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# Improvement of adherence and anticorrosion properties of an epoxy-polyamide coating on steel by incorporation of an indole-3 butyric acid-modified nanomagnetite

Anh Truc Trinh, Thu Trang Nguyen, Thu Thuy Thai,  
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**Abstract** In this study, synthesized magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles were treated with a corrosion inhibitor, indole-3 butyric acid (IBA) and incorporated in an epoxy-polyamide coating. The coating was applied on a carbon steel substrate. For comparison, coatings without particles or with nontreated  $\text{Fe}_3\text{O}_4$  particles were also prepared. The IBA-modified nanomagnetite (IBA- $\text{Fe}_3\text{O}_4$ ) was characterized by infrared spectroscopy and Zeta potential measurements. The inhibitive action of IBA was shown by electrochemical measurements (polarization curves) performed for a bare carbon steel in 0.1 M NaCl solution containing  $\text{Fe}_3\text{O}_4$  or IBA- $\text{Fe}_3\text{O}_4$  nanoparticles. Adherence and anticorrosion properties of the epoxy-based coatings containing  $\text{Fe}_3\text{O}_4$  or IBA- $\text{Fe}_3\text{O}_4$  were compared to those of the pure epoxy-polyamide resin by dry and wet adherence measurements and by salt spray test. The results showed significant improvement of the film adherence and higher corrosion protection of the carbon steel in the presence of IBA- $\text{Fe}_3\text{O}_4$ . It was

concluded that the IBA effect was restricted to the metal/coating interface.

**Keywords**  $\text{Fe}_3\text{O}_4$  nanoparticles, Epoxy-polyamide-based coating, Corrosion inhibitor, Carbon steel, Adherence tests, Salt spray test

## Introduction

Recently, the introduction of nanoparticles in protective coatings has attracted numerous investigations. The most commonly used nanoparticles are  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and clays.<sup>1–10</sup> For corrosion protection of metals, the addition of nanoparticles in organic coatings offers an acceptable environmental solution. The major documented benefit of the incorporation of nanoparticles in polymer coatings is reinforcement of barrier effect and improvement of mechanical properties. These effects are due to their tiny size and large specific surface area. The dispersion of nanoparticles induces additional interactions with the organic matrix and thus enhances the barrier properties. In addition, good dispersion of lamellar or plate-like shaped charges (e.g., clay platelets) in coatings increases the length of the diffusion paths of corrosive species through the film and thus improves the barrier effect.<sup>6,11</sup> The presence of nanoparticles can also reinforce the coating resistance against hydrolytic degradation and increase the coating adherence.<sup>10,11</sup> Iron oxide pigments are commonly used in organic coatings to protect ferrous substrates, particularly structural steels, due to their nontoxic, weather-resistant, and mainly opaque properties.<sup>12–19</sup> Magnetite iron oxide pigments ( $\text{Fe}_3\text{O}_4$ ) are known as black pigments and used for a wide range of applications. They confer high anticorrosion efficiency in various binders.<sup>13</sup> Although the protective mechanism is not yet well established, it has been proposed that incor-

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poration of magnetite in paints leads to interactions between the paint and the steel, delaying the corrosion process.<sup>14</sup> It has been also suggested that the magnetite pigments create an alkaline environment at the metal/coating interface which limits the corrosion process.<sup>16–18</sup> Moreover, the interactions between the magnetite pigments and carboxyl groups in alkyd (or polyester modified by fatty acid) binders can lead to metal soaps formation which can act as inhibitors at the metal/organic coating interface.<sup>16,19</sup> However, iron oxide pigments agglomerate easily due to their small size and high surface energy. This phenomenon affects their efficiency when they are directly incorporated in an organic matrix. To improve the dispersion, a modification of the surface of the nanoparticle is required. Recently, the magnetite nanoparticles were encapsulated by organic or polymeric compounds and used as corrosion inhibitors for carbon steel in acidic medium.<sup>20–22</sup> Their efficiencies were significant in 1 M HCl solution.

In continuation of our quest for developing corrosion inhibitors with high efficiency, the present work aims to prepare treated magnetite nanoparticles and then to incorporate them in an epoxy-based coating. In previous works, indole-3 butyric acid (IBA) was attached to montmorillonite clay (MMT) which is an inert filler.<sup>23,24</sup> It is well known that the main role of MMT within polymer matrixes is to improve their barrier effect. Resulting from this modification, the IBA-modified clay improved the corrosion performance of epoxy coatings by both an increase of the barrier properties of the film and by the inhibitive action of the IBA molecules at the carbon steel/coating interface.<sup>23,24</sup> In the present work, IBA was used with an active filler, the nanomagnetite. IBA-modified nanomagnetite was used as an additive in an epoxy-polyamide coating to enhance the corrosion protection, particularly the coating adherence on the steel surface. As a matter of fact, a high level of adherence is required between the paint and the metal to prevent delamination. Nanomagnetite was prepared by hydrothermal method and modified by the IBA molecules (IBA-Fe<sub>3</sub>O<sub>4</sub>). A salt spray test was conducted to evaluate the corrosion protection of the epoxy-based coatings containing or not the nanoparticles. Adherence of the coatings on carbon steel surface was measured by three-point bending and was also evaluated by cross-cut test after different immersion times in an aqueous solution.

## Experimental

### Materials

For the nanoparticles synthesis, FeCl<sub>3</sub>·6H<sub>2</sub>O, FeSO<sub>4</sub>·7H<sub>2</sub>O, and KOH were purchased from Merck. Indole-3 butyric acid (IBA), purchased from Sigma Aldrich, was used as received.

The epoxy resin was unmodified diglycidyl ether of bisphenol A, Epotec YD 011-X75. Epoxy equivalent weight was about 460–490 g eq<sup>-1</sup>. The hardener was a polyamide 307D-60; equivalent weight per active H was 266 g eq<sup>-1</sup>. Both compounds were purchased from Kukdo Chemical Co., Ltd. (Korea).

Carbon steel plates (150 mm × 100 mm × 2 mm) were used as substrates. The chemical composition of the steel in weight percent was C = 0.35, Mn = 0.65, Si = 0.25, P = 0.035, and Fe to balance. The sample surface was abraded with successive SiC papers from 80 to 600 grades and washed with ethanol. The magnetite (Fe<sub>3</sub>O<sub>4</sub>) and IBA-modified magnetite (IBA-Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were incorporated at a concentration of 3 wt% in the pre-polymer mixture with xylene as solvent. This content, optimized by preliminary tests, was sufficient to achieve the required properties. The pre-polymer mixtures (with or without particles) were applied by spin-coating at a speed of 600 rpm for 90 s. After polymerization and drying at room temperature for 24 h, the coatings were about 30 μm thick (measured by Minitest 600 Erichen digital meter).

### Synthesis and surface modification of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were prepared following the protocol previously used<sup>25</sup> and is briefly recalled here: a mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O/FeSO<sub>4</sub>·7H<sub>2</sub>O (molar ratio Fe<sup>2+</sup>/Fe<sup>3+</sup> = 1/1) was dissolved with distilled water. Under stirring, a KOH solution was added to the solution until the formation of a precipitate occurred. The resulting slurry mixture was transferred to a Teflon-lined stainless steel autoclave. Hydrothermal reaction was conducted at 150°C for 7 h. After reaction, the precipitate was washed with distilled water to remove impurity ions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>) and dried in a vacuum oven at 80°C for 12 h.

IBA (0.2 g) was dissolved in a 50 mL water/ethanol mixture (1/19 ratio). Then, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles (1 g) were dispersed by an IKA T10 Ultra-Turrax disperser (30,000 rpm for 10 min) and then mechanically stirred for 180 min. The precipitate was filtered and washed with ethanol several times to remove the excess IBA. The IBA-Fe<sub>3</sub>O<sub>4</sub> nanoparticles were finally dried in a vacuum oven at 60°C for 24 h. The synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles were previously characterized by X-ray diffraction.<sup>25</sup> All peaks on the XRD patterns properly correspond with the Fe<sub>3</sub>O<sub>4</sub> standard (symmetry *Fd-3m*, *a* = 8.378 Å, cubic crystal structure). Similar XRD patterns were obtained for IBA-Fe<sub>3</sub>O<sub>4</sub>.

### Analytical characterizations

Fourier transform infrared spectra were recorded with a Nexus 670 Nicolet spectrometer equipped with

DTGS KBr detector. Each spectrum was scanned 32 times at a resolution of  $4\text{ cm}^{-1}$  in the  $400\text{--}4000\text{ cm}^{-1}$  region. The transmission spectra were recorded using KBr pellets.

The amount of remaining IBA in the water/ethanol mixture was determined by UV–Vis spectroscopy at  $\lambda_{\text{max}} = 224\text{ nm}$  using GBC Cintra 40 spectrometer, from a calibration curve obtained for a series of standard solutions (from  $1 \times 10^{-3}$  to  $3 \times 10^{-2}\text{ mol L}^{-1}$  of IBA):

$$A = 138.8C + 0.0026,$$

where  $C$  is the concentration of IBA (in  $\text{mol L}^{-1}$ ) and  $A$  is the absorption intensity at  $224\text{ nm}$ .

The IBA loading on the  $\text{Fe}_3\text{O}_4$  particles was calculated from the remaining IBA content in the water/ethanol mixture and was about  $0.03\text{ g}$  ( $0.17\text{ g}$  of remaining IBA from  $0.2\text{ g}$  of the initial IBA mixture with  $1\text{ g}$  of  $\text{Fe}_3\text{O}_4$ ). Thus, the IBA loading was  $3\text{ wt}\%$  ( $15\%$  of the initial IBA were fixed on the  $\text{Fe}_3\text{O}_4$  nanoparticles).

The IBA release from the IBA– $\text{Fe}_3\text{O}_4$  nanoparticles at different pH values (3, 7, and 10) was also determined using the following protocol:  $0.05\text{ g}$  of IBA– $\text{Fe}_3\text{O}_4$  was stirred with distilled water ( $25\text{ mL}$ ) for  $24\text{ h}$ . Then, the solution was filtered and the IBA content was determined by UV–Vis spectroscopy at  $224\text{ nm}$ . Release experiments were performed in triplicate.

Field-emission scanning electron microscope (FE-SEM) observations were carried out to examine the surface morphology of the magnetite/epoxy polymer composite (using a Jeol JSM 7800F). The microphotographs were recorded at an accelerating voltage of  $5.0\text{ kV}$  at different magnifications.

The surface charge of the nanoparticles was determined at  $25^\circ\text{C}$  by Zeta potential measurements using a Zetameter Phoremeter IV. The particles were dispersed in distilled water with  $5\text{ mmol L}^{-1}$  of KCl in an ultrasonic bath before being injected in the Zeta cell. The Schmoluchowski equation was employed to calculate the Zeta potential values.<sup>25</sup>

### Electrochemical measurements

The polarization curves were obtained with a classical three-electrode cell in which the bare carbon steel electrode served as the working electrode with an exposed area of  $1\text{ cm}^2$ . A saturated calomel electrode and a large platinum sheet were used as reference and counter electrodes, respectively. The electrochemical cell was open to air and was kept at room temperature. The corrosive medium was a  $0.1\text{ M NaCl}$  solution. The polarization curves for the carbon steel in the solution containing IBA ( $10^{-3}\text{ M}$ ) or  $\text{Fe}_3\text{O}_4$  ( $3\text{ wt}\%$ ) or IBA– $\text{Fe}_3\text{O}_4$  ( $3\text{ wt}\%$ ) were recorded after  $2\text{ h}$  of immersion in the electrolyte, at a scan rate of  $1\text{ mV s}^{-1}$ , starting

from  $-0.9$  to  $-0.1\text{ V SCE}^{-1}$ . Two trials were performed to ensure reproducibility.

### Differential scanning calorimetry (DSC)

DSC experiments were carried out with a Mettler DSC 1 Star System apparatus to determine the glass transition temperature ( $T_g$ ) of the coatings. Aluminum pans containing about  $10\text{ mg}$  of paints were heated three times from  $0$  to  $160^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under a continuous flow of nitrogen. The  $T_g$  was determined as  $T_{g\infty}$  (after post-curing) by the onset point with a  $\pm 1^\circ\text{C}$  sensitivity.

### Salt spray test

Salt spray test was used in order to evaluate the corrosion protection of the samples. The test was performed according to ASTM B117 using a Q-FOGCCT-600 chamber. Scribes were made on the samples before exposure to the salt spray. The specimens were placed inside the salt spray chamber at an angle of  $20^\circ$  without any contact with each other or with any metallic material. A solution of  $5\%$  NaCl was sprayed on the samples. The spraying was maintained for the duration of the test. The temperature of the chamber was kept as  $35^\circ\text{C}$ . The samples were evaluated according to ASTM D1654 after  $240\text{ h}$  of exposure.

### Adherence tests

The crosscut adherence test was performed according to ASTM D 3359 method B to evaluate the adherence of the coatings during aging in distilled water. The adherence was measured using crosshatch cutter six blades with  $1\text{ mm}$  spaces between cutting edges. An adhesive test tape with adhesive strength of  $9.5\text{ N per }25\text{ mm}$  (ISO 2409) was immediately applied to the cross-cut coating surface. The tape was removed by a quick pull and the coating removal content was determined. The test was also performed after different immersion times in distilled water. The coatings were dried by clean tissue paper to remove the surface water and placed at room temperature for  $10\text{ min}$  to be sure of surface dryness. The adhesive strength was evaluated by using the following expression:

$$\text{Adhesive loss (\%)} = \frac{x}{25} 100,$$

where  $x$  is the number of squares of detached coating and  $25$  is the total number of squares on the intact coating.

To measure the adherence more accurately, the three-point bending test was carried out according to ISO 14679-1997. Before testing, coated steel plates were carefully sawn into samples of size  $50\text{ mm} \times 10\text{ mm}$ .

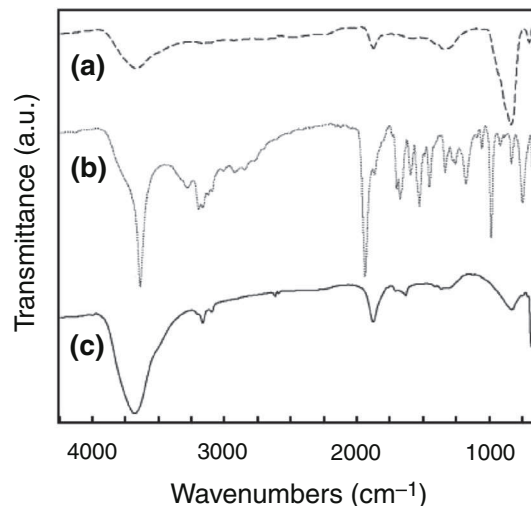
The samples were degreased with ethanol and ultrasonicated in an ethanol bath for 10 min. Then, they were placed in a silicone mold between two clamping plates. The assembly was closed and a 5 mL stoichiometric epoxy-amine ratio polymer mixture (Dow Chemical, Midland, MI, USA—DGEBA DER™ 332 and DETA from Aldrich, St. Louis, MO, USA, respectively) was injected into the mold. 25 mm × 5 mm × 4 mm stiffener epoxy blocks were made according to the ISO 14679-1997 Standard, and as described in previous work.<sup>26</sup> Stiffener block polymerization was carried out at ambient temperature ( $23 \pm 2^\circ\text{C}$ ) for 24 h. Then, the assembly was sequentially placed in a dry oven at  $60^\circ\text{C}$  for 3 h and at  $120^\circ\text{C}$  for 1 h. An Instron 3367 tensile testing machine (Norwood, MA, USA) was used with a 5000 N full-scale load cell with a sensitivity of  $\pm 0.5\%$  of the measured values, and a crosshead displacement speed of  $0.5 \text{ mm min}^{-1}$  ( $\pm 0.5\%$ ). Bluehill software (Instron) controlled the apparatus parameters. The ultimate load ( $F_{\text{max}}$  measured on the load–displacement curve) was taken as the adherence parameter. For each tested sample, the failure must be verified as an adhesive failure and not as a cohesive one. Good average values and low standard errors of  $F_{\text{max}}$  were achieved and validated by testing eight samples for each system.

## Results and discussion

First, FTIR spectroscopy and Zeta potential measurements were presented to show the presence of the IBA molecules on the nanomagnetite surface. Then, the inhibitive effect of IBA on the corrosion of the carbon steel was characterized by polarization curves. Afterward, the IBA content on the treated  $\text{Fe}_3\text{O}_4$  and the release of IBA from the IBA- $\text{Fe}_3\text{O}_4$  nanoparticles determined by UV-Vis spectroscopy were presented. Finally, the protection of the carbon steel was discussed from the salt spray test and from the adherence measurements by the three-point bending (before aging) and the cross-cut test (before and after aging).

### Characterization of the IBA- $\text{Fe}_3\text{O}_4$ nanoparticles

Figure 1 presents the FTIR spectra of pure IBA,  $\text{Fe}_3\text{O}_4$ , and IBA- $\text{Fe}_3\text{O}_4$  nanoparticles. The characteristic bands of the spectra are given in Table 1. The spectrum of the  $\text{Fe}_3\text{O}_4$  shows bands at 578 and  $454 \text{ cm}^{-1}$ .<sup>27,28</sup> These bands were also found in the spectrum of IBA- $\text{Fe}_3\text{O}_4$ . The hydrocarbon chain of the IBA molecule gave bands at 2946, 2853  $\text{cm}^{-1}$  and IBA- $\text{Fe}_3\text{O}_4$  presented similar bands at 2920, 2852  $\text{cm}^{-1}$ . The C=O and C-O-H characteristic peaks were observed at 1694 and  $1427 \text{ cm}^{-1}$  for the IBA molecule.<sup>29</sup> In the IBA- $\text{Fe}_3\text{O}_4$  spectrum, these peaks are shifted to 1629 and  $1385 \text{ cm}^{-1}$ . The comparison of the three spectra (Fig. 1) shows the presence of the



**Fig. 1:** FTIR spectra of: (a)  $\text{Fe}_3\text{O}_4$ , (b) IBA, and (c) IBA- $\text{Fe}_3\text{O}_4$

**Table 1:** Characteristic bands of FTIR spectra obtained for IBA,  $\text{Fe}_3\text{O}_4$  and IBA- $\text{Fe}_3\text{O}_4$

IBA ( $\text{cm}^{-1}$ )	$\text{Fe}_3\text{O}_4$ ( $\text{cm}^{-1}$ )	IBA- $\text{Fe}_3\text{O}_4$ ( $\text{cm}^{-1}$ )	Bond
–	578 454	579 434	Fe–O
2946, 2853	–	2920, 2852	– $\text{CH}_2$
1694	–	1629	–C = O
1427	–	1385	–C–O–H

IBA molecules on the surface of the  $\text{Fe}_3\text{O}_4$  nanoparticles.

Figure 2 shows the surface charge distribution for  $\text{Fe}_3\text{O}_4$  and IBA- $\text{Fe}_3\text{O}_4$  nanoparticles. The  $\text{Fe}_3\text{O}_4$  nanoparticles have an average surface charge value of about  $-20 \text{ mV}$ . The negative charge on the particles surface can be attributed to the adsorption of hydroxyl group from the alkaline medium during the hydrothermal reaction. For the IBA- $\text{Fe}_3\text{O}_4$  nanoparticles, the average surface charge was shifted to a more negative region, about  $-50 \text{ mV}$ . The increase in the negative charge of the IBA- $\text{Fe}_3\text{O}_4$  confirmed the presence of the IBA molecules on the nanoparticles.

The polarization curves obtained for the carbon steel in the 0.1 M NaCl solutions containing  $\text{Fe}_3\text{O}_4$  or IBA- $\text{Fe}_3\text{O}_4$  nanoparticles are presented in Fig. 3. The curves without nanoparticles (blank solution) and with IBA at  $10^{-3} \text{ M}$  are also reported for comparison. In the presence of “free” IBA in the solution, it can be seen that the corrosion potential is shifted in the anodic direction (about 100 mV) and the anodic current densities are significantly lower by comparison with the blank solution, particularly near the corrosion potential. This result confirmed the inhibitive properties of IBA<sup>23,24</sup> and showed that the compound is an anodic inhibitor. The polarization curves obtained in

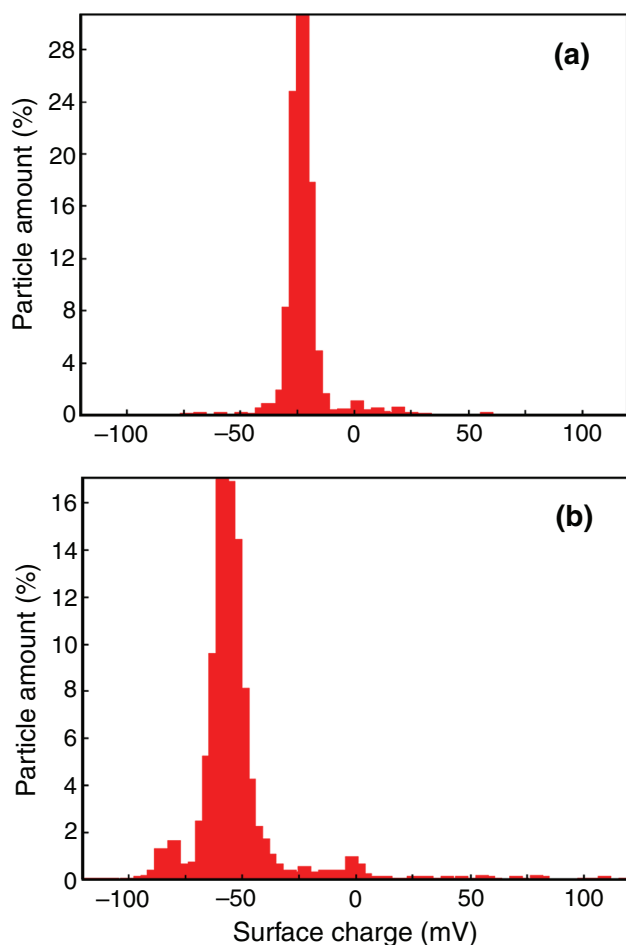


Fig. 2: Surface charge distribution on: (a)  $\text{Fe}_3\text{O}_4$  and (b)  $\text{IBA-Fe}_3\text{O}_4$  nanoparticles

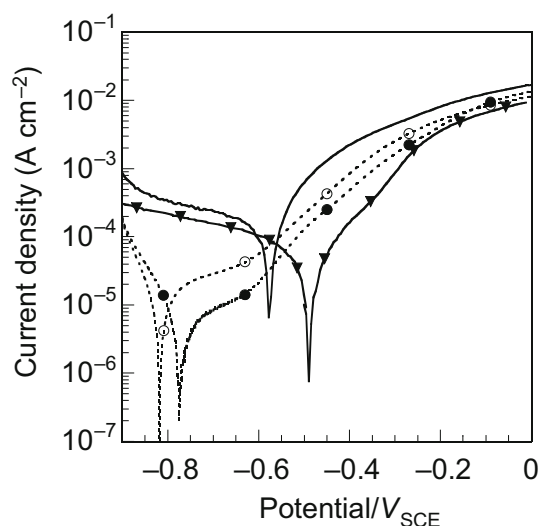


Fig. 3: Polarization curves obtained for the carbon steel electrode after 2 h of immersion in the 0.1 M NaCl solution: (○) 3 wt% of  $\text{Fe}_3\text{O}_4$ , (●) 3 wt% of  $\text{IBA-Fe}_3\text{O}_4$ , (▼)  $10^{-3}\text{M}$  IBA and (—) blank solution (pH 6)

the presence of  $\text{Fe}_3\text{O}_4$  or  $\text{IBA-Fe}_3\text{O}_4$  presented similar shape. The corrosion potential is shifted toward cathodic potentials by comparison with the blank solution and the current densities are significantly lower. For both types of magnetite, accumulation of particles on the carbon steel surface was observed after the electrochemical measurements. This observation can explain the results observed in the presence of the nanoparticles. However, for the solution containing the  $\text{IBA-Fe}_3\text{O}_4$ , the corrosion potential is shifted toward anodic values and the anodic current densities are lower, similar to the curve obtained in the presence of “free” IBA. The electrochemical results showed the inhibitive effect of the IBA on the corrosion of the carbon steel and confirmed that the IBA molecules are attached on the  $\text{Fe}_3\text{O}_4$  nanoparticles.

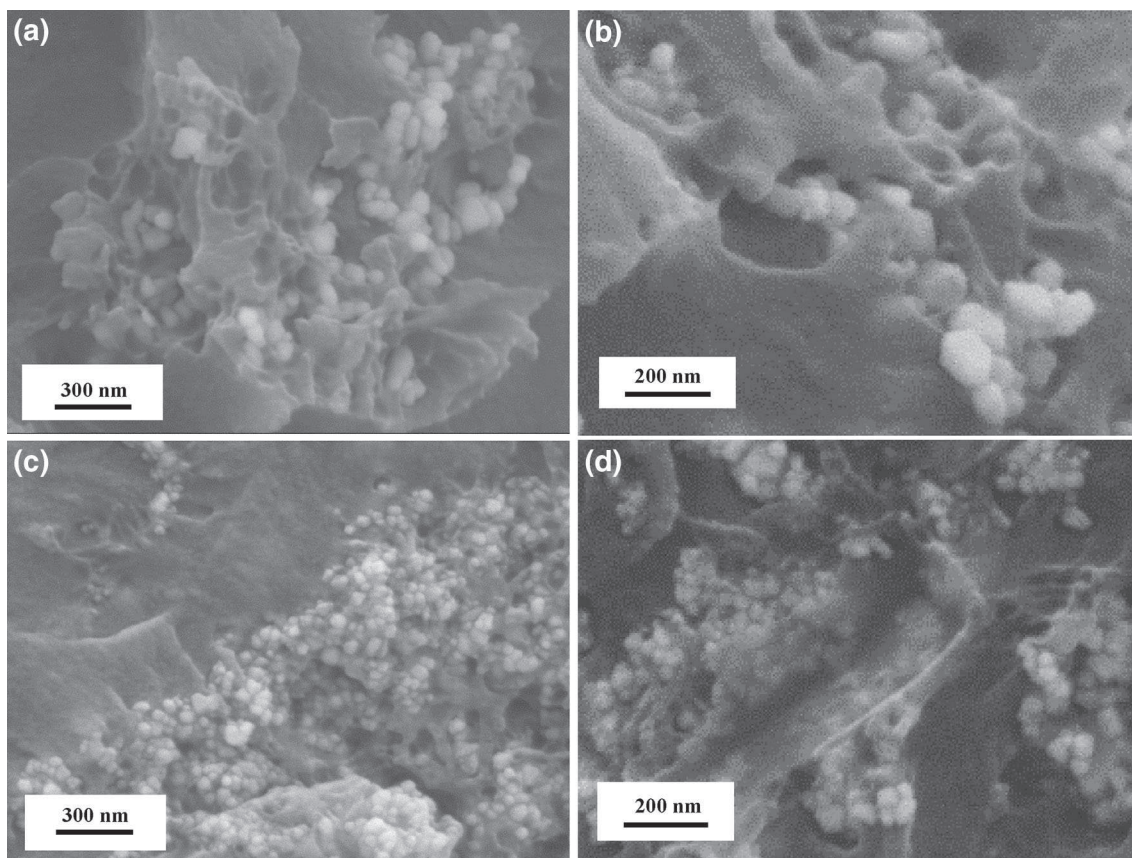
### Characterization of the epoxy-polyamide coatings

The glass transition temperatures,  $T_g$ , of the epoxy-polyamide coatings with or without nanoparticles were determined by DSC. The values are reported in Table 2. A slight decrease of the  $T_g$  values is observed for the coatings containing the  $\text{Fe}_3\text{O}_4$  and the  $\text{IBA-Fe}_3\text{O}_4$  nanoparticles.

Numerous investigations have examined the effect of nanoparticles addition on the glass transition temperature. On the one hand, the incorporation of nanoparticles (such as nanoclay or iron oxide) in a polyepoxy matrix often increases its  $T_g$ , due to an additional crosslinking which decreases the polymer mobility.<sup>23</sup> On the other hand, the addition of nanoparticles might decrease the  $T_g$  value due to the decrease of the crosslinking density and/or interphase formation.<sup>30–32</sup> In order to verify these hypotheses, fracture surface of the epoxy-polyamide coatings containing  $\text{Fe}_3\text{O}_4$  or  $\text{IBA-Fe}_3\text{O}_4$  were observed by FE-SEM and presented in Fig. 4. Nanoparticles have grain size of about 50 nm. For both coatings, particles agglomeration can be observed. In the presence of  $\text{IBA-Fe}_3\text{O}_4$ , some fragments of polymer remained attached to the fillers (Fig. 4d) and this feature was not observed in the presence of  $\text{Fe}_3\text{O}_4$  (Figs. 4a and 4b). This result revealed higher adherence between the polymer and the fillers and thus indicated a better compatibility between the epoxy-polyamide matrix and the  $\text{IBA-Fe}_3\text{O}_4$  surface which can explain the decrease of  $T_g$ .

Table 2:  $T_g$  values for the different coatings

	Pure epoxy-polyamide coating	Epoxy-polyamide coating containing $\text{Fe}_3\text{O}_4$	Epoxy-polyamide coating containing $\text{IBA-Fe}_3\text{O}_4$
$T_{g/\text{onset}}$ ( $^{\circ}\text{C}$ )	71	68	65



**Fig. 4:** FE-SEM micrographs of a fracture surface for the epoxy-polyamide coatings containing: (a, b)  $\text{Fe}_3\text{O}_4$  and (c, d) IBA- $\text{Fe}_3\text{O}_4$

### ***Corrosion protection performance***

Electrochemical impedance measurements were first performed to characterize the barrier properties of the coatings. The results are not presented here because the impedance diagrams were similar for the coatings containing the two types of nanoparticles indicating that there was no influence of the magnetite treatment by IBA on the impedance response. Nonetheless, the impedance results showed that the addition of treated or nontreated magnetite in the epoxy-polyamide coatings allowed the barrier properties to remain high during exposure to a 0.5 M sodium chloride solution while those of pure epoxy-polyamide resin continually decreased during immersion. This result underlined that the incorporation of  $\text{Fe}_3\text{O}_4$  or IBA- $\text{Fe}_3\text{O}_4$  improved the coating performance. Since the impedance results did not allow the IBA influence to be shown, salt spray test in the presence of a scratch was conducted as an accelerated corrosion test to evaluate the corrosion resistance of the carbon steel covered with the epoxy-polyamide coating containing or not the nanoparticles ( $\text{Fe}_3\text{O}_4$  and IBA- $\text{Fe}_3\text{O}_4$ ). Pictures of the samples after 240 h exposure to the salt spray are shown in Fig. 5 and the evaluation of the corrosion behavior, according to ASTM D1654, is presented in

Table 3. Numerous blisters associated with corrosion products are observed on the edge of the scratch for the pure epoxy-polyamide coating. This behavior corresponds to a loss of adherence of the coating.<sup>33</sup> Brown corrosion products are visible inside the scratch. Development of blisters and corrosion products are limited for the epoxy-polyamide coating containing  $\text{Fe}_3\text{O}_4$  and a few corrosion products in the scratch and few blisters around the scratch are observed for the sample with IBA- $\text{Fe}_3\text{O}_4$ . The rust creepage from the scribe for the pure epoxy system was higher than for the epoxy containing the nanoparticles (Table 3). According to the ASTM D1654, the rating number is 7 for the pure epoxy coating and 8 for the epoxy containing  $\text{Fe}_3\text{O}_4$  or IBA- $\text{Fe}_3\text{O}_4$  (after 240 h of exposure to the salt spray). The salt spray results indicated that the presence of  $\text{Fe}_3\text{O}_4$  or IBA- $\text{Fe}_3\text{O}_4$  improved the corrosion protection of the carbon steel.

To show the IBA effect on the corrosion protection, the release of IBA in distilled water, from the IBA- $\text{Fe}_3\text{O}_4$  particles was measured by UV-Vis spectroscopy for three pH values (Fig. 6). It is observed in Fig. 6 that the IBA release increases for the high pH value. It can be recalled that the corrosion process induces an increase of the local pH due to the cathodic reaction of oxygen reduction. Thus, the release of IBA, favored in

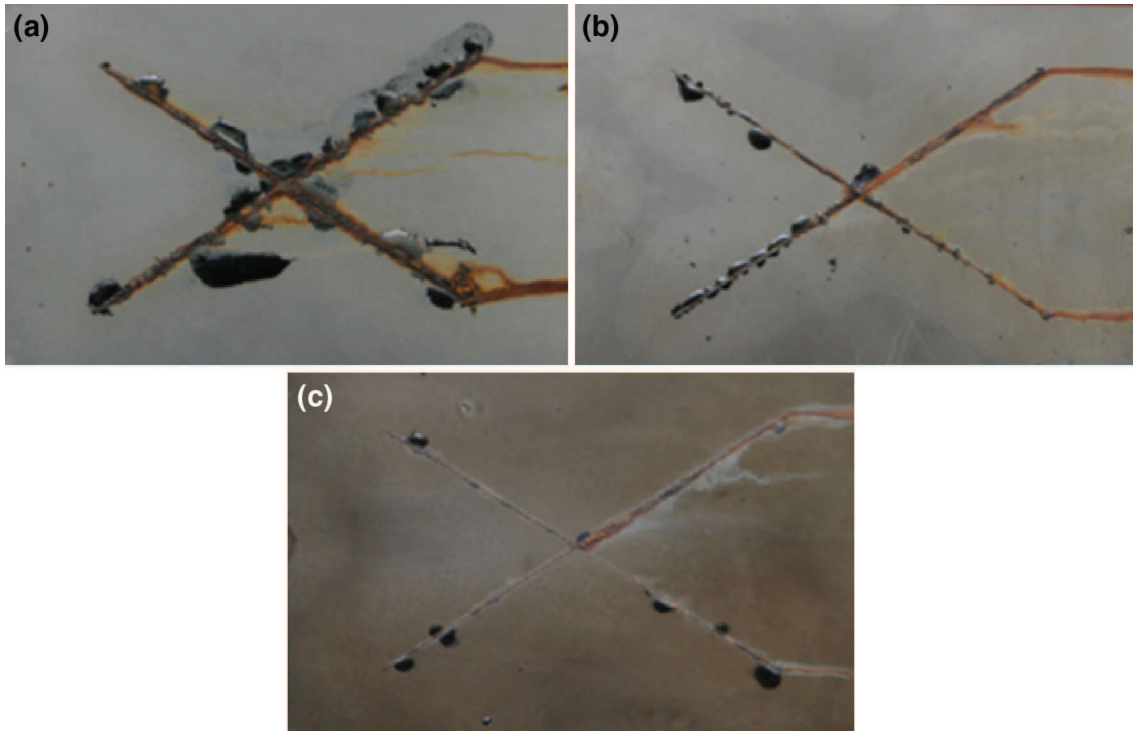


Fig. 5: Salt spray test results obtained after 240 h for the carbon steel coated with the epoxy-polyamide film: (a) without nanoparticles, (b) with  $\text{Fe}_3\text{O}_4$  and (c) with IBA- $\text{Fe}_3\text{O}_4$

Table 3: Salt spray test results after 240 h exposure according to ASTM D1654 standard

Samples	Creepage from scribe	
	Rust creepage (mm)	Rating number
Epoxy-polyamide coating	1.27	7
Epoxy-polyamide coating containing $\text{Fe}_3\text{O}_4$	0.79	8
Epoxy-polyamide coating containing IBA- $\text{Fe}_3\text{O}_4$	0.64	8

alkaline conditions, will lead to the corrosion inhibition of the carbon steel.

#### Adherence measurements

To characterize the effect of the  $\text{Fe}_3\text{O}_4$  particles on the behavior of the steel/coating interface, two adherence tests were performed. First, the cross-cut adherence test was performed to evaluate the influence of water penetration at the steel/coating interface during aging in distilled water. According to Funke,<sup>34,35</sup> the adherence under wet conditions is more meaningful for corrosion protection than dry adherence (initial adherence before aging). Many coatings showed excellent tensile adherence to metal but lost the adherence after exposure to pure water at room or elevated temperatures. A thin film of water at the interface is apparently responsible for the loss of adherence. Images of the coatings surface before (as-prepared

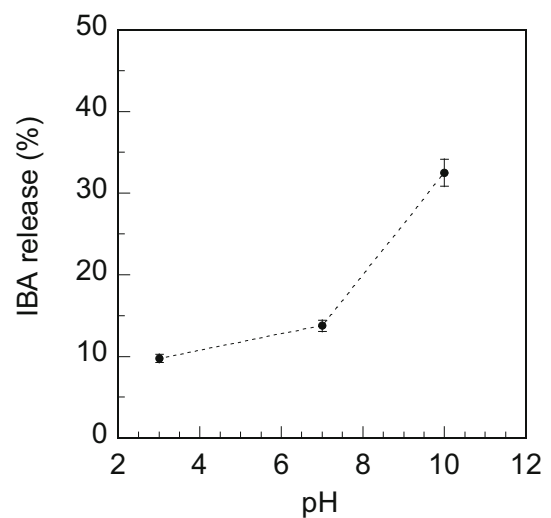
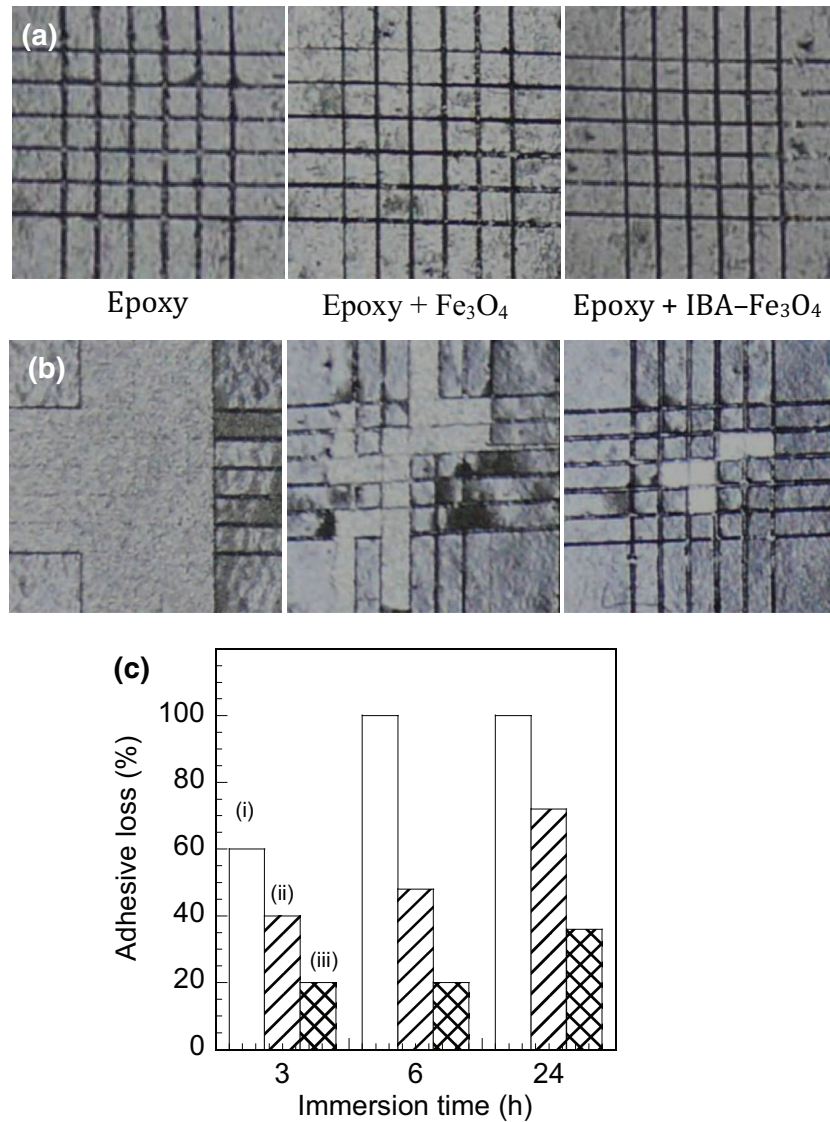


Fig. 6: Release amount of IBA from the IBA- $\text{Fe}_3\text{O}_4$  particles vs pH in distilled water

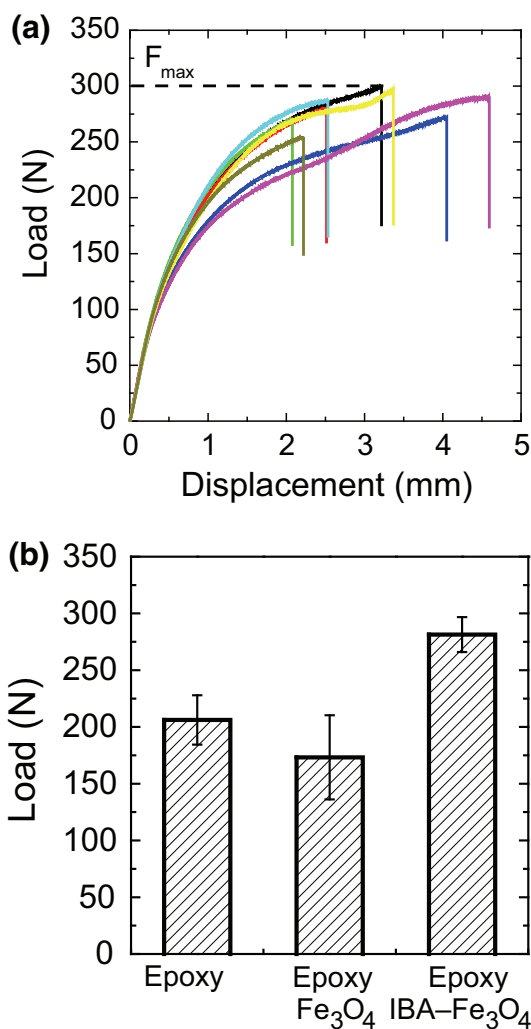


**Fig. 7:** (a) and (b) Images of the samples surface after the crosscut test: (a) dry adhesion and (b) wet adhesion after 6 h of immersion in distilled water; (c) delaminated area showing the adhesive loss vs immersion time in water: (i) coating without nanoparticles, (ii) coating with Fe<sub>3</sub>O<sub>4</sub>, and (iii) with IBA-Fe<sub>3</sub>O<sub>4</sub>

samples) and after wet adherence (6 h of immersion) are shown in Figs. 7a and 7b, respectively. It can be seen that for the as-prepared samples, the crosscut area is not significantly affected by the addition of Fe<sub>3</sub>O<sub>4</sub> and IBA-Fe<sub>3</sub>O<sub>4</sub>: there is no adhesion loss after the test for the three samples (Fig. 7a). On the contrary, after 6 h of exposure to distilled water, the film without nanoparticles is completely detached whereas only some squares of coatings are detached for the films containing Fe<sub>3</sub>O<sub>4</sub> or IBA-Fe<sub>3</sub>O<sub>4</sub> (Fig. 7b). The variation of the adhesive loss for the three coatings vs immersion time in distilled water is shown in Fig. 7c. It is observed that the adhesive loss of the coating without nanoparticles increases rapidly with the immersion time, while the adhesive loss of coatings containing the particles increases slowly, particularly

for the coating containing IBA-Fe<sub>3</sub>O<sub>4</sub>. This improvement can be explained by the cooperative bonds between the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the oxide layer at the steel/coating interface. For the coating containing IBA-Fe<sub>3</sub>O<sub>4</sub>, the wet adherence improvement can be also attributed to the IBA release in the presence of water, which reacted with iron oxides at the steel surface.<sup>36</sup> From the cross-cut test, it was not possible to discriminate between the adherences of the three systems at the initial state (as-prepared samples). Thus, the three-point bending test was performed to better characterize the interfacial phenomena (the failure initiation is well defined in this test) at the initial state (i.e., before aging).

Figure 8a gives, as an example, the load vs displacement recorded during the three-point bending test for



**Fig. 8:** (a) Load vs displacement for the steel surface covered by the epoxy-polyamide film containing IBA- $\text{Fe}_3\text{O}_4$  (results of eight independent trials are shown on the figure) and (b) Comparison of the adherence results obtained from the three-point bending test for the coatings: without nanoparticles, with  $\text{Fe}_3\text{O}_4$  and with IBA- $\text{Fe}_3\text{O}_4$

the coating containing IBA- $\text{Fe}_3\text{O}_4$ . The ultimate load values ( $F_{\text{max}}$ ) for the three systems are compared in Fig. 8b. It is interesting to note that the coating containing IBA- $\text{Fe}_3\text{O}_4$  presents the highest values for the ultimate load indicating an improvement of the adherence for this coating. For the other coatings (neat epoxy-polyamide coating and epoxy-polyamide coatings containing nontreated magnetite), the measured values were similar by taking into account the reproducibility. From these results, it is possible to show a higher performance for the coating containing IBA- $\text{Fe}_3\text{O}_4$  before aging which cannot be observed by the crosscut test.

From the adherence measurements coupled with the salt spray test, an improvement in both the adherence (dry and wet conditions) and the corrosion protection

when the IBA- $\text{Fe}_3\text{O}_4$  particles were incorporated in the coatings was seen. Thus, it can be concluded that the main action of IBA- $\text{Fe}_3\text{O}_4$  is limited at the metal/coating interface.

### Discussion

In aqueous solutions, IBA showed a significant inhibition effect. It is known that the inhibitive action of organic compounds containing S, N, and O is due to the formation of a covalent type bond between the metal and the lone pair of electrons in the molecule.<sup>37</sup> The chemisorption of IBA on the steel surface can take place between the  $\pi$ -electrons and the iron vacant  $d$ -orbital. More particularly, this adsorption can take place at the metal/coating interface when the IBA molecules are released from the  $\text{Fe}_3\text{O}_4$  particles due to the presence of water which penetrated through the coating. Moreover, it was shown that the IBA release (from the IBA- $\text{Fe}_3\text{O}_4$ ) was higher when the pH increases. Thus, in neutral and alkaline media, the IBA release could impede the corrosion process and confer self-healing properties to the coating. The salt spray test confirmed the beneficial effect of IBA on the corrosion protection of the carbon steel.

On the other hand, the improvement of the interactions between the coating and the metal surface was shown for the epoxy-polyamide coating containing IBA- $\text{Fe}_3\text{O}_4$  by the three-point bending test for the as-prepared samples. The adherence increase could be linked to the polymer network, as indicated by the decrease of  $T_g$  with the addition of  $\text{Fe}_3\text{O}_4$  (treated or nontreated by IBA). Previous works have shown that metal oxides are able to react with the monomers, leading to a competition with the polymerization reaction.<sup>38</sup> The decrease of  $T_g$  could be also linked to the decrease of crosslinking density with interphase formation all around the particles (Fig. 4), which can be attributed to an incomplete curing of the composites in the presence of the nanoparticles. The unreacted functional groups might have interactions with the metal/coating interface, reinforcing the adherence of the coating on the metallic substrate.<sup>59</sup> It could be also mentioned that the  $\text{Fe}_3\text{O}_4$  nanoparticles are magnetic and might migrate to the metallic surface during the curing process, changing the adherence behavior (in our case, increasing the adherence). The cross-cut tests in wet conditions clearly showed the role of the IBA- $\text{Fe}_3\text{O}_4$  nanoparticles at the metal/coating interface. Finally, it can be concluded that the corrosion protection was controlled by the adherence of the coatings and the action of IBA- $\text{Fe}_3\text{O}_4$  at the metal/coating interface was confirmed.

### Conclusions

The corrosion protection of the carbon steel by epoxy-polyamide-based coatings containing  $\text{Fe}_3\text{O}_4$  and IBA-

Fe<sub>3</sub>O<sub>4</sub> nanoparticles (3 wt%) was evaluated by the salt spray test and adherence tests. It was shown that the coatings were highly protective in the presence of IBA-Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The inhibitive action of IBA (anodic inhibitor) on the corrosion of the carbon steel was confirmed by the polarization curves, in agreement with previous results. In the scratch (salt spray test), its inhibitive action was observed due to the release of IBA from IBA-Fe<sub>3</sub>O<sub>4</sub> particles. However, the IBA content in the Fe<sub>3</sub>O<sub>4</sub> is relatively low. For the long-term protection of the carbon steel, a higher content of IBA on the Fe<sub>3</sub>O<sub>4</sub> particles is required. The IBA-Fe<sub>3</sub>O<sub>4</sub> played a role at the coating/steel interface by strengthening the adherence before and after aging (i.e., dry and wet adherence tests). This work demonstrates that the combination of accelerated corrosion tests and adherence tests provides relevant and complementary information for a better assessment of the corrosion protection by organic coatings.

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