

Incorporation of a Coumarate Based Corrosion Inhibitor in Waterborne Polymeric Binders for Corrosion Protection Applications

Diulia Quites, Jose Ramon Leiza, Daniele Mantione, Anthony Somers, Maria Forsyth, and Maria Paulis*

The incorporation of organic corrosion inhibitors into waterborne coatings is optimized in this work. Herein, *p*-coumaric acid (4-hydroxycinnamic acid) is modified by a butyl radical and its effectiveness as an anticorrosive free inhibitor in solution is confirmed by potentiodynamic polarization (PP). The molecule is then successfully incorporated into waterborne polymeric binders by employing different polymerization techniques in dispersed media. Whenever possible, the inhibitor is also blended into the bare latexes to compare the effect of the incorporating method. The anticorrosion performance of the obtained coatings is tested and compared by electrochemical analysis. Promising results are obtained for the coatings produced by semibatch emulsion polymerization even at the low concentration of 1.5 mg of inhibitor g^{-1} latex. The intact control coating without inhibitor shows an impedance of up to $10^6 \Omega$ and a phase angle of 72° after 1 h of immersion in the corrosive medium, meanwhile the coating with inhibitor shows higher values, $10^{6.7} \Omega$ and 80° . Active corrosion inhibition is observed in the coating with inhibitor in which a defect has been done, as the impedances drop to $10^{3.9} \Omega$ after 24 h of immersion in the saline solution while in the control scratched coating it drops to $10^{3.6} \Omega$.

1. Introduction

Mitigation of mild steel corrosion is still a challenge, and is the cause of worldwide economic loss, accidents, and environmental impacts.^[1] One of the most common and effective method for mitigation of corrosion in metallic materials is the use of organic coatings, mainly solvent-borne.^[2,3] However, recently there has been a push to reduce the concentration of volatile organic compounds (VOCs) present in these traditional solvent-borne coatings,^[4] so waterborne coatings have become an industrially viable alternative to fulfill such environmental regulations.^[5–7] These coatings are obtained from latexes, polymer particles dispersed in water, which form a continuous film by the coalescence of the particles, as the water present in the latex dries when applied on substrates.^[8,9] One of the major challenges to overcome for the industrial application of waterborne coatings on metallic surfaces is that the presence of water can contribute to the formation of flash rust.^[10,11]

Different polymerization techniques can be used to produce a latex, such as dispersion polymerization, emulsion polymerization, and mini-emulsion polymerization. In dispersion polymerization the system is initially composed by a single homogeneous phase containing monomer, initiator, stabilizer, and solvent. As the reaction proceeds, amphiphilic species produced by grafting of growing in stabilizer molecules self-aggregate forming polymer particles that grow by absorption of monomer and further polymerization.^[12] Emulsion polymerization is the most common and simple technique for the production of waterborne polymeric dispersions.^[4,13–15] The mechanism of an ab-initio batch emulsion polymerization initiated by aqueous phase soluble initiators can be summarized in three intervals:^[16] a) Nucleation of polymer particles by entry of oligoradicals into micelles (first interval). b) Particle growth by diffusion of monomer from the droplets to the growing particles (2nd interval). c) Once the monomer droplets are depleted, the remaining monomer in the polymer particles is consumed (3rd interval) to produce the final polymer particles dispersion or latex.^[4] The conventional emulsion polymerization is not suitable in the presence of very

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hydrophobic reactants or for the encapsulation of compounds. In those cases, miniemulsion polymerization is employed;^[6] here, energy is applied to a coarse emulsion to reduce the size of the monomer droplets, producing a dispersion of monomer nanodroplets. This nanodroplet dispersion is polymerized by the addition of initiator and degradation of the monomer nanodroplets (so called Ostwald ripening) is prevented by the use of a co-stabilizer. The co-stabilizer, a water-insoluble compound, retards the miniemulsion degradation by molecular diffusion because its slow rate of diffusion would permit the monomer to remain essentially equilibrated among the nanodroplets of different size.^[6]

A waterborne coating is formulated using the binder (latex) and a pigment dispersion that incorporated a series of additives including, among others, dispersing agents, plasticizers, anti-foaming agents, and specially corrosion inhibitors, when high-performance anticorrosion coatings are targeted. The main function of a coating is to form a physical protective barrier, limiting the diffusion of ions and other species from the corrosive media to the metal surface.^[5,17] In organic coatings, the barrier property is mainly provided by the polymer matrix. Corrosion inhibitors may be added to the coating by different methodologies to provide extra protection.^[18–20] As mentioned above, corrosion inhibitors are typically included in the pigment dispersion of the formulation. This results in a heterogeneous distribution of the inhibitor in the coating and may contribute to premature leaching of the inhibitors.^[21] An alternative technique is the incorporation of inhibitors into the binder during the polymerization reaction, which allows for a more homogeneous distribution of inhibitors and increases the leaching time.^[7,19,21]

Chromate-based inhibitors are known to be the most efficient corrosion inhibitors; nevertheless, they have been banned in nearly all cases due to their toxicity and environmental hazards.^[22,23] Hence, there is an increasing interest in the study of environmentally friendly inhibitors. Organic inhibitors are appealing due to their relatively easy synthesis and application, and importantly, their high protection. They are known for adsorbing onto the metal surface and acting predominantly as an anodic inhibitor.^[24] Here, the polar group of the molecule attaches directly to the metal and the nonpolar end is oriented in a vertical direction, forming a protective hydrophobic film.^[25,26]

Among the promising carboxylate compounds, *p*-coumaric acid (4-hydroxycinnamic acid) combined with new rare earth elements, has been reported to be an efficient free corrosion inhibitor in solution.^[2,21,27,28] A better performance was observed in 4-hydroxy cinnamate based sol-gel formulations after the successful incorporation of lanthanum.^[29,30] Recently, ionic coumarate corrosion inhibitors have been incorporated into acrylic UV coatings showing promising results in terms of corrosion inhibition.^[31–33] An interesting methodology for the industrial application of those carboxylate inhibitors would be to incorporate them into waterborne latexes. Conversely, conventional latexes are electrostatically stabilized by anionic surfactants and hence increasing ionic strength might destabilize the dispersion (coagulation). Therefore, the acid form of the carboxylate inhibitors is more suitable for its incorporation into waterborne systems.

For the present work, the molecule of *p*-coumaric acid (**Figure 1**) was modified by the addition of a butyl (H4) radical to its structure, according to the technique proposed by Naciri et al.^[34] The

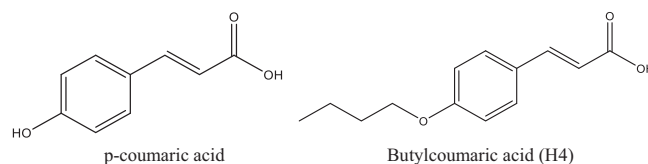


Figure 1. Chemical structures of *p*-coumaric acid (4-hydroxycinnamic acid) and butylcoumaric acid (H4).

nonpolar radical is supposed to contribute to the formation of a protective hydrophobic film where the molecule is adsorbed onto a metal substrate, in addition to decreasing its solubility in water, preventing a rapid leaching profile. The aim of the present work was the incorporation of the H4 corrosion inhibitor into waterborne polymer dispersions (latex) using industrially viable heterophase polymerization techniques. For this purpose, first the anticorrosion efficiency of H4 was assessed in solution. Then, and for the first time to the best of our knowledge, it was incorporated into polymer latexes synthesized by either dispersion, emulsion, or miniemulsion polymerization. Whenever possible, the inhibitor was also blended into the bare latexes to compare the method of incorporation into the anticorrosion properties of the coatings. The effectiveness of the obtained coatings was compared by electrochemical analysis.

2. Experimental Section

2.1. Materials

Methyl methacrylate (MMA), *n*-butyl acrylate (BA) (Quimidroga), and acrylic acid (AA, Aldrich) were used as received. Dodecyl diphenyl oxide disulfonate (Dowfax 2A1 45%, Dow Chemical Company), and sodium dodecyl sulfate (SDS, Aldrich) were used as anionic emulsifiers. Azobis(isobutyronitrile) (AIBN, Fluka), 2,2'-Azobis(2-methylbutyronitrile) (AMBN, Aldrich), and potassium persulfate (KPS, Aldrich) were used as radical initiators. Distilled water was used in the aqueous media of the reactions, and MilliQ water was used for the electrochemical tests. Hydroquinone (HQ, Aldrich) was used as a polymerization inhibitor to enable quantification of the conversion of reactions. Steel substrates (medium carbon steel with 0.5% of carbon) from UR-DURI 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. Electrochemical Analysis of H4 as a Free Inhibitor

The anticorrosive properties of H4 in solution were evaluated by electrochemical impedance spectroscopy (EIS) and PP experiments using a low current channel of the potentiostat BIOLOGIC VMP3 and EC Lab V11.26 software. The experiments were performed at room temperature and open to air, with a cell composed of reference electrode of Ag/AgCl (saturated with KCl), medium carbon steel substrates as the working electrode, and a graphite rod counter electrode. The tests were carried out using an exposure area of 1.1 cm². The open circuit voltage (OCV)

Table 1. Recipe used for the dispersion polymerization reactions.

	Components	Mass [g]
Initial charge	MMA	6.15
	BA	6.15
	Visiomer MPEG 2005 (22% wbm*)	5.4
	H4 (0/3% wbm*)	0 / 0.37
	Methanol/water (30/70%)	22.3
Solution of initiator	AMBN (1.7% wbm*)	0.2
	Methanol/water (30/70%)	10

*Weight based on monomer.

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^{-1} with 6 points per decade and a sinusoidal amplitude of 10 mV. Impedance responses were monitored for 24 h, followed by a PP experiment. $0.3 \times 10^{-3} \text{ M}$ of the inhibitor was dissolved in a 0.01 M NaCl corrosive solution of ethanol and water. Ethanol was added to enhance the solubility of the inhibitor, and the solution was heated for 2 h at low temperature to evaporate the ethanol. For comparison purposes, a control experiment with no inhibitor was also performed. Tests were done in triplicate.

The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) values were extracted from the PP curves by Tafel extrapolation. The linearity of the curves was found to be over a range of 10–25 mV at both sides of E_{corr} . The value of I_{corr} corresponds to the point on the graph in which the linear extrapolations of the anodic and the cathodic sections of the curves intersect. The inhibitor efficiency (IE) was calculated by Equation (1).

$$\text{IE} = \frac{I_{\text{corr control}} - I_{\text{corr inhibited}}}{I_{\text{corr control}}} \times 100 \quad (1)$$

2.3. Bulk Polymerization in the Presence of H4

Bulk polymerization reactions were monitored by proton NMR, in order to analyze the effect of the presence of H4 in the kinetics of MMA and BA (50/50) copolymerization. Bulk copolymerizations were carried out in NMR tubes at $70 \text{ }^\circ\text{C}$, with inhibitor concentrations of 0, 1, and 3% (g H4/100 g monomer). AMBN was used as the initiator at a concentration of 1% (g AMBN/100 g monomer). The vinyl protons of MMA (6.3–6.4 ppm) and BA (5.9–6.0 ppm) monomers were used to monitor the evolution of conversion. A representative spectrum taken during the copolymerization experiment with 1% of H4 at time 0 of reaction is shown in the Supporting Information.

2.4. Synthesis of Waterborne Poly(MMA/BA) Latex by Dispersion Polymerization (30 wt% Solids Content)

Dispersion polymerization reactions were carried out in a 100 mL round bottom flask immersed in a bath of water. The initial charge is homogeneous and it is composed by the reagents presented in Table 1. The solution was mixed for 10 min, then continuously agitated (250 rpm) and purged with N_2 for at least

Table 2. Recipe used for the emulsion polymerization reaction with 20% solids content.

	Components	Mass [g]
Organic phase	MMA	4.95
	BA	4.95
	AA	0.1
	H4	0 / 0.1
Aqueous phase	SDS	0.2
	H_2O	35
Initiator solution	KPS	0.1
	H_2O	5.0

15 min before addition of the initiator at $70 \text{ }^\circ\text{C}$. Latexes were produced with a H4 inhibitor concentration of 3% (g H4/100 g monomer), and a control latex (with no inhibitor) was also prepared for comparison purposes. The final latexes have solids content of 30%.

Additionally, as H4 is soluble in methanol, the inhibitors were blended with the control latex to form a final concentration of 3% (g H4/100 g monomer), equivalent to the latexes with the inhibitors incorporated in the polymerization step. The purpose was to compare both methodologies to analyze which one is more promising in terms of corrosion inhibition efficiency.

The partition of H4 between the polymer particles and the continuous phase is expected to be the main difference between both methods of inhibitor addition to the dispersion latex. In order to quantify the amount of inhibitor in the aqueous phase of the final latexes, calibration curves of H4 in methanol/water (70/30, m/m) were constructed using ultraviolet spectroscopy (UV 2550, Shimadzu). Then, samples of latex with H4 incorporated and with H4 blended were centrifuged for 6 h at $-4 \text{ }^\circ\text{C}$ and 13 000 rpm. The serum was analyzed in UV by triplicate. Using the data obtained by the calibration curve, the concentration of H4 located outside the particles was calculated.

2.5. Synthesis of Waterborne Poly(MMA/BA) by Emulsion Polymerization (20 wt% Solids Content)

H4 inhibitor was also incorporated in latexes by emulsion polymerization. The reactions were prepared according to the recipe described in Table 2, to obtain latexes with 20% solids content. Initially the aqueous and organic phases were mixed, agitated for 10 min, and finally placed in the round bottom flask. The solution was continuously agitated (250 rpm) and fed with N_2 for at least 15 min. When the system reached $70 \text{ }^\circ\text{C}$, the initiator solution was added, commencing the reaction.

2.6. Synthesis of Waterborne Poly(MMA/BA) by Miniemulsion Polymerization

2.6.1. Low solids Content Latexes (20%) by Batch Polymerization

Miniemulsion polymerization reactions were also performed in order to incorporate the H4 inhibitor into latexes. The reactions

Table 3. Recipe used for miniemulsion polymerization reactions with 20% solids content.

	Components	Mass [g]
Organic phase	MMA	4.95
	BA	4.95
	AA	0.1
	Octadecyl acrylate	0.4
Aqueous phase	H4	0/0.1
	SDS	0.2
Initiator solution	H ₂ O	35
	KPS	0.1
	H ₂ O	5.0

were prepared according to the recipe described in **Table 3**, to obtain latexes with 20% solids content. A co-stabilizer compound, octadecyl acrylate, was added to the organic phase to minimize the Ostwald ripening. Both the aqueous and organic phases were initially mixed and agitated for 10 min. Then, the mixture was sonified using a Branson Sonifier 450 for 5 min (operating at the 1-output control and 80% duty cycle in an ice bath and under magnetic stirring at 300 rpm) to reduce the size of the monomer droplets. The prepared miniemulsion was then placed in the 100 mL round bottom flask and it was continuously agitated (250 rpm) and fed with N₂ for at least 15 min. When the system reached 70 °C, the solution of initiator was added, and the reaction was continued for 3 h.

2.6.2. High Solids Content Latexes (50% SC) by Semibatch Emulsion Polymerization

In order to increase the solids content of the latexes containing the H4 inhibitor, a two stage seeded semibatch emulsion polymerization process was implemented. The seed latexes were prepared by miniemulsion polymerization containing H4 inhibitor. These polymerization reactions were carried out under N₂ atmosphere in a 250 mL glass-jacketed reactor. The temperature was maintained at 75 °C, and the impeller rotation speed at 200 rpm. Initially, a seed of 30% solids content with 1% H4 inhibitor (g H4/100 g monomer) was prepared by batch miniemulsion polymerization (as in Section 2.6.1). In the second stage a pre-emulsion of MMA, BA, water, and surfactant was continuously fed for 3 h in order to increase the solids content of the latex to 50%. Therefore, the concentration of H4 in the final latex was 1.5 mg H4 per gram latex (0.15% H4). A post polymerization step was performed at 90 °C for 1 h to eliminate traces of monomer. A control latex with no H4 was also produced for comparison purposes. The recipe used for the polymerizations is presented in **Table 4**.

2.7. Characterizations of Latexes and Coatings

2.7.1. Monomer Conversion and Particle size

Monomer conversion was followed by gravimetry. Samples were taken from the reaction over time and placed in a pre-weighed

Table 4. Recipe used for the two stage seeded semibatch emulsion polymerization reactions.

	Seed Components	Mass [g]
Organic phase	MMA	14.85
	BA	14.85
	AA	0.3
	Octadecyl Acrylate	1.2
Aqueous phase	H4 (0/ 1% wbm)	0/0.3
	SDS (2% wbm)	0.6
Initiator solution	H ₂ O	55
	KPS (1% wbm)	0.3
	H ₂ O	15
Preemulsion		
	Components	Mass [g]
Organic phase	MMA	34.65
	BA	34.65
	AA	0.7
Aqueous phase	SDS (1% wbm)	0.7
	H ₂ O	15
Initiator solution	KPS (0.5% wbm)	0.35
	H ₂ O	15

aluminum pan with droplets of hydroquinone (1 wt%) to stop the reaction. The pans were dried until a constant weight was obtained. The instantaneous conversion of each sample was obtained by Equation 2. The polymer particle sizes were measured by dynamic light scattering (DLS) using a Zetasizer Nano Series (Malvern instrument) after diluting the samples with deionized water.

$$X(t) = \frac{(\text{solids content}) - (\text{fraction of non polymerizable material})}{\text{fraction of monomers}} \quad (2)$$

2.7.2. Water Uptake of Free Films

To analyze the absorption of water in the films, latex samples were placed in silicone molds and dried at room temperature for 7 days. The films were peeled from the molds and immersed in distilled water. The water uptake was followed for 11 days, in triplicate and was measured by the difference between the weight of the film after immersion in water and the initial weight.

2.7.3. Preparation of Steel Substrates and EIS of Coatings

The steel substrate surfaces were used as received. The substrates were cleaned with abundant acetone and dried with compressed air before deposition of the latex. The samples were dried at room temperature for at least 1 day. The final thickness of the coatings

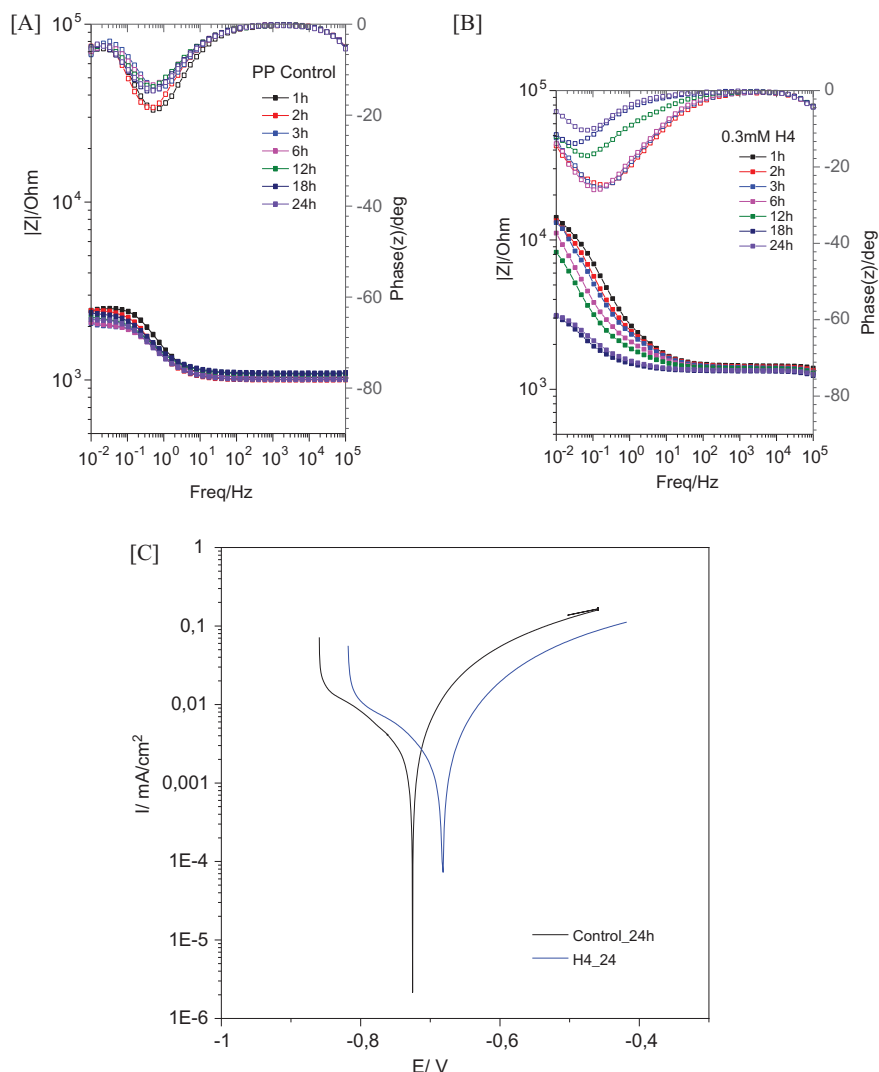


Figure 2. Bode spectra of steel immersed in A) the control solution (0.01 M NaCl) and B) the solution containing the H4 inhibitor (0.3×10^{-3} M H4 in 0.01 M NaCl) over 24 h; C) potentiodynamic polarization (PP) curves of the control and H4 solutions after 24 h at open circuit voltage (OCV).

was measured with a coating thickness gauge to ensure that the final film had an average thickness of 45 μm .

EIS was performed over 24 h according to the same procedure reported in Section 2.2, except that the concentration of the corrosive solution used was 0.005 M NaCl. In addition to these EIS measurements on the intact films, EIS measurements were also carried out for films in which an artificial scratch (1.1 cm in size and 0.1 mm thick) was made. EIS analyses were performed on the scratched coatings to determine if H4 imparts any active anticorrosive properties to the system where the barrier properties of the coating were removed.

3. Results and Discussion

3.1. Electrochemical Analysis of H4 as a Free Inhibitor

The anticorrosive property of H4 was investigated by EIS (Figure 2A (control) and Figure 2B (0.3×10^{-3} M H4)). This concentra-

tion was chosen as it is approximately the maximum solubility observed for the component in the system. The molecules of H4 dispersed in the corrosive solution are expected to diffuse from the bulk of the solution and adsorb onto steel surfaces, forming a protective layer. In the first hour of immersion, the solution with H4 shows higher impedance values ($10^4/Z/$) in the low frequency range and also a higher phase angle (27 degrees) when compared to the control ($10^{3.2}/Z/$, 19 degrees), demonstrating that H4 molecules do provide a degree of corrosion protection to the metal surface even at such low concentrations. However, a significant decrease in the impedance and phase is observed after 12 h of experiment, indicating that the concentration of inhibitors was not sufficient to maintain the corrosion protection of the system for 24 h.

The PP spectra are shown in Figure 2C. A shift in the corrosion potential (E_{corr}) toward a more positive value is observed in the solution of inhibitor. The average E_{corr} of the control was -717.1 ± 8.5 mV, whereas the solution with H4 yielded an average E_{corr} of

Table 5. Corrosion potentials (E_{corr}), corrosion current density (I_{corr}), Tafel anodic, and cathodic slopes (β_a and β_c) of the control and inhibitor sample.

Solution	E_{corr} [mV]	I_{corr} [mA cm^{-2}]	β_a [mV decade^{-1}]	β_c [mV decade^{-1}]	IE [%]
Control	-717.1 ± 8.5	1.87 ± 0.5	32.0 ± 1.3	46.25 ± 7.36	-
H4	-714.5 ± 28	0.64 ± 0.2	33.5 ± 1.6	42.33 ± 6.04	66

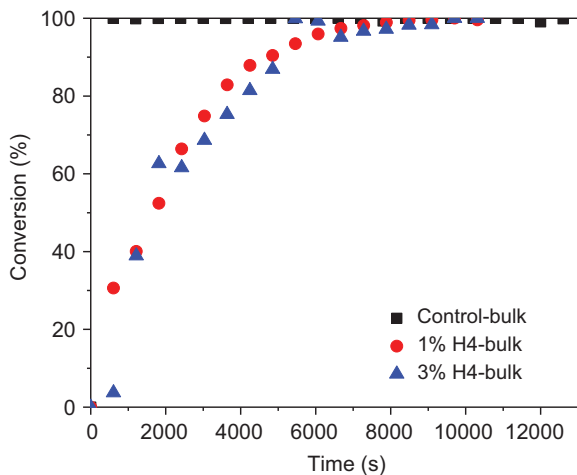


Figure 3. Conversion of methyl methacrylate (MMA) in bulk radical copolymerization of MMA/*n*-butyl acrylate (BA) in the presence of H4, as measured by ^1H NMR.

-714.5 ± 28 mV, indicating that H4 primarily suppresses the anodic reaction of corrosion. The corrosion current of the control was found to be 1.87 ± 0.5 mA cm^{-2} while the solution with H4 had a current of 0.64 ± 0.2 mA cm^{-2} , giving an inhibition efficiency of 66% (see Table 5).

Once the inhibitor effect of H4 in solution was assessed, its incorporation into waterborne coatings was investigated in order to provide longer term protection. It is important to highlight though, that even when the property of an inhibitor is well known, the outcome of its incorporation into a coating is not predictable.^[20]

3.2. Bulk Polymerization

In order to analyze the effect that H4 inhibitor molecules may have on the rate of monomer polymerization, the radical copolymerization of the MMA/BA mixture was carried out in bulk, in the absence and presence of H4 molecules. This study was monitored by ^1H NMR. It was observed that the conversion of MMA in the copolymerization of MMA/BA is retarded in the presence of H4 at 70°C (Figure 3). It is known that compounds with aromatic rings in their composition may retard free radical polymerization reactions.^[35,36] The kinetic profile observed in the system with 1% H4 (g H4/100 g monomer) is very similar to the one with 3% H4 (g H4/100 g monomer), and since precipitation of some of the H4 was observed in the bottom of the NMR tube containing the system prepared with 3% H4 (indicating that the concentration

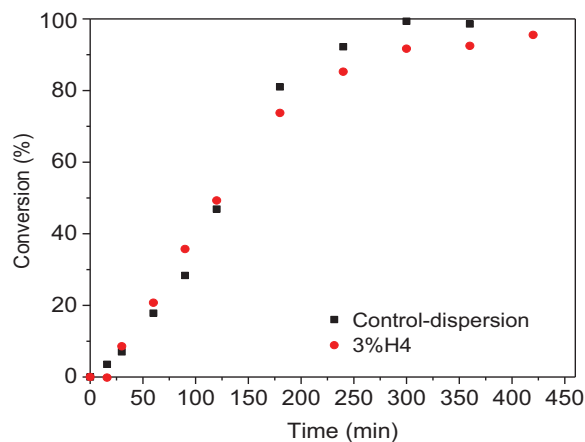


Figure 4. Kinetics of batch dispersion copolymerization reactions of methyl methacrylate (MMA)/*n*-butyl acrylate (BA) carried out in the absence (control dispersion) and presence of H4 (3%).

was over its solubility), a H4 concentration of 1% was adopted as the limit for the solubility/dispersibility of H4 into the MMA/BA (50/50) monomer mixture.

3.3. Coatings Made by Dispersion Polymerization Reactions with H4 Incorporated/Blended

Once the inhibitory effect of H4 on the radical polymerization of MMA/BA was identified, the first attempts to incorporate it in waterborne binders were carried out by dispersion polymerization. H4 was found to be soluble in the initial methanol/water/monomer phase used in the dispersion polymerization recipe,^[37] enabling its incorporation. The kinetics of the dispersion polymerization reactions performed in both the absence (control-dispersion) and presence (3% H4) of H4 molecules are presented in Figure 4. In principle, the radical reaction inhibitory effect of H4 is not so evident from these reactions, even though the final monomer conversion achieved in the presence of H4 was slightly lower than the control. Thus, the H4 molecules were successfully incorporated into the polymer particles dispersed in the continuous methanol/water phase. The average particle size of the control-dispersion latex, 135 nm, was determined to be larger than that of the latex with H4, which was 115 nm. Additionally, the control-dispersion latex was blended with H4 after the polymerization step, in order to analyze the effect of having the H4 molecules mainly in the continuous methanol/water phase.

To analyze the partition of the inhibitor between the continuous media and the polymer particles, a calibration curve of H4 in methanol/water (70/30) was constructed, and then the continuous phase of both latexes (after centrifugation) was analyzed. For the latex where H4 was incorporated in the copolymerization, 48% of the total amount of inhibitor was in the media, with the remaining 52% of the inhibitor in the polymer particles. On the other hand, in the dispersion obtained by blending the bare latex and the H4 inhibitor, 100% of the inhibitor was found in the media. Therefore, it is expected that this difference in availability

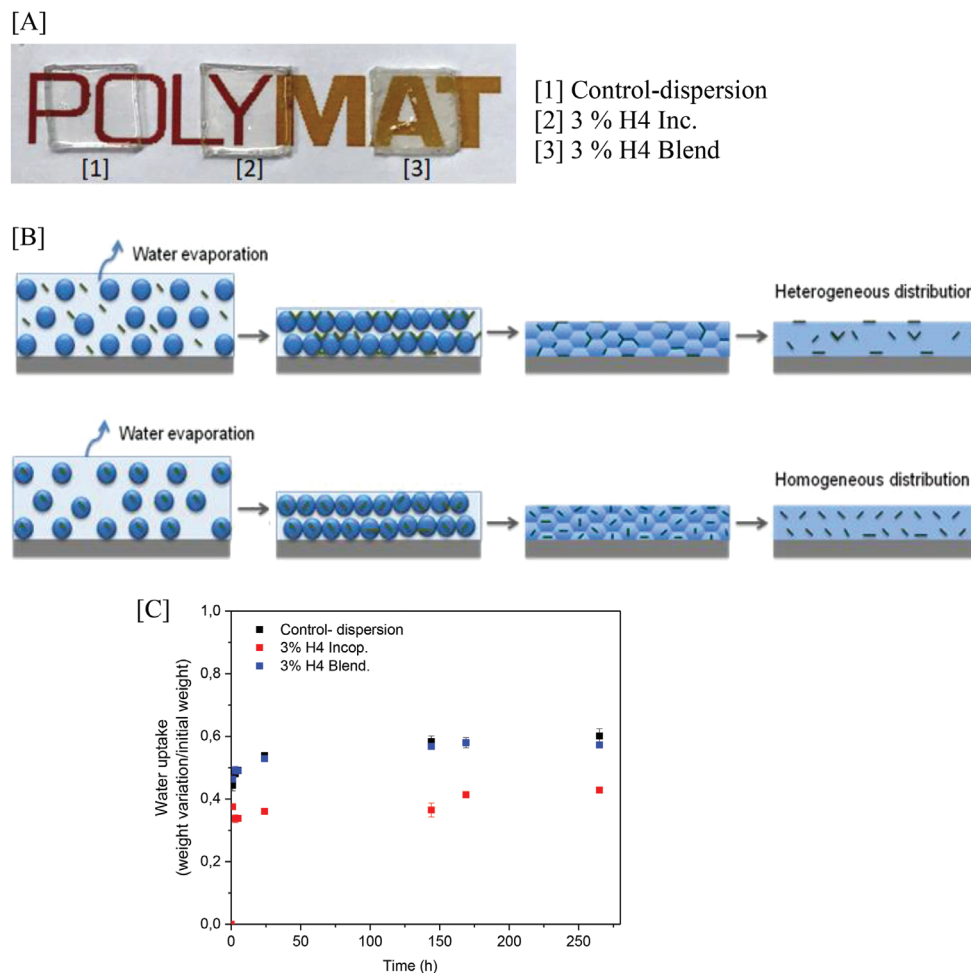


Figure 5. A) Images of the free latex films formed from control dispersion, dispersion with 3% H4 incorporated and 3% H4 blended. B) Scheme of H4 blending and incorporation in the latexes; when the inhibitor (black lines) is blended into the latex a heterogeneous distribution of it into the film is obtained but when incorporated into the binder (blue circles) an homogeneous distribution is reached. C) Water absorption of the free films over time.

of the H4 inhibitor will vary the corrosion inhibiting effect of the films produced from these latexes.

The free films formed from both the control-dispersion latex and the latex with H4 incorporated are transparent (Figure 5A). However, the free film obtained from the latex with H4 blended is opaque. It is likely that the opacity is due to an accumulation of inhibitor molecules in the interstices of the particles during film formation. This is in contrast to the events occurring during film formation from latex with H4, as the incorporation of H4 in the particles results in its higher dispersion in the final film (Figure 5B).

The water uptake of these three films is shown in Figure 5C. The absorption of water is nearly the same for the control film and the film with H4 blended, however, the film with H4 incorporated absorbs less water. This result indicates that the incorporation of H4 into the polymer particles and hence, its higher distribution during film formation, contributes to the film being more hydrophobic.

Finally, the corrosion inhibitory effect of these three films coated on steel was analyzed by EIS (Figure 6A–D), optical

images of the sample before and after the experiment were also taken. The Bode spectra of the control-dispersion coating (Figure 6B) is characteristic of soft coatings that allow diffusion of water, and it has no phase angle peaks at high frequencies that are normally associated with a barrier coating.^[38] The control-dispersion coating offers no significant anticorrosive protection to the bare steel substrate (Figure 6A,B). Therefore, any increase in impedance that is observed in the other coatings will exclusively result from the anticorrosive properties of the inhibitors in the films. Higher impedances are observed in the first 3 h of analysis for the coating with H4 blended and in the first hour for the film with H4 incorporated, highlighting the anticorrosive properties of H4. The difference between the two may be due to the availability of H4 in the system; in the coating in which H4 is incorporated, almost half of it is attached to the polymeric particles, as previously determined by calculation of the partition of H4 into the phases. On the other hand, in the coating with the blended H4, all of it is free in the medium. Therefore, when the coating is applied on the steel, a higher amount of H4 molecules are free to diffuse onto the metal surface to produce

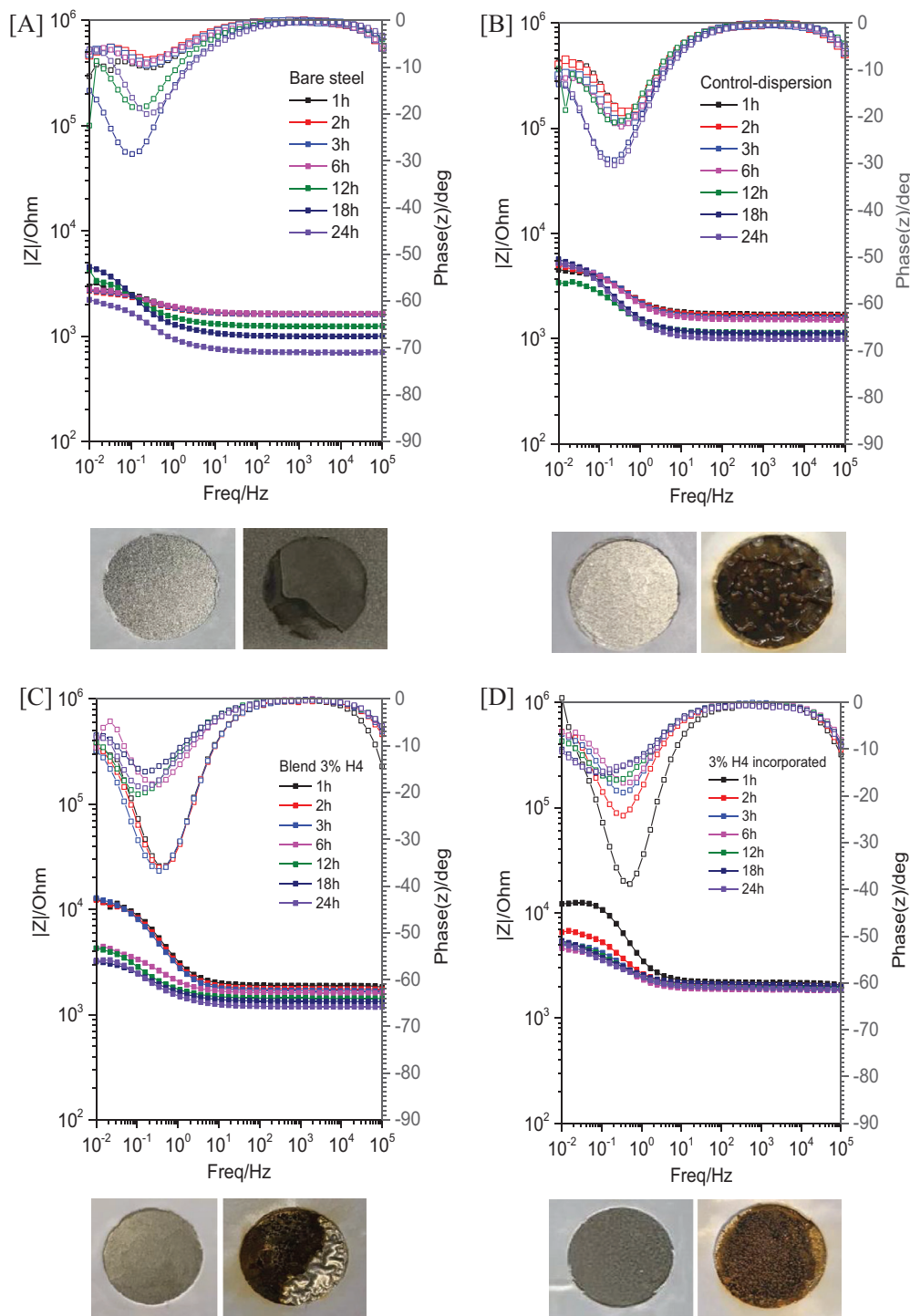


Figure 6. Electrochemical impedance spectra of bare steel and of coatings made by dispersion polymerization followed by optical images of the samples before (on the left) and after the experiment (on the right). A) Bare steel; B) control coating; C) coating with 3% H4 blended; and D) coating with 3% H4 incorporated.

the corrosion inhibitory effect in the blended system than in the case of the incorporated system. In any case, the anticorrosive effect of H4 does not last for 24 h in this system; this may be due to the poor barrier properties of the control-dispersion film or the low concentration of H4 in the system.

3.4. Coatings Made by Emulsion Polymerization with H4 Incorporated

As seen above, the inhibitory effect of H4 was observed in the dispersion latex coatings, but the low barrier properties of

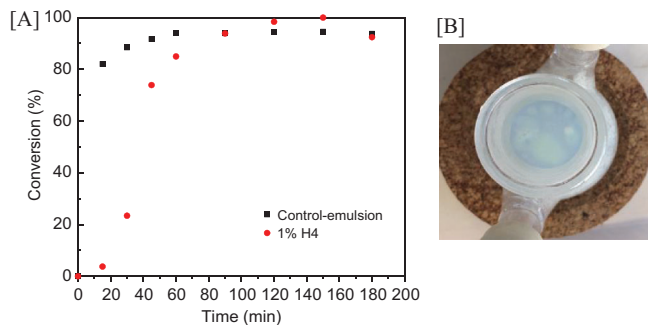


Figure 7. A) Kinetics of emulsion polymerization reactions (20% solids content [SC]); and B) supernatant observed at the end of the reaction with H4.

the control-dispersion film itself led to low corrosion protection films. This could be explained by the large amount of stabilizer (Visiomer) present in the recipe, which can increase the hydrophilicity and water permeability of the final films.^[39] In order to decrease the amount of stabilizer/emulsifier required to produce waterborne latexes containing H4, emulsion polymerization was used to synthesize the latex. However, two main drawbacks were found when this polymerization technique was used. On one hand, as displayed in **Figure 7A**, the conversion of the monomers was retarded by the presence of H4 molecules in the system. On the other hand, even if a stable latex was obtained from both formulas, a supernatant was observed at the end of the reaction from the H4 containing latex, which was confirmed to be mainly composed of H4 by NMR (Figure 7B). Due to the hydrophobic character of H4, its diffusion from the droplets of monomer to the polymer particles during the emulsion polymerization is difficult, preventing its incorporation in the polymer particles. As a result, H4 segregates and phase separates, ending up on the surface of the latex. Thus, the incorporation of H4 was not successful by emulsion polymerization.

3.5. Coatings Made by Miniemulsion Polymerization

Once the emulsion polymerization technique was discarded for the incorporation of H4 inhibitor to waterborne coatings, the

miniemulsion polymerization technique was pursued. In this polymerization technique, the monomer polymerizes directly in the monomer droplets, without needing to be transported through the water phase. Therefore, it was hypothesized that if the H4 molecules can be initially placed in the monomer droplets, they would remain in the final polymer particles. Two types of processes were tried by miniemulsion polymerization; one as a single stage batch to obtain a dispersion with solids content of 20%, and another using a two stage seeded semibatch emulsion polymerization, to achieve higher final solids content (50% SC). In the latter, the first stage was a batch miniemulsion polymerization where the H4 was incorporated.

3.5.1. Single Stage Batch Miniemulsion Polymerization (20 wt% Solids Content)

Batch miniemulsion polymerizations were carried out in the absence and presence of H4. It was observed that at 70 °C, the reaction was also retarded by the presence of 1% of H4 (**Figure 8A**). On the other hand, the presence of H4 in the system seems to contribute to the formation of smaller particles, as the average particle size of the control-miniemulsion latex was 90 nm, while that of the latex with 1% H4 was 80 nm. These latexes were applied onto steel substrates, and a brownish color, characteristic of flash rust was observed on the surface of the metal (**Figure 8B**). This flash rust was attributed to the high concentration of water in contact with the steel substrate for these low solids content (high water content) latexes. Therefore, as an attempt to prevent the flash rust, the formulation of the latexes was optimized in order to increase their solids content.

3.5.2. Two Stage Seeded Semibatch Emulsion Polymerization (50 wt% Solids Content)

Due to the exothermic character of polymerization reactions, batch polymerization reactions at high solids contents are not recommended, since thermal runaway could occur in these conditions. Therefore, first a low solids content latex (seed) was synthesized by miniemulsion polymerization incorporating all the

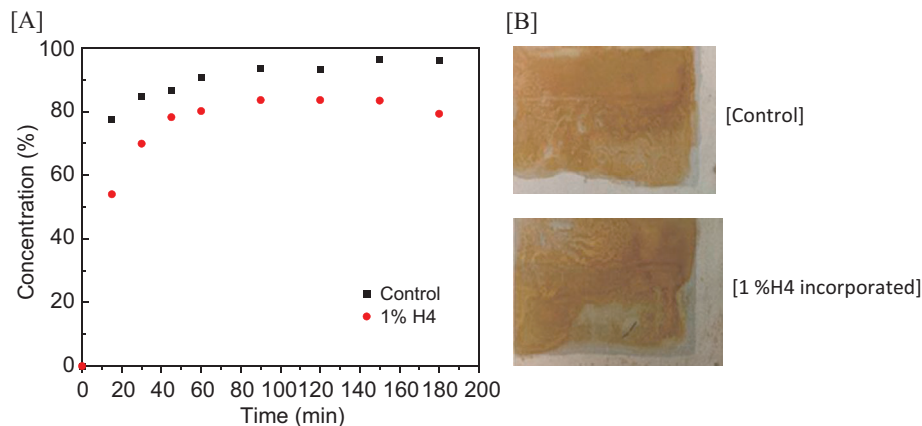


Figure 8. A) Kinetics of miniemulsion polymerization reactions (20% solids content [SC]); and B) images of the steel substrates coated with the latexes obtained with 20% SC, showing clear evidence of flash rust.

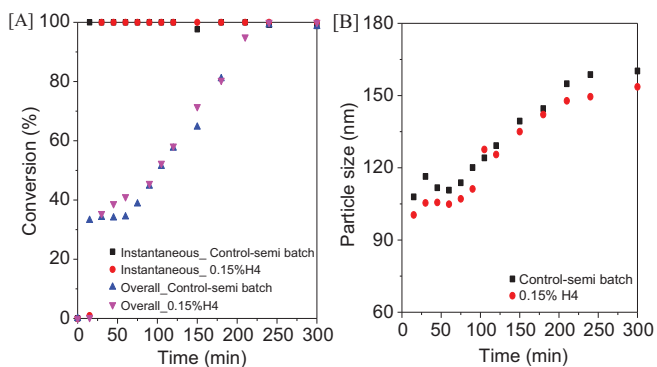


Figure 9. A) Kinetics of the semibatch emulsion polymerization reaction; and B) the average particle size obtained over the duration of the reaction.

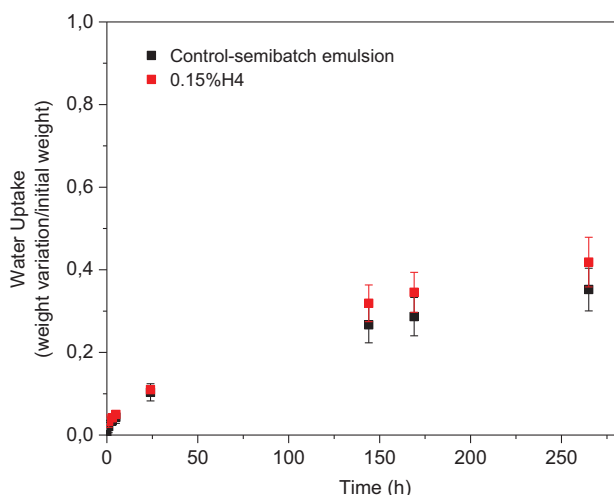


Figure 10. Water absorption of free semibatch emulsion films over time.

amount of the inhibitor H4 (1% based on the monomers in this step) in the formulation. This latex was then used as seed in the semibatch emulsion polymerization where the remaining MMA/BA monomers needed to produce a dispersion with 50% solids content were added as a preemulsion. The final H4 concentration in the latex was 0.15% based on total monomers. The polymerization reactions kinetics of this second process is presented in Figure 9A. It was observed that at 75 °C, the reaction was not retarded by the addition of H4. H4 may be partially hidden from the initiator radicals by the polymer in the seed, and its polymerization retardation effect may be therefore notably reduced. The instantaneous conversions are high and similar for both the control latex and the latex with H4. The evolution of the particle size over time is shown in Figure 9B. A similar particle size evolution can be seen in both cases, reaching 160 nm for the control-semibatch latex and 154 nm for the latex containing H4.

The water uptake of the free films is shown in Figure 10. The profile of the absorption of water is considerably different from the one observed in the films made via dispersion polymerization (Figure 5C). In the dispersion films, the absorption of water was rapid; the control-dispersion reached the maximum, 0.5 (weight

variation/real weight), after 24 h and remained constant until the end of the experiment. However, in the case of the films made by semibatch emulsion polymerization, the absorption of water was gradual, and the control-semibatch reached 0.35 (weight variation/initial weight) at the end of the experiment, after 24 h. This is related to the higher concentration of stabilizer (polyethylene oxide based macromonomer) used in the dispersion polymerization recipe, which is known to contribute to the absorption of water in waterborne films.^[39] There was no significant difference between the absorption of water of the free films formed from the emulsion-0.15% H4 and the control-semibatch over 24 h of immersion. This is an indication that the concentration of H4 incorporated into the film does not change the hydrophobicity of the film. However, after 144 h of immersion, the water uptake of the emulsion-0.15% H4 films was slightly higher than the control. This may be due to the creation of pores in emulsion-0.15% H4 film, as the inhibitor is leached out.

When these high solids content latexes were applied onto steel substrates, no flash rusting was formed. Therefore, their corrosion protection properties were measured by EIS, optical images of the sample surfaces before and after the experiment were also taken (Figure 11). A phase angle peak at high frequencies, normally associated with a barrier coating,^[38] is seen for the control-semibatch emulsion and also for the semibatch emulsion-0.15% H4. The EIS spectra indicate that the control-semibatch emulsion coating (Figure 9B) offers an effective barrier protection to the bare steel substrate (Figure 11A), showing impedances in the range of $10^{5.2}$ to 10^6 and phases angles of 54° to 72° from the moment immersed to 24 h after immersion in the corrosive medium. The coating with H4 incorporated shows more effective corrosion protection performance compared to the control-semibatch emulsion, with impedances in the range of 10^6 to $10^{6.7}$ and phases angles of 65° to 80° (Figure 11C) over the 24 h of immersion.

The phase angle approaches that for highly effective barrier coatings that show a capacitor behavior—phase angle of 90° .^[38] Optical images in Figure 11 of the bare steel and of the two coated systems before and after the 24 h of immersion also show the effective protection that the H4 containing semibatch emulsion gives the steel from corrosion. Therefore, it was confirmed that H4 is able to provide extra anticorrosive protection to the system, even in such low concentrations (1.5 mg H4 per gram polymer).

In a further analysis to assess the corrosion performance of the coatings when a defect is present, a scratch was made to both coatings applied on steel, and EIS measurements were conducted on these scratched samples. The spectra of the coatings with a scratch and the optical images of the sample surfaces before and after the experiment are presented in Figure 12 along with optical images before and after immersion. The impedance of the control-semibatch emulsion (Figure 12A) drops considerably faster than the one of the coating with H4 (Figure 12B). This phenomenon is mainly visible in the first hours of the experiment (1–6 h); the impedance of the coating with H4 incorporated dropped from $10^{4.2}$ to $10^{3.9}$ Ω , whereas the impedance of the control coating dropped from $10^{4.2}$ to $10^{3.6}$ Ω . This is an indication that even if H4 is incorporated into the polymer particles of the coating, it can be released and impart corrosion inhibiting properties. The effect does not last for long, probably because the

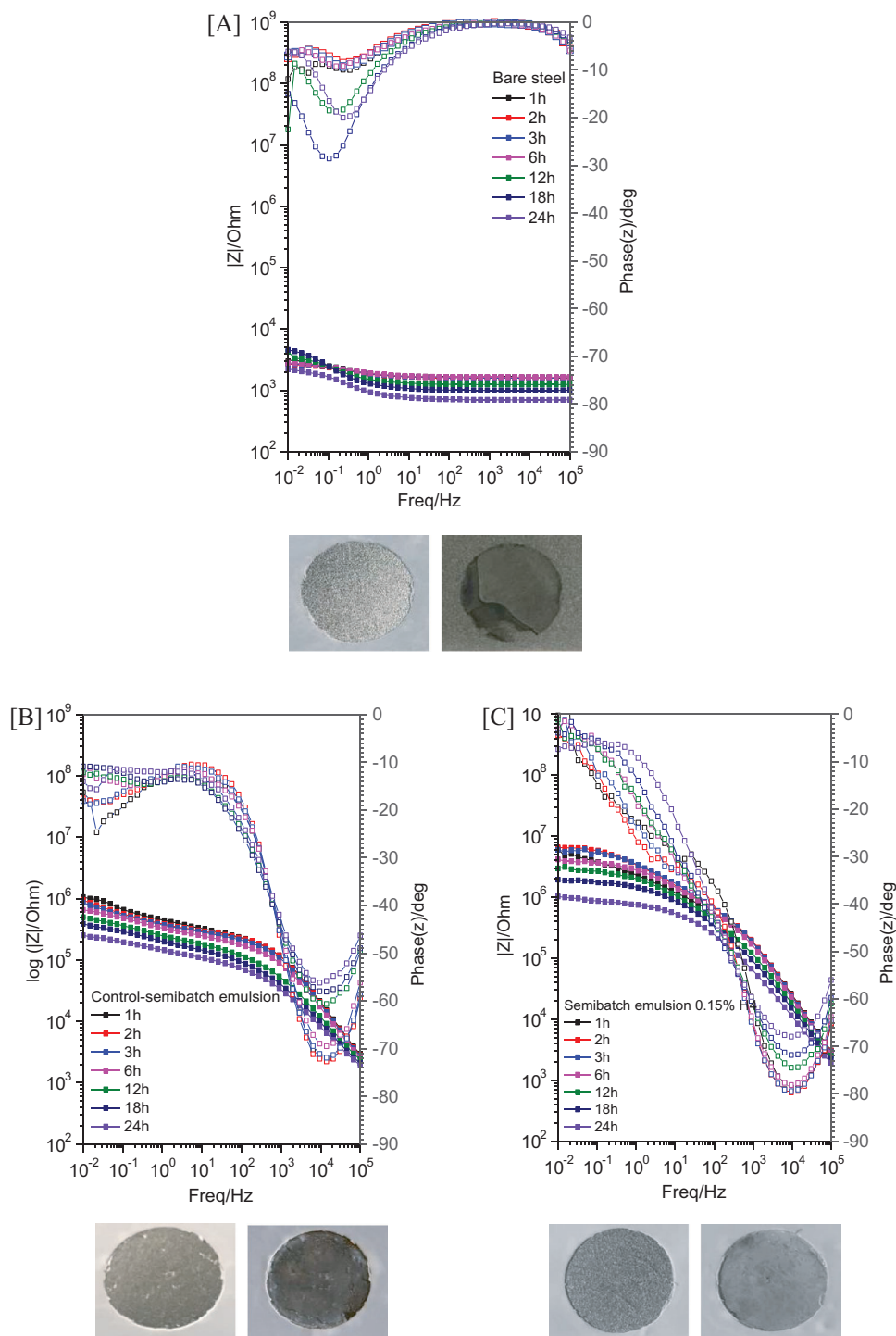


Figure 11. Electrochemical impedance spectra of coatings made by seeded semibatch emulsion polymerization and optical images of the sample before (on the left) and after the experiment (on the right) for A) the bare steel; B) the control coating; and C) the coating with H4.

concentration of inhibitor is low in this system. These findings were further proved by the fitting to equivalent circuit the EIS data obtained for intact and scratched coatings, as shown in the Supporting Information.

The optimum concentration of H4 is still under investigation. A higher amount of inhibitor in the system will most likely

be required, but the solubility of the inhibitor in the monomer system is limiting. It is also important to highlight that the recipe of the coating itself without inhibitors could be optimized to improve protection against corrosion, for instance by using more hydrophobic monomers and polymerizable functionalized surfactants.^[17]

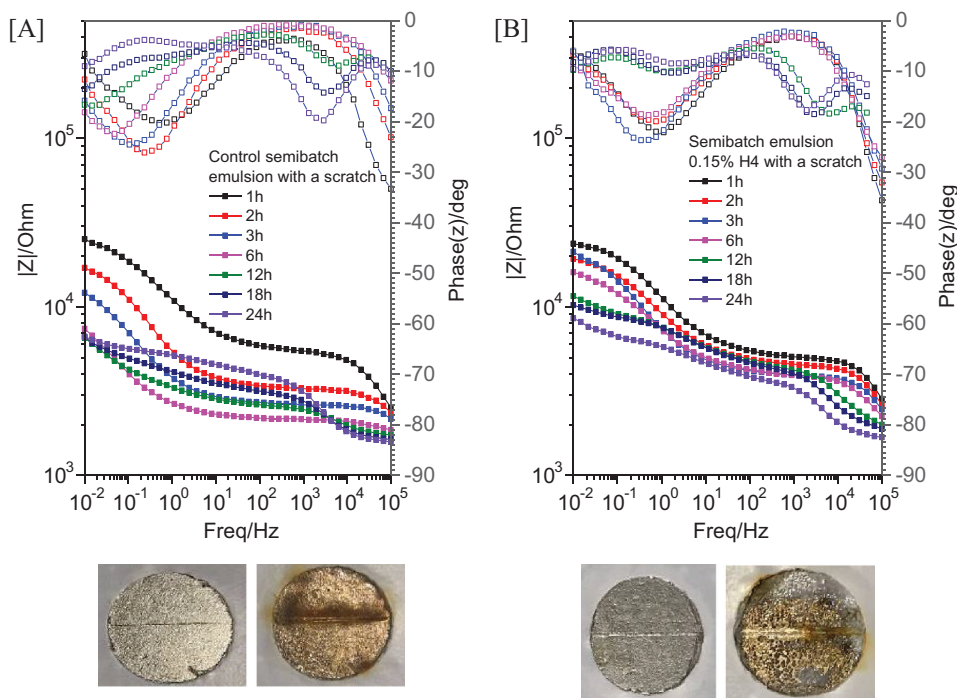


Figure 12. Electrochemical impedance spectra of coatings with a controlled scratch and optical images of the sample surfaces before (on the left) and after the experiment (on the right) for A) the control coating; and B) the coating with H4.

4. Conclusions

The anticorrosive property of H4 in solution was confirmed by potentiodynamic polarization (PP) analysis making it a suitable candidate to investigate as part of a coating system. It was not possible to incorporate H4 in waterborne binders by emulsion polymerization due to its resistance to diffusion through the water phase. However, H4 was successfully incorporated into the waterborne polymeric binder by dispersion polymerization, batch miniemulsion, and seeded semibatch emulsion polymerization with the H4 incorporated in the seed previously synthesized by miniemulsion polymerization. Blending H4 into the final latex, as opposed to incorporation into the separate polymer particles was possible only in the case of dispersion polymerization due to the presence of methanol that dissolves the inhibitor.

The coatings made by dispersion polymerization did not provide effective barrier protection to the steel substrate but in the presence of H4, either incorporated or blended, higher impedances were reached in the first hours of experiment. These results prove the concept that the presence of H4 in a coating can provide extra protection to the system. The coating with H4 blended provided protection for 6 h, while the one with H4 incorporated only provided it for the first hour. This difference was related to the availability of H4 in the system, as when blended, the inhibitor has higher mobility.

The coatings obtained by batch miniemulsion polymerization with low solids content were not able to avoid flash rust when applied to steel substrates. However, this could be avoided by increasing the solids content of the latex by seeded semibatch emulsion polymerization. These high solids content latexes provided an effective barrier protection to the steel surface and when the

inhibitor was incorporated, it gave extra protection to the system. Therefore, this methodology seems promising for the incorporation of inhibitors into the binder for development of waterborne coatings with anticorrosive properties. It is important to highlight that the latex recipe could still be optimized to obtain better results and the optimal concentration of H4 is still under investigation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

corrosion, corrosion inhibitors, organic coatings, waterborne latex

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