Corrosion Behavior of Low-Carbon Steel in Model Solutions, Containing Empty PB$_d$-PEO Vesicles

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Abstract—The present work reports the corrosion resistance of low-carbon steel in alkaline model solutions (saturated Ca(OH)$_2$) in the presence of empty vesicles of poly (butadiene-b-ethylene oxide) (PB$_d$-PEO). The main objective was to define the electrochemical response of the steel electrodes in chloride free and chloride containing solutions. Electrochemical Impedance Spectroscopy (EIS), Linear Polarization Resistance (LPR) and Cyclic voltammetry (CV) were performed at certain time intervals, whereas open circuit potential (OCP) was monitored continuously throughout the test. The motivation of this research was to evaluate the effect of PBd-PEO vesicles on the electrochemical response of steel in model solutions, prior to "loading" them with active substance and employing them as an additive to reinforced concrete. In other words, "empty" vesicles were subject to investigation in this work, where the obtained results serve as a control case for on-going work on self-healing in reinforced cement-based materials. The study reveals that, the addition of 0.025 wt.% empty PB$_d$-PEO vesicles has a positive effect on the protective properties of the passive film, formed on the treated steel surface in solutions with and without chloride. This enhancement in the surface film properties was assigned to the variation in the chemical composition and altered redox processes on the steel surface when PB$_d$-PEO vesicles were present.

Index Terms—corrosion, vesicles, model solution, PB$_d$-PEO, EIS

I. INTRODUCTION

Corrosion of the steel reinforcement, induced by carbonation or chloride ingress, is considered as one of the main degradation mechanisms which contribute to reduced durability of reinforced concrete structures [1]-[5].

In the frame of a novel approach to corrosion control in reinforced concrete, the application of polymeric nano-particulate aggregates was recently applied [6]-[9]. The investigated aggregates (micelles, vesicles, hybrid core–shell particles of a polymer shell, and a metal oxide core) proved to result in significant variation in the properties of reinforced concrete systems [7]-[9].

Previously studied polymeric aggregates were polymeric PS-PEO (polyethylene oxide-block-polystyrene), Pluronic 123 core-shell micelles (hydrodynamic radius of approximately 20 and 50 nm, respectively) [6]-[8] and polymeric PS-PEO vesicles (hydrodynamic radius of about 220 nm) [9]. These studies reported promising results in view of superior performance of both materials, i.e. enhancement of the corrosion resistance of steel reinforcement, together with improved properties of the cement-based bulk matrix (pore structure and transport properties).

Micelles are core–shell formations, comprising a hydrophilic "shell" and a hydrophobic "core". In PS-PEO micelles, PEO is the hydrophilic shell and PS is the hydrophobic core. Vesicles are nano-sacs that enclose a volume with a thin membrane. Hence, water-soluble compounds can be effectively entrapped in their interior.

The main objective of studying the application of polymeric micelles and vesicles in cement-based materials was to develop a multi-functional system for self-healing of corrosion damage. The approach involved studies of different polymer types which could potentially hinder and/or heal the corrosion-related degradation on the steel surface, at interfaces or in the bulk cement-based matrix with exposure to harsh conditions.

In the present work, preliminary testing of empty vesicles of poly (butadiene-b-ethylene oxide) (PB$_d$-PEO) in model solutions was considered as a potentially suitable alternative to the already reported polymeric particles [6]-[9]. PB$_d$-PEO polymer vesicles, also called polymersomes, are self-assembled structures composed of amphiphilic block copolymers that form a hydrophobic bilayer enclosing an aqueous cavity [10]. The PBd portion of these vesicles is not as brittle as the PS portion of the reported particles. Therefore, a point of interest within application of PBd-PEO in reinforced concrete would be their potentially better performance with concrete mixing and possibly superior micromechanical performance of the bulk matrix, if compared to PS-based admixtures.

In order to introduce PB$_d$-PEO vesicles as nano-carriers of active substance for self-healing of corrosion damage, the corrosion performance of carbon steel in the

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presence of "empty" vesicles becomes the first question that should be clarified. Consequently, the present work aimed to investigate the electrochemical response of low-carbon steel in model alkaline solution in the presence of empty PB_d-PEO vesicles.

II. EXPERIMENTAL

A. Materials

Steel electrodes (low carbon St37) with a defined surface area of 0.3 cm², were ultrasonically degreased in ethanol, grinded with successive grades of SiC empery paper up to 4000 grade and then polished using 3 μm and 1 μm diamond paste to mirror like surface. The electrodes were tested in saturated $Ca(OH)_2$ solutions with pH 12.5 at 25 ℃. The electrochemical response of the steel electrodes was recorded in model alkaline solutions, using a three electrode electrochemical flat cell. Saturated calomel electrode (SCE) was employed as a reference electrode and MMO Ti-mesh as a counter electrode. For each exposure conditions, two identical steels specimens (replicates) were tested.

The steel samples were immersed in chloride-free (control cases) and chloride-contacting (corroding cases) aerated model solutions of $Ca(OH)_2$, that in fact simulate concrete the pore solution of mature concrete. Their electrochemical behavior was recorded at different immersion periods starting from 1 hour up to 15 days.

The chloride content was adjusted by adding the relevant amount of NaCl as a solid. The effect of vesicles was studied by adding 0.025 wt.% of PBd-PEO vesicles to the original solutions.

The PB_d-PEO vesicles were prepared by dissolving poly(butadiene-b-ethylene oxide) block copolymers in a solution containing different concentrations of DTPA (ranging from 0.1 to 5 mM) and 10 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer [10]. The mixture was then stirred for a week. The pH of the solution was 7.4. The size of the vesicles was adjusted by extruding them several times through polycarbonate filters with a cut-of membrane of 200 nm. The remaining free DTPA was separated from the polymersomes using a Sephadex G-25 column [10].

Solution of 0.5 mg/ml of 200 nm size Poly (butadiene-b-ethylene oxide), $PB_{d(1900)}$-$PEO_{(900)}$, was used for preparation of the final test solutions. The $PB_{d(1900)}$-$PEO_{(900)}$ vesicles were prepared by following the above mentioned procedures [10].

The samples' designation and the composition of the saturated $Ca(OH)_2$ solutions are listed in Table I.

TABLE I.   TEST SAMPLES DESIGNATIONS AND COMPOSITION OF THE SATURATED CALCIUM HYDROXIDE SOLUTIONS

Sample designations	Chloride/ wt.%	PBd-PEO/ wt.%
C	0	0
CN	0	0.025
CC	3.5	0
CCN	3.5	0.025

B. Electrochemical Methods

Non-destructive electrochemical measurements were employed to follow up the progressive changes in the electrochemical response of the steel electrodes in control conditions and in 0.025 wt.% PBd-PEOd. The Open Circuit Potential (OCP) was monitored throughout the test and recorded at different time intervals. Electrochemical measurements were carried out using Metrohm Autolab-Potentiostat PGSTAT30. EIS was performed under potentiostatic control at OCP, from 50 kHz down to 10 mHz. An AC perturbation voltage signal of 10 mV (rms) amplitude was applied.

Periodic measurements of the polarization resistance (Rp) were carried out by using linear polarization resistance (LPR) measurements in the potential range around OCP from -20 mV to +20 mV with a scan rate of 10 mV/min. The corrosion current density (i_{corr}) was calculated by using the Stern-Geary equation [11], i_{corr} = B/Rp, where B is the Stern-Geary constant. A value of B = 26 mV, for active carbon steel, was used and 52 mV for passive steel [12], [13].

III. RESULTS AND DISCUSSION

A. OCP Evloution and Corrosion Current Density (i_{corr})

The variation of OCP and corrosion current density (i_{corr}) of the steel electrodes (low carbon St37), treated in saturated $Ca(OH)_2$ solutions with 0 and 3.5 wt.% chloride (C and CC samples) in the absence and in the presence of 0.025% wt.% PBd-PEO (C, CC, CN and CCN samples respectively), are shown in Fig. 1.

In chloride-free solutions, C and CN samples, an electrochemically stable passive film initiated and developed on the steel surface with time of conditioning. In both C and CN cases, more anodic (noble) *OCP* and lower i_{corr} values were monitored, Fig. 1, which resulted from the fact that the passive film acquired a stable thickness; consequently, low i_{corr} was observed [14], [15]. In the presence of 0.025% wt.% PBd-PEO (CN samples), the treated steel showed relatively more cathodic *OCP* and lower i_{corr} values than in case of C-samples (control). This changes in the electrochemical response of steel in the presence of 0.025% wt.% PBd-PEO was related to a possible accumulation of Fe^{2+} species on the steel surface and more negative potential values were recorded. However, the certain coordination between Fe^{2+} ions and PEO block, reported elsewhere [9], was expected to occur as long as Fe^{2+} species were formed. This interaction of the vesicles on the steel surface induced a barrier effect, that can explain the decrease in i_{corr} values.

In chloride-containing $Ca(OH)_2$ solutions, CC and CCN samples, the chloride content (3.5%) induced corrosion onset on all tested steel samples, Fig. 1. For the vesicle-free corroding samples (CC), corrosion was detected at early ages of immersion (in 1 hour). In this case, the OCP reached -0.54V vs. SCE and corrosion current density was ≈ 8 μA.cm⁻². This response was

maintained until the end of the test for CC-samples, due to corrosion propagation with prolonged treatment.

On the other hand, after 1 hour immersion in case of CCN-samples, no corrosion onset was detected. Initially more noble potentials (in the range of the control C samples, Fig. 1a), together with low current densities (again, comparable to the derived values for specimens C, Fig. 1b) were recorded. However, after 6 hours of treatment, the OCP for samples CCN becomes significantly more cathodic and comparable to the corroding samples in vesicles-free solutions, CC (Fig.1a, 0.25d stage). The OCP values are well in line with the increase in corrosion current at this stage (Fig. 1b).
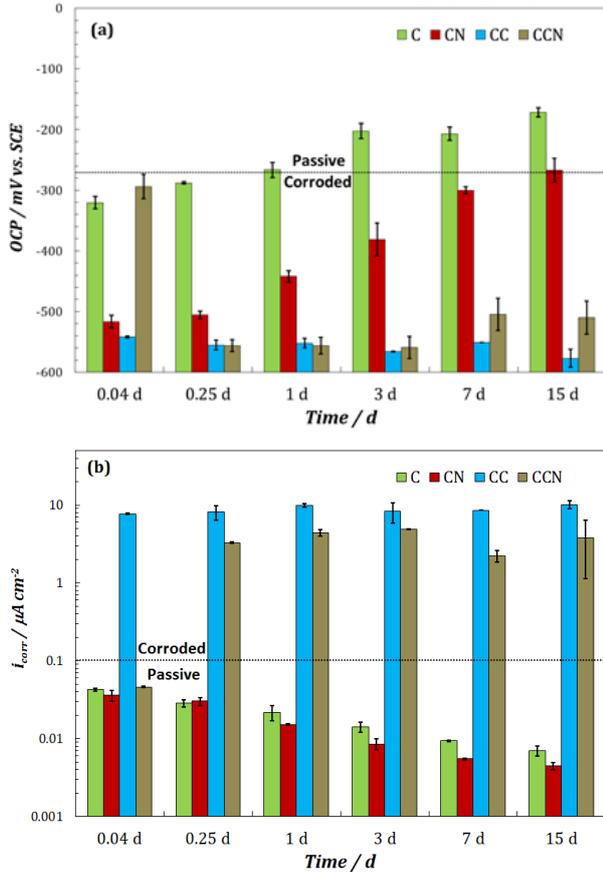

Figure 1.   Variation in (a) OCP and (b) corrosion current density of carbon steel in sat. Ca(OH)₂ solutions with and without chloride in presence of 0.025 wt.% PBd-PEO.

In the presence of PBd-PEO vesicles (CCN samples), however, corrosion propagation seemed to be limited, reflected by overall more anodic potentials and lower corrosion current densities with prolonged treatment, Fig. 1. This change in the corrosion propagation rate in the presence of PBd-PEO vesicles was probably related to the barrier effect of the vesicles themselves, also resulting in impeded   anodic reaction and overall corrosion rate respectively.

It has been reported [7], [9] that, chloride ions not only induce corrosion onset and propagation on the steel surface, but also affect the PEO component of the vesicles membrane, which can "shrink" in the presence of chloride ions [7], [9]. This leads to morphological changes of the vesicles by altering their shape i.e.

salting-out effect is a common phenomenon in these conditions. The chloride-induced modification of the vesicles themselves could also lead to variation in their barrier effects on the steel surface.

Furthermore, the composition of the corrosion products formed on the corroded samples, treated in the presence of polymeric additives was reported to be different from non-corroded steel [9]. In the former case (corroding steel in the presence of particles), γ-FeOOH and [Fe^{3+}(OOHCl)] will dominate, while in the latter case (control cases and passive state in the presence of particles) Fe_3O_4 and α-FeOOH will be the predominant compounds [9].

In control condition, the PBd-PEO vesicles stabilized the Fe^{2+} content in the passive film formed in case of CN samples, which suggested a possible enrichment of magnetite, resulting in a decrease in the measured i_{corr}. On the other hand, more noble *OCP* and low i_{corr} in case of CCN samples, with respect to CC samples, could account for a decrease in the iron oxyhydroxides and oxy(hydroxyl)chlorides species in the presence of PBd-PEO. These interactions of course, need a more in-depth investigation and confirmation.
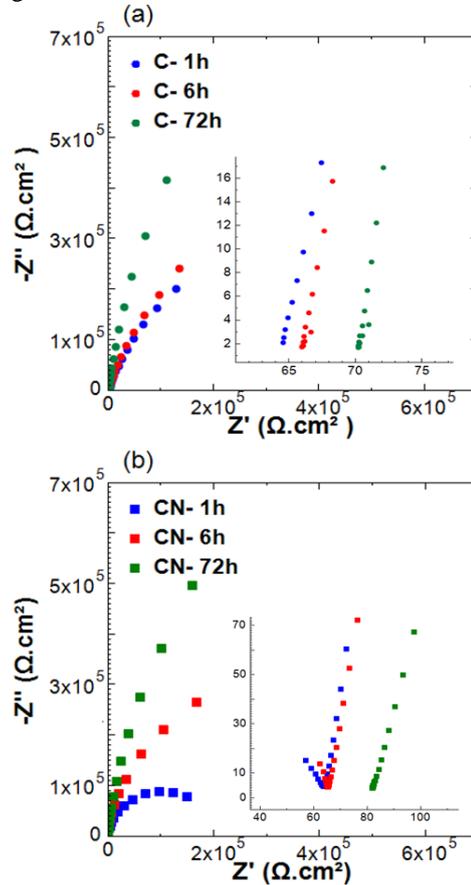

Figure 2.   EIS response represented in Nyquist diagrams of (a) control C- samples and (b) samples treated in presence of 0.025 wt.% PBd-PEO empty vesicles (CN- samples) in chloride-free sat. Ca(OH)₂ solutions after 1, 6, 72 hours.

B.   Electrochemical Impedance Spectroscopy (EIS)

The EIS response, represented in Nyquist diagrams, of the tested steel samples in chloride-free sat. Ca(OH)₂

solutions with and without PBd-PEO vesicles, and at early immersion time intervals (1, 6, 72 hours), are shown in Fig. 2.

In chloride-free $Ca(OH)_2$ solutions, both control samples (C-samples) and samples treated in the presence of PBd-PEO vesicles (CN) showed an increase in the overall impedance with treatment, Fig. 2. This increase in the impedance magnitude, with immersion time, was attributed to the passive film formation on the surface of C and CN samples, in accordance with the *OCP* and i_{corr} data, see Fig. 1.

Both high and low frequency response for the CN-samples, treated in presence of 0.025% wt.% PBd-PEO, was quite different from control specimens C. After 1 and 6 hours conditioning, the control C-samples presented a more capacitive response compared to CN cases, Fig. 2. However, after 72 hours the CN samples showed higher overall impedance than the C-samples. This increase in the impedance value after 72 hours suggested that the PBd-PEO vesicles induced both barrier effect and modifications in the redox processes occurring during film formation. Moreover, an additional high frequency time constant appeared in case of CN-samples, which probably results from certain interaction between the PBd-PEO polymeric vesicles, represented in PEO component, and the redox species in the film. This coordination between the polymeric vesicles and steel Fe^{2+} species in the film also confirmed elsewhere [9].

To confirm the expected modification in the redox processes in presence of the polymeric vesicles, EIS response in case C and CN after prolonged treatments, after 7 and 15 days, was also considered. Both Bode and Nyquist diagrams of C and CN samples are shown in Fig. 3.

The Nyquist diagrams indicated that, for control specimens, C, a more capacitive-like behavior was monitored at low frequency limits, than in case of CN cases, Fig. 3a. This variation in the capacitive response confirmed that the PBd-PEO affected the oxi/redox processes in the passive film. In addition, this variation in the impedance response could support the hypothesis that PEO content was able to interact and/or stabilized the Fe^{2+} species in the film, leading to a decrease in the capacitive response.

Overall, it can be seen that the EIS response of both control groups C and CN is quite similar if the complex plane (Nyquist plot) is only considered. A difference in the HF response can be observed (inlet in Fig. 3a), which can be denoted to concentration polarization on the steel surface due to the presence of vesicles. Additionally, the contribution of a barrier effect on the steel surface of CN is also possible to be linked to higher values in the HF domain. This is, in fact, confirmed by the appearance of a second time constant in the HF to MF domain for the case of CN specimens, well observable in the Bode plot (Fig. 3b). As can be seen, in the frequency range between 1 kHz and 10 Hz, a clear variation in the phase between C and CN samples was observed. In other words, the presence of vesicles resulted in variation of

the film composition and/or distribution, which would add-up to the global corrosion resistance of the steel surface. The phase in the low frequency limit remains almost identical to the vesicles-free specimens C, reaching approx. 80 degrees. This accounts for passive state in both C and CN samples.
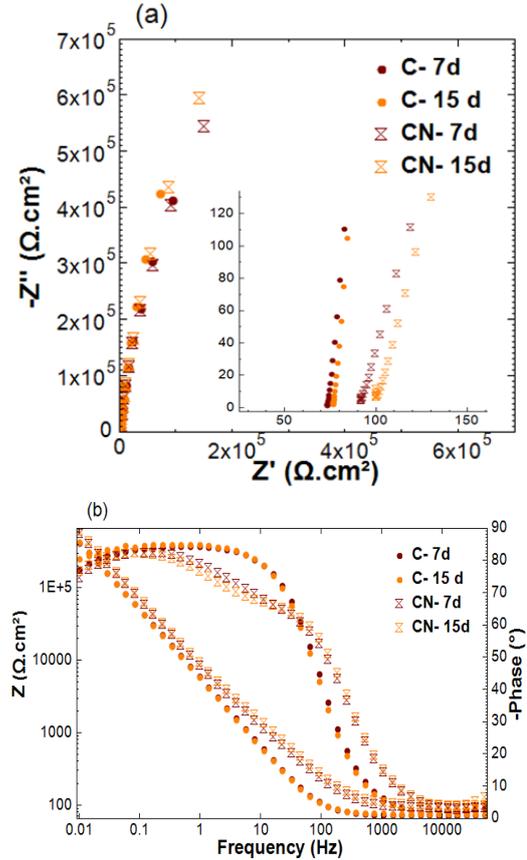

Figure 3. (a) Nyquist and (b) Bode diagrams, of steel treated in sat. $Ca(OH)_2$ solutions in absence and presence of 0.025 wt.% PBd-PEO vesicles (C and CN samples,) after 7 and 15 days immersion.

Obviously, quantitative analysis of the EIS response is necessary to elucidate further the phenomena, related to both oxidation/reduction and barrier effects only. The qualitative interpretation of the EIS results are in accordance with the recorded *OCP* and i_{corr} data (Fig. 1).

In $Ca(OH)_2$ solutions with 3.5% sodium chloride, the EIS response of CC and CCN samples after 7 and 15 days are shown in Fig. 4.

In case of CC samples, the corrosion initiation was detected at early exposure stage, Fig. 1. Consequently, as a result of the corrosion propagation on CC samples, the overall impedance decreased with exposure time, reaching the lowest recorded value after 15days, Fig. 4. The accumulated corrosion product on the CC surface after 15 days hindered the ingress of more aggressive chloride to the corroded steel surface, and impeded corrosion propagation was observed. Consequently, the global |Z| values and changes in the low frequency response were probably related to limitation in mass transport through the corrosion product layer, Fig. 4b.

Concerning the steel treated in case of CCN samples in presence of PBd-PEO vesicles, the displayed data in

Fig. 4 indicated that, although corrosion was also detected and propagated, the impedance magnitude in case of CCN samples was higher than in case of CC samples, at the same exposure conditions (7 or 15 days), see Fig. 4a. The higher global |Z| in case of CCN samples suggested that the in the presence of 0.25 wt.% PBd-PEO vesicles, overall corrosion resistance increased.
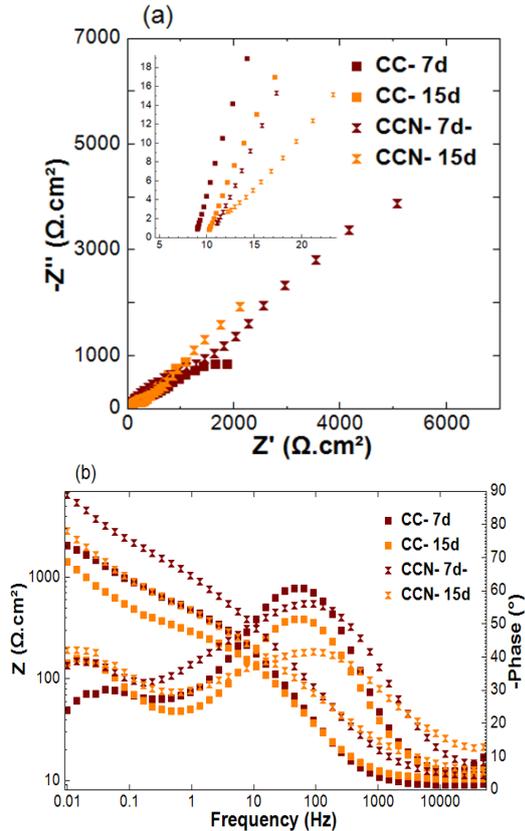

Figure 4. (a) Nyquist and (b) Bode diagrams, of steel treated in chloride-containing sat. Ca(OH)$_2$ solutions with 3.5% Chloride in absence and presence of 0.025 wt.% PBd-PEO vesicles (CC and CCN samples, respectively) after 7 and 15 days immersion.

A closer look at the Bode plot reveals some specific information as follows. For the CC specimen (vesicles-free) the response is composed of at least two time constants: between 500 Hz and 100 Hz, where the phase depicts maximum values of approx. 60 degrees at 7 days and ca.50 degrees at 15 days, and a second one between 0.1 Hz and 10mHz, where the phase adopts values of around 35 degrees at 7 days and 40 degrees at 15 days. Reduction in phase angle at the MF range, accompanied by reduction in the LF range, which along with depressed semi-circle in the Nyquits plot, reflect enhanced corrosion activity, reduced charge transfer and accumulation of a corrosion product layer on the steel surface. After 15 days, the phase in the MF droped, but increased in the LF domain. This accompanied by a tale in the Nuquist plot, accounts for mixed kinetics i.e. mass transport and charge transfer. Corrosion resistance was therefore reduced, although the corrosion product layer seems to have increased in volume or spread over a larger surface.

For the CCN specimens, similar distribution of time constants can be observed. The phase angle in the MF

domain at 7 days is slightly lower, compared to the values for specimens CC i.e. ca. 55 degrees and further reduces to 40 degrees after 15 days. These were accompanied by an increase only in the phase at LF, reaching 45 degrees after 15 days. The response at 7 days presents a less pronounced diffusion control in the LF, while at 15 days, diffusion limitations increase, also reflected by the Nyquits plot.

Since global |Z| values are higher for specimens CCN, compared to specimens CC, it can be concluded that both barrier effects and charge transfer alterations for specimens CCN result in globally higher corrosion resistance, compared to that for specimens CC. In order to clarify the contribution of charge transfer and oxi/redox resistance to the overall corrosion rate in each case, quantitative analysis of the EIS data is required. The detailed analysis will also elucidate the contribution of the vesicles to one or another step in the electrochemical process and/or the formation and properties of the corrosion product layer.

The qualitative interpretation of EIS results for the corroding specimens is also in line with the observed OCP and i_{corr} values, where lower currents were measured for the CCN specimens and slightly higher corrosion activity was recorded for the CC specimens.

IV. CONCLUSION

To conclude, the aforementioned results confirmed the positive effect of empty polymeric PBd-PEO vesicles in enhancing the barrier effect of the passive film in model solutions without chloride, leading to an improvement of corrosion resistance. For chloride containing solutions, the vesicles induced structural changes in the corrosion product layer, leading to an overall higher corrosion resistance, compared to the product layer on steel in vesicles-free solutions. The difference in global performance for the corroding cases is not significant. Nevertheless, EIS response shows variation in the reaction control mechanism, from kinetic to mixed and vice versa, depending on time of immersion and composition of the external medium. Consequently, a detailed quantitative analysis is required, prior to identifying these vesicles as potentially applicable admixture to reinforced concrete systems, in view of corrosion control.

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