



# Corrosion Protection Performance of Nanoclay-Polyester Nanocomposite Coatings

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## ABSTRACT

In this paper, polymer-based nanocomposite powder was applied on the surface of plain carbon steel by electrostatic device and then was cured by microwave. The effect of adding nanoparticles on the corrosion resistance properties of the coatings was investigated by Electrochemical Impedance Spectroscopy and immersion test in 3.5% NaCl solution. Coatings structure and the morphology of nanoparticles both were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results of Electrochemical Impedance Spectroscopy and immersion test showed that the corrosion resistance of coating is increased significantly (more than one order of magnitude) by adding nanoclay because of barrier properties of nanoparticles. In addition, embedded nanoparticles in polyester coating resulted in a denser, more uniform and less porous coatings in comparison with pure polyester ones. Surface roughness of coated samples was higher for nanocomposite coatings. Prog. Color Colorants Coat. 9 (2016), 223-232 © Institute for Color Science and Technology.

## 1. Introduction

Use of protective polymer coatings is the most widely accepted approach for corrosion resistance [1, 2], but the low corrosion resistance and also low wear properties are the most important problems in polymeric coatings such as polyesters [3, 4]. Recently, nanoparticles were used in the polymer matrix coatings to improve the corrosion resistance of these coatings. There are many researches in which the corrosion resistance has been increased by adding nanoparticles in polymeric coatings [3, 5]. Higher corrosion resistance of nanocomposite coatings can be attributed to the barrier properties of nanoparticles [6]. For example, incorporation of clay nanoparticles in the

polymer matrix leads to the increase of abrasion resistance, thermal stability and barrier properties of these coatings [7, 8]. Ashasisorkhabi et al. [9] showed that the stiffness, hardness, corrosion resistance and wear resistance of epoxy coatings are enhanced by addition of ZnO nanoparticles in polymeric matrix. Also, Bagherzadeh et al. [10] in their study showed that water absorption in pure epoxy coating was three times more than nanocomposite coatings containing 1 wt% nanoclay, so penetration of corrosive solution in nanocomposite coating is lower and corrosion resistance enhances.

In this paper, polyester powder as the matrix was

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combined with clay nanoparticle as reinforcement to form polymer-based nanocomposites which were then applied on steel substrate using electrostatic technique. The purpose of this research was to improve the corrosion resistance properties of the coating and study the effect of adding clay nanoparticles on structure and morphology of nanocomposite coatings.

## 2. Experimental

### 2.1. Materials

The polyester powder (10–60  $\mu\text{m}$ , NikfamGostar Company, Iran) and Alumina nanoparticle (10–30 nm, commercial grade) were used. SEM micrograph of pure polyester powder as well as SEM and TEM images of clay nanoparticles are shown in Figure 1.

### 2.2. Preparation of nanocomposite powders

The nanocomposite powder was prepared as follows: I) Dispersing 2.5 and 5wt% nanoclay in distilled water by ultrasonic homogenizer (200 W and 20 kHz) for 3h; II) Adding polyester to this solution and redistribution in ultrasonic homogenizer for 6 h; III) mechanical mixing with the rate of 2000 rpm for 12 h; IV) ball milling by rate of 300 rpm for 12 h.

### 2.3. Substrate preparation

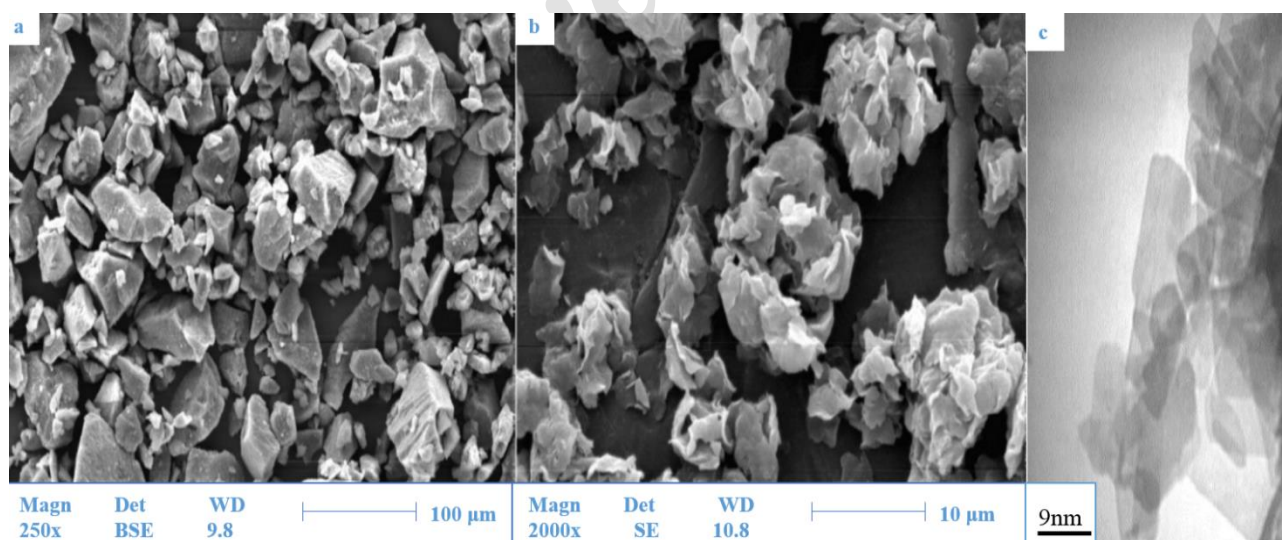
Carbon steel substrates (0.2% C, 0.37% Al, 1.38% Si, 0.2% Mn and the rest of iron) with dimensions of  $6 \times 5 \times 0.5 \text{ cm}^3$  were first polished by 800 and 1200 sandpapers and then were degreased by methanol in an ultrasonic bath and finally were washed with distilled water and dried in a blowing hot air.

### 2.4. Coating method

Coating was applied by electrostatic device equipped with Corona-model gun at 100 kV, 0.1 mA and distance of 10 cm on both sides of the steel panels. At last, the curing treatment was done in a microwave with the power of 900 W for 12 minutes.

### 2.5. Measurements and characteristics

The shapes and structures of clay nanoparticles were considered by using TEM (EMIOC model - Germany) and the voltage of the filament was fixed in 80kV. The structure of polyester powder and moreover, the surface structural with cross sections of coatings considered by using SEM (Philips-XL30 model).



**Figure 1:** (a) SEM image of pure polyester powder, (b) SEM images of clay nanoparticles, (c) TEM image of nanoclay.

**Table 1:** The characteristics of the coated samples.

Sample Name	Nanoparticle (wt%)	Curing method
PM	---	Microwave
PM-2.5	2.5	Microwave
PM-5	5	Microwave

## 2.6. Corrosion Tests

The effects of clay nanoparticles on the corrosion resistance of coated samples were studied using immersion and EIS tests. In the immersion test, the coated samples were immersed into the 3.5% NaCl solution for 10000 minutes and the variation of potential values with time was recorded in the various times of immersion. EIS measurements were carried out in 3.5% NaCl solution using EG&G Potentiostat-Galvanostat (model 273A) coupled with a frequency response analyzer (Model Schlumberger Si1250) in open circuit potential (OCP) under atmospheric conditions at 25 °C. Conventional three-electrode cell was used in which a saturated calomel electrode (SCE) was used as a reference electrode and platinum foil was selected as an auxiliary electrode. The coated samples were used as working electrode. In EIS measurements, the sample area exposed to corrosive electrolyte was 0.785 cm<sup>2</sup>. Prior to EIS measurements, the applied potential amplitude was chosen to be 10 mV with frequency ranging from 65 KHz to 0.01 Hz. The collected data were analyzed with an equivalent circuit using “ZView2” software.

## 3. Results and discussions

### 3.1. Microstructure of the coated samples

Figure 2 shows SEM micrograph of the cross section of polyester coating (PM) and nanocomposite coatings (PM-2.5 and PM-5) on the metal substrate. SEM images of the cross section of nanocomposite coating containing 2.5wt% nanoclay represents a homogeneous structure, no cracks, good adhesion to the substrate and

almost compact for PM-2.5 coating which affecting their corrosion properties, while the structure of pure polyester coatings have many cracks and pores which may have negative effect on protective properties of the coatings [6, 11]. The presence of these nanoparticles increased the density of coatings, so the interfaces between the coatings and the substrate are increased [12]. By increasing the amount of nanoclay to 5wt%, the quality of coatings decreased and proportional to coatings by 2.5wt% nanoclay, have more defects and pores. So, the nanocomposite samples have suitable quality and wetting to the substrate but the pure polyester samples didn't have a suitable cohesion to the substrate.

Fabricated coatings were studied in terms of homogeneity and surface morphology (see Figure 3). Samples containing nanoclay have a higher level of quality compared to pure polyester samples and the cavity and surface defects are less than pure polyester coating. Also surface roughness of nanocomposite sample was more than pure samples because nanoparticles enhanced the roughness of nanocomposite coatings.

Surface roughness of coated samples was showed more roughness for nanocomposite coatings. The problem may be due to the addition of nanoparticles to the polymer matrix. Ra (arithmetic average roughness) is the average of valleys and peaks. Therefore by addition of nanoparticles to the matrix, peaks are increased and therefore roughness is increased. Also, as can be shown with increasing amount of nanoparticle, roughness is increased.

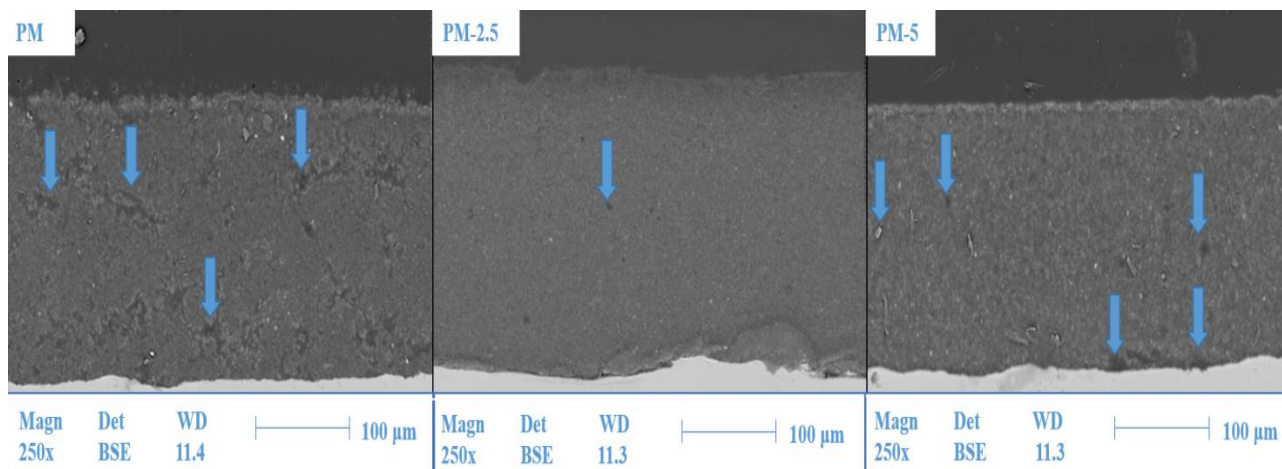


Figure 2: Cross-section SEM images of coated samples.

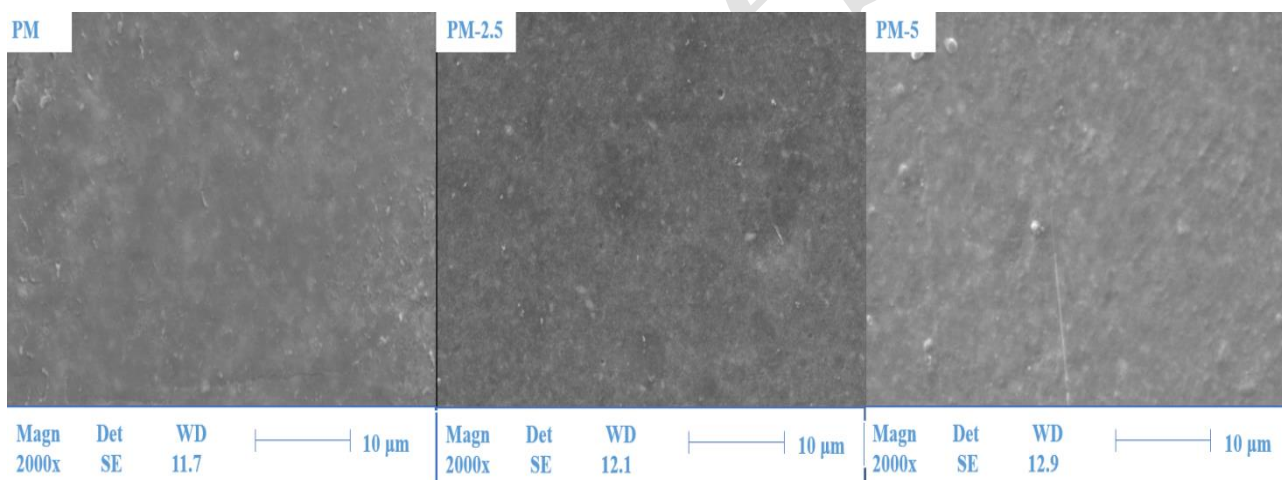


Figure 3: SEM images of top surface of coated samples.

Table 2: Surface roughness of coated samples.

Samples	$R_a$ ( $\mu\text{m}$ )
PM	0.144
PM-2.5	1.36
PM-5	2.12

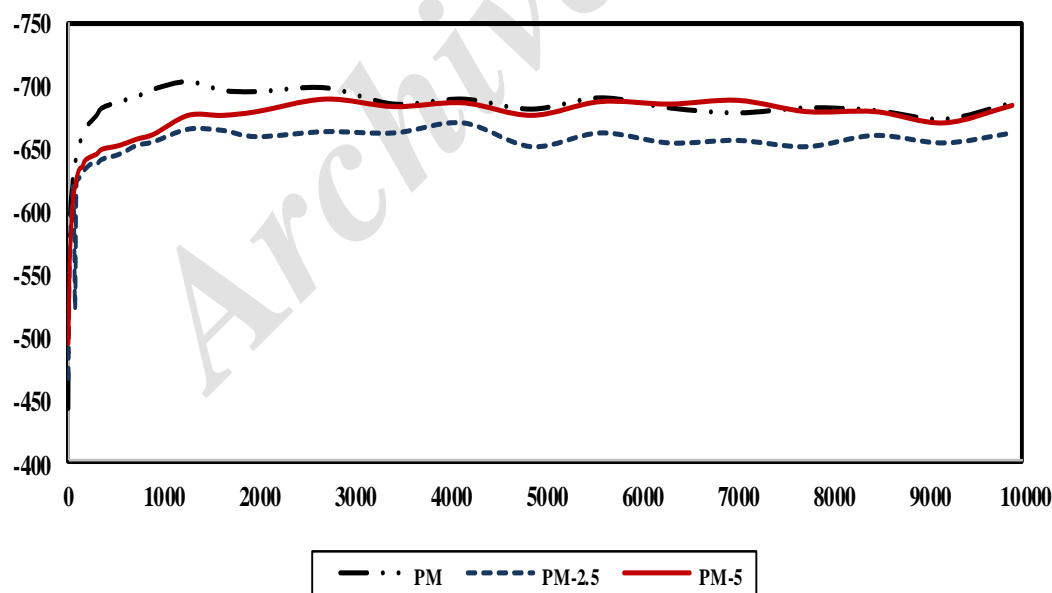
## 3.2. Corrosion protective behavior

### 3.2.1. EIS Test

Electrochemical impedance spectroscopy is a well-known method for prediction of corrosion resistance [13, 14]. Usually the Nyquist plots are used to investigate and describe the coating protective properties [14, 15]. Nyquist diagrams of coatings after one hour immersion in 3.5% NaCl solution are shown in Figure 4. Equivalent electrical circuit with 2 time constants was used to analyze EIS data [9]. In the proposed circuit, the constant phase element was introduced because of depression loops. In Figure 5,  $R_s$  is the resistance of the solution;  $R_{corr}$  is the charge transfer resistance;  $R_{coat}$  is the coating resistance,  $C_{coat}$  is the capacitive element of coating and  $C_{dl}$  is the capacitive element of double layer [16]. Zview software was used to calculate impedance parameters. Impedance parameters calculated are shown in Table 3. Corrosion resistance of coatings on steel substrate was evaluated by coating resistance ( $R_c$ ) and impedance at low frequency ( $|z|_{0.01Hz}$ ) after immersing for an hour in the electrolyte solution [17]. Corrosion resistance of

the coating can be explained inversely with the rate of corrosion [18]. When there are defects in the coating, water molecules and corrosive ions diffuse through the coating [19] and corrosion rate increases.

Table 3 and Figure 4 show that the corrosion resistance of PM-2.5 nanocomposite coatings is markedly higher than PM-5 and PM coatings. Also coating capacitance is sensitive to the amount of water in the coating, therefore as is shown in Table 3, after immersion in the electrolyte solution, nanocomposite coatings absorb less water than pure polyester coatings and have better corrosion protection compared to pure polyester coatings. Therefore, a decrease in this parameter is corresponding to the diffusion of electrolyte through the pores and defects into the coating [19]. It can be argued that the presence of nanoparticles in the coatings has a positive effect on both coating resistance and coating capacitance due to the delays in the penetration of water, oxygen and ionic components through the coating containing nanoparticles and decrease pores and defects of coating [9].

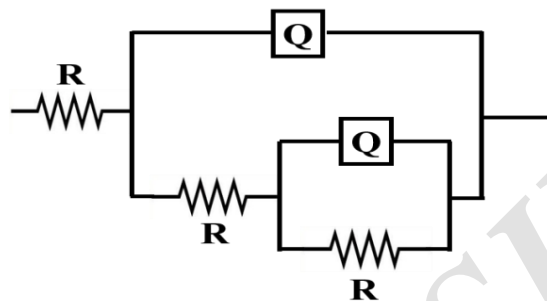


**Figure 4:** Fitted Nyquist impedance spectra of coated samples after an hour of immersion.



**Table 3:** Impedance parameters obtained by fitting of Nyquist diagrams.

Sample	$R_{\text{coat}}(\text{K}\Omega.\text{cm}^2)$	$C_{\text{coat}}(\text{F}.\text{cm}^2)$	$R_{\text{corr}}(\text{K}\Omega.\text{cm}^2)$	$C_{\text{dl}}(\text{F}.\text{cm}^2)$
PM	33.1	4.6E-8	677	4.5E-7
PM-2.5	1990	8.6E-9	11352	2.3E-8
PM-5	631	1.3E-9	3687	5.8E-9

**Figure 5:** The equivalent circuit model used to simulate the impedance behavior.

The Bode plot also shows that impedance value for nanocomposite coating is more than that of pure coating [21]. The impedance values in high frequency range in Bode plots show the protective performance of coatings, whereas the impedance values in low frequency range represent the corrosion behavior at the substrate/coating interface ( $|Z|_{0.01\text{Hz}}$ ). According to Figure 6, the impedance values for nanocomposite coating with 2.5 wt% nanoparticle in both high and low frequency ranges is higher than that of other coatings. This may be attributed to better corrosion resistance of PM-2.5 in comparison to PM and PM-5 [21, 22].

The addition of nanoparticles to the polymeric coatings leads to a decrease in penetration of water and electrolyte into the coatings. The occupation of pores with nanoparticles may decrease the preferred paths for the diffusion of electrolyte [23]. However, the penetration rate of water into the nanocomposite coating is lower than that of pure polyester coating. According to the previous researches, the mixture of nanoparticles can lead to enhance the properties of coating/substrate interface.

### 3.2.2. Immersion Test

The barrier, cohesion and inhibition properties of a coating play a dominant role in its life time. The sustainability of a coating on metal surface is related to

the duration of direct exposure in the corrosive medium, variation in the adhesion strength and barrier properties. Aging, diffusion of corrosive agent such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{H}^+$  ions into the metal/coating interface can be cause to blistering, reducing the stability of adhesion bond, increasing the cathodic reaction and thus led to destruction of coating and substrate[10, 21].

To investigate the effect of nanoparticles in reducing the penetration of corrosive agent toward the coating/metal interface, immersion measurements were performed. To do this, the coated sheets were immersed in 3.5 wt% NaCl electrolyte for 10000 h and open circuit potential values were measured.

Figure 7 shows open circuit potential (OCP) changes compared to the immersion time for different samples. OCP values of the coating contains nanoparticles over time is more positive than pure polyester coatings. It is known that adding nanoclay to the coating greatly improves the barrier properties of coating. So nanoparticles can control the penetration of corrosive agents, and will prevent corrosion [18]. The lack of clear pores on the surface of the nanocomposite coating (Figure 2) shows better resistance to water penetration of this coating.

Evaluate the protective properties of coating at different times of exposure in electrolyte release that

nanoclay nanoparticles play a dominant role in protective properties of coating which they act as following:

- A barrier against diffusion of electrolyte and

corrosive ions.

- A barrier against diffusion paths of ions between local cathode and anode at the interface of coating and substrate.

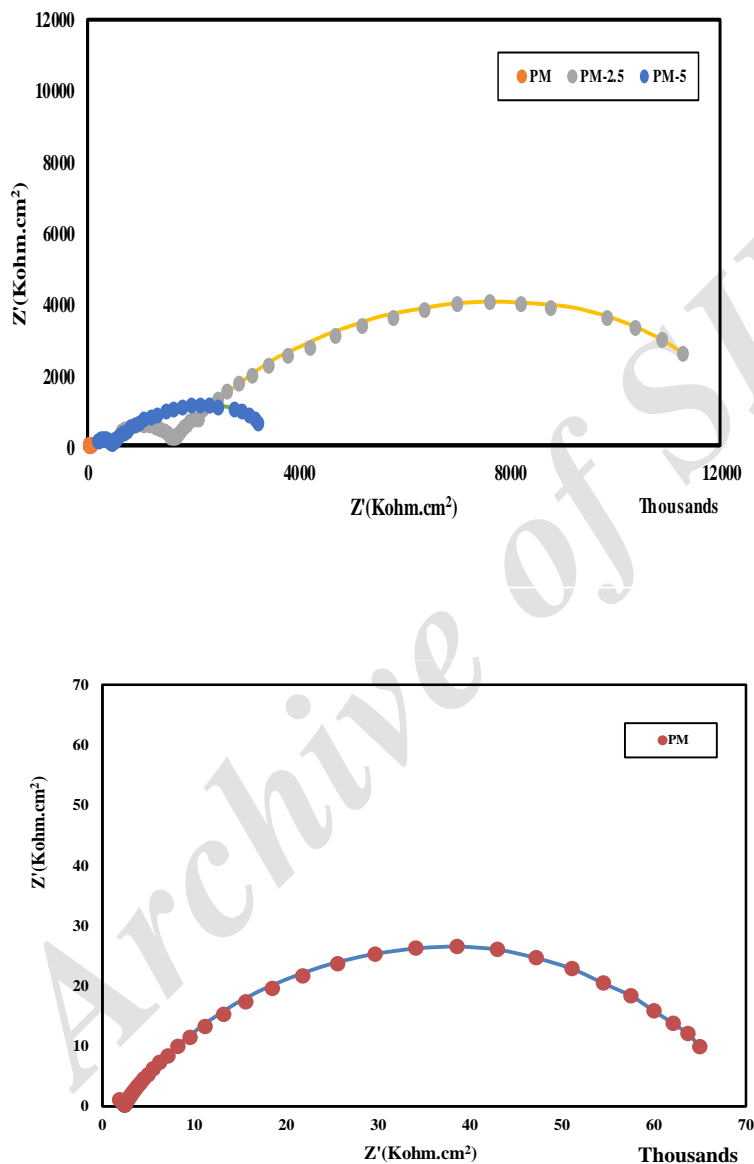


Figure 6: Fitted Bode diagrams of coated samples after an hour of immersion.

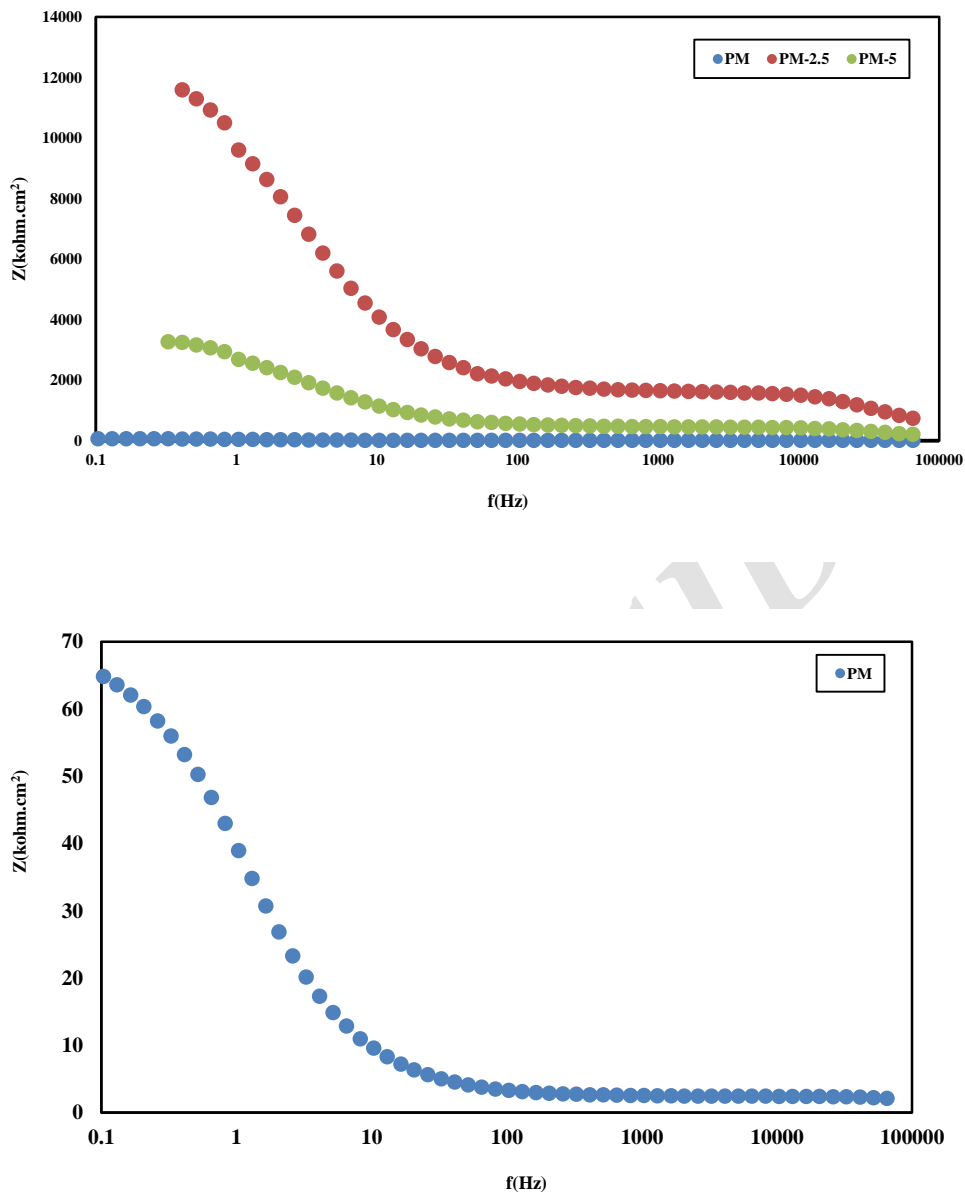


Figure 7: OCP changes compared to the immersion time for different samples.

#### 4. Conclusion

Embedding Nanoparticles in polyester coating fabricates a denser coating, more uniform and less pores in comparison with the pure polyester coating. Fabricating a barrier against penetration of corrosive electrolytes with little pores and flows, increase the corrosion resistance properties of nanocomposite coatings. Corrosion test results revealed that the

samples containing 2.5 wt% nanoclay showed the best corrosion resistance. It seems that, the agglomeration of nanoclay in the samples containing 5 wt% may reduce the corrosion resistance of these samples. In general, it can be concluded that the presence of nanoparticles will be helpful greatly to increase the corrosion resistance of polyester coatings.



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## کارایی حفاظت از خوردگی پوشش‌های نانوکلی-پلی‌استر

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### چکیده

در این مقاله، پودر نانوکامپوزیتی پایه پلیمری به کمک دستگاه الکترواستاتیک بر روی فولاد ساده کربنی اعمال شد و پوشش به دست آمده با استفاده از امواج مایکروویو پخته شد. تاثیر افزودن نانوذرات بر روی خواص خوردگی پوشش‌ها، توسط آزمون طیف‌سنجی امپدانس الکتروشیمیایی و آزمون غوطه‌وری در محلول ۳.۵٪ نمک مورد بررسی قرار گرفت. همچنین ساختار و ریخت شناسی پوشش‌ها و نانوذرات توسط میکروسوپ الکترونی عبوری و روبشی بررسی شد. نتایج آزمون طیف‌سنجی امپدانس الکتروشیمیایی و آزمون غوطه‌وری نشان می‌دهد که با افزودن نانوذرات، مقاومت خوردگی پوشش‌ها به صورت قابل توجهی افزایش می‌یابد که علت آن نقش سدکنندگی نانوذرات است. همچنین حضور نانوذرات باعث متراکم‌تر و یکنواخت‌تر شدن پوشش و کاهش منافذ آن می‌شود. همچنین میزان زبری پوشش نانوکامپوزیتی بیش از پوشش پلیمری ساده است.

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