



Development of waterborne anticorrosive coatings by the incorporation of coumarate based corrosion inhibitors and phosphate functionalization

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ABSTRACT

Waterborne coatings are more industrially appealing for corrosion protection due to their low toxicity when compared to traditional solvent based coatings. In waterborne latex systems, the presence of surfactants is crucial, which can nevertheless contribute later to a poor performance of the final films in terms of barrier protection. This can be avoided by the use of polymerizable surfactants covalently bonded to the polymeric chains. In this work, particles of a latex loaded with an organic corrosion inhibitor, methoxy p-coumaric acid (H1), are further functionalized by the incorporation of a polymerizable surfactant, Sipomer® PAM-200 (SIP), by semibatch emulsion polymerization. The proposed system was hypothesized to ideally have higher barrier and corrosion protection properties due to the combination of H1 and SIP. However, the Electrochemical Impedance Spectroscopy results of the latexes cast on metal substrates indicate an antagonistic effect on the corrosion inhibition process rather than synergistic, as both species compete for the same moieties of the metallic surface. Thus, while the control coating with SIP (13.3 mg of SIP/g of polymer) showed impedances of $10^{7.1}$ – $10^{6.4}$ Ω and phase angles of 84–88 degrees over 24 h, the coating with H1 (3.3 mg of H1/g polymer) and SIP (13.3 mg of SIP/g of polymer) showed a less stable behavior with changes in impedances with time from $10^{7.1}$ to $10^{5.5}$ Ω and in phase angle from 86 to 72 degrees. The production of a bi-layer system avoids this antagonistic effect.

1. Introduction

One of the best ways to protect mild steel from corrosion is the use of protective coatings [1–3], with waterborne coatings being a more appealing choice due to their low toxicity when compared to conventional solvent based coatings [4]. Surfactants are crucial for the production of waterborne coatings, since they are responsible for the stability of the particles of the latex [5–7]. However, as the latex dries forming a polymeric film, the presence of surfactants can be the source of problems such as the formation of hydrophilic pathways [8], creation of hydrophilic pockets, aggregation through the formed film, or migration towards the film-air or film-substrate interface [9–11]. Therefore, migration of surfactant may adversely affect different properties of the final polymeric film such as adhesion, shear, and peel strength [12,13], as well as water resistance [5,12,13] and gloss [13].

To avoid the negative effects of conventional surfactants an alternative is the use of reactive surfactants in the formulation [7,14,15]. The

use of polymerizable surfactants, frequently referred to as surfmers [7,16], has attracted special attention in the last few years [15,17]. A promising surfactant for the field of corrosion protection is Sipomer® PAM-200 (SIP). It has a methacrylic function present in its structure that allows its co-polymerization into the polymeric backbone and a phosphate group (hydrophilic part), that provides efficient stabilization of the polymer particles in the aqueous dispersion.

Recently, good corrosion resistance was found in waterborne (meth) acrylic films with phosphate functionality, achieved by using SIP [18–22]. Excellent properties were obtained when the latex was dried under a slow drying rate with controlled conditions of temperature and relative humidity (23 °C, RH = 60 %) [20]. Besides the formation of more homogeneous films, lower drying rates allow the interaction of the phosphate groups of the surfactant with the hydroxyl groups of the steel surface, producing a thin iron phosphate passive layer at the coating/metal interface, covalently bonded to the polymeric film [20]. Therefore, the phosphate functionalization of waterborne binders seems to be

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a promising strategy for reducing the water sensitivity of the final film and also increasing its barrier property due to the formation of the phosphate layer on the substrate.

The addition of corrosion inhibitors in polymeric coatings have also attracted attention, mainly when looking for substitutes for the toxic chromate inhibitors. Organic inhibitors have appeared as interesting substitutes, due to their relatively easy synthesis and application, which relies on the adsorption of their polar group to the metal surface, while the nonpolar end is oriented away from it, forming a protective hydrophobic film [3,23]. Compounds based on p-coumaric acid (4-hydroxycinnamic acid) derivatives have demonstrated efficient corrosion inhibition properties as free inhibitors in solution [24,25], when integrated with sol-gel coatings [26,27] and acrylic UV-cured coatings [28] and also when incorporated into waterborne polymeric binders [4,29]. In the case of incorporation of hydrophobic species into waterborne polymeric dispersions, it was found that miniemulsion polymerization was the most effective technique, as hydrophobic species initially present in the monomer droplets that nucleate to create polymer particles do not need to diffuse through the water phase [4,30].

A range of p-coumaric based inhibitors with different radicals were also compared in terms of anticorrosive properties when dissolved in solution, as well as when incorporated into the coating by batch miniemulsion polymerization, in the concentration of 1 g inhibitor/100 g monomer [29]. The barrier corrosion protection of the coatings produced from these hybrid latexes was analyzed by Electrochemical Impedance Spectroscopy (EIS) showing that coatings with methoxy p-coumaric acid (H1), gave the highest impedances and phase angles ($10^{6.3}$ to $10^{6.7}$ Ω and 82–84 degrees, respectively) for the intact coatings, which approached capacitive coating behavior.

The objective of this paper is to further improve the corrosion protection properties of the coating with H1 inhibitor incorporated. The particles of the latex containing H1 will be further functionalized by the incorporation of Sipomer® PAM-200 (SIP) by semibatch emulsion polymerization. A control latex, with no inhibitor, was also functionalized for comparison purposes. The final latex with SIP and H1 in its composition would ideally have higher barrier properties due to the combination of both components, and the active protection provided by H1 in case of the presence of a defect in the coating is also expected. The films formed from the new latex with combined functionality were cast on metal substrates and dried at two different conditions; 1) under non controlled room temperature conditions and 2) under controlled conditions of $T = 23$ °C and $RH = 60$ %. The coating corrosion protection ability was analyzed by EIS for both an intact coating and when a controlled scratch was made. The effect of having both corrosion protection groups in the latex was analyzed, to determine if this provided better performance than having just one of them. For comparison purposes, the corrosion protection of a blend of latexes having H1 inhibitor or SIP was also analyzed, as well as the protection provided by a bilayer system. To the best of our knowledge, it is the first time that this combination of a p-coumaric based inhibitor and a polymerizable surfactant is carried out and the corrosion protection properties of the synthesized polymeric binder are measured.

2. Experimental

2.1. Materials

The monomers methyl methacrylate (MMA), and n-butyl acrylate (BA) (Quimidroga) were used for the polymerization reactions as received. Sipomer® PAM-200 (Solvay) was used as a polymerizable surfactant, and potassium persulfate (KPS, Aldrich) as a radical thermal initiator. Distilled water was used in the aqueous media of the polymerization reactions and MiliQ water was used for the electrochemical tests. Sodium bicarbonate (NaHCO_3 , Aldrich) was used as a buffer, and ammonium hydroxide solution (NH_4OH , 28.0–30.0 %, Aldrich) to increase the pH. Hydroquinone (HQ, Aldrich) was used as a

polymerization inhibitor for quantification of the reaction conversion. Steel substrates (medium carbon steel with 0.5 % of carbon) from URDURI ACEROS were used as metallic substrates for application of the latex. High purity NaCl (Corrosalt, Ascott-Analytical) was used for preparation of corrosive solutions for the electrochemical tests.

2.2. Synthesis of poly (MMA/BA) latex by semibatch emulsion polymerization

To functionalize the latexes with phosphate moieties, semibatch emulsion polymerization reactions were carried out using latexes containing H1 inhibitor that were previously synthesized by batch miniemulsion polymerization [29]. Briefly, H1 was incorporated in the organic phase containing MMA and BA monomers, before its miniemulsification with the aqueous phase containing the Dowfax 2A1 surfactant [29]. This miniemulsion was polymerized in batches for 3 h, by the addition of potassium persulphate initiator. The latex obtained by miniemulsion polymerization containing H1 was named Mp_H1. A control latex was synthesized for comparison purposes, Mp_Control, with no H1. The subsequent semibatch emulsion polymerization reactions were carried out in a 100 mL round bottom flask immersed in a bath of ethylene glycol. The temperature was maintained at 70 °C, under agitation of 250 rpm, and N_2 atmosphere. The reactions were prepared according to the recipe described in Table 1. Initially, the seed (Mp_Control or Mp_H1), synthesized in the previous work [29], was loaded in the round bottom flask, to which a buffer (NaHCO_3) was added to control the pH. The seed was continuously agitated and fed with N_2 for 15 min before the addition of the initiator solution. A pre-emulsion composed of Sipomer® PAM-200 (SIP), monomer and water was prepared and its pH was adjusted with drops of NH_4OH to 7. A pump was used for feeding this pre-emulsion into the round bottom flask at the rate of 0.157 mL/min for 3 h. To maintain the homogeneity of the pre-emulsion, it was continuously agitated on a stirring plate during the whole experiment. Two latexes with 40 % solids content were produced using this method, one containing phosphate functionality (Ep_SIP) and the second containing H1 and phosphate functionality (Ep_H1_SIP). Ep_SIP latex has 5.3 mg of SIP/g latex (13.3 mg of SIP/g of polymer), and Ep_H1_SIP has 1.3 mg of H1/g latex (3.3 mg of H1/g polymer), and 5.3 mg of SIP/g latex (13.3 mg of SIP/g of polymer). Fig. 1 presents a scheme of the synthesis procedure followed.

A representation of the polymeric particles obtained by the polymerization reactions is presented in Fig. 2. The particles of Ep_SIP latex are characterized for having phosphate functionalization (Fig. 2 a), while particles of Ep_H1_SIP latex have in their composition SIP and H1 incorporated (Fig. 2 b). In order to analyze the influence of the particles composition on the final film, in terms of location/distribution of H1 and SIP, a blend of Mp_H1 (seed) and Ep_SIP in a ratio 1:1 of polymer particles was also prepared. In this blend, half of the particles are functionalized with SIP and the other half are loaded with H1 (Fig. 2 c). Therefore, the blend has the final concentration of 2 mg of H1/g latex (5 mg of H1/g polymer) and 2.6 mg of SIP/g latex (6.6 mg of SIP/g

Table 1
Recipe of phosphated poly (MMA/BA) waterborne latex.

	Reactive	Initial load (g)	Stream (g)
Seed	Mp_Control / Mp_H1	15	–
	NaHCO_3	0.014	–
	MMA	–	6
	BA	–	6
Pre-emulsion	Sipomer® PAM-200 (SIP)	–	0.24
	H_2O	–	16
	NH_4OH	–	drops ^a
	Solution of initiator	KPS	0.12
		H_2O	2
	Feed rate	0.157 mL/min	

^a Minimum quantity necessary for adjusting the solution to pH 7.

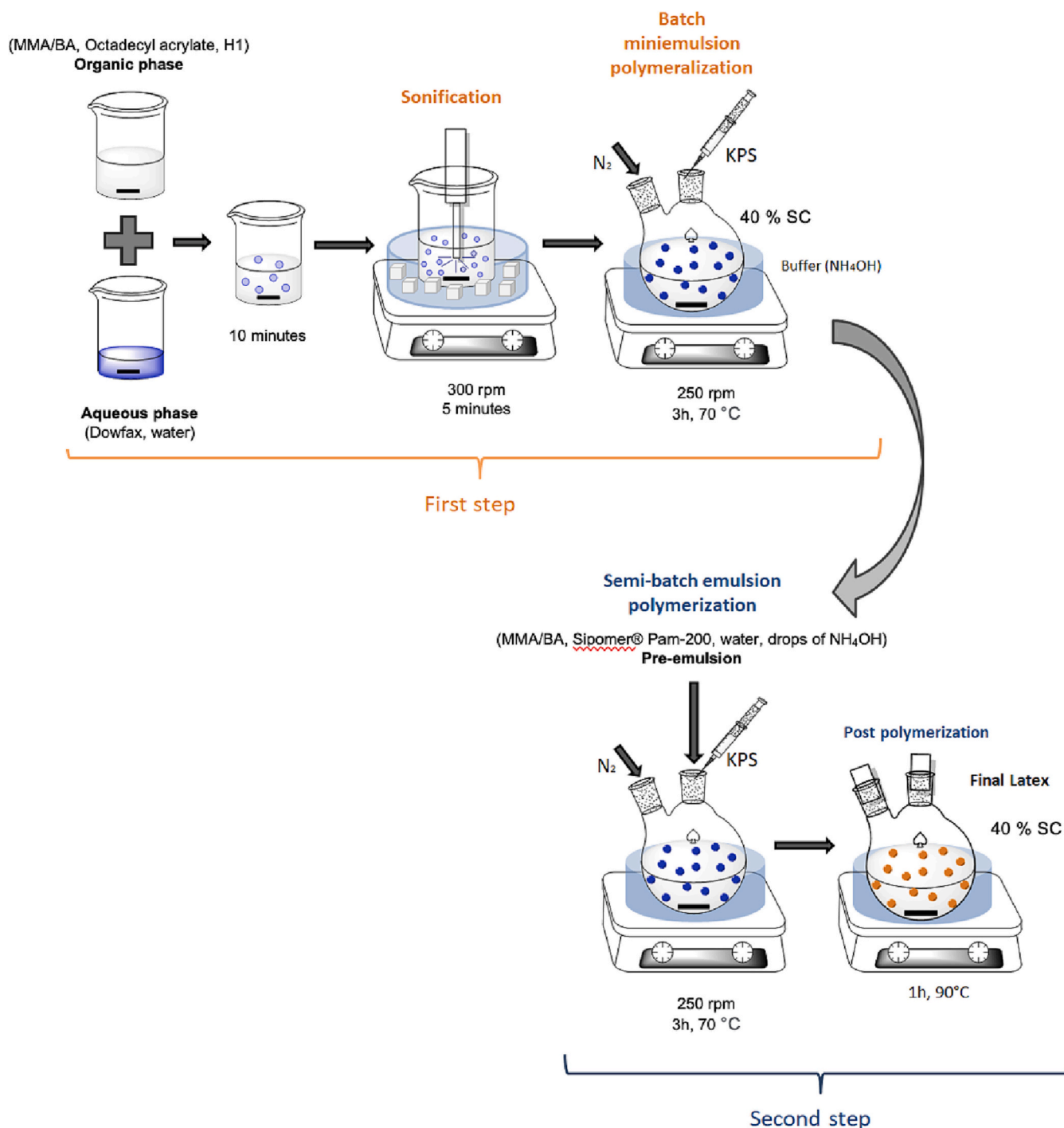


Fig. 1. Synthesis of latexes containing H1 and phosphate functionalities by semibatch emulsion polymerization.

polymer).

2.3. Characterization

The emulsion polymerization kinetics were followed by monitoring monomer conversion and particle size evolution. Monomer conversion was measured by gravimetry, while polymer particle sizes were measured in diluted samples by dynamic light scattering (DLS) using a Zetasizer Nano Series (Malvern instrument).

The water resistance of the free polymeric films was analyzed by measuring their water uptake. Samples of latex were placed in silicone molds and dried for 7 days at room temperature. The formed films were

taken from the mold and immersed in distilled water. The water uptake was followed for 24 h, in triplicate, through measuring the fraction of weight increase, determined by the difference between the initial weight of the film and the weight after immersion in water.

These latexes were used to prepare coatings on the steel substrate with subsequent characterization of the corrosion protection properties of the resultant films. The metallic substrates were cleaned with abundant acetone and dried with compressed air before deposition of the latex with a doctor blade applicator. Coated samples were dried in two different conditions; 1) at room temperature without controlling the relative humidity, and 2) under controlled conditions of temperature and relative humidity (23 °C, RH = 60 %) in a humidity chamber, for at

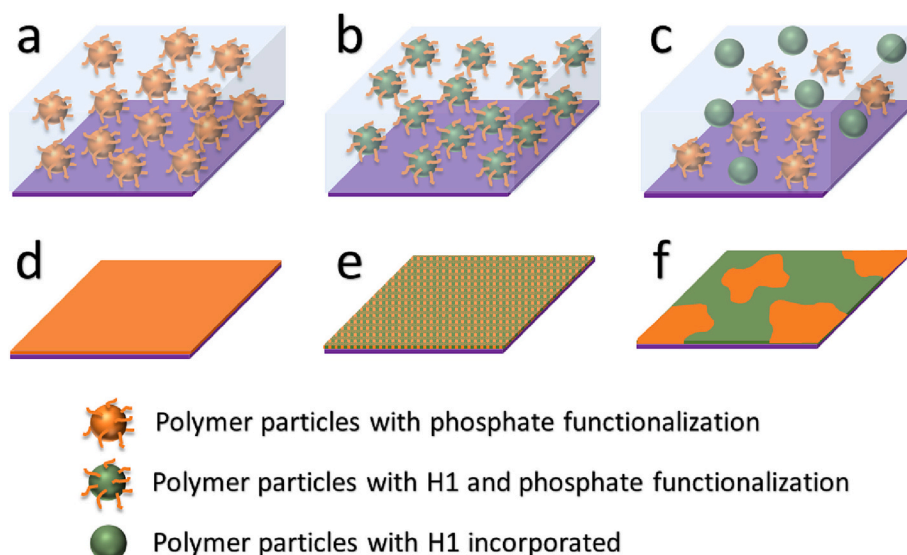


Fig. 2. Representation of the deposition of waterborne polymeric particles on the metallic substrate: a) Ep_SIP, b) Ep_H1_SIP, and c) Blend (Ep_SIP + Mp_H1) and the proposed surface composition after the film formation: d) phosphate functionalization, e) mixed presence of H1 and phosphate groups and f) patchy structure with H1 and phosphate functionalities.

least 24 h. It was previously shown for similar SIP containing latexes that this controlled humidity condition resulted in the formation of a phosphate film on the substrate surface [20]. The final thickness of the coatings was measured with a coating thickness gauge to ensure that the final film had an average thickness of 45 μm .

The coated samples were immersed in NaCl containing solution and monitored for 24 h at room temperature by electrochemical impedance spectroscopy (EIS), using a low current channel of a BIO-LOGIC VMP3 potentiostat with EC Lab (V11.26) software. The electrochemical cell was composed of a Ag/AgCl (saturated with KCl) reference electrode, a medium carbon steel substrate as the working electrode, and a graphite rod counter electrode. The coated sample exposure area was 1.1 cm^2 and the concentration of the corrosive solution used was 0.005 M NaCl. The open circuit voltage (OCV) was monitored for 47 min over the frequency range from 100 kHz to 10 mHz, followed by EIS at a scan rate of 0.167 mV/s with 6 points per decade and a sinusoidal amplitude of 10 mV.

3. Results and discussion

3.1. Polymerization kinetics

Semibatch emulsion polymerization reactions were successfully performed using the latexes with and without H1 incorporated as seeds (Mp_H1 and Mp_Control respectively). Full conversion was reached after 180 min for the reaction Ep_SIP, using Mp_Control as the seed, and a conversion of 80 % was obtained for the reaction Ep_H1_SIP, using Mp_H1 as seed (Fig. 3 a). The lower conversion rate of this reaction may be due to some kind of retardation from the interaction of H1 with SIP in the system. In both cases coagulum free latexes were obtained with a final particle size of 170–180 nm (Fig. 3 b).

To determine the effect of incorporating SIP and H1 in the coatings on water uptake, free films with them added separately (Mp_H1 and Ep_SIP) and combined (Ep_H1_SIP and the blend of Mp_H1 and Ep_SIP) were prepared and their water absorption was measured for 24 h (Fig. 4). The coating Ep_SIP (13.3 mg of Sipomer®/g polymer) had the lowest absorption of water, as expected, since SIP was reported to

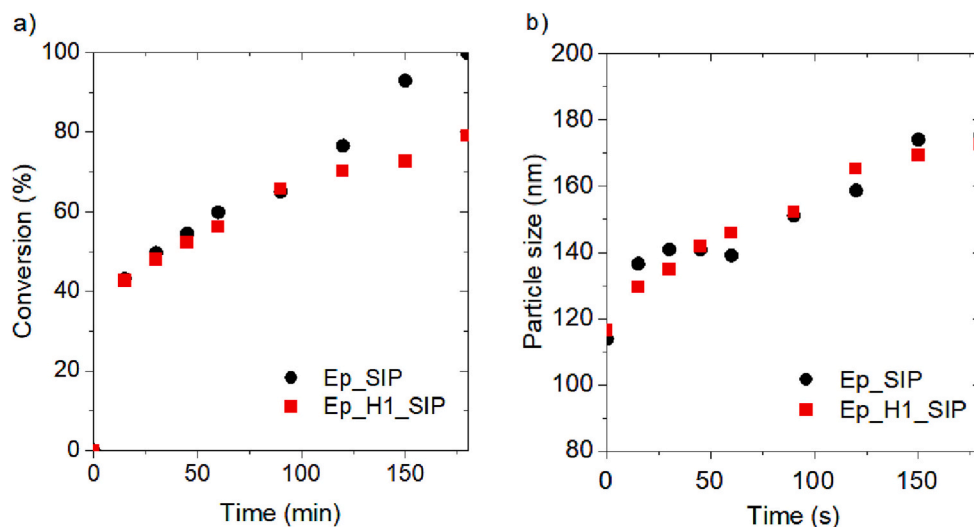


Fig. 3. Semibatch emulsion polymerization reaction a) kinetics, and b) particles size evolution.

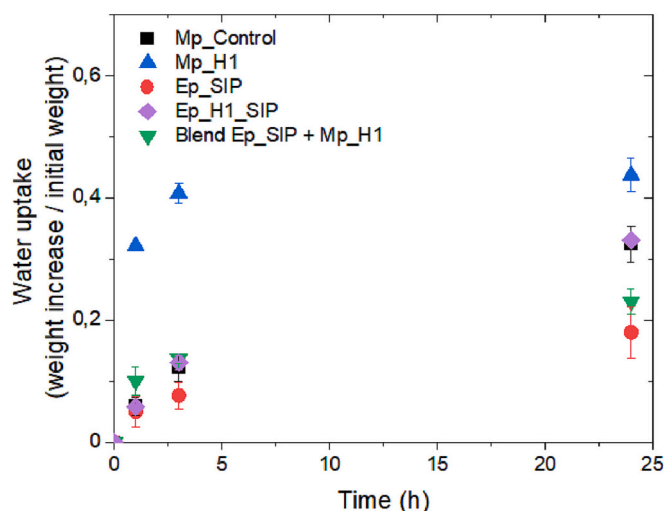


Fig. 4. Water absorption of free films.

contribute to reduce the water sensitivity of the film [19,22]. On the other hand, the film with the highest water uptake was Mp_H1. This is due to the high concentration of H1 (10 mg H1/g polymer), that is slightly soluble in water [29]. Therefore, the presence of H1 incorporated into the particles improves the hydrophilicity of the polymeric film. This is also supported by the considerably lower water uptake of Mp_Control (that has no H1 incorporated). Nevertheless, it is relevant to mention that, in this case, higher water uptake is not necessarily related to worse anticorrosive performance, as previously observed [29]; Mp_H1 coating had shown higher impedances ($10^{6.7} \Omega$, and 84 degrees.) than Mp_Control ($10^{5.2} \Omega$ and 66 degrees), due to the active anticorrosive protection given by H1.

Ep_H1_SIP (3.3 mg of H1/g polymer, and 13.3 mg of SIP/g of polymer) film, showed considerably higher water uptake when compared to the Blend Ep_SIP + Mp_H1 (5 mg of H1/g polymer and 6.6 mg of SIP/g polymer), even though the blend has a higher concentration of H1 in its composition. This is an indication that the distribution of H1 between the particles that form the film (Fig. 2) have an influence in the absorption of water, since the absorption of water is higher when H1 is present in all of the particles (Fig. 4).

3.2. Electrochemical characterization

In order to check their corrosion protection properties, the latexes were cast on metallic surfaces and dried at two different conditions; 1) room temperature with non-controlled RH, and 2) $T = 23^\circ\text{C}$ and $\text{RH} = 60\%$. The corrosion protection properties of the coatings were measured by EIS and presented in Fig. 5. In these graphs, the phase angles were plotted as empty symbols, and the impedances as full symbols.

When the coating Ep_SIP was dried at room temperature, it showed impedances of $10^{4.7}$ – $10^{5.4} \Omega$ at low frequencies, and phase angles of 78–82 degrees at high frequencies over 24 h (Fig. 5 a), which are very similar to those observed for the latex Mp_Control ($10^{5.2} \Omega$ and 66 degrees) [29], used as the seed. Therefore, the presence of SIP did not show any significant improvement when compared to the seed, when dried under a condition that does not enable the formation of the phosphate layer [20]. When comparing Ep_SIP with Ep_H1_SIP, dried at room temperature without controlling the relative humidity, it was observed that they had similar impedances and phase angles, except that the impedance values obtained for Ep_H1_SIP were more stable through the experiment, maintaining a higher impedance at 24 h, which is probably due to the presence of H1 providing additional protection to the system. In any case, for both cases (Fig. 5a and c) there is a peak emerging in the phase angle at low frequency, indicating corrosion at the interface,

which agrees with the change in phase angle at high frequency due to a reduction in the barrier properties and an overall lower total impedance.

When Ep_SIP was dried at 23°C with a relative humidity of 60 %, it showed considerably higher and constant impedances at low frequencies ($10^{7.1}$ – $10^{6.4} \Omega$) and phase angles of 84–88 degrees at high frequencies throughout the 24 h experiment time, similar to coatings previously reported with SIP (Fig. 5 b). The improvement of impedance is due to the formation of the phosphate layer that provides extra barrier property to the system [20]. Nevertheless, the impedances obtained for Ep_H1_SIP dried in the same controlled conditions, were considerably less stable through the experiment. In the first three hours of experiment, Ep_H1_SIP showed impedances in the range of $10^{7.1}$ – $10^{6.7} \Omega$ and 96–72 of phase angle, similar to the values obtained for the Ep_SIP. However, the values dropped with time reaching $10^{5.5} \Omega$ and 72 degrees, after 24 h of experiment, similar to the values obtained for Ep_H1_SIP, when dried at room temperature ($10^{5.3}$ – $10^{5.5} \Omega$ and phase angles of 72–76 degrees), in which the phosphate layer is not formed. This may be an indication that the coexistence of H1 and SIP incorporated into the same latex particles is not compatible for corrosion protection. Both SIP and H1 are known for attaching to the metallic surface and forming a protective film. Therefore, it is possible that some kind of steric competition may be occurring, precluding the formation of a homogeneous phosphate layer. If these results are compared to a similar binder of MMA/BA/AA produced by semibatch emulsion polymerization with a similar amount of inhibitor (3 mg/g polymer of butyl coumaric acid), that presented an impedance drop from $10^{6.7}$ to 10^6 at low frequencies during 24 h, it can be said that the presence of SIP enhanced the corrosion protection properties, and the combined presence of H1 and SIP worsened them [4].

In order to further investigate the influence of the distribution of H1 into the anticorrosive properties of the film, the latex Ep_SIP was blended with the latex Mp_H1 (Blend Ep_SIP + Mp_H1) in the proportion 1:1. The EIS results for the sample dried at room temperature without controlling the relative humidity and for the one dried at $T = 23^\circ\text{C}$ and $\text{RH} = 60\%$ are presented in Fig. 6. The EIS spectra of the sample dried at room temperature (Fig. 6 a) show higher impedances and phase angles ($10^{5.3}$ – $10^{5.8} \Omega$ and 80–75 degree), when compared to Ep_SIP dried in the same conditions (Fig. 5 a), indicating that H1 was able to give some additional protection to the system. On the other hand, the impedances obtained for the Blend Ep_SIP + Mp_H1, dried at $T = 23^\circ\text{C}$ and $\text{RH} = 60\%$ (Fig. 6 b) are very similar to the ones obtained when the sample is dried at room temperature (Fig. 6 a) and much lower than the impedances obtained for Ep_SIP dried under controlled conditions (Fig. 5 b), indicating an antagonistic influence of the particles loaded with H1, whereby their presence restricts the formation of a complete homogeneous phosphate layer (see Fig. 2f) and therefore leads to poorer corrosion barrier properties.

To test the active protection of the proposed coating systems, the coated steel samples were dried at $T = 23^\circ\text{C}$ and $\text{RH} = 60\%$, and a scratch was made in the coatings before the EIS measurements were carried out. The results are presented in Fig. 7. A drop is observed in the impedance values of the coating Ep_SIP (Fig. 7 a) in which the phosphate layer is homogeneous. However, while the impedance of Ep_SIP dropped from $10^{4.4}$ to $10^{4.2} \Omega$ after the 24 h of experiment, the impedance of Mp_Control [29] dropped from $\approx 10^{4.6}$ to $10^{4.1} \Omega$ in the same experiment. It is an indication that the phosphate present in Ep_SIP coating contributed to a more stable impedance profile when compared to Mp_Control.

The spectra obtained for the Ep_H1_SIP (Fig. 7 b) is complex, indicating that a number of processes are taking place, as observed by the changes of profile in the phase angles and impedances in the intermediate frequencies throughout the duration of the experiment. On the other hand, the impedances at low frequencies are maintained relatively constant at around $10^{4.2} \Omega$. We note that the complex impedance behavior in this system was also observed for the intact coating (Fig. 5 d); unstable impedance values were observed. A smaller decrease in

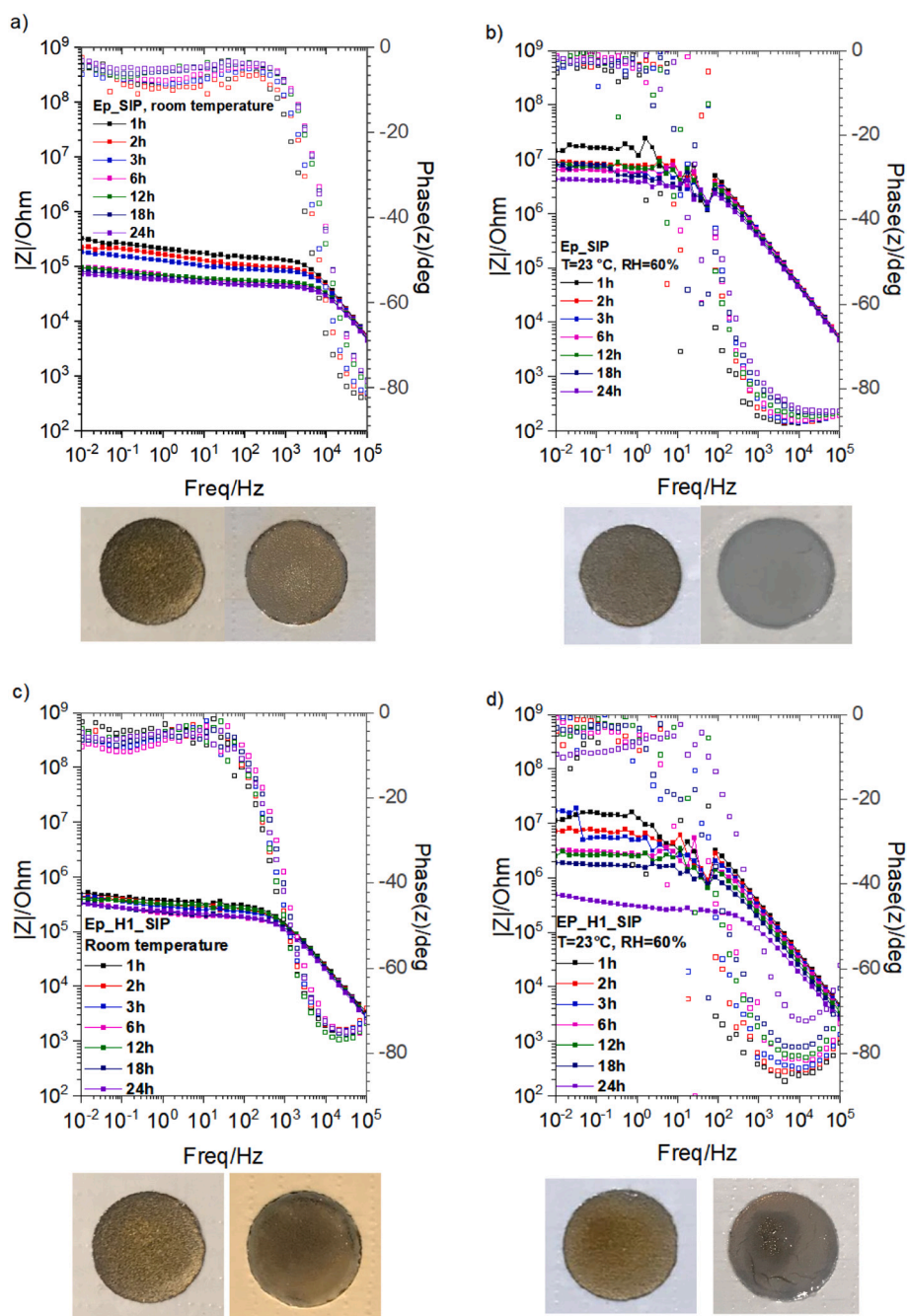


Fig. 5. Electrochemical impedance spectra of coatings and optical images of the samples before (on the left) and after the experiment (on the right). Ep_SIP dried at a) room temperature, and b) $T = 23\text{ }^{\circ}\text{C}$ and $\text{RH} = 60\%$. Ep_H1_SIP dried at c) room temperature, and d) $T = 23\text{ }^{\circ}\text{C}$ and $\text{RH} = 60\%$.

impedance is observed in the coating Ep_H1_SIP, suggesting that H1 is providing some level of active protection to the system when incorporated inside the particles with SIP (Fig. 2 b). The same is not observed in the Blend Ep_SIP + Mp_H1, as H1 is distributed in a different configuration (Fig. 2 c).

In summary, the presence of the phosphate layer only (Ep_SIP) shows a higher initial impedance, but this declines at a greater rate when H1 and SIP are both present in all particles (Ep_H1_SIP). In H1_SIP, while it maintains a consistent impedance, the presence of H1 appears to interfere with the phosphate formation, and so the coating presents a lower initial impedance. When the coating contains both H1 and SIP, but in separate particles (Ep_SIP + Mp_H1) it does not have either the higher initial impedance of SIP only coating, again likely due to competition with H1, or maintains the impedance of the Ep_H1_SIP coating, probably

due to a lower level of H1 present. While this experiment confirms that SIP results in the formation of a phosphate film that is initially protective and the presence of H1 improves the ongoing protection, there is not a synergistic effect when both are present together, but rather a reduction in the effect of both is observed.

Therefore, it can be said that the corrosion protection mechanism seen in our systems is an improvement in the barrier properties, most likely due to phosphate layer formation. The EIS response to the effect of the curing conditions confirm it, as when SIP containing latexes are dried under controlled humidity that produce the phosphate layer, the corrosion protection improves. H1 appears to be competing with this corrosion protection mechanism. In the defect samples, the slight improvement in performance for SIP may also be due to the phosphate layer formation reducing penetration under the coating, which explains

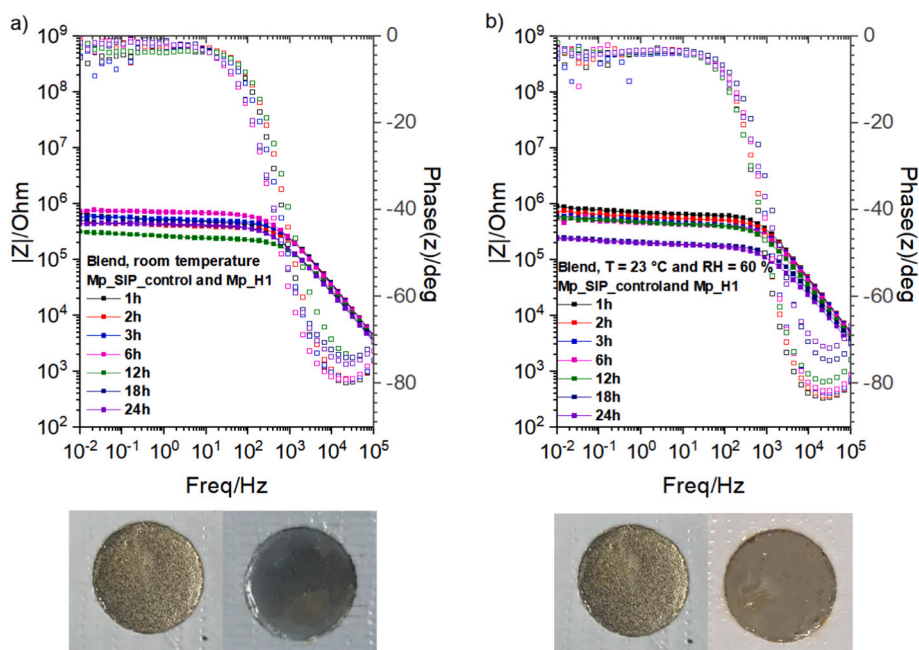


Fig. 6. Electrochemical impedance spectra of the coating formed by the blend of the latex Ep_SIP + Mp_H1 (1:1), dried at; a) Room temperature; b) $T = 23\text{ }^{\circ}\text{C}$ and $\text{RH} = 60\%$.

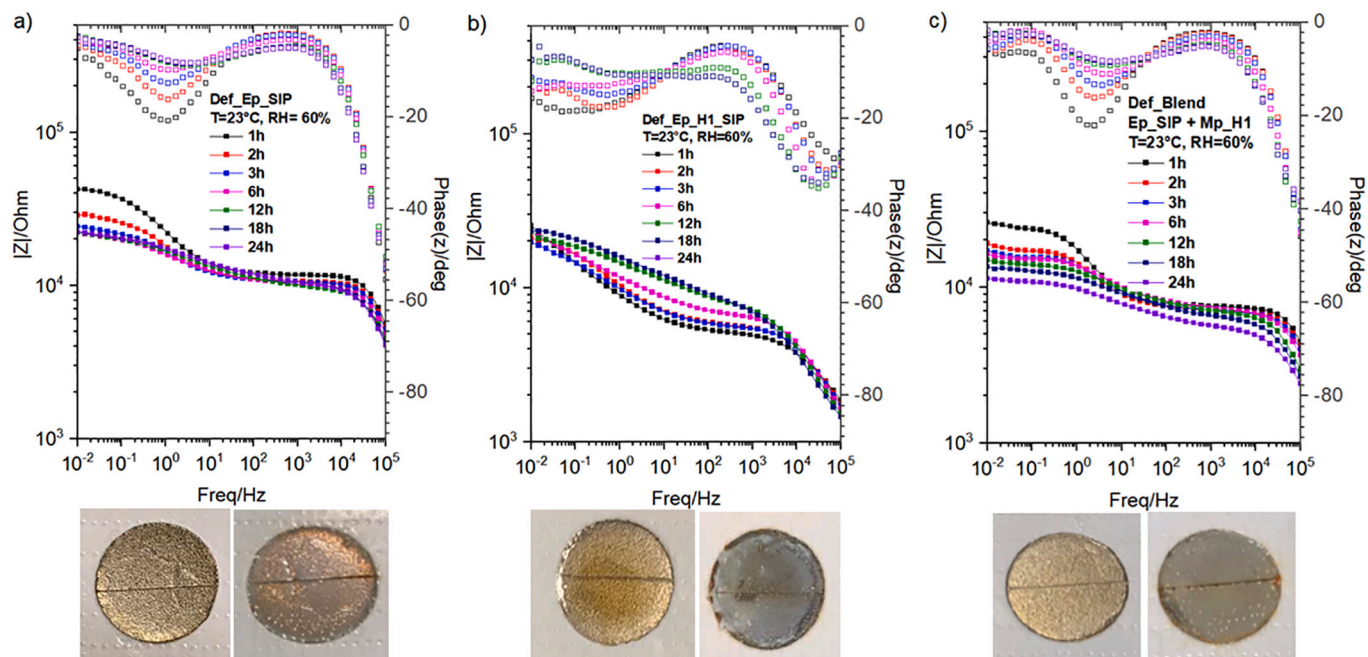


Fig. 7. Electrochemical impedance spectra coatings dried at $T = 23\text{ }^{\circ}\text{C}$ and $\text{RH} = 60\%$, with a controlled scratch followed by optical images of the samples before (on the left) and after the experiment (on the right). a) Ep_SIP, b) Ep_H1_SIP, c) Blend Ep_SIP + Mp_H1.

why the initial response is similar, but maintains a higher impedance and also appears to have less corrosion than the others.

In an attempt to optimize the corrosion protection, and after considering the antagonistic effect that H1 and SIP have on the corrosion protection properties of the coatings, a system composed of two layers of coatings was proposed. The first layer was prepared with the latex Ep_SIP dried at $T = 23\text{ }^{\circ}\text{C}$ and $\text{RH} = 60\%$, that has previously shown the highest impedance in the previous tests ($10^7\ \Omega$, Fig. 5 b), and the second layer was prepared with the latex Mp_H1 that has shown high impedances and some active protection due to the presence of H1 in its

composition [29]. This sample was named 2 L - Ep_SIP / Mp_H1. A control sample with the second layer prepared with the latex Mp_Control, was also prepared for comparison purposes (2 L - Ep_SIP / Mp_Control). Each layer had the thickness of approximately $45\ \mu\text{m}$, therefore the final thickness of the system was around $90\ \mu\text{m}$. The 2-layers-systems were measured by EIS, and the results are shown in Fig. 8.

The impedance spectra obtained for the 2-layer-coating 2 L-Ep_SIP / Mp_Control was very similar to that obtained for the 1 - layer coating Ep_SIP (Fig. 5), even though the 2-layer-coating was thicker. The impedances obtained for the 2-layer-coating 2 L-Ep_SIP / Mp_H1 (Fig. 8 b)

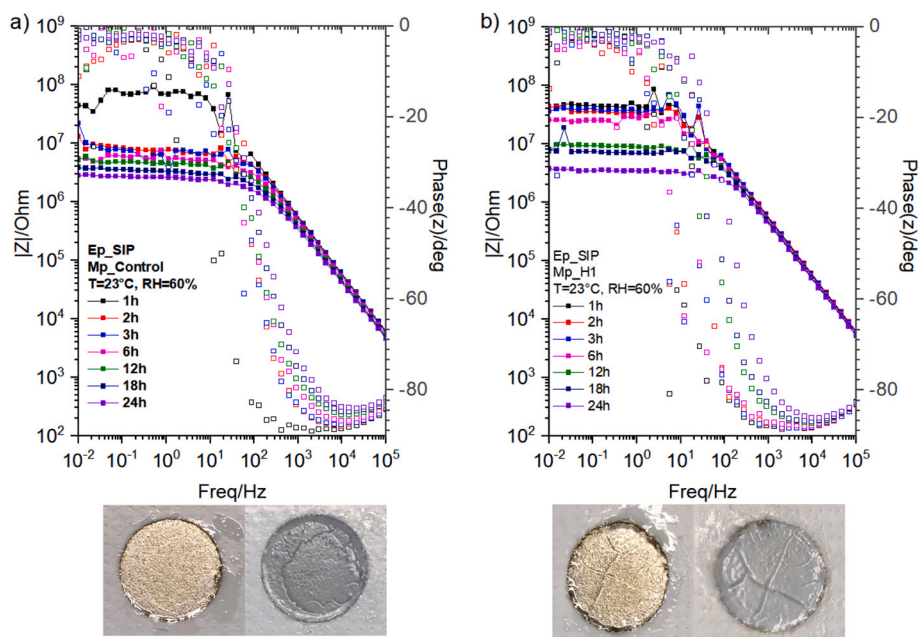


Fig. 8. Electrochemical impedance spectra of 2-layer-coatings dried at $T = 23\text{ }^{\circ}\text{C}$ and $\text{RH} = 60\%$ of intact coatings a) 2 L - Ep_SIP / Mp_Control, b) 2 L - Ep_H1_SIP / Mp_H1, followed by optical images of the samples before (on the left) and after the experiment (on the right).

were higher in the first hours of experiment, when compared to the 2-layer-coating 2 L-Ep_SIP / Mp_Control (Fig. 8 a), indicating that the presence of H1 in the second layer of the coating contributes to improve the barrier properties of the proposed system. The 2 layer coating provides additional evidence that combining both SIP and H1 in the same layer leads to an antagonistic effect found between SIP and H1 with respect to forming a protective surface and leads to the need to separate these two compounds in different coating layers to obtain an optimized corrosion protection performance.

4. Conclusions

The phosphate functionalization of a latex containing methoxy p-coumaric acid (H1) inhibitor was performed by semibatch emulsion polymerization with the addition of Sipomer® PAM-200 (SIP) polymerizable surfactant. When this latex and a control latex without H1 were cast on steel and dried at room temperature without controlling the relative humidity, in which the phosphate layer is not formed, the impedances obtained for the intact coatings were comparable to those observed for the latexes without SIP. However, higher impedances were obtained when the latexes were dried under the controlled conditions that allow the formation of the phosphate layer ($23\text{ }^{\circ}\text{C}$, $\text{RH} = 60\%$). The control coating with SIP showed fairly stable impedances of $10^{7.1}$ – $10^{6.4}\ \Omega$ and phase angles of 84–88 degrees over 24 h. However, the corrosion protection of the coating with H1 and SIP was less stable than the control, showing changes in impedances with time from $10^{7.1}$ to $10^{5.5}\ \Omega$ and in phase angle from 86 to 72 degrees. This could be an indication that the coexistence of H1 and the phosphate function in the particles is not compatible during the corrosion inhibition process. As both components are known for protecting the surface by being attached to it, some competition may be occurring between them.

The coating obtained from the blend of Ep_SIP with Mp_H1 (1:1), in which half of particles were loaded with SIP and the other half with H1 did not show higher impedances when dried at $23\text{ }^{\circ}\text{C}$, $\text{RH} = 60\%$, as seen from the other coatings with SIP incorporated. This may be due to an inability to form a complete, homogeneous phosphate layer in the presence of MP_H1 particles that are also in contact with the metallic surface and do not contain the phosphate on their particle surfaces.

The analysis obtained from the proposed 2-layer-coatings composed

of a polymeric layer with SIP followed by a layer with H1 incorporated, has shown high impedances and also suggests that the presence of H1 in the second layer contributes to better corrosion protection of the system in the first hours of the experiment ($\sim 6\text{ h}$).

CRediT authorship contribution statement

Diulia Quites: Investigation, Formal analysis, Writing – original draft. **Anthony Somers:** Writing – review & editing, Data curation, Formal analysis. **Maria Forsyth:** Conceptualization, Writing – review & editing, Supervision. **Maria Paulis:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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