



EFFECT OF ZrO₂ NANOPARTICLES ON THE MECHANICAL AND ANTICORROSION PROPERTIES OF EPOXY COATING

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ABSTRACT

Homogeneous epoxy coatings containing ZrO₂ nanoparticles were applied on Grade A naval steel substrates. The morphology of the coating was characterized by optical microscopy and scanning electron microscopy. The effect of nanoparticles on the corrosion resistance of the hybrid coating was investigated by potentiodynamic polarization method. ZrO₂ (1wt. %) doping increased the microhardness of coating up to 15%, from 12.5 (kgf/mm²) to 14.4 (kgf/mm²). The coated steel samples were electrochemically monitored over the 30 days of immersion in 5 wt. % NaCl solution. As shown by the polarization resistance and corrosion rate, the nanoparticles have a beneficial role, significantly improving the corrosion resistance.

KEYWORDS: nanoparticle, epoxy coating, Tafel curves, corrosion parameters

1. Introduction

Epoxy coatings have been widely used as a material to protect the metallic structures [1-3] and represent one of the most used coating systems in naval field. The protective coatings for marine steel structures work in very demanding conditions. Epoxy coating is suitable for these multiple requirements, because of its excellent chemical resistance, good electrical insulating properties and strong adhesion to steel substrates, but often is susceptible to damage by surface abrasion and wear [4, 5] and also is poorly resistant to the propagation of cracks [6].

Usually, epoxy coatings reduce the corrosion of a metallic substrate subject to an electrolyte. It is acting as a physical barrier layer against the ingress of a deleterious species and represent a reservoir for corrosion inhibitors. The barrier features of epoxy coatings can be enhanced by the incorporation of nanosized inorganic filler particles dispersed within the epoxy matrix, to form an epoxy nanocomposite.

Thereby, the following benefits can be obtained:

- Improving the integrity and durability of coatings by dispersion of fine particles in the cavities of epoxy matrix [7-9] which cause crack bridging [10];

- Preventing epoxy disaggregation during curing, resulting in a more homogeneous coating, due to tendency of nanoparticles to occupy small hole defects formed from local shrinkage during curing of the epoxy resin and act as a bridge, interconnecting more molecules;

- Offering significant barrier properties for corrosion protection, by reducing the total free volume and increasing cross-linking density [11, 12].

In this work it is discussed the influence of ZrO₂ nanoparticles on the surface morphology, microhardness and anticorrosion parameters of epoxy coatings. A better understanding of the mechanisms through which nanoparticles interact with epoxy matrix is very important to offer subsequent guidelines in design of epoxy coatings with high performances in corrosion protection of steel.

2. Experimental details

2.1. Materials

The epoxy resin, the hardener and the solvent used for coating deposition, commercially known as DER 353, I 3100 and D 309 respectively, were obtained from S.C. "Policolor" S.A. (Bucharest).



ZrO₂ nanoparticles with diameter below 100nm, were purchased from Sigma Aldrich (Steinheim, Germany). Sodium chloride (NaCl) used for corrosion test was purchased from S.C. Silal Trading S.R.L. (Bucharest). As substrate it was used rectangle steel samples (50x20mm) of grade S235JR+AR according to EN 10025-2004; the steel substrates have the following chemical composition: 0.12% C, 0.48% Mn, 0.015% Si, 0.013% P, 0.006% S, 0.039% Al, 0.016% Cu, 0.029% Cr, 0.024% Ni, 0.001% V, 0.003% Mo, 0.001% Ti, 0.001% Nb, Fe in rest. The composition and mechanical properties are similar to those of naval steel grade A.

2.2. Deposition of coatings

Steel substrates were initially cleaned with acetone, sand-blasted to the grade "Sa 2½" and cleaned by immersion in acetone. To remove the microparticles remained on the surface after sand-blasted, the substrates were sonicated for 10min. in acetone. Two types of coatings were prepared: epoxy and epoxy modified with ZrO₂ nanoparticles. The weight ratio of the epoxy resin to the hardener was 2:1. Before mixing, both resin and its hardener were diluted by solvent with a 1:1 weight ratio [13]. After that, the two solutions were stirred (1400rpm) using a Heidolph MR Hei-Tech magnetic stirrer, mixed and sonicated 10min. using a bath. For nanocomposite coating, at this resulted solution were added ZrO₂ nanoparticles, (1%) of the total weight of resin and hardener. The steel substrates were dipped into the obtained mixture, using a home-made dip-coater, at different withdrawn speed of 2.5, 5 and 10cm/min, respectively. After each layer deposited, the samples were kept at room temperature for 30min. and placed in an oven (Model FN 055 Nüve) at 90°C for 30min. Finally, the samples were kept at room temperature for 30min.

The following groups of samples were obtained: epoxy coating (six layers) and ZrO₂ modified epoxy coatings (two layers noted with I and six layers noted with II) (Table 1). All the coated samples were kept at room temperatures for 14 days, to allow full curing for the subsequent mechanical and anticorrosion tests.

2.3. Characterization of coatings

The Thickness of the Dried Film (DFT) was measured by a nondestructive echo-sound test, using a 345 type Elcometer. The DFT values are presented in Table 1. The surface morphology and the cross-section for the nanocomposite sample covered by six layers at withdrawn speed of 10 cm/min, were analyzed by Scanning Electron Microscopy (SEM) (model Zeiss EVO MA 15). *Microhardness* measurements were realized for the samples covered by six layers, using a specific system (model PMT-

3), according to EN ISO 6507/1 – 2002 [14] and equation (1),

$$HVF=1.8544 \cdot F/d^2 [\text{kgf/mm}^2] \quad (1)$$

where F is strength test and d is diagonal of square trace remained after test.

The anticorrosive performance of nanocomposite coatings was investigated by potentiodynamic weak polarization method. The samples were kept immersed in corrosive solution (5wt.% aqueous NaCl solution) over the 30 days and the measurements of corrosion parameters were carried out periodically using Voltalab PGP 201 Radiometer Analytical equipment, with three electrodes: the epoxy coated steel sample served as the working electrode, while the counter electrode and the reference electrode used were a platinum grid and a saturated calomel - Ag/AgCl (Sat. KCl), respectively. A special cell ensures the reproducibility of the experimental parameters, especially the distances between electrodes and the free sample surface (0.5024cm²) in contact with the corrosive solution. The steel was polarized around its corrosion potential, in general in the potential range of -1000mV÷ +200mV by a direct current (DC) signal, at a scan rate of 0.2mV/s. The results were processed with the application VoltaMaster software, version 4, using the following experimental parameters: diameter of the free surface of the sample (8mm); solution expose surface area (50.24mm²); steel sample density (7.8kg/dm³) and iron valence (2).

3. Results and discussion

3.1. Effect of nanoparticles on the morphology of epoxy coating

Optical top-view images of the investigated samples are shown in Figure 1, which indicates that cured epoxy coatings have a relatively homogeneous morphology, the ZrO₂ modified epoxy coatings are denser and apparently showed no sign of nanoparticles agglomeration. The average thickness of the epoxy coatings for the sample studied, estimated from its cross-sectional view (as shown in Fig. 2a) is in accordance with the thickness of the coating measured by nondestructive echo-sound test. Six layers epoxy coating has the same range DFT with two layers ZrO₂ modified epoxy coatings (I). These coatings are much thinner than the six layers ZrO₂ modified epoxy coatings (II) (Table 1), which are very homogeneous in value. As it can be seen in Figure 2a, the surface of coating has small roughness, the coating shows a good compliance and adherence to the substrate, is very compact, without boundaries between the deposited layers.

The sample studied has some agglomeration of zirconia nanoparticles, revealed by cross section view

(see zone A of $24.38\mu\text{m}^2$) (Fig. 2a) and chemical analysis (Fig. 2b).

3.2. Effect of nanoparticles on the mechanical properties – microhardness

As the indentation depth in microhardness measurements done on PMT-3 system is around $3\mu\text{m}$

and the coating thickness is above $25\mu\text{m}$, the contribution of steel substrate to the final results of microhardness is negligible. In this work we presume that all the coatings have identical mechanical properties over the entire thickness and the results of microhardness so measured are the representative value of the whole coatings.

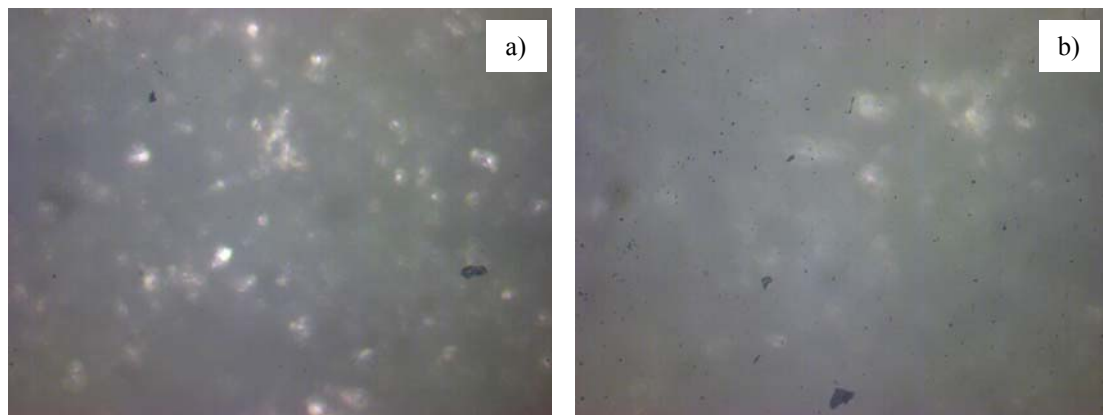


Fig. 1. Optical micrographs of epoxy coatings obtained by six layers, at withdrawn speed of 10cm/min: a) plain epoxy; b) nanocomposite coatings

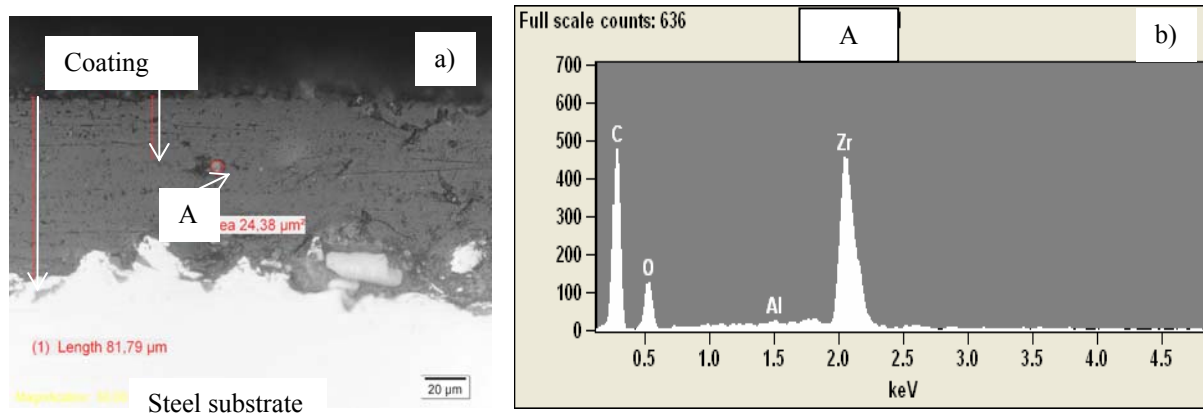


Fig. 2. SEM images of nanocomposite coatings obtained by six layers, at withdrawn speed of 10cm/min: a) cross sectional view, indicating a thickness of $82\mu\text{m}$; b) chemical analysis specific for region A

Table 1. DFT of the samples at different withdrawn speed

Type of coating	No. of layers	Withdrawn speed (cm/min)	DFT (μm)
Epoxy	6	2.5	32 ± 10
		5	50 ± 10
		10	70 ± 15
ZrO ₂ -Epoxy nanocomposite (type I)	2	2.5	35 ± 5
		5	45 ± 5
		10	50 ± 8
ZrO ₂ -Epoxy nanocomposite (type II)	6	2.5	80 ± 12
		5	95 ± 10
		10	112 ± 18

Figure 3 shows the values of microhardness calculated considering the average thickness of film coatings, for the samples covered by six layers, measured in two different stages: as prepared (a) and after salt spray test chamber (480 hours) (b). The incorporation into epoxy of small amount of ZrO₂ nanoparticles (1wt.%) have a beneficial role, improving the microhardness of coating, up to 15% for the homologous samples obtained for the withdrawn speed of 2.5cm/min and maintains the values of microhardness upper or sensitive to values equal in rest.

This beneficial role is particularly relevant in time, when the coating has worked in demanding conditions (after salt spray test chamber).

3.3. Effect of nanoparticles on the corrosion resistance of the coated steel

The corrosion potential, corrosion current, polarization resistance and instantaneous rate were estimated from the measured potentiodynamic polarization curves of epoxy-coated steel.

Fig. 4 shows the temporal evolution of instantaneous corrosion rate and polarization

resistance (R_p) of steel samples coated at withdrawn speed of 2.5 cm/min, during the 30-day immersion in 5wt.% NaCl solution. To conclude on the beneficial role of introducing nanoparticles into epoxy matrix, it is better to compare the temporal evolution of the corrosion parameters for plain epoxy with nanocomposite type I, the two coatings having DFT closer as values.

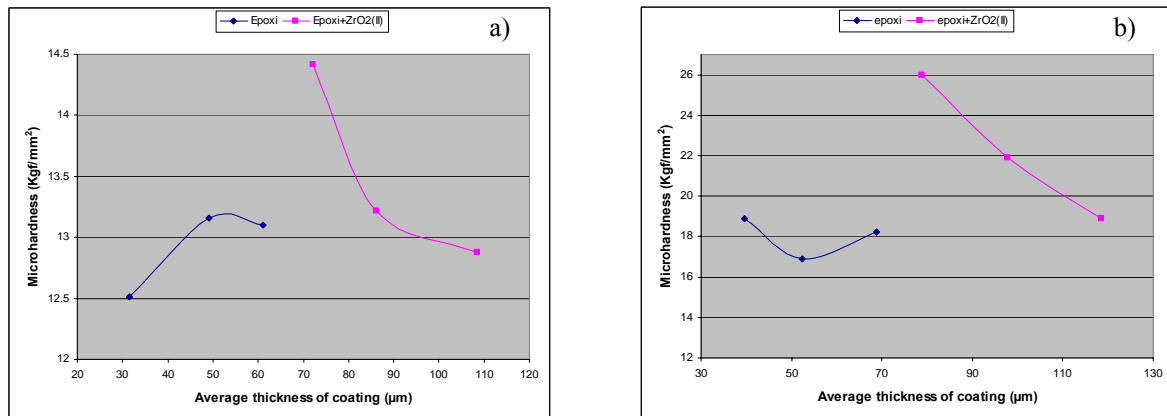


Fig. 3. Microhardness values calculated considering the average thickness film, for plain epoxy and the ZrO₂ modified epoxy coating (II) (six layers): a) as prepared; b) after salt spray corrosion test

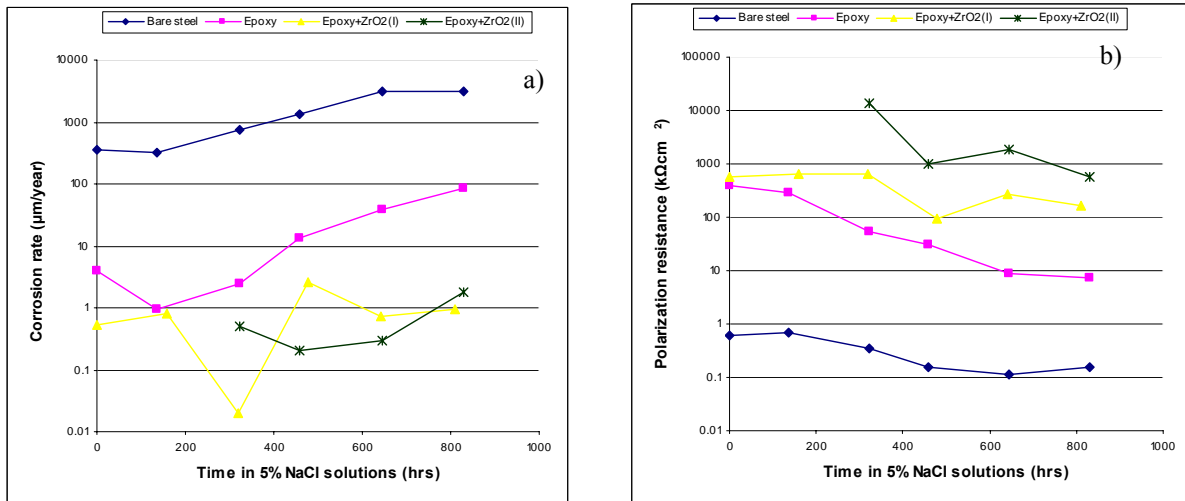


Fig. 4. Temporal evolution of: corrosion rate - a); polarization resistance - b), for samples coated at withdrawn speed of 2.5cm/min, measured in 5wt% aqueous NaCl solution, at different times of immersion

In case of nanocomposite type II, the beneficial role could be the result both of the presence of ZrO₂ nanoparticles and the thickness obtained after six layers deposited. So, the incorporation into epoxy coating of small amount of ZrO₂ nanoparticles (1wt.%) significantly reduced the corrosion rate of the epoxy-coated steel over the 30-day immersion in 5wt.% NaCl solution, up to 80 times after 800 hours (Fig. 4a), and consequently leads to the adequate

improving corrosion resistance of the epoxy-coated, up to 20 times (Fig. 4b). It can be noted that R_p for nanocomposite type II in comparison with similar value for nanocomposite type I, is maintained higher by 3-27 times, while the corrosion rate at some moments of tests are better for nanocomposite type I. It is assumed that in the type I nanocomposite coatings, the nanoparticles were better dispersed, the two layers were thinner opposite to nanocomposite II,



in which some nanoparticles agglomeration were highlighted. For samples covered with six layers, each layer deposited leads to increasing the internal stress, the source for micro-cracks and pinholes [11, 12], decreasing mechanical strength and corrosion resistance.

Conclusions

ZrO₂ nanoparticles were successfully dispersed in epoxy based coatings at a concentration of 1%.

The electrochemical monitoring of coated steel over the 30 days of immersion in 5wt.% NaCl solution suggested the beneficial role of nanoparticles in significantly improving the corrosion resistance of the coated steel. The epoxy coating modified with ZrO₂ nanoparticles showed an important enhanced microhardness value.

The hardness remains at good values for samples subjected to corrosion test for long time.

For future research, it would be important to investigate ways to improve dispersion of the nanoparticles in the coating matrix, further effect of increasing ZrO₂ nanoparticles content on the anticorrosive performance for epoxy coating; the potential application of the nanoparticles as reservoirs

of corrosion inhibitors, for the storage and for releasing them in some conditions will be investigated.

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