Development of Anticorrosive Polymer Nanocomposite Coating for Corrosion Protection in Marine Environment

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Abstract. The marine environment is considered to be a highly aggressive environment for metal materials. Steels are the most common materials being used for shipbuilding. Corrosion is a major cause of structural deterioration in marine and offshore structures. Corrosion of carbon steel in marine environment becomes serious due to the highly corrosive nature of seawater with high salinity and microorganism. To protect metallic materials particularly steel against corrosion occurrence various organic and inorganic coatings are used. The most used are the polymeric protective coatings. The nanostructured TiO_2 polymer coating is able to offer higher protection to steel against corrosion, and performed relatively better than other polymer coatings.

1. Introduction

Marine atmosphere with its high level of salinity and humidity is very corrosive, and the effects of corrosion are allegedly responsible for 30% of failures on ships and other marine equipment. The effects of corrosion are expensive costs to vessel, structural and equipment operations, compounded by the financial penalties on breakdowns, outages, and repairs [2].

The Port of Constanta is located on the Western Coast of the Black Sea, through which the Danube flows into the sea. The two breakwaters located northwards and southwards shelter the port creating the safest conditions for port activities. Constanta harbour is a major port on the western coast of the semi-enclosed Black Sea. Its brackish waters and low species richness make it vulnerable to invasions. The intensive maritime traffic through Constanta harbour facilitates the arrival of alien species. In marine and brackish water environments, shipping is considered the main vector of alien species introductions [2].

Inside Constanta harbour at the end of July 2009, average values of salinity, temperature and dissolved oxygen at the surface were 12.1 PSU, 25°C and 14 mg/L, respectively. At the end of August 2010, average values of the parameters registered in the same locations inside the harbour were 13.8 PSU, 27.3^{o}C and 9.4 mg/L [2].

The majority of the pH results was found in the domain of most natural waters that falls in the 6 to 8.5 range [3,4].

The unique hydrological and hydro chemical characteristics of the Black Sea confer the status of the largest anoxic basin in the world. The Black Sea is subject to environmental variations due to the natural influences (e.g., climate change, global warming, sea level rising, coastal erosion) [3].

The corrosion of steels in fresh and brackish waters is known to be a function not so much of

salinity itself but rather of the calcium–calcium carbonate balance (alkalinity and hardness) of the water and how this is influenced by its pH [5].

One of the most widely used methods for protection against metallic corrosion is the application of organic polymeric coatings, often described as paintings. Among the main organic coatings that improve the corrosion resistance of steel are paintings with an epoxy resin, in which inorganic particles or passivating compounds may be incorporated, in order to delay the corrosion phenomenon.

The resin exerts a barrier effect, separating the metal from the corrosive aqueous medium. However, the barrier properties are often insufficient, since aggressive ions can penetrate through the pores of the coating, initiating the corrosive process [6-7].

Polymeric coatings have been widely used for corrosion protection of metallic substrates because they are easy to apply with a reasonable cost. Among possible choices of polymeric coatings, have been extensively used due to its excellent gloss, good durability as well as relatively low cost [6].

2. Experimental set-up

2.1. Materials

Three different coatings were painted (table 1) on 3 mm thickness *E 32* naval steel plates. The chemical composition of the steel substrate is shown in table 2 and immersed in seawater harvested from the port of Constanta. Seawater parameters are shown in table 3.

Table 1. Tested sample types.

Coat code	Description
E 32	Uncoated naval steel
E32G	Primer: Two-component polyamide adduct cured, high solids, high build epoxy paint.
E32GNP	Primer: Two-component polyamide adduct cured, high solids, high build epoxy paint, blended with TiO_2 nanoparticles.

The corrosion experiments were performed on naval steel EN32, uncoated or coated with a two-component polymeric primer or two-component polymeric primer with epoxy polyurethane paint layer. For corrosion measurements, all the samples were cut to dimensions of 25 x 25 x 2 mm.

After that the surface was covered with a polymeric primer two-component polyamide adduct cured, high solids, high build epoxy paint. (having a dry thickness (DFT) equal to 40 μm). Finally this polymeric primer was coated with two-component glossy acrylic polyurethane with DFT equal with 80 μm.

Table 2. The chemical composition of the E32 naval steel.

	C [%]	Cr [%]	Mo [%]	Mn [%]	Ni [%]	Si [%]	P [%]	S [%]	N [%]	Al [%]	Cu [%]	As [%]	Fe [%]
E32	0.18	0.2	0.08	1. 6	0.4	0.5	0.035	0.035	0.008	0.06	0.35	0.08	Balance

Samples used in the experimental protocol, have been bonded with copper wire and insulated with epoxy resin to obtain a measurable area. The naval steel samples were degreased with alcohol and acetone. The samples covered with polymers have been degreased with water and detergent.

In order to perform the corrosion experiments it was used a standard three-electrode cell consisting of the tested samples as working electrode, a Pt-Rh grid used as auxiliary electrode and Ag/AgCl

electrode (saturated KCl solution, E = 200 mV vs. normal hydrogen electrode (NHE)) as a reference electrode.

Table 3. Black Sea water characteristics.

pH	Salinity [ppt]	Conductivity [mS]
7.93	11.9	20.9

The experiments were done using a Potentiostat/Galvanostat PGZ 100 and the data were recorded with VoltaMaster 4 software.

3. Results and discussion

3.1. Open Circuit Potential
Corrosion tests were initiated by monitoring the evolution of open circuit potential, after immersion in the tested solution, until they reached a stationary steady state. The potential-time measurements of the four different surfaces studied in sea water are shown in figure 1. The evolution of OCP was monitored for 12 hours for each sample.

The OCP trend of uncoated E 32 naval steel decreases slight from the value of - 488 mV to -705 mV vs. Ag/AgCl during the immersion. The potential shift towards negative direction indicates that this material is unable to form a protective oxide layer on its surface after exposure to marine environmental conditions [8-9].
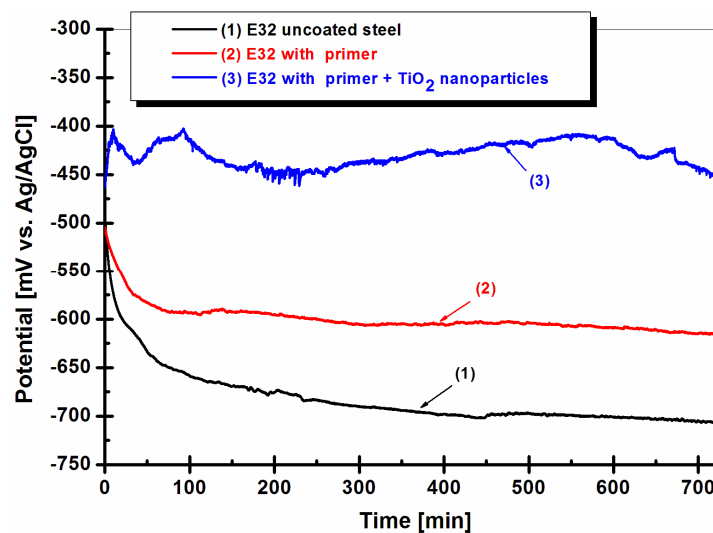

Figure 1. Variation of open circuit potential with time immersed in sea water for: (1) uncoated E 32, (2) E 32 coated with primer, (3) E 32 coated with primer and blended with TiO_2 nanoparticles.

For E 32 steel coated with polymeric primer, the OCP is almost constant in all over the immersion period and the steady state potential is already achieved. This almost constant potential of polymeric primer coating at a value around -599 mV vs. Ag/AgCl, is associated with an improved corrosion resistance.

For E32 coated with polymeric primer with TiO_2 nanoparticles the value growing slowly from – 483mV to -442 mV vs. Ag/AgCl.

Generally a steady potential indicates that the film remains intact and protective. Comparing the steady state potential of the three different surfaces studied in sea water, it is clearly revealed that the uncoated E 32 naval steel does not reach a noble steady state potential, while the two types of polymeric coatings applied on E 32 naval steel offers improvement in its corrosion performances.

3.2. Evolution of Polarization Resistance during immersion time

The evolution of polarization resistance it was performed by linear polarization method around free potential value with a very small potential difference ($\pm$ 40 mV) in order to keep the steady state surface. Linear polarization resistance is the only corrosion monitoring method that allows corrosion rates to be measured directly, in real time. From figure 2 (a), it can be seen that the lowest polarization resistance (R_p) value is attained by the uncoated E 32 naval steel being equal to 0.195 kohm·cm^2.
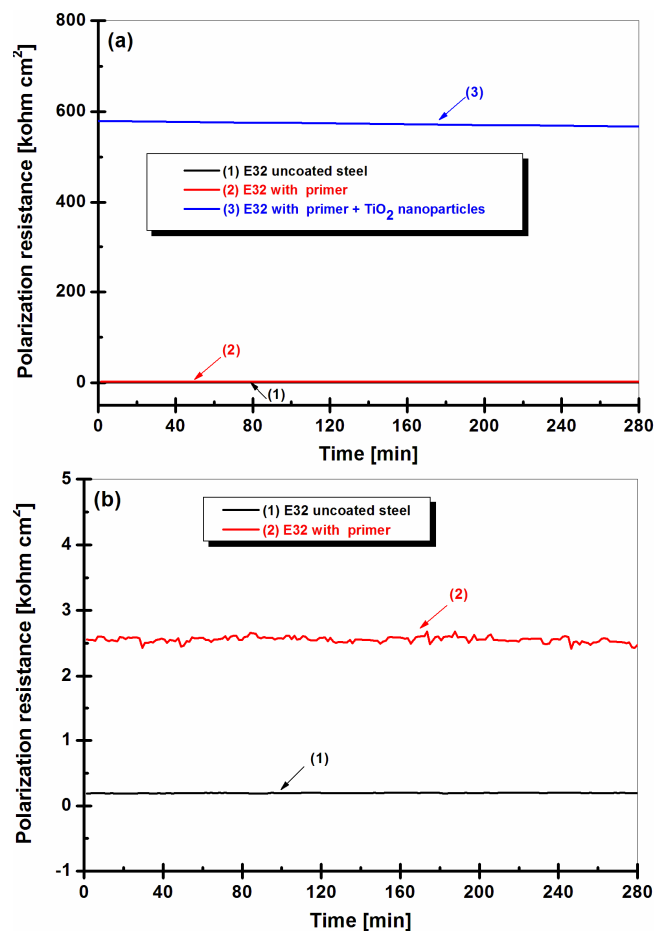

Figure 2 (a). The evolution of R_p values during immersion time of: (1) uncoated E32, (2) E32 coated with primer,(3) E32 coated with primer and blended with TiO_2 nanoparticles, (b). Zoom of polarization resistance diagrams from Fig. 2 (a) for: (1) uncoated E32, (2) E32 coated with primer.

This R_p value corresponding to uncoated EN32 naval steel remains constant during the immersion time in sea water. By applying the polymeric primer onto the E 32 naval steel the R_p increases to a mean value around 2.557 kohm·cm^2, being higher than that of uncoated E 32 naval steel. For E32 coated steel with polymeric primer blended with TiO$_2$ nanoparticles the R_p value is around 573.391 kohm·cm^2. An increased value of polarization resistance it means a lower corrosion current density and therefore a lower corrosion rate, as it can be seen from figure 2 (b). The higher corrosion current density value corresponds to E32 coated steel with polymeric primer and primer blended with TiO$_2$ nanoparticles.

According with the data presented in figure 3 it can be seen that the higher corrosion rate, as penetration rate, correspond to uncoated E32 naval steel compared with two types of polymeric primer coatings. From corrosion rate evolution, as penetration rate showed in figure 3 it can be seen that coated steel with primer and primer plus TiO$_2$ nanoparticles have very low values of 29.922 μm/year and 0.141 μm/year respectively as compared with uncoated steel which reveal a corrosion rate value of 386.79 μm/year. These results suggest that the two types of polymeric primer coatings increase the corrosion resistance of E32 naval steel and are in good agreement with the polarization resistance data results.
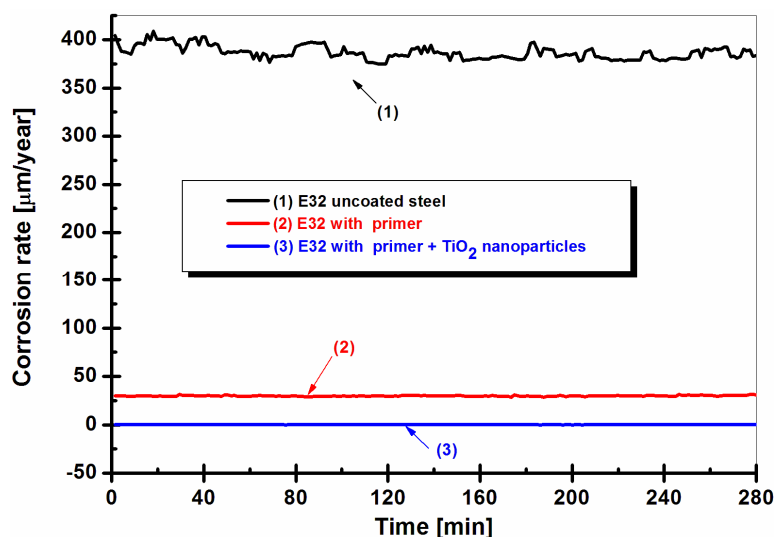

Figure 3. The corrosion rates, as penetration rate versus time corresponding to all three analysed surfaces immersed in seawater.

3.3. Cyclic voltammetry

In figure 4 (a, b) are presented the cyclic voltammograms of all three studied surfaces in seawater. These diagrams were recorded in the potential range of -1500 mV vs. Ag/AgCl to +1500 mV vs. Ag/AgCl at a scan rate of 5 mV/s and then reversed with the same scan rate till the starting potential to form one complete cycle.

Highlighting the localized corrosion susceptibility in the presence of chloride ions in the seawater of uncoated naval steel E32 can be seen very well due to the specific hysteresis aspect which presents the anodic transpassivation part of the curve (1) from figure 4 (a). The specific hysteresis aspect indicates that uncoated naval steel E32 is susceptible to pitting and crevice corrosion in marine environment. The steel coated only with polymeric primer show a smaller passive domain as compared with primer mixed with nanoparticles. Also some small hysteresis are revealed on cyclic voltametry, probably do to some porosity of coating. The steel coated with primer mixed with TiO$_2$ nanoparticles don't show the transpassive domain (anodic current did not increase) and reveal the absence of specific hysteresis for localized corrosion.
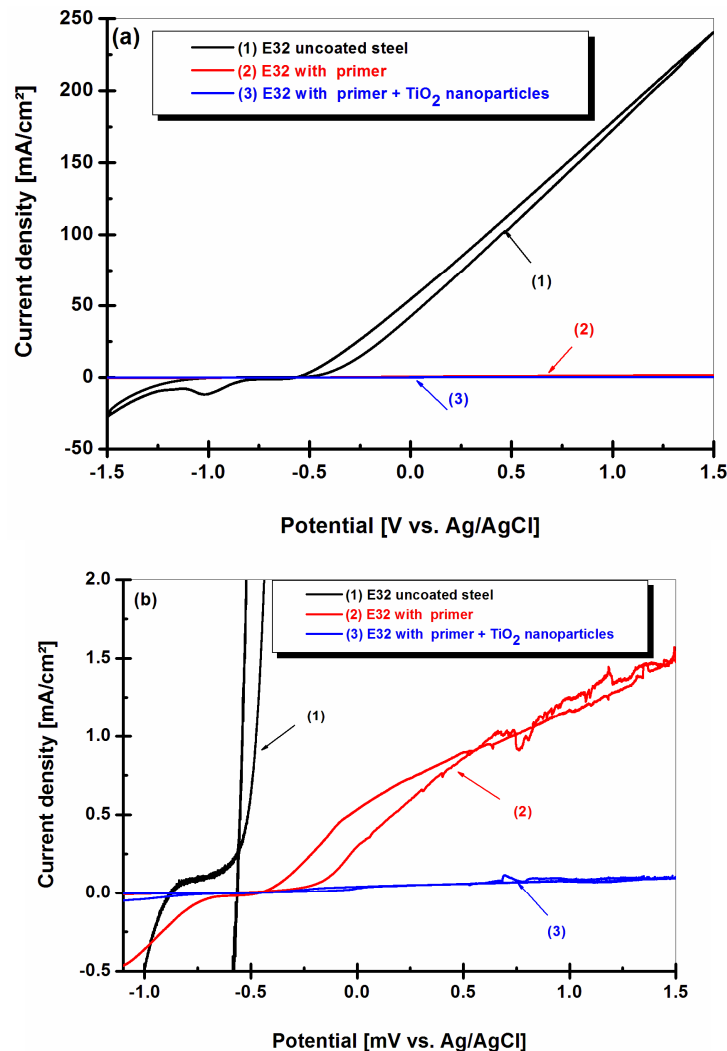
Figure 4 (a). Cyclic voltammograms of: (1) uncoated E32, (2) E32 coated with primer, (3) E32 coated with primer and blended with TiO_2 nanoparticles, (b). Zoom of Cyclic voltammograms in the lower range of current densities for: (1) uncoated E32, (2) E32 coated with primer, (3) E32 coated with primer and blended with TiO_2 nanoparticles.

From figure 4 it can be observed that upon the onset of the transpassive region the current still raises up until the potential is reversed in the case of uncoated naval steel E32 immersed in seawater indicating a susceptibility to pitting corrosion. On the other hand, the current density is almost constant for the naval steel coated with polymeric coatings on entire studied range of potential.

The recorded polarization curves of uncoated naval steel E32 are characterized by narrow passive regions, as shown in the figure 4 (a). The end of this narrow passive region denotes the pitting potential, E_{pit}, above which the passive film breaks down and pits initiate on the uncoated steel surface. This is indicated by the rapid increase in the passive current density without any sign for oxygen evolution, as a consequence of the passivity breakdown. These narrow passive regions of uncoated naval steel E32 reflects without any doubt the severity nature of the pitting attack induced by

Cl⁻ anions, compared with polymeric primer coatings.

The polymeric primer coatings have revealed the extended passive domains indicating once again a much higher corrosion resistance compared with uncoated naval steel E32.

4. Conclusion

From the present experimental research work and the obtained results, the following can be concluded:

By coating the naval steel with polymeric primer, the open circuit potential is shifted to more positive values from E=-681 mV to E=-599 mV. Adding to polymeric primer TiO_2 nanoparticles, the open circuit potential is even more shifted to positive values confirming the beneficial effect of TiO_2 nanoparticles.

From 200 point linear polarization, it was calculated the evolution of polarization resistance (Rp), resulting the highest value for modified polymeric primer with TiO_2 nanoparticles. Thus, Rp of steel coated with polymeric primer plus TiO_2 is about two hundred times higher than Rp of primer without naoparticles and about 1000 time higher than uncoated steel.

The good effect of TiO_2 nanoparticles addition to polymeric primes is also revealed by the corrosion rate, as penetration rate, which is smallest for coated steel with primer modified with nanoparticles, having the value of 0.141 μm/year. The uncoated steel show a higher corrosion rate of 386.79 μm/year, which was diminished only to 29.92 μm by coating with simply polymeric primer.

The cyclic voltametry measurements proved the better behavior of steel coated with primer plus TiO_2 nanoparticles, showing the highest passive domain in the scanned potential range. Also from cyclic voltametry it was revealed that uncoated steel is sensitive to localized corrosion, by showing the specific hysteresis. The steel coated with primer mixed with TiO2 nanoparticles don't show the transpassive domain (anodic current did not increase) and reveal the absence of specific hysteresis for localized corrosion.

The polymeric coatings increases the lifetime for naval steel and this is materialized in lowering maintenance costs.

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