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Improvement of corrosion protection of steel by incorporation of a new phosphonated fatty acid in a phosphorus-containing polymer coating obtained by UV curing

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A B S T R A C T

Six formulations containing diacrylate monomers (from 89 to 92.5% (w/w)) as well as a phosphonated methacrylate monomer (from 1 to 10% (w/w)) were prepared. All formulations were UV-cured and the corrosion performance of the resulting coatings applied onto a steel substrate was assessed by electrochemical impedance spectroscopy (EIS). It was first shown that the coatings containing phosphonic acid methacrylate (MAPC1(OH)₂) instead of methacrylate phosphonic dimethyl ester (MAPC1) presented higher corrosion protection related to the strong adhesive properties of phosphonic acid on the metal substrate. A minimum MAPC1(OH)₂ content of 2.5% was determined to provide the highest impedance values (best efficiency). Then, a new bio-based compound, i.e. phosphonic acid-bearing oleic acid (phosphonated fatty acid), was synthesized and added as an inhibitor to the formulations. In the presence of this compound, the corrosion protection was notably improved. The beneficial effect of phosphonated fatty acid was explained by its inhibitive action at the steel/coating interface and by the improvement of the barrier properties.

Keywords:

Phosphonated methacrylate
Coating
Phosphonated fatty acid
Inhibitor
Electrochemical impedance spectroscopy

1. Introduction

In recent years, phosphorus-containing products have gained significant development due to their interesting properties in various applications. For example, dental adhesives, ion-exchange resins and adhesion promoters are three of the more common applications [1–7]. Furthermore, flame retardants containing phosphorus atoms progressively came to replace halogenated ones [8–12]. Phosphorus-containing compounds are excellent promoters with respect to adhesion, and thus improve anti-corrosion effects. Commercial anti-corrosion polymers are generally formed from Sipomer[®] or Phosmer[®] monomers, which are *phosphate*-type (meth)acrylates, and can be readily polymerized via emulsion or solution [13,14]. Sheffer et al. [15] reported the enhanced corrosion protection of sol-gel films on aluminum substrate by entrapping phosphonate group in organosilanes. However, phosphonate groups which remain as additives in a physical mixture can lead to dynamic phenomena such as aggregation, phase separation or leaching by solvent or water with time. Such

disadvantages can be overcome if the phosphonates form part of polymer network. Kannan et al. [16,17] reported the synthesis of a highly cross-linked methacrylate-phospho-silicate hybrid by copolymerizing 2-(methacryloyloxy)ethyl phosphate (EGMP), containing a polymerizable methacrylate group and functional phosphate group with 3-[(methacryloyloxy) propyl] trimethoxysilane (MEMO) which possesses a polymerizable methacryloxy group at one end and alkoxy silane groups capable of forming inorganic networks via sol-gel route at the other end. Protection of steel substrates with these hybrid coatings was explained by the strong interfacial acid-base interactions of P=O⁻ groups from phosphate with the Mⁿ⁺ from the metal substrate [17]. Polymers with some phosphonate functionality have long been established as excellent adhesives and anti-corrosion compounds [18–25]. However, there has been very little investigation into the use of *phosphonate*-type methacrylates for the same purpose [13,14,26]. In an effort to synthesize new types of phosphonated methacrylate monomers, we have proposed a series of monomers with the following general formula: CH₂=C(CH₃)C(O)O(CH₂)_nP(O)(OR₁)(OR₂). The synthesis was achieved by using several organic pathways such as the well-known Arbusov reaction [27,28] or by using hydroxyl-phosphonate compounds under Schotten-Bauman conditions [29] ending with methacrylates bearing spacer *n* values from 1 to 11. More

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recently, new N,N-amino-bisphosphonic-containing methacrylates (MAC_nNP₂) [30] and new gem-bisphosphonic-containing methacrylates (MAC_nP₂) [31] have also been synthesized and polymerized under UV-light. The resulting coatings, evaluated by salt spray test, showed efficient corrosion protection of steel after over 900 h of exposure. Posner et al. [32] already reported UV curable coatings based on acrylate/styrene copolymers to be efficient against corrosion, but no phosphonate-containing methacrylate compound has been used so far.

The aim of the present study was to evaluate the corrosion protection of coatings obtained from UV polymerization based on (meth)acrylate compounds and more specifically diacrylate monomers as well as phosphonated methacrylate monomers. The coatings were applied on a steel substrate and the behavior of the steel/coating interface was characterized during immersion in 0.1 M NaCl by electrochemical impedance spectroscopy [33–37]. In the first part of the study, the influence of the phosphonic acid methacrylate content on the corrosion protection was investigated. Then, in a second step, a new phosphonated fatty acid was synthesized and added to the formulation prior to the UV polymerization. Note that this molecule does not participate in the UV cross-linking with acrylate monomers but was incorporated in the formulation as an inhibitive compound to enhance the corrosion protection of the steel.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich and used without further purification.

Two phosphonated methacrylate monomers MAPC1 and MAPC1(OH)₂ were synthesized according to a previously described procedure [26]. Their chemical structure is shown in Fig. 1.

Low-carbon steel Q-Panel plates (SAE1008/1010, R type) 150 mm × 75 mm × 0.8 mm were used as substrate.

2.2. Synthesis of a new phosphonated fatty acid (phosphonic acid-bearing oleic acid)

In a first step, the phosphonation of methyl oleate was carried out in a glass reactor containing 0.249 g (0.00170 mol) of di-*tert*-butyl peroxide, 10 g (0.034 mol) of methyl oleate and two molar equivalents of dimethyl phosphite. The mixture was heated to 125 °C for 12 h. After cooling to room temperature, excess dimethyl phosphite was removed under high vacuum. Phosphonic ester-bearing oleic methyl ester was obtained with 78% yield. This synthesis was performed by Specific Polymers and sold under the SP-3S-10-001 trademark.

¹H NMR (CDCl₃, δ, ppm): 3.70 (d, 6H, PO(OCH₃)₂), 3.63 (s, 3H, COOCH₃), 2.26 (t, 2H, CH₂-COOCH₃), 0.84 (t, 3H, CH₃-CH₂). ³¹P (CDCl₃, δ, ppm): 37.7.

In a second step, 10 g (0.025 mol) of phosphonic ester-bearing oleic methyl ester and 50 g of dioxane were introduced into a single-necked round bottom flask equipped with a condenser

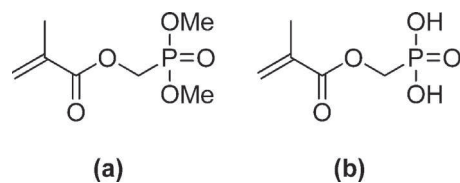


Fig. 1. Structures of the monomers: (a) methacrylate phosphonic dimethyl ester (MAPC1) and (b) phosphonic acid methacrylate (MAPC1(OH)₂).

Table 1

Composition of the different formulations prepared for the electrochemical characterization. Each formula contains 6% Darocur.

Formulation	Acrylates (wt. %)	MAPC1 (wt. %)	MAPC1(OH) ₂ (wt. %)	New phosphonated fatty acid (wt. %)
1	92.7	1.3	–	–
2	92.7	–	1.3	–
3	91.5	–	2.5	–
4	89	–	5	–
5	84	–	10	–
6	89	–	2.5	2.5

and a magnetic stirrer. Subsequently, two molar equivalents of hydrochloric acid were added dropwise. Then, the solution was vigorously stirred under dioxane refluxing for 6 h. After purification, phosphonic acid-bearing oleic acid was obtained with 55% yield. This synthesis was performed by specific polymers and sold under the SP-3S-10-009 trademark.

¹H NMR (CD₃OD, δ, ppm): 5.03 (s, 4H, PO(OH)₂), 2.30 (t, 2H, CH₂-COOH), 0.92 (t, 3H, CH₃-CH₂). ³¹P (CD₃OD, δ, ppm): 33.2.

The chemical structure of the products was determined by ¹H and ³¹P NMR (Bruker AC 400 MHz) at room temperature in CDCl₃ solutions. Abbreviations s, d, t, q, m stand for singlet, doublet, triplet, quadruplet and multiplet, respectively. The INVGATE procedure with delay D1 of 10 s was used to quantify the final yield.

2.3. UV photopolymerization of methacrylate monomers and coating preparation

The UV polymerization of mixtures of (meth)acrylates (composed of tripropyleneglycol diacrylate, hexanedioldiacrylate and phosphonated methacrylate MAPC1 or MAPC1(OH)₂), and Darocur 1173 (6%, w/w) as a photoinitiator was studied by real time FT-IR spectroscopy with a Nicolet Nexus apparatus with 2 cm⁻¹ accuracy using OMNIC software. The UV intensity was measured using a Solatell UV spectroradiometer apparatus (4D Controls Limited, Cornwall, UK). The kinetics of (meth)acrylate monomer conversion have already been published [38]. The reagents were blended without solvent. Six different formulations were prepared. The compositions are indicated in Table 1. The first composition (F1) was composed of acrylates, MAPC1 and photoinitiator, while the four subsequent compositions (F2–F5) contained acrylates and various amounts of the MAPC1(OH)₂ with photoinitiator. The last formulation (F6) contained 2.5% MAPC1(OH)₂ as well as 2.5% new phosphonated fatty acid.

The steel substrates were degreased with methyl ethyl ketone (MEK) and dried in warm air for 30 min. Then, the liquid formulation was uniformly applied on the steel sample to obtain a uniform layer after curing. The films were applied with a SHEEN bar coater. Coated samples were then photopolymerized. The UV source was placed perpendicular to the sample surface and induced the crosslinking reaction, monitored in real-time via FT-IR. Complete conversion of monomer to polymer was obtained after ca. 60s, confirmed by following the intensity of IR absorption at 812 cm⁻¹ (characteristic of the C=C methacrylate monomer double bond). The dry film thickness was 20 ± 2 μm (measured by a Bykotest 7500 digital meter).

2.4. Electrochemical measurements

A three-electrode electrochemical cell was used in electrochemical impedance measurements. A coated specimen was used as working electrode. A cylindrical Plexiglas tube was assembled on top of the coated sample (exposed surface area: 29 cm²) and

filled with the aggressive solution prepared from distilled water by adding 0.1 M NaCl (reagent grade). A large platinum sheet and a saturated calomel electrode were used as counter and reference electrodes, respectively. The electrochemical cell was kept at room temperature and open to air. Electrochemical impedance measurements were carried out using a Solartron 1287 electrochemical interface connected to a Solartron 1250 frequency response analyser. Impedance diagrams were obtained over a frequency range of 65 kHz to a few mHz with six points per decade using a 20 mV peak-to-peak sinusoidal voltage. The linearity of the system was checked by varying the amplitude of the ac signal applied to the sample. The electrochemical behavior of the steel/coatings interface was characterized for different exposure times to the aggressive solution ranging from 2 h to 72 h (3 days).

2.5. Scanning electron microscopy (SEM) observations

SEM, coupled with X-ray diffraction (SEM-EDX), was used to visualize the morphology of the coatings and define localized concentrations of phosphorus. Analyses were performed on cross-sections of the coating material. SEM-EDX analyses were performed using a LEO 435VP electron microscope operating at 8 kV. The phosphorus profiles were obtained from 64 measurements through the whole coating thickness.

3. Results and discussion

Impedance measurements were performed to evaluate the effects of the phosphonated methacrylate monomers on the corrosion protection of the steel coated by the different formulations. First, the influence of the methacrylate monomers (MAPC1 or MAPC1(OH)₂) was investigated. Then, the influence of the addition of the new phosphonated fatty acid was studied. It can be mentioned that corrosion appeared relatively rapidly indicating that the coatings offered a low corrosion protection. Albeit unsatisfactory it is helpful to rapidly discriminate the effect of the additives. For this reason, the impedance results were compared for only 24 h of immersion in the NaCl solution.

3.1. The effect of both the nature and the content of the phosphonated methacrylate monomer (ester or acid groups) on corrosion protection

Fig. 2 reports the impedance diagrams obtained after 24 h of immersion in the 0.1 M NaCl solution for the two formulations (F1 and F2). The diagrams are characterized by two time constants: the high-frequency (HF) part of the diagrams (from 10⁵ to 1 Hz) is related to the coating and attributed to the barrier properties of

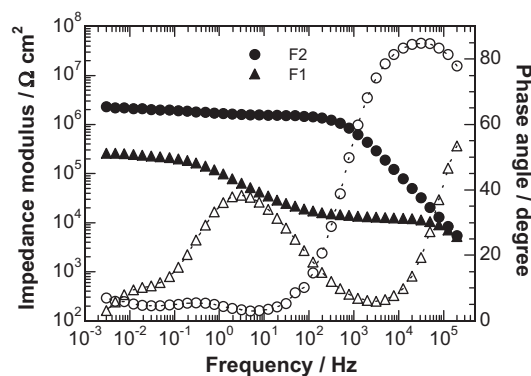


Fig. 2. Electrochemical impedance diagrams (Bode representation) obtained for the F1 and F2 samples after 24 h of immersion in 0.1 M NaCl solution.

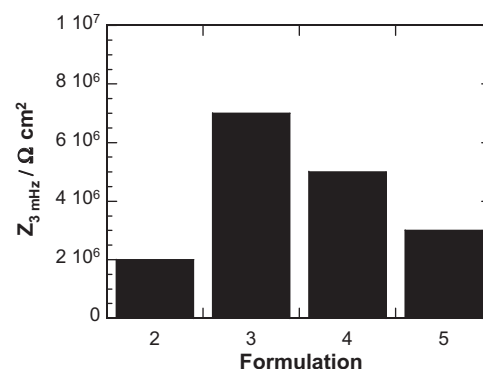


Fig. 3. $|Z|_{3\text{mHz}}$ after 24 h of immersion in 0.1 M NaCl solution for the formulations with different MAPC2(OH)₂ concentrations.

the film, while the low-frequency (LF) part (from 1 to 10⁻³ Hz) corresponds to the reactions occurring at the metal/coating interface through defects and pores in the coating [39,40]. For the F1 coating, the barrier effect (HF range) is significantly lower than for the F2 coating: the impedance value is only $2 \times 10^4 \Omega \text{ cm}^2$ (plateau in the HF range). In addition, the impedance modulus at 3 mHz is low which indicates that the F1 coating is poorly efficient at protecting the steel surface which is also a consequence of the poor barrier effect. The diagram for the F2 coating reveals a higher impedance modulus in the HF range ($2 \times 10^6 \Omega \text{ cm}^2$) compared to F1 indicating that the barrier effect was improved. The barrier effect leads to a decrease of the surface area in contact with the electrolyte (high impedance modulus in the LF range) and as a consequence coating F2 was more protective.

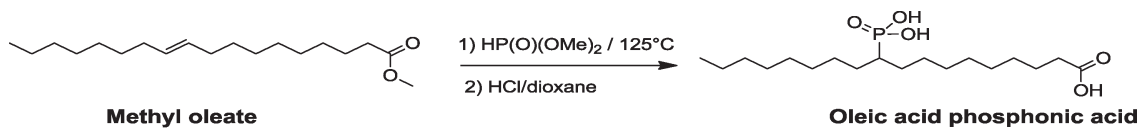
From this first set of experiments, it can be concluded that the coating containing acid methacrylate instead of ester methacrylate conferred a more efficient corrosion protection to the metal substrate. Thus, in the remainder of the study only MAPC1(OH)₂ was used.

The influence of the MAPC1(OH)₂ content in the coating for the corrosion protection of the steel was investigated. Similar formulations were prepared and only the MAPC1(OH)₂ content was changed (1%, 2.5%, 5% and 10%). The impedance diagrams presented the same shape and are not reported here. It can be mentioned that the HF part of the impedance diagrams was poorly modified in the presence of different MAPC1(OH)₂ concentrations and only the LF part changed. This result indicates that MAPC1(OH)₂ acts mainly at the metal/coating interface. It was proposed by Kittel et al. [41] and the group of Bierwagen [42–44] that the impedance modulus at low frequencies ($|Z|_{3\text{mHz}}$ in the present study) could serve as an estimation of the corrosion protection of a painted metal. Fig. 3 reports $|Z|_{3\text{mHz}}$ after 24 h of immersion in the NaCl solution for the four formulations with different MAPC1(OH)₂ contents. It can be seen that the impedance modulus is the highest for the F3 formulation (2.5%) and decreases when the MAPC1(OH)₂ concentration increases (F4 and F5). However, the decrease is not significant and the data in Fig. 2 allow a minimum efficient MAPC1(OH)₂ concentration to be determined. This concentration is around 2.5%.

3.2. Influence of the addition of new phosphonated fatty acid on the corrosion protection of coated steel

3.2.1. New phosphonated fatty acid

In the present study, the phosphonation of methyl oleate was investigated. The chemical incorporation of phosphonic acid moieties onto methyl oleate was done via a two-step pathway, as depicted below:



Synthesis of phosphonic acid-bearing oleic acid (phosphonated fatty acid)

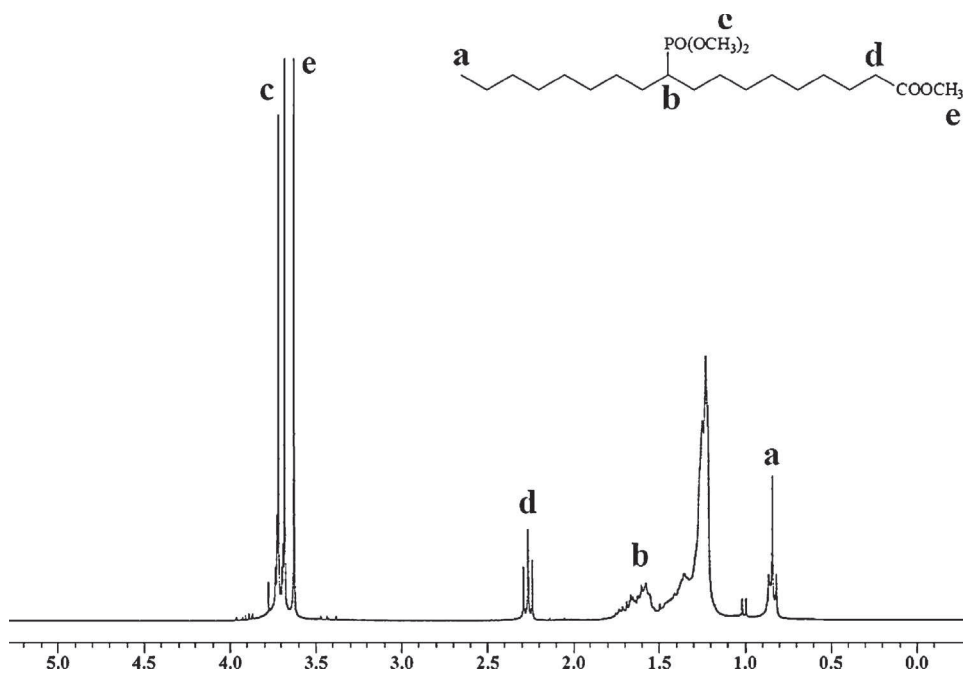


Fig. 4. ^1H NMR (CDCl_3) of phosphonate-bearing methyl oleate.

(a)

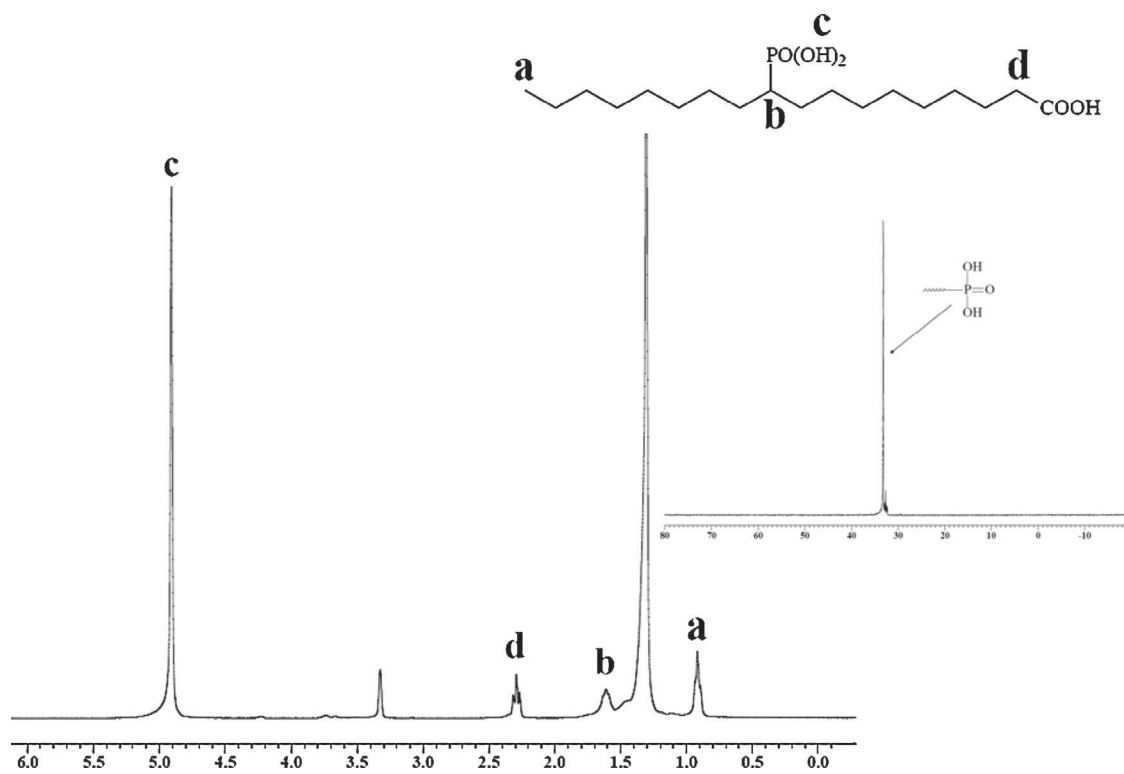


Fig. 5. ^1H NMR and ^{31}P NMR (CDCl_3) of phosphonic acid-bearing oleic acid.

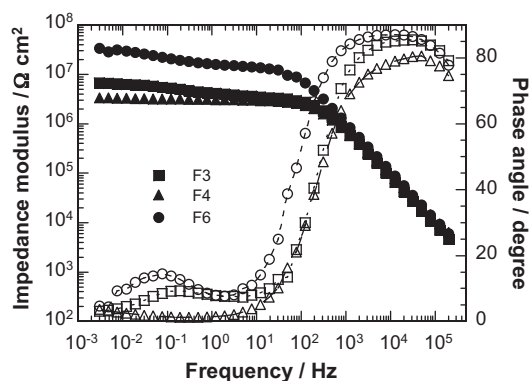


Fig. 6. Electrochemical impedance diagrams (Bode representation) obtained for samples F3, F4 and F6 after 24 h of immersion in 0.1 M NaCl solution.

The first step corresponds to the radical addition of dimethyl phosphite onto the unsaturated C=C of the acid. As with thiolene radical coupling [45], radical addition of methyl oleate (MO) with dimethyl phosphite, used as chain transfer agent (CTA) was carried out at high temperature with an excess of CTA compared to double bond. In these reaction conditions, phosphonation was accomplished after 12 h and the resulting MO-phosphonate was obtained at about 80% yield. In Fig. 4, ^1H NMR shows that the CH_3 protons of the methylphosphonate ester appear at 3.70 ppm. Moreover, the vinyl protons of MO, centered at 5.34 ppm, are no longer present, indicating successful phosphonation. Furthermore, ^{31}P NMR showed a single peak centered at 37.7 ppm (not reported here).

Phosphonated fatty acid was obtained in a second step by hydrolysis of methyl ester groups of phosphonate moieties with hydrochloric acid in a dioxane solution. In these reaction conditions, the methyl ester of methyl oleate was also hydrolyzed to lead to the corresponding carboxylic acid. Fig. 5 shows the ^1H NMR and ^{31}P NMR spectra of the phosphonated fatty acid. The CH_3 protons of the methylphosphonate ester, centered at 3.70 ppm, are no longer present, indicating successful hydrolysis. In support of this, the peak of $\text{P}-\text{O}-\text{CH}_3$ at 37.7 ppm is shifted to 33.2 ppm for $\text{P}-\text{OH}$.

3.2.2. The corrosion protection of coated steel with the addition of oleic acid phosphonic acid

It was seen that in the presence of methacrylate $\text{MAPC1}(\text{OH})_2$, the highest impedance value was obtained when it was incorporated into the formulation at a concentration of 2.5% (F3 coating). The performance of the coating containing the phosphonated fatty acid (F6 formulation) was compared to the F3 coating. The impedance diagrams obtained after 24 h of immersion in the NaCl solution are reported in Fig. 6. The impedance of the F4 coating (5% $\text{MAPC1}(\text{OH})_2$) is also shown in order to separate the role played

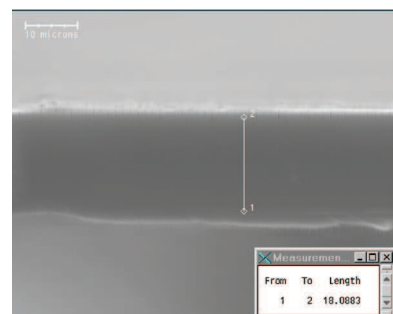


Fig. 8. SEM micrograph (cross-section) for coating F6.

by the addition of the phosphonated fatty acid and the role of the acid in the methacrylate $\text{MAPC1}(\text{OH})_2$. It can be seen in Fig. 6, that the addition of phosphonated fatty acid improved the barrier properties of the coating. For the F3 and F4 coatings, the impedance values in the HF range were between 2×10^6 and $3 \times 10^6 \Omega \text{ cm}^2$. With the addition of the phosphonated fatty acid, the impedance value in the HF range was about ten times higher ($2 \times 10^7 \Omega \text{ cm}^2$). The impedance modulus at 3 mHz was $4 \times 10^7 \Omega \text{ cm}^2$ showing that the corrosion protection was improved.

Photographs of the electrode surface were taken at the end of the electrochemical test (72 h of immersion in the NaCl solution) and are shown in Fig. 7. The surface of coating F6 appears poorly corroded, and in contrast, the surfaces of the coatings F3 and F4 are damaged and corrosion products are clearly visible. The photographs corroborate the electrochemical results and underline the beneficial effect of the addition of phosphonated fatty acid on the corrosion protection of the steel surface.

To analyze the role of phosphonated fatty acid, SEM/EDX analyses were performed. The aim was to detect the phosphorus through the whole coating thickness and particularly at the metal/coating interface and to show (if possible) a phosphorus gradient concentration. For each sample two different zones were studied. Fig. 8 shows a cross-section of the F6 coating. The coating has a uniform thickness. Phosphorus profiles were obtained for F4 and F6 coatings (Fig. 9). In Fig. 9a, it can be seen that through the whole coating thickness, the quantity of phosphorus is constant. A progressive decrease can be observed at the outer part of the coating which can be explained by the SEM probe resolution. In contrast, in Fig. 9b, the phosphorus profiles are significantly modified at the metal/coating interface and reveal a higher phosphorus content. It can be seen that about $3 \mu\text{m}$ of the internal zone of the coating was enriched in phosphorus. However, EDX is not a suitable technique to determine the thickness of this interfacial zone accurately. The difference between the two samples (Fig. 9a and b) was only the presence of the phosphonated fatty acid. Thus, it can be concluded that in the F6 coating the phosphonated fatty acid can migrate through the

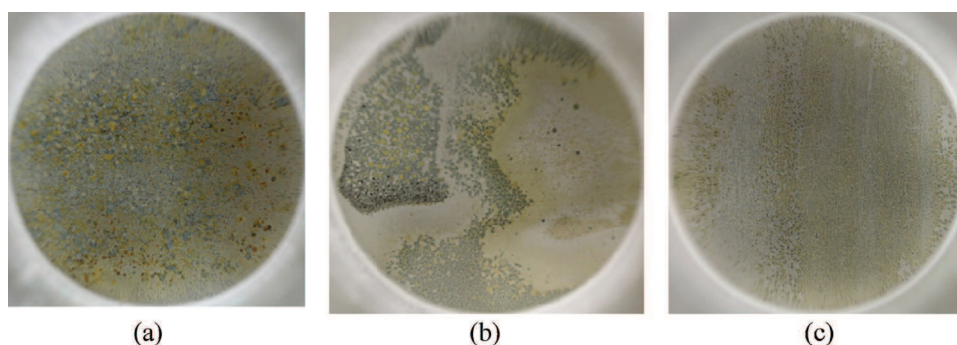


Fig. 7. Photographs of the electrode surface after 72 h of immersion in 0.1 M NaCl solution for samples: (a) F3, (b) F4 and (c) F6 (Surface area: 29 cm^2).

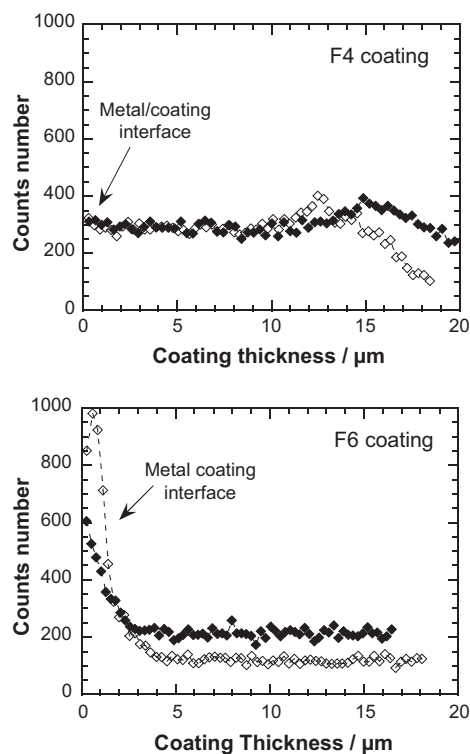


Fig. 9. Phosphorus profiles along the coating thickness for coatings F4 and F6 (◆,◇: results of two independent measurements on the same sample).

film and reach the substrate to inhibit the corrosion of the steel [46,47]. As a consequence, corrosion resistance was improved. It can be noted that the phosphorus content was higher for the F4 coating in agreement with the higher MAPC1(OH)₂ content.

4. Conclusions

Different formulations containing diacrylate monomers, phosphonic methacrylate and a newly synthesized phosphonated fatty acid were deposited on a carbon steel substrate and polymerized by UV curing. The corrosion protection afforded by the different coatings was investigated by EIS. From the impedance data, it was found that:

- (i) Phosphonic acid methacrylate provided higher corrosion resistance in comparison with ester methacrylate.
- (ii) The best corrosion protection was obtained with 2.5% phosphonic acid methacrylate. An increase of the concentration did not improve the corrosion resistance of the steel.
- (iii) The addition of the synthesized phosphonated fatty acid in the formulation significantly enhanced the protective properties of the coating. This performance was explained by both the barrier properties and the corrosion inhibition at the steel surface due to the presence of the phosphonic group on the molecule.

Finally, integrating phosphonated fatty acid in a bio-based coating using vegetable oils [48] seems to be promising. This study is still under investigation and should be the subject of a forthcoming publication.

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