic deformation theory, H and E_r values can be extracted from the experimental data (load-displacement curves) using Oliver and Pharr method (Oliver & Pharr, 1992). Each time the nanoindentation experiments were conducted on the external layer of the tested samples. Taking into account that the thickness of each layer exceeds the overall dry thickness of $50 \cdot 10^{-6}$ m ($2 \cdot 10^{-3}$ in), the presence of the internal layers has no effect on the measured nanomechanical properties.

Electrochemical impedance spectroscopy. The corrosion resistance of the developed coatings was evaluated by EIS. The measurements were conducted in a three-electrode flat cell, composed of a working electrode with 10^{-4} m² exposed area ($1.08 \cdot 10^{-3}$ ft²), a saturated silver/silver chloride electrode as reference and platinum foil as the counter electrode at room temperature. A 3.5% wt.NaCl solution was used as an electrolyte. AC impedance data were obtained by a Solartron SI 1260 impedance/gain phase analyzer connected to a PAR263 potentiostat. The coating quality and corrosion behavior was examined for a period of 17 days and the spectra were analyzed with the Zview Software.

RESULTS & DISCUSSION

CNTs Characterization

In Figure 1a, the SEM images of the produced carbonaceous materials after the purification/functionalization process at two magnifications are presented. As observed, the produced carbonaceous material consists mainly of MWCNTs with diameters in the range of $20\text{--}40 \cdot 10^{-9}$ m ($6.6 \cdot 10^{-8}\text{--}13.2 \cdot 10^{-8}$ ft) and length $> 10^{-6}$ m ($3.3 \cdot 10^{-6}$ ft). FTIR spectra of pristine MWCNTs, MWCNT-COOH and MWCNTs-Amino are shown in Figure 1b. Comparing the pristine MWCNTs and MWCNTs-COOH, it can be observed that some new peaks appeared in the spectrum of MWCNTs-Amino. Especially, the C=O stretching frequencies shifted from 1704cm^{-1} (MWCNT-COOH) to 1660cm^{-1} (MWCNTs-

Amino) and a new peak appears at 1564 cm^{-1} which can be assigned to N-H inplane. These bonds represent the existence of a secondary amine, on the sidewalls of MWCNTs-Amino.

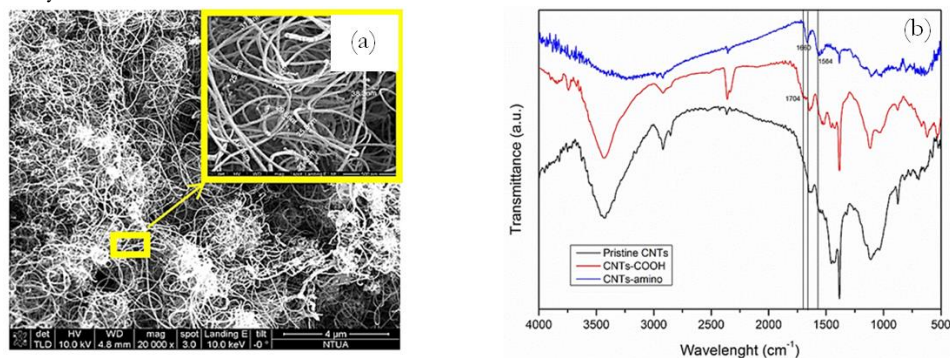


Figure 1 SEM image of MWCNTs and comparative FT-IR spectra of pristine and functionalized MWCNTs.

Nanomechanical Testing

In Figure 2a load-unload curves of the primer paint formulations at $3.5 \cdot 10^{-3}\text{N}$ ($7.9 \cdot 10^{-4}\text{lb}_F$) maximum applied load, are presented. Generally, it is observed that the addition of different concentrations of MWCNTs-COOH, results in different nanomechanical behavior, depending on MWCNTs concentration. Especially, it can be seen that the addition of low concentrations of MWCNTs-COOH (0.05 and 0.1%wt.) results in similar plastic behavior and resistance to applied loads with the pure formulation coating (EP_{Ref}). However, medium concentrations (0.2%wt.) led to a significant improvement of resistance to applied loads, whereas higher addition of MWCNTs-COOH (0.4%wt.) into the primer formulation, results in softening, since higher indentation depths are recorded for the same applied load. This behavior is probably attributed to the formation of MWCNTs agglomerations at higher concentrations. It is well known that the presence of these agglomerations leads to degradation of mechanical properties of the composite material (Nadler, Werner, Mahrholz, Riedel, & Hufenbach, 2009). Load-unload curves of the antifouling coatings (pure and containing 0.1% wt. MWCNTs with different functional groups) at $4 \cdot 10^{-3}\text{N}$ ($8.9 \cdot 10^{-4}\text{lb}_F$) maximum applied load, are presented in Figure 2b. It is observed that the addition of 0.1% wt. CNTs without any surface functionalization (A1) and functionalized with carboxyl ($-\text{COOH}$) end groups (A2) into the paint decreases the resistance to applied loads and the tip enters deeper in the paint formulation for the same applied loads. On the contrary, it can be seen that the addition of 0.1% wt. MWCNTs-Amino (A3) results in slightly higher resistance to applied loads compared to the reference sample (A_{Ref}).

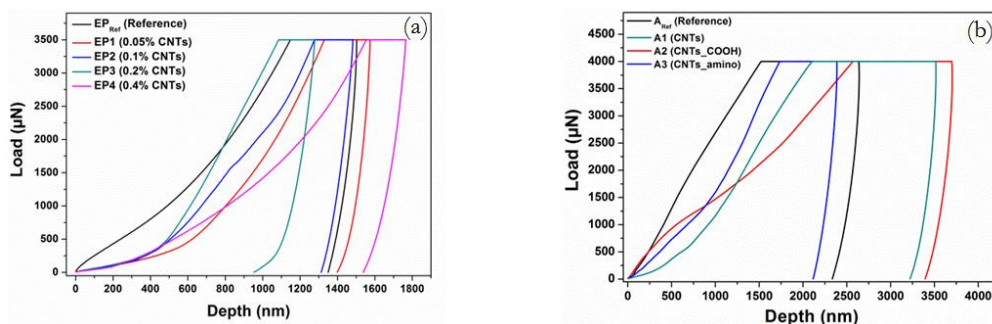


Figure 2 Load-unload curves of (a) the primer formulations at $3.5 \cdot 10^{-3}\text{N}$ ($7.9 \cdot 10^{-4}\text{lb}_F$) maximum applied load for EP_{Ref} , EP1, EP2, EP3 and EP4 samples and (b) the antifouling coatings (pure and containing 0.1% CNTs with different surface functionalization) at $4 \cdot 10^{-3}\text{N}$ ($8.9 \cdot 10^{-4}\text{lb}_F$) maximum applied load.

The reduced modulus and hardness values of each primer coating sample are shown in Figure 3. Concerning reduced modulus values, generally the addition of MWCNTs-COOH results in lower values, ranging between 10% for EP1 and 30% for sample EP2 (0.1% wt.), compared to the reference epoxy sample (EP_{Ref}) (Figure 3a). It is observed that sample EP3 (0.2% wt. MWCNTs-COOH) exhibited higher hardness value by 41.7%, while sample EP4 (0.4% wt. MWCNTs-COOH) lower by 23.5%, compared to the reference sample (EP_{Ref}) (Figure 3b). For the rest of the coating samples, no significant variations become apparent, compared to the reference sample (EP_{Ref}).

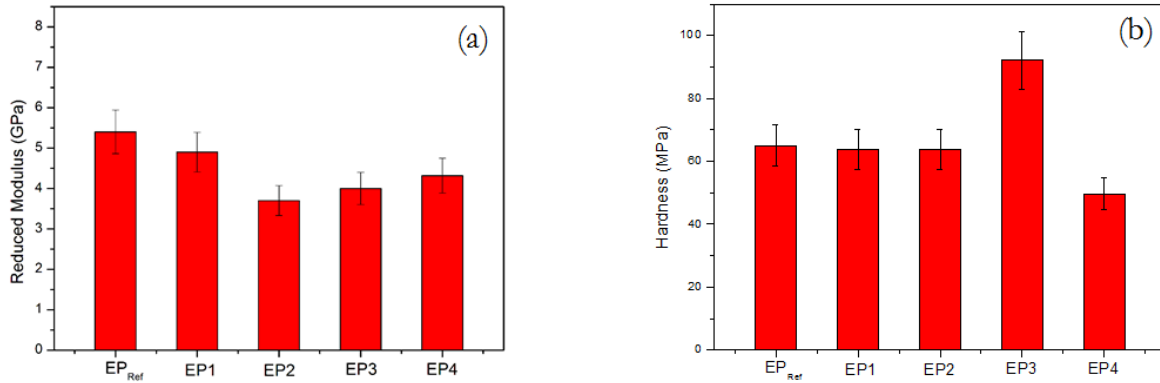


Figure 3 Reduced modulus (a) and hardness (b) values of samples EP_{Ref} , EP1, EP2, EP3 and EP4.

The reduced modulus and hardness values of each top coating are shown in Figure 4. It is obvious that samples A1 and A2 present lower reduced modulus values by 29.5% and 27.2%, compared to the reference (A_{Ref}), respectively (Figure 4a). On the other hand, samples A1 and A2 exhibited reduced hardness values by 46.4% and 50.6% compared to A_{Ref} , respectively (Figure 4b). As concerns the sample that contains 0.1% wt. MWCNTs-Amino (A3), higher hardness values by 26.6% were measured, while lower reduced modulus values by 15.9% compared with A_{Ref} were detected. The improved performance of antifouling coating containing MWCNTs-Amino could be attributed to sufficient interfacial bonding between the amino functional groups and the polymeric matrix, resulting in an efficient load transfer across the CNTs–matrix interface, a necessary condition for improving the mechanical properties of the final composite coating (Papanicolaou, Charitidis, Portan, Perivoliotis, & Koklioti, 2014).

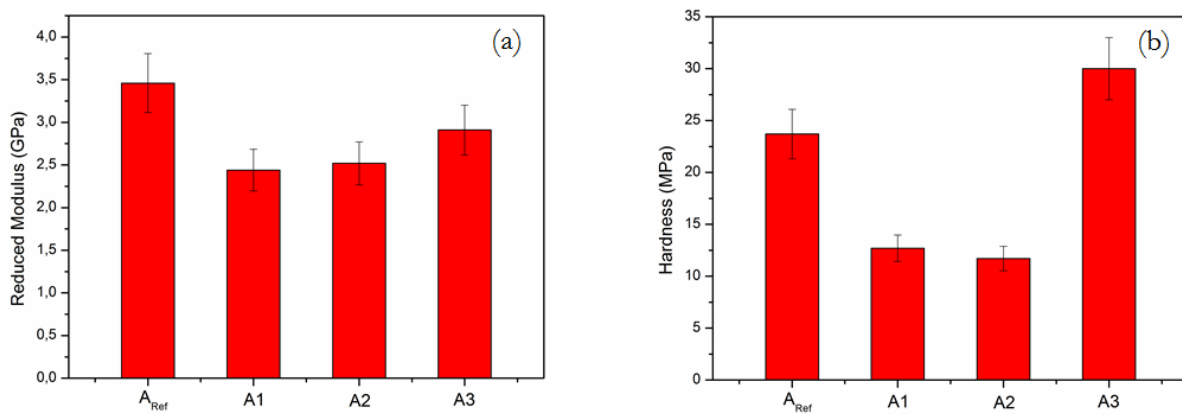


Figure 4 (a) Reduced modulus and (b) hardness values, of pure antifouling coating (A_{Ref}) and CNTs containing antifouling coatings (A1, A2 and A3).

Electrochemical Testing

Generally, changes in the overall corrosion performance may be attributed to the nature, thickness, MWCNT's content and their adhesion with each layer. In Figure 5a the EIS spectra of the epoxy primer coating for the first 17 days of immersion are shown. The samples EP_{Ref} and EP1 have a capacitance response, within the whole frequency range allowed by the instrumentation; the slope does not change and the phase angle remains at -90°. On the contrary, samples EP2, EP3 and EP4 show a significant change, which is related to the decrease in pore resistance that occurs as the electrolyte penetrates the coating and creates a path to the surface of the underlying metal. The Bode plots for the sample EP2 exhibit a capacitance response until the 3rd day of immersion as shown in Figure 5b. From the 4th day a finite element is shown corresponding to the coating's pore resistance which indicates the electrolyte's diffusion into the polymeric matrix. The observed overall electrochemical performance indicates that the incorporated MWCNTs do not further enhance the coating's stability over the corrosive conditions. On the contrary, we may assume that the MWCNTs content deranges the coating's integrity allowing aggressive ions to penetrate the coating layer.

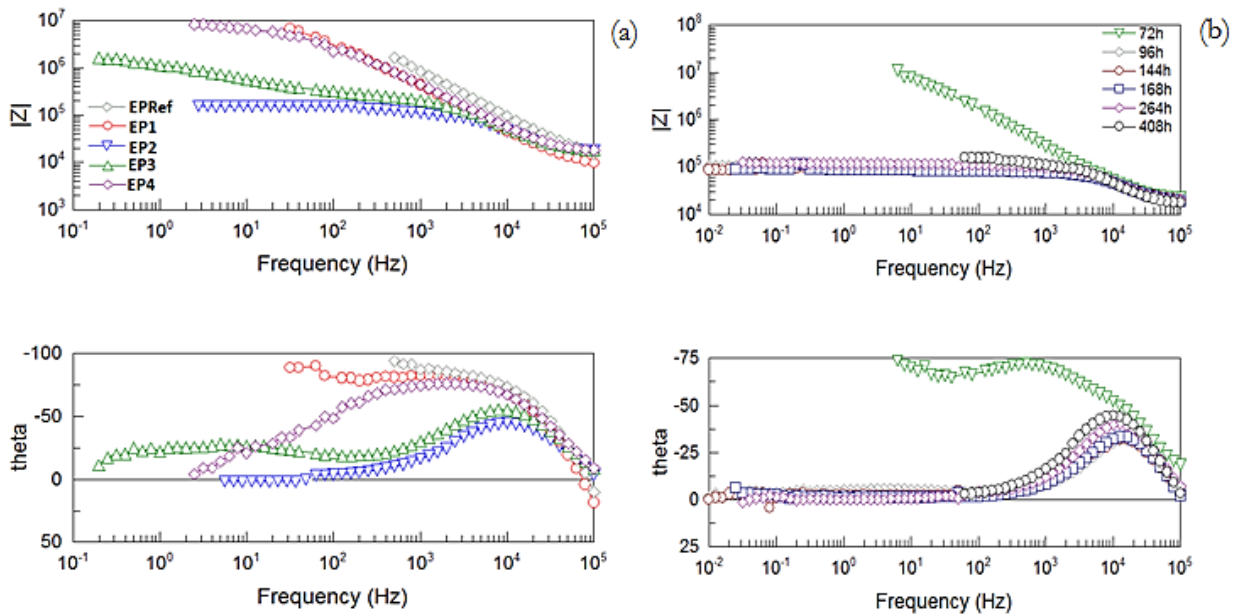


Figure 5. (a) EIS Bode plots for the epoxy primer with the incorporated CNTs after 17 days of exposure to 3.5% wt. NaCl solution (b) the evolution of the electrochemical behavior for the sample EP2.

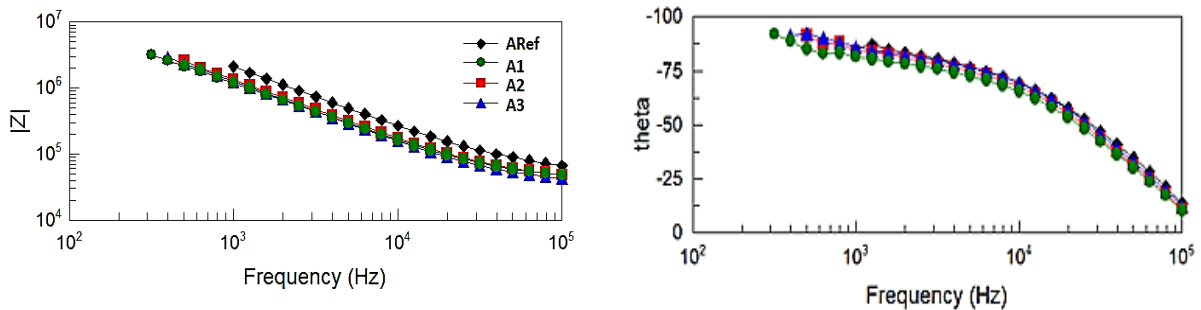


Figure 6. EIS Bode plots of the samples A_{Ref}, A1, A2 and A3 after 24 days of exposure in 3.5% wt. NaCl solution.

According to literature two controversial observations are reported. Some authors claim that the incorporation of MWCNTs increase the electrical conductivity of the epoxy layer and create a conductive path for the electron current flow through the polymeric matrix decreasing its barrier properties (Vahedi, et. al, 2013). On the other hand, some studies report the improvement of the corrosion performance of the coating with increasing the MWCNTs content. This is attributed to the increment of pore resistance due to the blocking of pores (Khun, et. al, 2014). In the present study, EIS spectra indicated that the barrier properties of the epoxy paint layer deteriorated by the presence of MWCNTs for the epoxy based primer coatings, while no significant changes of the anticorrosion performance of antifouling paint system were observed.

CONCLUSION

The influence of MWCNTs addition in both epoxy primer layer and antifouling topcoat layers was studied. To achieve a homogeneous dispersion of MWCNTs in polymer matrices, different surface functionalization was applied. It was found, that the incorporation of carboxyl functionalized MWCNTs in the epoxy primer leads to increased hardness values for 0.2% wt. loading sample, but deteriorates its anticorrosion performance in all cases. Concerning the antifouling paint system, the presence of amino-functionalized MWCNTs in antifouling topcoat improves significantly its mechanical performance without any effect on its anticorrosion behavior. To conclude, the proposed antifouling paint system which is efficient in terms of both mechanical and anticorrosion resistance to applied loads and corrosive environment, consists of an epoxy primer layer without MWCNTs, an anticorrosion intermediate layer and an antifouling colophony based topcoat containing 0.1% wt. amino-functionalized MWCNTs. This coating system provides both improved mechanical integrity and acceptable anticorrosion behavior.

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NOMENCLATURE

AC	=	Alternative Current
ASTM	=	American Society of Testing Materials
EIS	=	Electrochemical Impedance Spectroscopy
CDP	=	Controlled Depletion System
CNTs	=	Carbon Nanotubes
CVD	=	Chemical Vapor Deposition
DMF	=	Dimethylformamide
FT-IR	=	Fourier Transform Infrared Spectroscopy
LC	=	Load Control
MWCNTs	=	Multi Walled Carbon Nanotubes
MWCNTs-Amino	=	Multi Walled Carbon Nanotubes with Amino Groups
MWCNTs-COOH	=	Multi Walled Carbon Nanotubes with Carboxyl Groups
NaCl	=	Sodium Chloride
SEM	=	Scanning Electron Microscopy
SOCl ₂	=	Thionyl Chloride
THF	=	Tetrahydrofuran

Subscripts

- r = reduced
 Ref = reference

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