

# Effect of Quartz Filler on Epoxy Coatings Behavior

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(Submitted 23 September 2002)

The effect of quartz (0-60 wt.%) on the mechanical, anticorrosive, and dielectric properties of pretreated steel coatings in a 3.5 wt.% NaCl solution was studied by abrasion and impact resistance, pencil and Shore D hardness measurements, visual observations after salt spray tests, as well as by electrochemical impedance spectroscopy and water permeability measurements. Results revealed that coatings with a quartz load up to 30% exhibit a noticeable improvement of their mechanical characteristics as well as better dielectric and anticorrosive behavior than that of pure epoxy coatings. Further increase of the quartz content results in a lower degree of their behavior improvement or even in their worsening, with the exception of the coatings' surface hardness that increases with the increase of the quartz content.

**Keywords** corrosion, inorganic pigments, mechanical properties, protective coatings, quartz

## 1. Introduction

It is a universal practice that high anticorrosive protection of metallic structures is offered by suitable organic coatings.<sup>[1,2]</sup> The corrosion resistance of a coated steel surface is generally considered to depend on the metal characteristics, the surface pretreatment, the thickness of the coating, as well as on several properties of the coating such as mechanical strength, adhesion to the metallic substrate, permeability, and dielectric and chemical properties of the system.<sup>[3]</sup> Requirements of improved mechanical properties of the coatings lead to the use of composite systems with the addition of polyamide, glass, or graphite fibers in the polymeric matrix.<sup>[4,5]</sup>

Composite systems having discrete particles dispersed randomly in the polymeric matrix have proven to be highly heterogeneous, deviating significantly from ideal Debye behavior.<sup>[6]</sup> This inhomogeneity becomes even more pronounced as water penetrates the bulk of the coating after immersion in a corrosive environment. Electrochemical impedance spectroscopy (EIS) has been widely used as a means of understanding the contributions of the specific corrosion processes occurring in complex systems such as epoxy-based barrier coatings on metal substrates, by fitting impedance data to theoretical electrical circuits.<sup>[7-10]</sup>

In this work, the effect of quartz filler on the mechanical and anticorrosive behavior of epoxy coatings of steel specimens was investigated. Quartz has been used due to its high Mohs hardness value.<sup>[11]</sup> The mechanical characteristics of the coating were determined using Shore D hardness, pencil hardness, abrasion resistance, and impact resistance to falling weight. These results were correlated with those concerning the modification of dielectric and anticorrosive characteristics of these

coatings in a 3.5 wt.% NaCl solution that was determined using EIS measurements. Since the longevity and reliability of the coatings are strongly affected by the water sorption,<sup>[12]</sup> the water permeability of the coatings was measured on free membranes of the same composition with the coatings examined by standard test method (cup test).

## 2. Experimental Procedure

### 2.1 Materials

The test specimens were flat plate samples cut from steel sheets in a rectangular shape of 10 cm × 10 cm and 10 cm × 20 cm. The wt.% composition of the steel substrate was the following: Fe (99.28%), C (0.12%), Mn (0.5%), P (0.005%), and S (0.05%).

The organic coating used was a bisphenol-A based epoxy resin of molecular weight about 1025 with epoxy equivalent weight 500-535 g/Aeq (grams resin containing one epoxy equivalent), viscosity 30-40 s (DIN 53211,<sup>[13]</sup> 4 mm, 20 °C) in solution 50 wt.%, and density 1.18-1.20 g/cm<sup>3</sup> at 20 °C. The curing agent was a high viscosity polyaminoamide with amine value 240-260 (DIN 16945<sup>[14]</sup>) and density 0.95-0.97 g/cm<sup>3</sup> at 20 °C. The resin/curing agent ratio was 200/50 by weight, in accordance to the proportions range given by the suppliers. This system was used either in this formulation, as a reference system (RES), or filled with quartz powder (grain size 70 μm) in contents of 15% (X15), 30% (X30), 45% (X40), and 60% (X60) by weight. The filler used was opaque crystalline quartz of Greek origin exhibiting Mohs hardness value equal to 7, density 2.6 g/cm<sup>3</sup>, and measured oil absorption number equal to 27.5 leading to a critical pigment volume concentration (CPVC) of 58%. Quartz's wt.% composition was the following: SiO<sub>2</sub> (99.7%), Fe<sub>2</sub>O<sub>3</sub> (0.05%), Al<sub>2</sub>O<sub>3</sub> (0.03%), Na (0.01%), K (0.01%), Ti (0.005%), H<sub>2</sub>O (0.2%-0.3%), and CO<sub>3</sub><sup>2-</sup> (0%).

### 2.2 Sample Preparation

The metallic substrate was cleaned by immersion in a strong solution of HCl with an organic corrosion inhibitor, washed with water, polished with emery paper (up to 320 grit), degreased for 10 min in boiling xylene, and stored before coating

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in a desiccator containing silica gel, to avoid any influence of moisture. Organic coatings were deposited on the metal surface by a film applicator and the coated specimens were initially cured at ambient temperature for 24 h followed by postcuring at 40 °C for another 24 h. The dry film thickness of the coatings was 180 μm ± 12%. Corrosive environments of 3.5 wt.% NaCl solution at ambient temperature or 5 wt.% NaCl solution at 32 °C (salt spray cabinet) were used.

### 2.3 Test Instrumentation

The mechanical behavior of the coatings was investigated by determination of their pencil hardness (ASTM D3363-00), measurements of Shore D hardness (ASTM D2240-97), measurements of abrasion resistance (ASTM D968-81/91), and measurements of impact resistance, using the falling weight method (ISO 6272:1993 (E)).

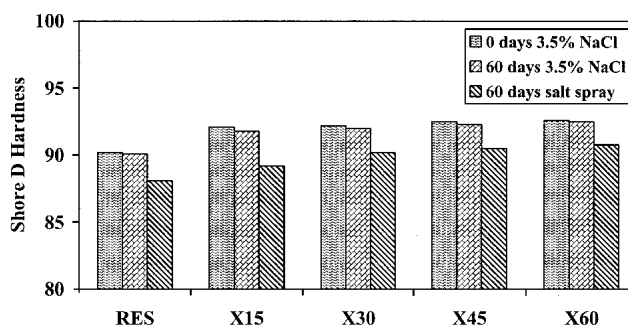
The anticorrosive performance of the coated steel specimens was investigated by EIS, water permeability measurements (cup test ASTM E96-90) of free films having the same composition of coatings, and visual observations according to ASTM D610-85 (rust degree) and ASTM D714-87 (blisters classification) for specimens exposed to the salt spray chamber (Erichsen Model 606 apparatus, Hemer, Germany).

The electrochemical cell for EIS consisted of a hollow Teflon cylinder, fixed with adhesive to the surface of the metal substrate and creating the vessel for electrolyte (3.5 wt.% NaCl). In EIS measurements, a two-electrode setup was used that was fully shielded to minimize noise.<sup>[10,15,16]</sup> The working electrode was the coated specimen having an exposed surface area equal to 15.904 mm<sup>2</sup>, and the second electrode was a silver disk.<sup>[10]</sup> The perturbation amplitude was 15 mV in a sine wave form imposed by means of an impedance analyzer (LF4192A, Hewlett-Packard, Palo Alto, CA) in the frequency range of 5-13 MHz. Each value was the mean value of five measurements in a logarithmic sweep of the frequencies (20 points per logarithmic unit). Measurements were carried out at ambient with the electrolyte in contact with air, periodically between 0-180 days of exposure. The spectra were measured at the open-circuit potential of the samples. Data obtained by impedance measurements were processed through a ZSIM program, to fit experimental data to equivalent circuits.

## 3. Results and Discussion

The mechanical properties of the coatings have been examined through several tests. Their hardness was determined using a Shore scleroscope (Bareiss, Inc., Willow Grove, PA) as well as a pencil hardness tester. It is known that hardness is a complex subject having a different meaning to different engineers.<sup>[17]</sup> The Shore D hardness, belonging to the rebound hardness test, measures the mechanical properties during very short time intervals. Figure 1 presents Shore D hardness of coated specimens exposed to 3.5 wt.% NaCl solution as well as to the salt spray chamber.

It is obvious that Shore D hardness increases with the addition of quartz, indicating that the incorporation of a material characterized by high Mohs hardness number in the epoxy matrix creates a composite coating with relatively improved hardness characteristics, even though the differences resulting



**Fig. 1** Shore D hardness of all types of coated specimens before and after 60 days of exposure to 3.5 wt.% NaCl solution as well as after 60 days of exposure to salt spray chamber

from the increase of the quartz content are not very significant. The increased hardness values remain stable after two months of exposure, both to 3.5 wt.% NaCl solution and accelerated conditions of salt spray test. In the latter case, the corresponding somewhat lower hardness values of all types of coated samples could be attributed to the severity of the conditions. These results are in accordance with those of a pencil hardness test (Table 1). The composite coatings show greater rigidity than that of the pure epoxy coating that increases with the increase of the quartz content at least up to 45 wt.%.

Resistance to abrasion is a factor related to physical characteristics of a coating such as hardness, tensile strength, elasticity, and toughness. In the case of coatings examined from Fig. 2, it is deduced that the addition of quartz in the epoxy matrix enhances the elastic characteristics of the coating.

When the coating is elastic, the mechanical energy transferred on its surface by the impacting sand is mainly returned to the sand, instead of being expended in the damage of the coating surface. If the deformation caused by the falling sand is not elastic, damage will be caused on the impacted material. The quartz particles in the epoxy matrix largely absorb the transferred energy, which then dissipates on the quartz particles boundaries. The resulting damage is lowered, and the corresponding abrasion resistance is increased, at least for quartz content up to 30 wt.%. Higher quartz content, though, still increases abrasion resistance of the composite coatings compared with that of the pure epoxy coating, leading to coatings exhibiting less favorable abrasion characteristics than the less filled composite coatings. This could be attributed to a possible approach to their critical pigment volume concentration.

The situation given in Fig. 2 for coatings that clearly do not exceed the critical pigment volume concentration, that is

$$(\Delta l/l)_{\times 30} > (\Delta l/l)_{\times 15} > (\Delta l/l)_{\text{RES}}$$

where  $l$  is the original length and  $\Delta l$  the change in length, gives information about the ranking of the Young's modulus of those coatings. Taking into consideration that in all cases the applied force  $F$ , per unit of original cross-sectional area  $A$ , remains stable, the equation which gives the Young's modulus  $E$ , of the coatings in terms of those parameters,

$$E = (F/A)/(\Delta l/l)$$

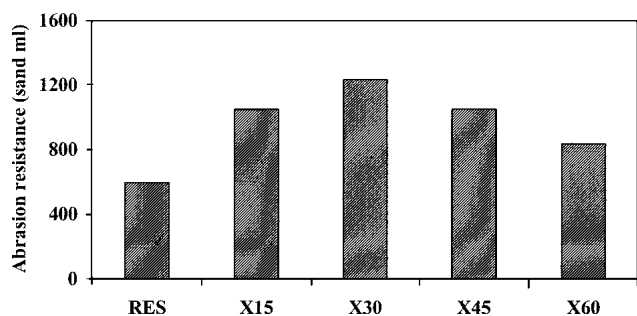


Fig. 2 Abrasion resistance of all types of coated specimens as a function of quartz content

Table 1 Results of Pencil Hardness Test

System of Organic Coating	Pencil Hardness	Range in Hardness From Softest to Hardest
RES	B	6B-B
X15	3H	HB
X30	4H	F
X45	5H	H
X60	5H	2-6H (9H)

Table 2 Coating Resistance to Falling Weight

System of Organic Coating	Analytical Results				
	RES	X15	X30	X45	X60
Weight, g	2000	2000	2000	2000	2000
Height, mm	1000	1000	1000	900	775
Results	Pass	Pass	Pass	Fail	Pass
	Pass	Pass	Fail	Fail	Pass
	Pass	Pass	Pass	Pass	Fail
	Pass	Pass	Pass	Pass	Pass
	Pass	Pass	Fail	Pass	Fail

leads to the following ranking of Young's modulus:

$$E_{\text{res}} < E_{\text{X15}} < E_{\text{X30}}$$

The impact resistance of the coatings has also been determined using the method of the falling weight. According to the ISO 6272:1993(E) standard, the test was performed to determine the weight times height of the dropped weight required to produce cracking detachment of the coating. The results of the tests performed by impacting the coating directly (coating facing upward) are given in Table 2.

Clearly, pure epoxy resin coatings as well as those containing 15 wt.% quartz exhibit the best behavior, as no damage is caused on their surface in all drops with the combination of maximum weight and maximum height of drop. Somewhat inferior results are observed in the behavior of coatings with 30 wt.% quartz content. Further increase of quartz concentration in the epoxy matrix leads to an increased reduction of the maximum height of drop at which damage on the coating surface is observed if the same maximum weight as above is dropped.

This is equivalent to a decrease of the resistance of the coating to falling weight with the increase of the filler content, for at least values > 30 wt.%. This result is in accordance with those of the abrasion resistance. The ranking of the coatings' resistance was the same when reverse (indirectly coating facing downward) impact measurements were performed, but the values of minimum weight and drop height were always significantly lower. This result is expected, since it is much more difficult for a coating to resist reverse impact than direct impact on the surface, because the coating of reverse impact is heavily stressed.<sup>[18]</sup> For this reason, reverse impact is sometimes used as a test for coating adhesion and extensibility.

The influence of quartz on the protective properties of the coatings was estimated through (1) the results of the accelerated degradation of the specimens evaluated by visual inspection of blister formation; and (2) the degree of rusting during the exposure of the samples to the salt spray cabinet (Table 3).

The addition of quartz improves the performance of the coatings as it concerns the blister formation. In all cases composite coatings do not form blisters, while on pure epoxy coatings, after about 20 days of exposure, blisters increasing in size and density with exposure time are formed. After 23 days of exposure, rust is observed in all cases with the exception of the coating with 15% quartz. The degree of rust increases with time for all types of coatings, but that of coatings with 15 and 30% quartz remains always lower than that of pure epoxy coatings, while that of coatings with 45 and 60% quartz is developed in higher values. This could be attributed to the diminution of the necessary volume of polymeric matrix for sufficient wetting of the total amount of quartz filler. This lack of volume should induce an excess of water diffusion paths, thus increasing the accessibility of water to the coating-steel interface and leading to a higher amount of rust formation. Note that the content of 60% quartz was the highest amount that was possible to be incorporated in the polymer matrix under the laboratory conditions.

Water sorption is an important factor in determining the duration and reliability of a coating. Corrosion protection offered depends on three aspects: water sorption of the coating, transport of water in the coating, and accessibility of water to the coating-substrate interface.<sup>[12]</sup> The penetration of water through a simple coating membrane without substrate was estimated by water permeability measurements using the cup method. The mass of water that had passed through the membrane  $M_t$ , determined according to

$$M_t = (W_0 - W_t)/W_0$$

and the rate of water flow  $dW/dt$  was calculated, where  $W_0$  and  $W_t$  are the weight of the cup at times 0 and  $t$  respectively (Fig. 3, 4).

For all types of coatings, the water penetration mechanism, followed throughout the total immersion time, deviates from the classic Fickian model (i.e., proportionality between mass gain and the square root of immersion time).<sup>[19,20]</sup> Up to 30 wt.% quartz content, a two-step penetration mechanism is observed, while higher filler content leads to the appearance of a third penetration step. The first step could be characterized as the result of direct diffusion of water molecules through the

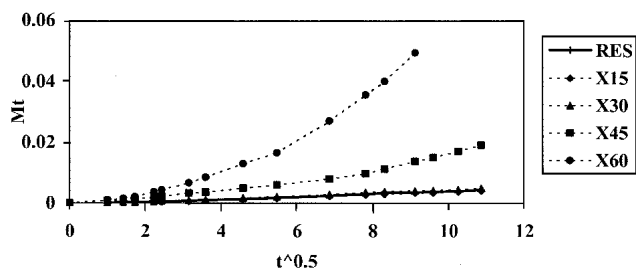


Fig. 3 Weight fraction of water passed through membrane as a function of square root of time

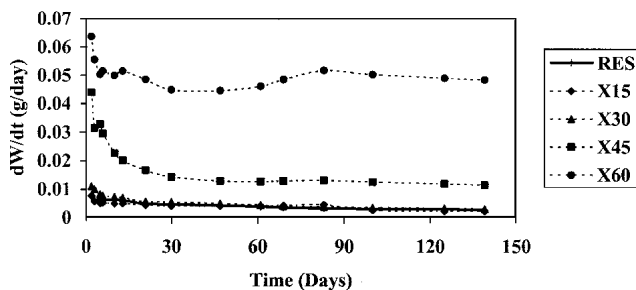


Fig. 4 Rate of water flow through membranes as function of time

Table 3 Results of Visual Observations in Salt Spray Cabinet

Organic Coating System	Salt Spray Test			
	Exposure Time: 23 Days		Exposure Time: 60 Days	
	Blisters	Rust	Blisters	Rust
RES	No. 6 Few	8	No. 4 Medium	6
X15	...	10	...	9
X30	...	9	...	9
X45	...	7	...	5
X60	...	6	...	5

epoxy matrix (ideal Fickian behavior), while the second one could be due to the flow of water molecules along the quartz particles–epoxy matrix interfaces, followed by diffusion through the epoxy matrix. Finally, the third one could be due to the transport of water through microcracks within the polymeric matrix owing to swelling, or through pores or small channels already presented in the matrix or generated by the high filler content.

Filled coatings exhibit a higher initial rate of water flow that increases with the filler content increase. This suggests that interfacial water transport or even flow through microdamages in the material is the dominant mechanism from the first stages of penetration, although water diffusion through the bulk of the polymer also appears.

Note that the time of the first change in the slope of the curves, which indicates the initiation time of the appearance of the second water penetration mechanism, lowers with the increase of quartz content, leading to the following rank order:

$$t_{x15}(\sim 530 \text{ hr}) > t_{RES} \\ \approx t_{x30}(\sim 216 \text{ h}) > t_{x45}(\sim 127 \text{ h}) > t_{x60}(\sim 69 \text{ h})$$

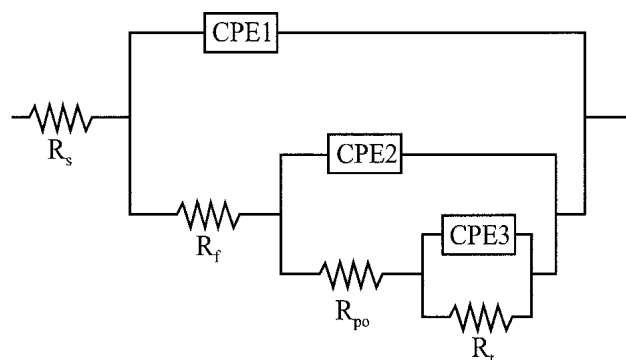


Fig. 5 Equivalent circuit for EIS analysis for nonbarrier coating.  $R_f$ , resistance of bulk coating;  $R_{po}$ , resistance of pores;  $R_t$ , polarization resistance. CPE<sub>*i*</sub> suffixes 1,2,3 correspond to bulk coating, pores, and double layer, respectively.

This ranking is also valid for the transition from the second to the third step in the case of high filler content, since the sharp change in the slope starts at 1314 h for X45 and ~893 h for X60, respectively. These results are in accordance with the visual observations after exposure in a salt spray cabinet.

The change with time of the dielectric properties of the organic coatings was examined by EIS measurements. Real and imaginary components of impedance measured were analyzed, based upon the equivalent circuit of Fig. 5. In this circuit, ideal resistor capacitor (RC) elements of a generally accepted equivalent circuit for a nonbarrier coating<sup>[21,22]</sup> have been replaced with distributed elements, such as constant phase element (CPE),<sup>[23]</sup> which accounts for the inhomogeneity that characterizes such complex systems.

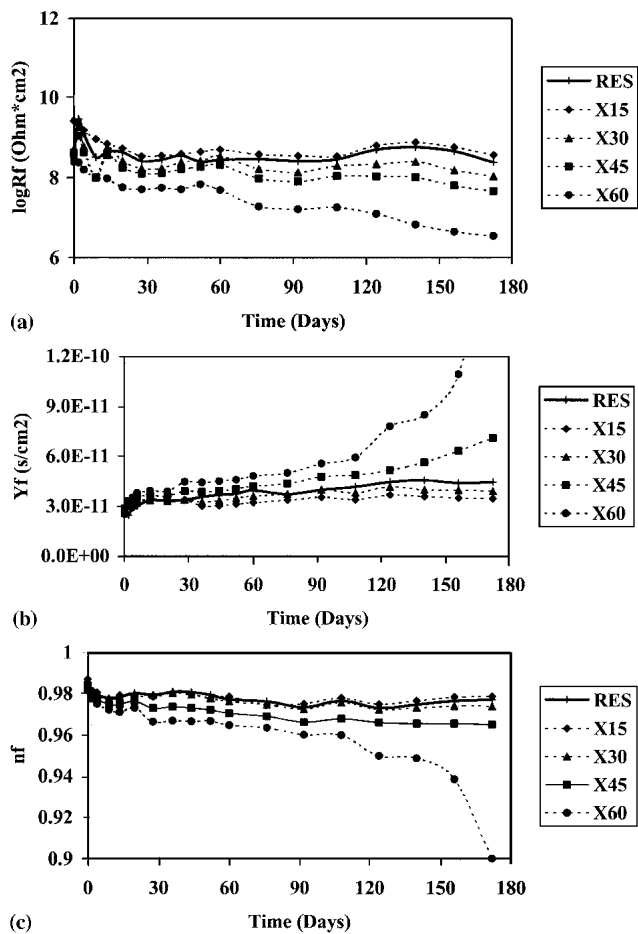
Typically, the CPE indicates the distribution of the relaxation times within a system and is defined by the following equation:<sup>[24,25]</sup>

$$Z = (j\omega)^{-n}/Y_0$$

where  $\omega$  is the angular frequency ( $\text{rad s}^{-1}$ ),  $Y_0$  is the amplitude of the constant phase element ( $\Omega^{-1}$ ), and  $n$  is the CPE power,  $n = \alpha\pi/2$ , where  $\alpha$  is the constant phase angle of the CPE (rad).

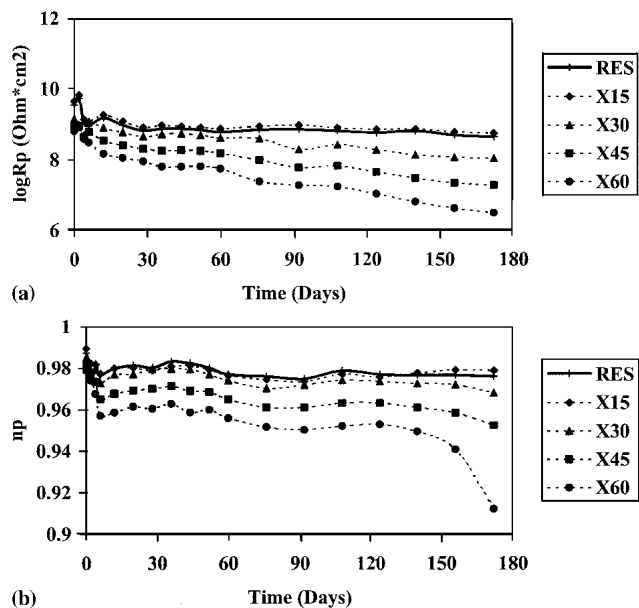
Time dependence of bulk coating resistance is presented in Fig. 6(a). Just after exposure to the corrosive environment for a short period, the resistance,  $R_f$ , of all types of coatings decreases followed by an increase which leads to a more or less plateau value for coatings containing 0-30% quartz. Just after exposure, water penetrates the capillaries and microdefects of the coatings, resulting in an increase of coating permittivity and consequently in a decrease in the coating resistance values.

The early stage increase of the coatings' permittivity also arises from the initial increase of the CPE constant  $Y_f$  values (Fig. 6b). Thereafter, the sorbed water of the coating is transported through the capillaries into the bulk of the coating, provoking local swelling effects which result in reduced capillaries and consequently to the observed increase of  $R_f$  values. The almost steady state  $R_f$  value of coatings containing 0-30% quartz remains higher than about  $5.10^8 \text{ Ohm} \cdot \text{cm}^2$ , which suggests that there is no significant change with time of the coat-



**Fig. 6** (a) Variation of resistance  $R_f$ , for bulk coatings as a function of exposure time; (b) variation of CPE constant  $Y_f$ , for bulk coating as function of exposure time; (c) variation of CPE power  $n_f$ , for bulk coating as a function of exposure time

ing's electrical characteristics, indicating thus, the maintenance of a protective behavior of these coatings.<sup>[26]</sup> The  $R_f$  plateau value for the coating filled with 15% quartz remains about the same as that of the pure epoxy coating during the whole exposure time. This is also valid for the values of CPE power  $n_f$ , whereas  $Y_f$  seems somewhat lower for the composite coating with 15% quartz. The behavior of coatings with 30% quartz is similar, while the filler's further increase generates changes in the inherent characteristics of the coatings. This, in turn, leads to a significant increase of  $Y_f$  values and to a decrease of  $R_f$  values of about two orders of size, suggesting thus a worsening of their behavior. The same behavior is also evident in the variation of CPE power  $n_f$  values (Fig. 6c). The behavior of the CPE depends on  $n$  in the following manner: for  $n = 1$ , the CPE becomes a simple capacitor, and for  $n = 0$  or  $n = -1$ , the CPE becomes an ideal resistor or inductor, respectively. Coatings containing quartz up to 30 wt.% exhibit  $n_f$  values of about 0.98 or even higher throughout the exposure time, indicating a high degree of homogeneity for the coating and the maintenance of its protective characteristics,<sup>[27,28]</sup> a result that is in agreement with those of visual observations. For coatings with quartz content higher than 45%,  $n_f$  acquires lower values from



**Fig. 7** (a) Variation of resistance  $R_p$ , of the coating pores as a function of exposure time; (b) variation of CPE power  $n_p$ , for coating pores as a function of exposure time

the beginning of the exposure, but the difference becomes more pronounced after about 120 days of immersion and especially for coatings containing 60% quartz. This could characterize a nonhomogeneous multiphase system (epoxy-quartz grains-water inclusions), due to a possible approach of the critical pigment volume concentration. These results are in agreement with those of the resistance  $R_p$ , and CPE power  $n_p$ , of the coating pores (Fig. 7a,b). Coatings with 15% quartz exhibit about the same  $R_p$  and  $n_p$  values as those of the pure epoxy coating, while for coatings with 30% quartz these values are somewhat lower, especially after three months of exposure. Those of coatings with higher filler content are significantly lower, indicating an increased water penetration as well as an increase in the area of pores.

## 4. Conclusions

The investigation of the effect of quartz filler on epoxy coating characteristics has led to the following conclusions:

- As it concerns the mechanical characteristics of the coatings, addition of quartz in the epoxy matrix, especially up to 30 wt.% filler content, enhances the coating's elastic characteristics, resulting in an increase in abrasion resistance. Composite coatings containing 15 wt.% quartz as well as pure epoxy resin coatings exhibit the best behavior regarding their impact resistance to falling weight.
- Shore D hardness and pencil hardness of the coatings increase with the increase of quartz content.
- Visual observations after the salt spray test evidenced an improvement of the anticorrosive performance of all composite coatings as it concerns blister formation, while the

degree of rust is lowered only for coatings with a quartz content up to 30 wt.%.

- Coatings with 15 wt.% quartz present almost the same dielectric behavior as those with pure epoxy coatings, which are characterized by the maintenance of their protective properties. The behavior of coatings with 30 wt.% quartz is similar, while further filler content increase generates changes in the inherent characteristics of the coatings, leading to a worsening of their behavior. These results are in accordance with the higher values of the initial rate of water flow through the epoxy matrix in the case of filled coatings. The water transport rate increases with the filler content increase.
- In general, the addition of 15 wt.% quartz seems to be the most favorable condition, leading to amelioration of almost all the examined characteristics of the coatings, with the exception of the dielectric ones, which remain the same as those of the pure epoxy coatings. A similar result was found in the behavior of coatings with 30 wt.% quartz.

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