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Corrosion Protection in Chloride Environments of Nanosilica Containing Epoxy Powder Coatings with Defects

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Abstract

This paper describes the use of innovative, nanosilica containing epoxy powder coatings for the corrosion protection of steel. Two types of nanosilica particles (hydrophilic -HL- and hydrophobic -HB-) were mixed by ball milling with the powders (0.75 wt.%). The adequate homogeneity and embedding of nanoparticles were verified by transmission electron microscopy. The corrosion performance of the coatings as-received, and with HL and HB additions, were analyzed in 3.5 wt.% NaCl solutions. The mechanism and rate of delamination of defective coatings under drops simulating atmospheric conditions were analyzed by Scanning Kelvin Probe measurements for 30 days. The results show that the corrosion attack progresses through a cathodic delamination mechanism. Besides, fully-immersed samples, with and without defects, were monitored by electrochemical impedance spectroscopy. In defective coatings under these conditions, the occurrence of anodic undermining is proved. The results obtained reveal that the corrosion driven coating failure is delayed in the case of the epoxy coatings containing nanosilica. This delay is larger in the case of HB additions than HL additions in both atmospheric and immersion conditions. The corrosion mechanism observed is dependent upon exposure conditions. It is proposed that the nanoparticles delay water absorption, thus delaying corrosion attack.

Introduction

Among the different organic coatings used to protect metals against corrosion, powder organic coatings are now becoming increasingly widespread. A recent article by IndustryArc estimated that the powder coatings market had a value of \$ 10.6 million in 2018 and predicted that it would increase by 6.1% in the period from 2019 to 2025¹. These types of coatings have great advantages, in terms of energy, material and economic savings². Primarily, their main benefit is that they do not contain volatile organic compounds (VOCs), which makes them more ecofriendly than conventional liquid coatings³. Restrictions against these VOCs have increased in order to protect health and the environment so powder coatings with optimized performances are of great interest to industry and science^{4,5}.

In addition, among the different types of powder organic coatings, epoxies are the most common due to their high mechanical (i.e. wear resistance, hardness, stiffness) and corrosion protective properties⁶⁻¹⁰. These types of organic coatings can be found in many different applications, such as domestic appliances, street furniture and in the automotive and aeronautics sectors^{8,11}, as well as in flow-handling components such as pipelines^{6,12}. They are also used in marine applications¹³ where exposure to chloride solutions is unavoidable.

Many of the frequent failures of organic coatings begin from defects due to scratches, impacts or abrasive/erosive wear¹⁴, from which the damage proceeds. Erosive wear is caused by the impact of particles against the surface of the coating, progressively reducing its thickness until the generation of small local breaks¹⁵. On the other hand, abrasive wear occurs when organic coatings are in contact with a harder material under relative movement, causing friction between both of them, and consequently, wearing the surface of the coating¹⁶.

In order to achieve good in-service performance of organic coatings, the first important aspect is to enhance their mechanical properties, that is, increase their resistance against mechanical damages that could cause the metal to be exposed to the environment. Secondly, in the case where local failure of the organic coating occurs, it would be of interest for the corrosion process to proceed as slowly as possible to minimize the electrochemical damage of the metallic component¹⁷. From the defect, the damage proceeds through the metal-coating interface by anodic delamination (if the anodes are located close to the delamination front of the coating) or cathodic delamination (if the cathodes are located close to the delamination front) mechanisms, allowing the spreading of corrosion over the metal surface. Hence, for guaranteeing its durability, it is necessary to use coatings on the steel that have good mechanical as well as corrosion protective properties.

Recent years have seen an intense search for new alternatives to increase the durability of coatings in the protection of metal substrates¹⁸. Nanotechnology stands out among these alternatives¹⁹. At present, it has already been demonstrated that the performance of some organic coatings can be improved by adding different types of nanomaterials^{20,21} to form composite coatings. Several studies have shown that the nanoadditions of SiO₂ allow some of the properties (such as corrosion and wear resistance) of conventional liquid epoxy coatings to be improved. An increase in the mechanical properties has sometimes been reported²²⁻²⁴. Other studies have focused on improvement in corrosion resistance when silica mesoporous nanoparticles have been used as nanocontainers for corrosion inhibitors²⁵. Besides that, there are other studies that report improvements on both properties²⁶⁻³⁰, relating the improvement in the corrosion behavior to an increase in barrier properties of the coating and a hindering of transport/diffusion of aggressive species. Focusing on powder coatings, the information is much more limited, but the improvement of the mechanical properties of epoxy-based coating with the use of SiO₂ nanoparticles as reinforcement has been demonstrated^{31,32}.

The mixing method is one of the most critical aspects in the manufacturing of composite coatings. If proper homogeneity is not achieved, the organic coatings will not be able to provide better in service performance than the commercial coatings and some of their initial properties will probably worsen due to the concentration of stresses in the heterogeneities³³, and the initial barrier effect of the coating could also be eliminated²¹. Up to now, extrusion has definitely been the most widely used method for mixing powder organic coatings with nanoreinforcements^{8,18,20,34,35}. However, bearing in mind environmentally-friendly factors, other manufacturing methods that use less energy should be considered, such as the ball milling mixing method. This method is also quicker and more economical than the traditional extrusion, as it does not require a second grinding stage to obtain the powder before the application of the coating on the substrates. Moreover, it does not require the use of temperature in the mixing process, which increases its advantage in economic terms.

Until now, the ball-milling mixing method has not been studied in depth, although there are results that prove it allows homogeneous powder organic coatings to be obtained in systems such as an epoxy powder coating with SiAlON nanoparticles³⁶ and a polyester powder coating with SiO₂ nanoparticles³⁷.

Improvement in the mechanical properties when hydrophobic (HB) as well as hydrophilic (HL) particles are dispersed in epoxy powders by ball-milling has also been already shown³². From this last study, it was concluded that 0.75 wt.% HB nanoparticles promoted a great increase in wear resistance, while in the case of HL nanoparticles, a clear improvement in the wear resistance of functionalized coatings was noticed for the interval of 0.25-0.75 wt.%. However, no information

regarding the effect of these additions on the corrosion performance of the HB and HL functionalized organic coatings has to date been reported.

Cathodic delamination from a defect in organic coatings on steel has been extensively studied in the previous literature, often resorting to the Scanning Kelvin Probe (SKP) technique³⁸. This method has already been used to analyze the performance of epoxy conventional liquid systems^{13,14,39,40}, as well as other types of organic coatings^{41,42}. In addition, some authors have obtained better corrosion resistance results when studying the effect of nanoadditions in different polymer matrixes⁴¹⁻⁴⁴. However, no literature was found pertaining to the use of SKP to study the cathodic delamination of powder organic coatings. At the same time, it has also been reported that, in certain exposure conditions, anodic undermining can also occur in steel substrates when they are under defective coatings^{13,45}. Hence, it is of interest to check the mechanism that allows the attack to progress in defective powder epoxy coatings, which has not yet been studied by SKP. Moreover, studying the effect of silica nanoparticles on the progress of the corrosive attack in this type of coatings is also of relevance.

Taking into account the previous context, this work aims to study the influence of two types of silica nanoparticles (hydrophilic, HL, and hydrophobic, HB) on the corrosion performance of epoxy powder coating under drops for 30 days -using a SKP-, and also during longer full immersion exposure -while monitoring by an electrochemical impedance spectroscopy (EIS)-.

Experimental

Materials and samples preparation

In this study, a commercial epoxy powder coating (provided by Cubson International Consulting S.L.) was used. This commercial powder contains as fillers dolomite (24 wt.%), talc (14 wt.%) and TiO₂ (2wt.%). Two types of silica nanoparticles were used: HB and HL. The characteristics of each type of nanoparticle –according to the supplier Aerosil® (Evonik, Essen, Germany)- are shown in Table 1.

The selection of the percentage of the silica nanoparticles added in this study (0.75wt. %) is based on the optimization of the wear resistance and hardness of the epoxy powder coatings published in other work²⁵. The mixing method used to obtain homogeneous organic coatings was the ball milling process. A two-body planetary ball mill Pulverisette 5 (Fritsch, Germany) was used. The mixtures were made under dry conditions during 10 min at 200 rpm, in a 250 cm³ vessel. Stainless steel balls with an 8 mm diameter were used and the ratio of material/balls was 1:10.

The epoxy based powder coatings were applied on degreased carbon steel sized samples of 0.8 mm thickness. The powders were sprayed with an electrostatic spray gun (Pulverizadora Manual Easyselect) with a control unit OPTITRONIC (ITW GEMA, Switzerland) and the voltage source used was 100 kV DC. The curing of the epoxy powder coatings was performed in an oven (180 °C and 15 min) according to the manufacturer's conditions for non-modified epoxy coatings. The suitability of these conditions for this type of functionalized powder was verified in a previous work ³².

Three types of coatings were studied: the coating manufactured with the as received powder (labeled as AR), the coating manufactured with powders mixed with hydrophilic silica nanoparticles (labeled as 0.75%HL), and the coating manufactured with powders mixed with hydrophobic silica nanoparticles (labeled as 0.75%HB). The final coating thicknesses obtained were determined with a thickness gauge (Elcometer 456, Manchester, UK) and were about 60±10 µm.

Physical characterization of the powders and coatings

In order to study the homogeneity of the two types of silica nanoparticles in the epoxy powder, a study was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Powder mixtures were analyzed by SEM, coupled with energy dispersive X-ray spectroscopy (EDS), using Teneo-LoVac (Thermo Fisher Scientific Inc., USA) equipment with a 10 kV electron beam.

Then, the samples were characterized by means of high resolution transmission electron microscopy (HRTEM) using a Philips Tecnai F20 Transmission Electron Microscope (TEM) (Philips, Eindhoven, The Netherlands) operated at 200 kV with a Scanning Transmission (STEM) module and High Angle Annular Detector (HAAD) for Z-contrast imaging. The microstructure of the samples was studied using bright field (BF) TEM images and the composition was measured by means of EDS in STEM-mode. The samples were prepared using a carbon grid.

Water absorption values were obtained from samples following both 2 and 7 days of immersion in 3.5 wt.% NaCl at 93% relative humidity (RH). For this purpose, coating films were manufactured on a Teflon plate, curing them under the same conditions as coatings on steel (180 °C and 15 min). The water absorption in both cases was calculated from the three films of each epoxy coating. The thickness of each film was 200±20 µm and with the dimensions of 1.5x1.5 cm approximately. The water absorbed was gravimetrically determined with a balance of ±0.1 mg accuracy.

SKP measurements

The delamination of the organic coatings was measured by SKP (SKP5050, KP Technology, UK). SKP is a non-destructive and non-contact technique for measuring the potential between the sample (the working electrode) and the reference electrode^{13,46}. In this study, samples with a size of 30x20 mm were used with a defect of 10x10 mm. An electrolyte reservoir was created around the defect with a methacrylate adhesive, using a glue gun to place the 3.5 wt. % NaCl solution. A diagram of the test can be observed in Fig. 1. The reference electrode (SKP tip) used was a vibrating stainless steel probe with a diameter of 500 μm . The probe was set to vibrate at 65 Hz frequency and the probe amplitude was in the range of 40 μm . All the measurements were performed in a controlled chamber with 93% RH and at 17 ± 1 °C. Potential measurements refer to the standard hydrogen electrode (SHE) after the calibration of stainless steel electrode against Cu/CuSO₄. The procedure is explained by Leng et al.⁴⁶

Before the first measurement, the samples were placed in the humidity chamber of the SKP for 24 h in order to allow equilibrium to be reached at high humidity. Then, a drop of 3.5 wt.% NaCl solution (with a volume of 5 μl approximately) was added to study the progress of the attack. Tests were carried out in situ until the 30th day after the drop-placement. The drops were not allowed drying during the 30-day testing period. The measurements were carried out at seven specific times after placing the droplet (1, 2, 3, 6, 12, 20 and 30 days). The probe was scanned from the defect towards the epoxy coating along a 6 mm line. Two samples of each coating were tested. For each sample and testing time, 12 profiles were measured. The position of the delamination front is quantified considering the criterion established in previous studies^{47,48}.

Corrosion immersion tests

Steel samples with defective and non-defective coatings -of the 3 types under study- were immersed in 3.5 wt.% NaCl solutions at room temperature. To prepare the defective coatings, artificial defects were made, using a sharp tool with a 1 mm wide blade (as that proposed for making scribes in ASTM D1654 standard). The defects had an area between 1.7 and 2.5 mm². Their electrochemical behavior was monitored by EIS. The measurements were carried out in triplicate in each condition. The measurements were carried out using a BioLogic potentiostat SP200 (BioLogic, France) for defective coatings and a Gamry 600+ potentiostat (Gamry Instruments, USA) for non-defective ones. A three-electrode cell was always employed. For defective coatings, an Ag/AgCl electrode was the reference electrode, a stainless steel grid was the counter electrode, and steel coated samples acted as working electrode, with an area of approximately 3 cm². For non-defective coatings, a saturated calomel reference electrode (SCE), a stainless steel wire as a counter electrode, and steel coated samples as working electrode were used. The study was carried out at open circuit potential (OCP) with a signal amplitude of 10 mV_{rms}. Frequency ranges were 10^5 to $5 \cdot 10^{-3}$ Hz and 10^5 to 10^{-2} Hz for defective and non-defective

coatings, respectively. The low frequency limit of measurements carried out for non-defective coatings was determined by the high resistance of the systems at these frequencies, which hinder accurate impedance determinations at minor frequencies as the inner impedance of the potentiostat is overcome. The subsequent analysis of EIS spectra was performed in the ZView software (Scribner Associates).

The exposure of immersed defective coatings lasted up to 50 days. After that, the epoxy coatings were carefully detached, the rust was cleaned with nitric acid and the morphology of the defects was analyzed. A digital microscope (model VHX-100, lens zoom VH-Z100R, Keyence, Japan) and an optoelectronic microscope (Olympus DSX500, Olympus Corporation, Japan) were used for this study in order to obtain 3D images.

Methacrylate tubes (with a 1.6 cm diameter) were bonded on non-defective coatings to carry out measurements in these areas. The exposure was extended up to one year due to difficulties in obtaining EIS spectra for such coatings.

The EIS spectra of non-defective coatings was normalized using the area of the coatings exposed to the solutions, while, for the defective coatings the original area of the defects was used for these calculations.

Results and discussion

Homogenization of silica nanoparticles in the epoxy powder

One of the most critical issues when coatings are functionalized with nanoparticles is to obtain their homogeneous distribution in the polymer, since agglomerates can worsen the initial coating properties⁴⁹. Therefore, it is necessary to verify that good distributions have been achieved, and also that the nanoparticles are well embedded in the epoxy matrix, so they can have a positive effect on the final properties.

SEM observations do not allow distinguishing the nanoparticles on the epoxy powders due to their small size and good dispersion achieved. After an extensive EDS analysis of the chemical composition of the particles covering the surface of the epoxy powders (an example can be seen in Fig. 2a), no isolated particle can be identified with SiO₂ composition. Therefore, no agglomerates have been detected using the SEM technique, even when observations at higher magnifications are carried out (Fig. 2b), and the presence of silica agglomerates can be discarded. The mixing procedure promotes the breaking-up of pre-existing silica agglomerates and the incorporation of nanosilica to the epoxy powders as isolated particles. Isolated nanoparticles are so small that they cannot be observed by SEM, but agglomerates, if they existed, would have been visible.

In Fig. 3, higher-resolution TEM images corresponding to ball-milled epoxy powder with silica nanoparticles (HL in Fig. 3a and HB in Fig 3b) are shown. The main objective of this study was to check if small particle aggregates -that would be undetectable by SEM because of its resolution- exist. Both silica nanoadditions (HL and HB) are found isolated in the epoxy powders and they can be visualized as spherical silica particles partially embedded on the powder surface. Moreover, the presence of aggregates of nanoparticles has not been observed. The composition of the nanoparticles was checked by EDS analysis. The results of the TEM study also show that there is good adhesion between the two types of silica nanoparticles and the epoxy powder. These observations demonstrate that, in principle, both nanoparticles can be used to reinforce this epoxy powder coating.

The use of the ball milling, a mixing method of interest because it consumes less energy and is more economical than the conventional extrusion method, has been confirmed as adequate for manufacturing these types of functionalized coatings. The good interaction between the nanoparticles and the matrix observed in Fig. 3 is consistent with their success in improving the mechanical properties observed for HB and HL additions for both types for coatings manufactured through ball milling³².

In Fig. 4, the results of the amount of water absorbed by the 3 coatings under study are plotted. The water absorption was measured after exposure for 2 and 7 days to a 93% RH (H) environment and after being immersed in a 3.5 wt.% NaCl (I). No additional weight gain was observed for longer test times, indicating that the coatings are water saturated after a week of exposure. It can clearly be observed that the specimens that have been immersed absorb a higher percentage of water than those that have been exposed to 93% RH.

Regarding the results obtained for the different coatings (Fig. 4), it can be seen that the commercial AR absorbs the highest amount of water on both exposure conditions, H and I, with values around 1.35% and 1.4% respectively after 7 days. On the other hand, the 0.75%HB organic coating presents the lowest tendency to absorb water in its structure after 7 days, with mass gains of 1.05% (H) and 1.21% (I). The 0.75%HL coating shows an intermediate behavior, with 1.18% for the H samples and 1.27% for the I samples, after 7 days. The lower water absorption can be related to a higher crosslinking of the epoxy thanks to the SiO₂ nanoparticles^{10,32}, and they can also become an obstacle for water molecule diffusion through the coatings. In addition, HB nanoparticles could help to repel water compared to the other organic coatings.

SKP measurements

The SKP measurements were carried out in order to study the effect of both types of silica nanoparticles when defective epoxy powder coatings on carbon steel are exposed to 93% HR

under 3.5 wt.% NaCl drops (Fig. 1). With the SKP, it is possible to measure the potential of the steel under the intact coating, obtaining information about the corrosion mechanism that occurs underneath the coatings. It was necessary to extend the duration of the testing to 30 days as no meaningful changes were observed for short times.

The SKP profiles obtained are similar to those obtained in other previous studies carried out on coated steels^{14,42}, where cathodic delamination occurs. Some examples obtained at different exposure times can be seen in Fig. 5. All samples show low potential value in the region of the defect, indicating an anodic behavior, corresponding to active iron corrosion⁴⁵. On the other hand, the regions located at a certain distance from the defect always have a high potential value, slightly positive, which corresponds to the intact metal under the still adherent coating^{42,48}. For steel with defective epoxy coatings, other authors have identified the cathodic behavior with potential values of about -200 mV vs. SHE⁴⁵. Between these regions, an intermediate one appears, corresponding to the cathodic activity under detached coatings^{Error! Marcador no definido.,47,50}. The ohmic drop due to the ingress of the electrolyte under the coating also contributes to the potentials observed in this region.

The potential difference between the defect region and the still adherent coating decreases with the testing time. For the AR coatings, the averaged potential differences decrease from about 0.71 V the first day to 0.45 the last one. Concurrently, the averaged potential difference decreases from 0.69 V to 0.30 V for the HL coating, and from 0.71 to 0.53 V for the HB, in the same testing period.

For these measurements, the location of the delamination front is assumed to be at an intermediate point between the anode and the intact metal surface (theoretically in contact with one end of the cathodic region). In the present study, the location of the delamination front is determined by the first derivative of the potential, following the method explained in other works^{47,48,50}. From graphics such as those in Fig. 5, the location of the delamination fronts has been calculated and its average advance for the different types of coatings under study is plotted in Fig. 6.

In previous researches, it has been often assumed that the cathodic delamination process is exclusively controlled by the diffusion rate of Na⁺ cation from the bulk of the drop to the cathodic region^{13,51}, to allow a local increase of the OH⁻ concentration in that region which is high enough to cause the debonding of the coating⁵². This mechanism should provide a parabolic relationship between the advance of the delamination front and the exposure time^{42,47,53}. For the studied coatings, the fittings related to the advance of the delamination front with time are included in Fig. 6a. The experimental relationship found is far from being parabolic (a parabolic

relationship would imply a time -x- exponent of 0.5 approximately, and in these cases, they range between 0.25 and 0.28, Fig. 6a). To understand the present results, it must be borne in mind that many of the pioneering, basic studies of cathodic delamination with SKP were carried out using thin and/or non pigmented coatings with high O₂ permeability^{40,54}, so the diffusion of this substance through the coating is easy and has a negligible impact on the kinetics. The use of high quality coatings, together with their partial saturation with water due to the high length of the test (Fig. 4), should affect O₂ diffusion. The influence of changes on the O₂ concentration in the progress of the cathodic delamination has already been demonstrated by other authors^{41,55,56}. Moreover, as has already been stated, under certain circumstances, the oxygen diffusion rate through the coating can control the delamination kinetics on steel⁴¹. For the studied systems, under drops and in an environment with 93% HR, there is a complex mechanism controlling the progress of the attack, which makes the kinetics different from those exclusively governed by a simple Na⁺ diffusion. From the results plotted in Fig. 6a (with exponent about the half of the typical parabolic curves), it can be clearly deduced that the rate of the cathodic delamination decreases with the exposure time more markedly than parabolic kinetics.

It is very important to point out that the progress of the delamination front is faster for the AR coating than for the other two functionalized coatings under study (Fig. 6). Moreover, the 0.75%HB coating behaves much better, since its delamination front progresses at a lower rate than that corresponding to the 0.75%HL. The first days, the differences between the AR and 0.75%HL are small, being the 0.75%HB the coating always with smaller progress of the delamination front. As an example, after 6 days, the 0.75%HB coating has a delamination of less than 1 mm, while the AR and 0.75% HL present a value of around 1.5-1.7 mm. Then, the 0.75%HL starts to show clear differences from AR. After 20 days, the delamination front values of AR, 0.75%HL and 0.75%HB coatings are 2.1, 1.8 and 1.4 mm respectively. Though other factors can influence the rate of advance of the delamination front, it is often assumed that it depends on the resistance of the bonds formed between the metal surface and the coating³¹ to the alkaline pH generated by the cathodic reaction of oxygen reduction ($O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$) that occurs in this region. The highest crosslinking in SiO₂ containing coatings (shown also in a previous work³²), suggested by their lower water absorption (Fig. 4) and improved mechanical properties and wear resistance of coatings³², is usually associated with an increase in the adhesion of the coatings to the metal substrate³¹. In this case, the SiO₂ additions seem to succeed in improving the adhesion of the coating to the steel, reducing the advance of the delamination front. However, the aggressiveness of the media in the coating-metal junction can be another key point and the stronger this bond is, the better the coating performs. The lowering of O₂ permeability due to enhanced crosslinking can also affect the progress of the delamination front. Khun *et al.*⁴² have also found improvements in the delamination resistance by adding carbon nanotubes to a

polyurethane coating, related to the blocking of transport pathways of water and oxygen molecules through the organic coating. Glover *et al.*⁴¹ also demonstrated similar mechanisms after adding graphene nano-platelets to their coatings. Moreover, the lower water absorption promoted by the nanosilica additions (Fig. 4) and the higher crosslinking of the polymer drawn from the increase on the mechanical properties³² are consistent with coatings with lower water and oxygen permeability. Moreover, the thickness of the coatings (about 60 μm) contributes to make this effect more noticeable.

In Fig. 6b, the progress of the delamination front for the different coatings has been plotted against the square root of the exposure time. Fitting them using linear relationships starting from the origin –which would correspond to simple parabolic kinetics- would be clearly unacceptable. However, a two-step kinetic could be reasonable as has been shown in previous works⁵⁵. The proposed hypothesis considers that the delamination for all the coatings could follow an initial fast kinetic and then change to a slower one due to changes in the mechanism. Both kinetics would be parabolic, as corresponds to phenomena controlled by diffusion. In this case, the first step of the delamination can be controlled by Na^+ diffusion, and after a time, by O_2 diffusion. Initially, when the coating was not water-saturated, the O_2 diffusion through it must have been high and its effect on corrosion rate less noticeable. However, the amount of O_2 that water can dissolve is lower than that present in air, so when the coating is water saturated, the O_2 permeability is reduced and the O_2 concentration that reaches the metal-coating interface starts to limit the advance of the delamination front. The transition time from the first step to the second would depend on the quality of the coating, being shorter for 0.75%HB coatings (in fact, it would take place before the first measurement was carried out), but it would last nearly one week for the AR coating.

From the results in Fig. 5, it can also be observed that the potential difference between anodes and cathodes decreases with time. This is due to the fact that the potential of the defect tends to increase with time because of the formation of corrosion products in this region. The oxides formed during the electrochemical attack can augment the Volta potential of the steel, as has already been reported in some recent studies^{57,58}. The power of the corrosion cells is related to the difference existing between the potential of the active steel surface in the defect (anode) and the potential of the passive iron under the coating⁴⁵. These decreasing potential differences can also contribute to explain, at least partially, the slowing of the kinetics with time shown in Fig. 6, which is much more marked than that predicted by Fick's law.

The anodic front is the distance from the defect where an almost constant anodic potential can be observed. An example has been marked for the AR curve corresponding to 30 days in Fig. 5. The evolution of the length of this region has been plotted in Fig. 7. There is an obvious relation

between the data in Fig. 7 and that in Fig. 6. The progress of the delamination front under the coating allows the anodic region to grow, and confirms the positive effect on the epoxy coating durability that HB additions can have. The increase in the size of the anodic region (Fig. 7) was accompanied by an increase in its potential (Fig. 5). This could be related to the observed decrease in the rate of the attack (Fig. 6).

Immersion tests

Epoxy coatings are often part of the painting systems used to protect marine applications¹³ that are likely to be exposed to full immersion in a chloride environment during their in-service lives. An EIS monitoring of the AR, 0.75%HL and 0.75%HB coatings when they are fully immersed in NaCl 3.5 wt.% solution has been carried out in the present research. The study is mainly focused on the performance of defective coatings, but also considered the non-defective coatings as an interesting reference.

In Fig. 8, examples of the EIS spectra obtained after one-year immersion of the three non-defective coatings can be observed. The impedance values demonstrate the outstanding protective effect of the different epoxy coatings. The impedance modulus of the organic coatings that contain nanoparticles is slightly greater than the AR coating. After such long immersion times, the values of the impedance at high and medium frequencies are very similar for all the tested samples. The identical capacitive behavior observed in these regions (phase angles close to 90° and modulus of the impedance, $|Z|$, which increase as the frequency decreases) suggests that the eventual water absorption (which affects the dielectric constant of the coatings, and so their capacitance) has been very similar. There is resistive behavior defined at low frequencies (phase angles close to 0° and almost constant values for $|Z|$) that can be identified with the resistance of the pores. The multiplicity of the tests carried out indicates that the differences among coatings shown in the examples of Fig. 8 are not meaningful, as fitted values of spectra (Table 2) shows. For the studied coatings, this parameter is only dependent on small local heterogeneities of the coatings caused by the application, but not by the nanoadditions.

Regarding the samples with defects, the coatings were detached after 50 days of immersion, and the rust present on the metal surfaces was cleaned. In Fig. 9, the appearance of the defects and their surroundings after exposure can be seen. Moreover, optoelectronic images of the topography of the defects have been included in the lowest image row of Fig. 9. The color scale bar at the bottom-right of the figure allows understanding the depth of the attack. AR and 0.75%HL coatings exhibit an intense corrosive attack in the region that surrounds the initial defects (blue and purple areas), while the surfaces directly exposed to the bulk solution have only suffered a mild attack (they are green colored). The anodic process has also taken place around

the defect caused in the 0.75%HB coating and some slight metal dissolution has occurred (green and blue areas surrounding the purple/blue regions). However, in this coating, the most intensive corrosion has occurred in the surface directly exposed to the bulk solution.

Obtained results demonstrate that, when the corrosion occurs in defective coatings, its mechanism is different if the process develops under small drops (Fig. 5) or under full immersion conditions (Fig. 9). The different oxygen access to the corroding region can explain this change in the corrosion mechanisms, which are schematically summarized in Fig. 10. Under drops (Fig. 10a), the surface of the coating around the defect is exposed to the air. The usually high O_2 permeability of non-water-saturated polymers⁴² allows the O_2 concentration reaching the metal surface close to the coating-substrate interface to be higher than the O_2 concentration in the surface under the middle of the NaCl solution drop (the limited solubility of air in aqueous solutions is still lower when they have dissolved salts). Thus, the activity under the central part of the drop is anodic, as less O_2 reaches this region and, hence, the metal is oxidized there. The corresponding cathode is located under the coating, where a high alkaline environment is generated and the metal-coating bond is destroyed. This is the well-studied cathodic delamination mechanism of organic coatings, which often occurs when steel corrodes under drops¹³. A higher number of bonds and a lower O_2 diffusion through the coating can explain the inhibitory effect of the tested nanodadditions in the progress of the attack, as it has been already discussed.

In Fig. 10b, a mechanism that can explain the observations in Fig. 9 is proposed. When the organic coatings are water saturated (Fig. 4), the O_2 diffusion is obviously reduced. If a thick layer of electrolyte covers all the surface of the specimen, there is no preferential access of O_2 to the metal-coating interface, so a cathodic detachment process can hardly occur. In full immersion conditions, it is logical to assume that the O_2 access to the metal surface would take place more easily for uncoated surface than through a water saturated organic coating. Moreover, the penetration of corrosive ions through the detached coating from the bulk solution to the electrolyte close to metal-coating bond cannot be completely discarded. So, the occurrence of intense anodic undermining can be understood in this case.

It has been previously published that, under full immersion in chloride solutions, other epoxy coatings suffered cathodic detachment, through a degradation mechanism similar to that studied for corrosion under drops¹³. However, the influence of O_2 concentration has been shown to be a key factor in the development of a corrosive attack under defective coatings⁵⁵. The thickness and highly protective nature of the coatings under study could also have influenced the development of an anodic undermining attack under these conditions.

Obviously, for the AR and 0.75%HL coatings, before the onset of the anodic undermining attack, a generalized corrosion has taken place on the uncoated surface (in Fig. 9, it can be seen that the region corresponding to the original defects has suffered a moderate loss of metal for the AR and 0.75%HL coatings). After a time, when the coating-metal bonds at the boundaries of the defects have weakened -due to rust generation, pH changes, or other processes- the metal oxidation is focused under the coating. The anodes locate in the regions with lowest O₂ access and the uncoated region becomes preferentially cathodic (Fig. 10b), hindering the metal dissolution there.

The images in Fig. 9 corresponding to the 0.75%HB coating can be understood considering the higher number and/or quality of the metal-coating interactions in this coating, which may have led to a delay in the onset of the attack under the organic coating. This hypothesis would explain the deepest attack on the defect area (blue and purple color), as the cathodic protection for the initial defect region that the anodic undermining implies has just started to act in the 50-day exposure period. This initial stage of general corrosion should also have taken place for the other two coatings under study, but with a shorter length (the region corresponding to the original defect is green and yellow, but only very locally blue).

During the 50-day immersion period of the defective coatings, the OCP also show values typical of an actively corroding steel. For all the systems, this parameter reaches its minimum, quite stable value after 30-40 s of exposure (from -700 to -720 mV vs. Ag/AgCl). As exposure proceeds, the E_{corr} values show a slow increase for all the systems up to about -675 or 670 mV vs. Ag/AgCl. This increase could simply correspond to ohmic drop introduced by the oxides that are formed during the attack. These values are clearly lower than those observed for the long term test of non-defective coatings, whose EIS spectra have been shown in Fig. 8.

In Fig. 11a, examples of the EIS spectra obtained during the immersion of the 3 coatings with defects can be seen. Impedance of the non-defective regions of the full immersed coating is so high (Fig. 8) that its contribution to the spectra is negligible and the electric signal finds a preferential way through the defect. Accordingly, the initial area of the defects has been used to plot the results in Fig. 11.

It can be confirmed that spectra are quite similar for the 3 systems under study. The global impedance measured for all the systems always decreases with the exposure time. An example corresponding to 0.75%HL coatings is shown in Fig. 11b and similar trends are observed for the impedance of defective AR and 0.75%HB coatings under immersion.

For an adequate simulation of the experimental impedance data, an equivalent circuit such as that shown in Fig. 12a is needed. In this circuit, R_s is the resistance of the electrolyte in the

bulk solution, R_1 and CPE_1 are used to simulate the resistive and capacitive behavior of an electrochemical process taking place in the oxide layer, probably the oxidation of Fe^{2+} cations to Fe^{3+} . The observation of an increasing appearance of the typical red-brown colored Fe_2O_3 oxides as exposure continues can confirm this hypothesis. The R_2 and CPE_2 can simulate the charge transfer resistance and the double layer capacitance of the corrosion process. The time constant at low frequencies (R_3 and CPE_3) hardly appears in the measurement frequency range used but it determines the shape of the spectra at the lowest frequencies. It has been included in the equivalent circuit to achieve a good fitting of the spectra, but the values obtained for these parameters are not reliable because they correspond to resistive and capacitive behaviors that are not clearly defined until frequencies quite lower than those of the measurement range. This time constant likely corresponds to the oxygen diffusion impedance, which usually exerts a certain -but not determining- influence on the corrosion kinetics of the steel in neutral solutions with chloride concentrations that are high but under 5%⁵⁹.

The quality of the simulation achieved with this circuit in Fig. 12a can be verified in Fig. 11. Later on, the fitted values for the parameters (i.e., R_1 , R_2 , CPE_1 and CPE_2) will be presented and analyzed (Fig.13 and 14).

On the other hand, the impedance response of the electrochemical process taking place on the metal under the organic coating must be non-uniform. The organic coating has a non-conductive nature, so the electrical signal goes through the very thin electrolyte layer existing between the organic coating and the metal. Theoretically, the use of a transmission line model (Fig. 12b)^{60,61}, would be necessary to understand the contribution of these areas. However, the resistance per surface unit of this layer of electrolyte is very high due to its low thickness⁶⁰ and the electrolyte resistance under the coating also increases the impedance corresponding to these regions. Hence, the contribution of the electrochemical process under the coatings is shifted very far away of the frequency range used in the measurements and its effect in the spectra becomes negligible for all the cases under study. Obtaining information from the process taking place in regions inside a debonded coating is not easy. In the reviewed paper published by Mahdavi et al⁶¹, it is reported that other authors studying cathodic delamination of organic coatings have found no correlation between EIS parameters and the debonded area.

In Fig. 13, the values obtained from the simulation for R_1 and R_2 are plotted. After the first hours of exposure, the decrease in both parameters becomes evident for the 3 systems studied. This decrease suggests that both processes can have a certain autocatalytic nature. If R_1 is related to charge transfer associated to the oxidation of Fe^{2+} to Fe^{3+} , the increase on the amount of Fe^{2+} should affect this redox process. The effect of the oxides' transformation on EIS spectra has been previously commented in the literature^{62,63}. A two order of magnitude decrease on R_1 value takes

place during the exposure, with its values being almost negligible for the 3 systems during the last weeks of exposure.

Conversely, R_2 , which is related to the process that controls the kinetic of the attack, that is to say, the charge transfer process, also decreases after the first day of immersion, although to a lesser extent than R_1 . The effect of the already formed oxides can explain this fact. The iron oxides are very effective cathodes, especially when they are Fe(III)-rich, so stable layers of these compounds can favor the attack on metal surfaces not covered by oxides. In addition, a local decrease of the pH on anodic sites can also foster the metal dissolution and be related to this trend.

If it is assumed that the anodic process taking place under the anodic coating hardly affects the impedance spectra, it can be assumed that the intensity of cathodic reaction occurring on the non-coated defects determines the R_2 value when the attack proceeds through an anodic undermining mechanism. It is worthwhile recalling that, when uncoated steel corrodes in 3.5 wt. % NaCl, the kinetic of process is also controlled by the cathodic semireaction⁵⁹. Thus, the corrosion rate in this case is probably influenced by the oxygen content of the solution.

In Fig. 14, the values obtained from the simulation for the CPE are plotted. Both CPE_1 and CPE_2 exhibit stable values during their first week of exposure, and then, their values increase, with the rise being more pronounced with time for CPE_2 than for CPE_1 . The capacitive elements used in the simulations, besides the CPE values plotted in Fig. 14, comprise values for the n parameter, which measures the deviation from an ideal capacitor behavior, with the deviation being higher as the n value is lower. The values obtained for n_1 are always around 0.8 for all the coatings and time studied. For n_2 , the values for the three coatings are initially very high; they exhibit values higher than 0.90 for the spectra acquired during the beginning of the immersion and then they decrease to values around 0.7. The decrease starts taking place before for the AR and 0.75%HL defective coatings, about the first 6-8 h, while it occurs on the 6th day of exposure for the 0.75%HB coating. The non-uniformity in the distribution of the corrosion process on the metal surface can easily explain this phenomenon.

Therefore, obtaining electrochemical information about the progress of the corrosive attack under defective coatings is not easy, at least for non-localized electrochemical techniques^{Error! Marcador no definido.,⁶⁴}. Differences in the mechanism as those reflected in Fig. 9 cannot be directly monitored with spectra such as those in Fig. 11, but information about the decrease in the global impedance of the defective coating systems are obtained. Quantification of the parameters that control the kinetic of the electrochemical reactions on the defects informs that an attack with an autocatalytic mechanism is taking place.

Conclusions

The aim of this article was to evaluate the effect of the nanoaddition of two different silica nanoparticles on the corrosion performance of an epoxy powder coating. After the study, the following main conclusions can be drawn:

- The TEM images confirm that the ball-mixing method allows good homogeneity of the two types of SiO₂ employed (HL and HB) in the epoxy matrix of powder coating.
- The addition of silica nanoparticles slows down the water absorption in a high RH environment and in immersion. The hindering of the water absorption process is more marked for HB coating than for HL
- For the coatings under study, when the attack takes place under drops and the coating just close to the defect is exposed to the air, it proceeds through a cathodic delamination mechanism, while for defective coatings immersed in 3.5 wt.% NaCl solutions, the corrosion proceeds by anodic undermining.
- The addition of silica nanoparticles to the epoxy powder allows the coating to be more resistant to the progress of corrosion from defects. HB additions are more effective than HL in delaying the progress of the cathodic delamination, as well as in delaying the onset of the anodic undermining attack.
- The EIS results demonstrate a decrease in the impedance of the 3 defective coatings as the immersion proceeds by an autocatalytic mechanism, but this technique is unable to reflect the influence of the anodic undermining attack.

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Tables:

Table 1. Characteristics of the SiO₂ nanoparticles used in this study according to the manufacturer.

	Model	Surface area (m ² ·g ⁻¹)	Average size (nm)	Groups on the surface
Hydrophilic SiO₂ (HL)	Aerosil® 90	75-105	20	Si-OH
Hydrophobic SiO₂ (HB)	Aerosil® R202	80-120	14	Si-CH ₃

Table 2. Values obtained from the fitting of the EIS spectra for the coatings without defects (Fig. 8).

Coating	C (nF·cm ⁻² ·s ⁿ⁻¹)	n	R (GΩ·cm ²)
AR	0.16±0.01	0.96±0.01	0.5±0.5
0.75%HB	0.25±0.01	0.93±0.01	0.6±0.4
0.75%HL	0.24±0.03	0.95±0.02	0.5±0.1

Figure Captions:

Fig. 1: Diagram of the SKP test.

Fig. 2: SEM images corresponding to the surface of a 0.75%HB powder particle: a) x4000 and b) x16000.

Fig. 3: Bright Field TEM images of a) HL and b) HB SiO₂ nanoparticles embedded in the epoxy powder after ball milling.

Fig. 4. Water absorption corresponding to the epoxy coatings under study in a 93% RH environment (H) and immersed in 3.5% NaCl (I) after 2 and 7 days.

Fig. 5: SKP potential profiles of the three organic coatings at different exposure times under 3.5% NaCl drops.

Fig. 6: Delamination front (mm) of all the organic coatings vs a) time of exposure and b) square root of the exposure time (in the equation, x is the time and y is the delamination front).

Fig. 7: Anodic front (mm) of all the organic coatings vs time of exposure (days).

Fig. 8: Example of the EIS spectra (Bode) acquired during the immersion of the organic coatings without defects after one year of exposure. The equivalent circuit used to simulate data is shown.

Fig. 9. Images of the damage that has taken place in the defect region after 50 days of immersion in 3.5% NaCl.

Fig. 10: Diagram of the corrosion mechanism taking place for the coating in chloride media: a) cathodic delamination under drops; b) anodic undermining in full immersion conditions.

Fig. 11. Example of the EIS spectra acquired during immersion of the organic coating with defects: a) Nyquist plot of the spectra corresponding to AR, 0.75%HL and 0.75%HB coatings after 22 h of exposure; b) Bode plot spectra corresponding to 0.75%HL coating after 4 h, 2 days, 30 days and 50 days of exposure. The dots correspond to the experimental data and the continuous lines plot the fitted results after simulation (Fig. 12a).

Fig. 12. Equivalent circuits. a) Used to fit the experimental data. b) Transmission line circuit, where each Z represents the 3 RCs elements shown in Fig.12a.

Fig. 13. Time evolution of the resistance values obtained from the fitting of the EIS spectra for the defective coatings.

Fig. 14. Time evolution of CPE values for capacitive elements in the circuit.