Corrosion barrier properties of PMMA-silica coatings for protection of reinforcing steel

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Abstract

Corrosion of steel metal structures is the principal cause of failure of reinforced concrete and the absence of preventive maintenance results in financial, social, and environmental implications. To overcome this problem, research efforts are directed toward eco-friendly coatings based on organic-inorganic hybrids developed for effective protection of metal surfaces. PMMA (methyl polymethacrylate)-silica were prepared by polymerization of methyl methacrylate (MMA) and 3-(Trimethoxysilyl) propyl methacrylate (MPTS), using the thermal initiator benzoyl peroxide (BPO) and the sol-gel hydrolytic condensation of tetraethoxysilane (TEOS) and MPTS. Several micrometer thick coatings were deposited on carbon steel by dip-coating. The results of the structural analysis performed by infrared spectroscopy confirmed the formation of PMMA-silica hybrid. The electrochemical impedance spectroscopy measurements in 0.6 mol L^{-1} NaCl solution showed excellent corrosion resistance of up to 100 $G\Omega\ cm^2$ (low-frequency impedance modulus), with a durability of more than 250 days, while similar corrosion resistance but somewhat lower lifetime was obtained in simulated carbonated and alkaline concrete pore solution.

Keywords: organic-inorganic hybrid, sol-gel process, reinforcing steel, anticorrosion coating

Introduction

In construction, steel is extensively used in reinforced concrete structures (RCS) due to its low-cost and ready availability as raw material. Despite the high susceptibility of reinforcing steel to corrosion, the service the life of RCS is increased by the ability of the concrete layer to prevent the diffusion and aggressive species (chlorides, oxygen, etc.) [1]. However, the long-term corrosion-induced deterioration of reinforcing steel is the principal cause of failure of RCS, which in the absence of preventive maintenance has serious financial, social, and environmental consequences.

In general, two factors cause corrosion and affect the stability of the passive film formed on the steel surface: (i) the carbonation of concrete by the diffusion of CO_2 through the concrete pores, causing a pH drop, and (ii) the activity of chloride ions introduced or initially present in the cementitious products [1]. To overcome the problems caused by corrosion of metallic structures different protection methods were developed, including the addition of corrosion inhibitors to concrete, high-performance concrete formulations, cathodic protection, use of alloys with high corrosion resistance, galvanized steel, and application protective coatings [2-

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4]. In the latter protection strategy, coatings have advantages such as relatively low production costs, environmental compatibility, and high performance as a barrier against the diffusion of aggressive species [4-6].

Organic coatings composed of purely polymeric materials such as epoxy, polymethyl-methacrylate (PMMA), polyurethane (PU), among others, despite their easy application on surfaces with different geometries, present disadvantages such as low thermal stability, the tendency of swelling, and poor adhesion to metal surfaces [3]. Inorganic coatings composed of metal oxides, phosphates, and others present micro-cracks, residual porosity, high internal stress, resulting in thickness limitations, thus impairing their anti-corrosion performance [7].

The combination of both phases in form of organic-inorganic nanocomposites has shown very promising results in the development of coatings for application as an efficient diffusion barrier to protect against corrosion of metal surfaces, with emphasis on formulations based on PMMA-silica [3,8-11]. The covalent conjugation between the organic phase (PMMA) and silica on molecular-scale results in a new material that exhibits unique properties. The silica phase plays an important role in cross-linking and contracting of polymeric segments [9-11] and promoting a strong adhesion between the film and the metallic substrate [20], while PMMA hermetically seals the structure, preventing the permeation of corrosive species [9,10].

Considering the potentiality of hybrid materials, the present study aims to develop environmentally compatible a highly efficient PMMA-silica for the protection of reinforcing steel by studying the influence of the proportion of thermal polymerization initiator (benzoyl peroxide, BPO) on the hybrid structure and its long-term barrier performance after exposure to saline and simulated concrete pore solutions.

Methodology

Hybrid synthesis

The hybrids were prepared by polymerization of methyl methacrylate (MMA) and 3-(trimethoxysilyl)propyl methacrylate (MPTS) using the thermal initiator benzoyl peroxide (BPO) and isopropanol as a solvent, followed the sol-gel hydrolytic condensation of tetraethoxysilane (TEOS) and MPTS. The MPTS molecule acts as a coupling agent by covalently conjugating the organic and inorganic phases. The organic solution (MMA+MPTS) was prepared at 80 °C for 4 h under stirring and reflux, and in parallel, the sol-gel reactions of TEOS occurred in an acidic (pH 1) ethanol/water solution during 1 h at 25 °C. Finally, both phases were mixed for 5 min at 80 ºC, and the resulting homogeneous hybrid solution was used to coat the reinforcing carbon steel substrates. The following molar ratios were kept constant MMA/MPTS = 8, TEOS/MPTS = 2; ethanol/H_2O = 0.5, Si/H_2O = 3.5 [9]; and the different proportions between BPO/MMA = 0.025, 0.05, and 0.1 were evaluated. The PMMA-silica hybrids were denoted B0.025, B0.05 and B0.1 according to the BPO/MMA proportion.

Substrate preparation and deposition

The reinforcing steel substrates (Ø 25 mm x 2 mm) were obtained by cutting the commercially acquired steel rebars with a nominal chemical composition of C = 0.35%; Si = 0.50%, Mn = 1.50%, P = 0.05%, S = 0.05% and EC (Carbon equivalent) = 0.55%. Before deposition, the reinforcing steel substrates were sanded using silicon carbide abrasive paper in the grit sizes of 320, 600, and 1500, cleaned in isopropanol for 10 min in an ultrasonic bath and dried with nitrogen.

The hybrids were deposited by dip-coating on carbon steel substrates, at room temperature at an immersion/emersion rate of 14 cm min^{-1}, and three depositions with an air-drying interval of 10 min between each immersion. The remaining solution was placed in Teflon® cups to obtain unsupported films. The coated substrates and the solution were subjected to heat treatment at 60 °C for 24 h and 160 °C for 3 h to ensure, after elimination of solvents, the complete polymerization of reactive groups and a high degree of polycondensation of the hybrid structure.

Characterization techniques

The structural characterization of the hybrid coatings was performed with a Bruker Hyperion 2000 Infrared microscope with Fourier Transform (FTIR) by attenuated total reflection (ATR) using germanium crystal, in a resolution of 4 cm^{-1}, 32 scans, and absorption spectral 4000 cm^{-1} to 500 cm^{-1}.

The surface morphology of the coatings was studied by atomic force microscopy (AFM) measurements using an Agilent Technologies 5500 instrument, operated in tapping mode. Topographic images allowed to determine the RMS (root means square) surface roughness (R_{RMS}) of the coatings with the Gwyddion software, in three different regions with a scanning area of 2 μm^2. The coating thicknesses were determined by optical interferometry using a Filmetrics F3-CS spectrometer, and their uniformity was assessed using an optical microscope (XJM900, Kozo).

The porosity (P) of the unsupported hybrids was calculated ($V_{Pt} = V_B – V_{Sk}$, $P = V_{Pt}/V_B \times 100\%$) from the values of real skeletal (V_{Sk}) and apparent bulk (V_B) volume and total porosity (V_{Pt}). The measurements were performed by helium (AccuPycc 1330, Micromeritics) and dry fluid (GeoPyc 1360, Micromeritics) pycnometry, respectively.

The contact angle measurements were performed using an OCA system, DATAPHYSICS, coupled with a CCD camera, and using the SCA20.2.0 software. For each sample, the average value of the contact angle formed between the hybrid coating and the 7 µL drop of distilled water was determined.

Pull-off tests were performed according to the ASTM D4541 method to assess the adhesion of the coatings to reinforcing steel surface using a Pull-Off Adhesion Tester (Elcometer F510-20T) employing a pull rate of 0.8 MPa s^{-1}. The coating surfaces were lightly roughed with SiC abrasive paper (600 grade) to promote the mechanical adhesion of the glue (Araldite® 2000+) and the aluminum dolly (Ø 10 mm), fixed perpendicularly. After application, the glue was cured at 100 ºC for 3 h. The equipment was calibrated according to the ASTM E74–13a standard (UKAS Calibration Laboratory No. 0157, 2017), and the adhesion strength obtained refers to the average of 2 measurements.

The anti-corrosion efficiency of the coatings in neutral 0.6 mol L^{-1} NaCl and simulated concrete pore solutions, SCPS1 and SCPS2 (Table 1), was evaluated by electrochemical impedance spectroscopy (EIS) measurements, at 25 °C, in a three-electrode cell: an Ag|AgCl|KClsat (0.6 mol L^{-1} NaCl and SCPS2) or Hg/HgO (SCPS1) reference electrode, a counter electrode (platinum wire) and the working electrode were then coated reinforcing steel substrate with an active area of 1 cm^2. A fourth platinum electrode connected to a 0.1 μF capacitor was connected in parallel to the counter electrode to avoid high-frequency phase changes. A sinusoidal potential of 10 V_{rms} was applied after checking the open circuit potential (OCP) stability for 1000 s. The frequency was varied between 1 MHz to 4 mHz, using a Gamry Reference 600 Potentiostat. To avoid instabilities and fluctuations in the potential of the Ag/AgCl electrode in alkaline solution, caused in the absence of chloride by reactions of the AgCl precipitate forming Ag_2O [13], a Hg/HgO electrode for was used. The measurements were performed in duplicate using 80 mL of neutral saline and the concrete pore solutions simulating fresh (SCPS1) and aged carbonated concrete pore liquid (SCPS2), shown in Table 1. The pH values for the solutions were verified with the digital pH meter PG2000 Gehaka.

Table 1. Composition and pH of simulated concrete pore solutions (SCPS).

Solution	**Compounds added (mol L^{-1})**						
	$Ca(OH)_2$	**NaOH**	**KOH**	**$NaSO_4$**	**$CaCO_3$**	**NaCl**	**pH**
SCPS 1	0,01	0,1	0,3	0,002	-	-	14
SCPS 2	-	-	-	0,002	0,001	0,014	8

Results and discussion

The evaluation of the formation of the organic-inorganic hybrid network, combining the polymerization reactions and the sol-gel process, was performed using FTIR/ATR spectra (Fig. 1a) recorded for hybrid coatings prepared with different molar proportions of BPO/MMA. In the absorption spectra, it is possible to highlight some absorption characteristic bands of PMMA, such as stretching of the carbonyl group (C = O) of the ester at 1720 cm^{-1}, and of silica, asymmetric stretching of 1060 and 1157 cm^{-1} of Si-O-Si [14,15]. The polymerization of methyl, methacrylate was evidenced by the disappearance of the stretching band in 1639 cm^{-1} of the vinyl group (C=C) using the carbonyl absorption (C=O) in 1720 cm^{-1} as reference, as shown in the inset of Figure 1a, including the MMA spectrum as a reference.

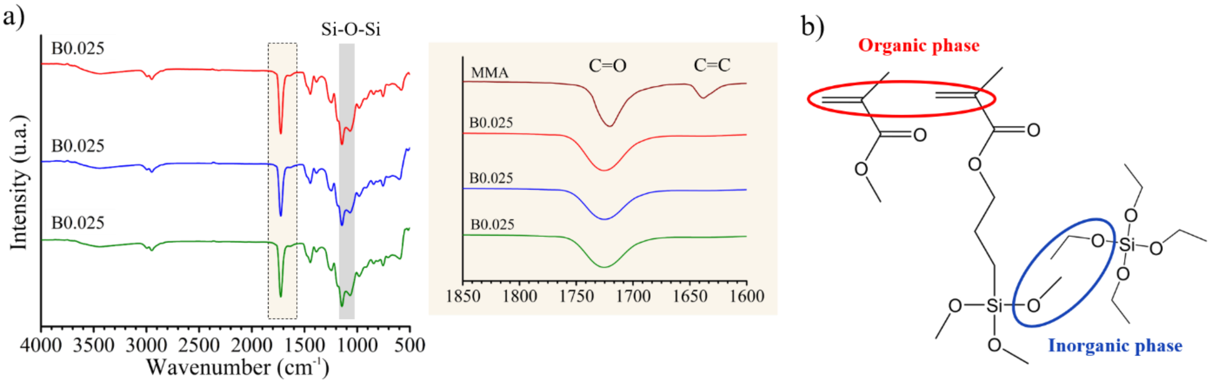

Figure 1. a) FTIR spectra of PMMA-silica hybrids prepared using different BPO/MMA ratios, b) Representation of the molecular structure of PMMA-silica hybrid precursors, showing the reactive groups of acrylate (organic phase) and silicon alkoxides (inorganic phase).

Other relevant requisites for coatings with high anticorrosive performance are homogeneity, low porosity, and strong adhesion to metallic substrates. The optical evaluation (Fig. 2a-b) showed that the hybrid coatings deposited on reinforcement steel are transparent, colorless, homogeneous, free of macroscopic defects and pores. The thickness of the coatings increases from 12 µm to 14 µm, as a result of subtle variations of the viscosity of the precursor hybrid solution with an increase in the BPO/MMA ratio.

Low RMS surface roughness were determined by AFM (Fig. 2c) for the hybrid coatings with values of 0.4 nm, 0.5 nm, and 2.2 nm for B0.025, B0.05 and B0.01, respectively. The surface wettability, evaluated by contact angle measurements, revealed a slightly hydrophilic character of the coatings. Compared to the contact angle of 71° found for bare steel, hybrid coatings exhibit a slightly higher values of 74 ° (B0.025 and B0.05) to 79 ° (B0.1), the latter attributed to its higher nano-roughness determined by AFM. The presence of the silica phase provides a more hydrophobic character to the hybrid coating when compared to pure PMMA, which is considered a hydrophilic polymer with water contact angle values of ± 68 ° [19].

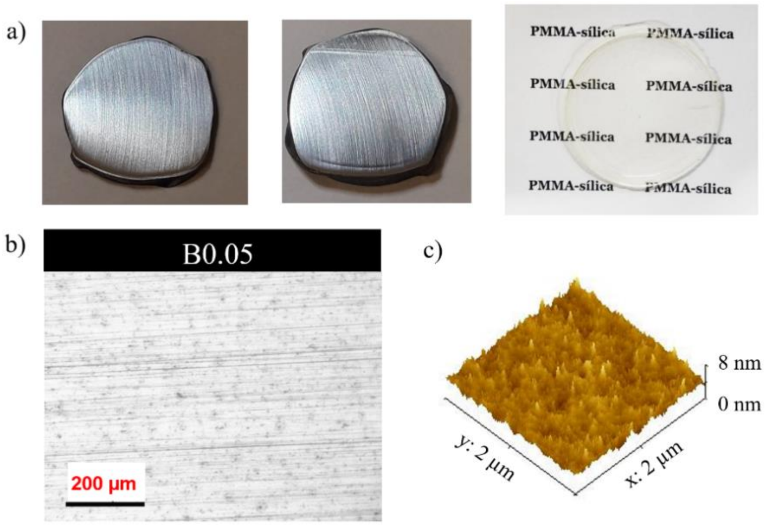

Figure 2. (a) Representative images reinforcing steel uncoated and coated with PMMA-silica hybrids, and unsupported film (monolith), (b) Optical micrograph of hybrid films deposited on reinforcing steel substrate (the dots come from the substrate), and (c) AFM 3D topographic image of deposited coatings on reinforcing steel for B0.05.

The pull-off assays showed for the hybrid coatings a high critical tensile adhesion strength between 13.7 MPa and 15.6 MPa, which is significantly higher than those reported for a pure PMMA coating of 6.7 MPa [9]. The excellent adhesion of hybrid coatings to the reinforcing steel substrate is a result of covalent bonding between silanol groups of the hybrid and iron oxyhydroxide groups present in the steel/coating interface [12]. The highest adhesion value (15.6 MPa), achieved for the B0.05 sample with intermediate BPO/MMA ratio, indicates for a sensitive balance between the proportion of both phases, resulting in a structure with high mechanical and thermal stability (Table 1).

Pycnometry measurements confirmed the presence of a highly cross-linked structure, with a low percentage of porosity for unsupported PMMA-silica hybrids with a density of 1.20±0.1 g/cm^3. The porosity of B0.05 and B0.1 hybrid was below the detection limit of the equipment resulting in negative percentages, in which the apparent density is higher than the skeletal density. On the other hand, the sample B0.025 presented a small percentage of residual porosity (0.4%), indicative for the presence of residual nanopores that may act as percolation paths facilitating the permeation of the electrolyte towards the coating/steel interface, thus impairing the anticorrosive properties.

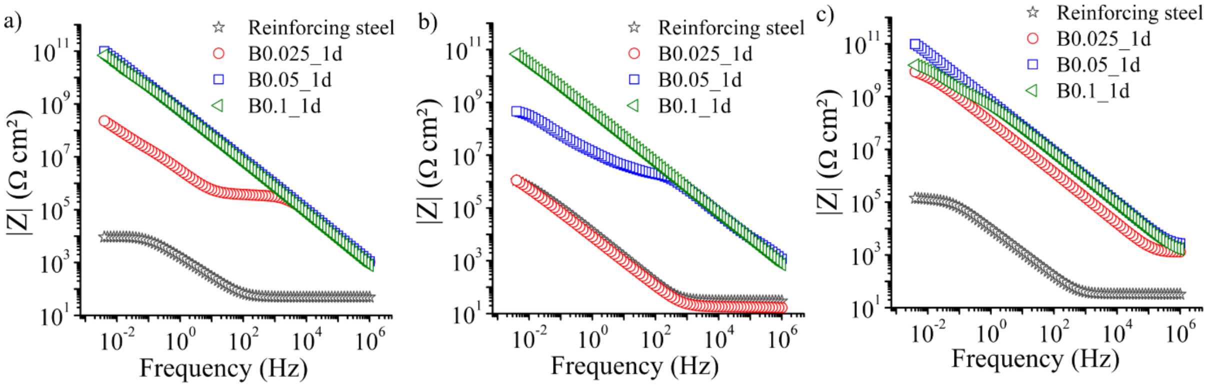

Figure 3. Bode graphs of the impedance module versus frequency for PMMA-silica hybrid coatings prepared with different BPO/MMA proportions, after 1 day of immersion in a) 0.6 mol L^{-1} NaCl, b) SCPS1 (pH 14), and c) SCPS2 (pH 8) solution (25 °C).

The intrinsic barrier properties of the coated samples were investigated using electrochemical impedance spectroscopy (EIS) in marine environment (0.6 mol L^{-1} NaCl) and the simulated concrete solutions present in the pores of fresh concrete (SCPS 1, pH 14) and after the carbonation process caused by CO_2 diffusion (SCPS2, pH 8). The low-frequency impedance modulus was used as a parameter to assess the corrosion resistance of the coatings. In general, coatings that provide excellent corrosion protection have low-frequency impedance modulus ($|Z|_{lf}$) values higher than 100 MΩ cm^2, while values below 1 MΩ cm^2 indicate a poor barrier property [9].

Figure 3 shows Bode plots of the impedance module versus frequency for the uncoated and coated steel samples after 1 day of exposure to the electrolyte solutions (NaCl, SCPS1, and SCPS2). In all environments the hybrid coated samples showed an excellent corrosion protection efficiency. With exception of the B0.1 sample in ACPS 1 solution, all coatings presented a low-frequency impedance modulus (4 mHz) in the range from 0.1 GΩ cm^2 to 100 GΩ cm^2, values up to 7 decades higher than those of bare steel. Comparing the low-frequency impedance modulus of the coatings, it is evident that the B0.25 and B0.1 sample show the best anti-corrosion performance in the studied electrolytic solutions. This result is in agreement with their structural properties, showing a less defective polymeric phase, indicated by thermogravimetry, and low porosity, evidenced by pycnometry measurements. The residual porosity of the B0.025 coating may facilitate the rapid formation of percolation paths, giving the electrolyte access to the coating/steel interface.

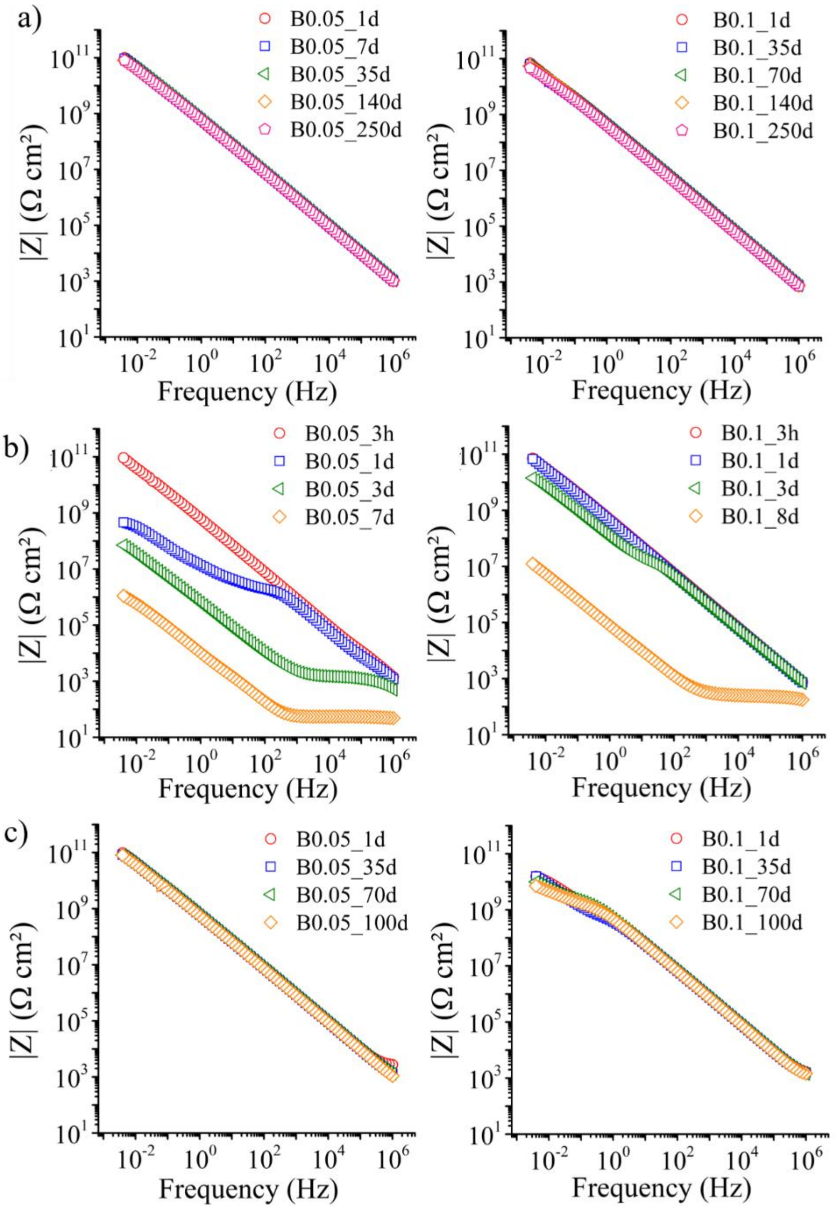

Figure 4. Time dependence of Bode plots of the impedance modulus versus frequency for B0.05 and B0.1 PMMA-silica coatings, immersed in solution (25 °C) of: a) 0.6 mol L^{-1} NaCl, b) SCPS1 (pH 14) and c) SCPS2 (pH 8).

The EIS measurements as a function of time were recorded for the B0.05 and B0.1 coating, confirming their excellent anticorrosive performance. The low-frequency impedance modulus remained essentially unchanged during 250 days of exposure to neutral saline solution and 100 days in carbonated concrete pore solution (SCPS2, pH 8), with no evidence of localized corrosion or delamination. However, it is possible to observe that when the coatings are exposed during 7 days to a solution with high pH, a noticeable drop of their electrochemical performance can be observed (Figure 4b). An impedance modulus close to that of the bare steel indicates a local degradation of the coating initiating the corrosion of the metal surface.

The hybrid coating PMMA-silica with the intermediate proportion of BPO (B0.05) showed the highest resistance to corrosion ($|Z|_{lf}$) and the best long-term stability in all tested electrolytic solutions. The results obtained are comparable to hybrid coatings with the best anticorrosive performance for protection of steel surfaces reported so far [3-6,8-11]. Although exposure to an aggressive environment with high basic pH (pH > 12) results in reductions in long-term stability and anti-corrosion efficiency, this work gives an important contribution to the development of efficient coatings for the protection of reinforcing steel in concrete structures. Additionally, the use of isopropanol as a solvent for the preparation of the PMMA-silica coating represents an environmentally compliant alternative for the use of harmful solvents such as tetrahydrofuran (THF), among others [3,8-11].

Conclusions

Homogeneous PMMA-silica coatings with small thickness (13 - 15 μm), free of pores and high adhesion to the reinforcing steel substrate (> 13 MPa), were prepared by varying the ratio between the polymerization thermal initiator and the methacrylate monomer methyl (BPO/MMA) in the range of 0.025 - 0.1, using the isopropanol as green solvent. The structural analysis, performed by infrared spectroscopy, confirmed the formation of the PMMA-silica hybrid structure, identifying the functional groups characteristic of the PMMA and SiO_2 absorption bands. For these coatings, the presence of a highly cross-linked structure with a porosity below the detection limit was evidenced by pycnometry measurements. The results of electrochemical impedance spectroscopy in 0.6 mol L^{-1} NaCl and SCPS2 (pH = 8), showed that these coatings have an excellent corrosion resistance with low-frequency impedance modulus of up to 100 GΩ cm^2 (B0.05) and a long-term durability of >250 days in saline solution, and more than 100 days in SCPS2. A similar corrosion resistance, however, with shorter durability was obtained in SCPS1 concrete pore solution (pH 14). All results suggest that PMMA-silica coatings represent a promising and environmentally compatible alternative to conventional coating systems used for the protection of reinforcing steel structures.

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