

POLYMERIC NANO-MATERIALS FOR CORROSION CONTROL OF STEEL IN CONCRETE

M. Varini¹, D.A. Koleva¹, A.G. Denkova², J.M.C. Mol³, H. Terryn^{3,4}, K. van Breugel¹

¹*Civil Engineering & Geosciences, Materials & Environment, Delft University of Technology, Stevinweg 1, 2628 CN Delft, NL; m.varini@tudelft.nl*

²*Reactor Institute Delft, Delft University of Technology Mekelweg 15, 2629 JB Delft, NL*

³*3mE, Surfaces & Interfaces, Delft University of Technology, Mekelweg 2, 2628CD, Delft, NL*

⁴*Vrije Universiteit Brussel, Electrochemical & Surface Engineering, Pleinlaan 2, B1050, B*

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ABSTRACT

Polymeric nano-materials utilization in reinforced concrete, aiming to deal with steel corrosion was developed in previous works. Promising results were obtained with PEO-*b*-PS nano-formations, both in terms of enhanced bulk matrix properties and improved steel corrosion resistance. Recent research has been focusing on a cheaper and commercially available polymer, Pluronic P123. Pluronic is able to self assemble into micelles and/or vesicles but their sensitivity towards the environmental medium is a drawback: for this reason, a study on Pluronic micelles stability in different solutions has been carried out. A stabilization process against dissociation of micelles was also performed. Both stabilized and non-stabilized micelles were tested in model solutions in terms of their influence on steel corrosion resistance.

1. INTRODUCTION

Steel corrosion in reinforced concrete is a worldwide problem that affects stability and durability of civil structures. Former works developed a novel approach to corrosion control based on nano-formations, able to improve the cement-based bulk matrix characteristics and steel surface properties. The final result was “self-healing” by restoring the environment at the steel/cement paste interface in the event of corrosion. Previously investigated was the addition of PEO₁₁₃-*b*-PS₂₁₈₍₇₆₀₎ micelles and vesicles to plain and reinforced mortar. In their presence (of only 0.006 wt.%), improved bulk matrix properties (reduced permeability, porosity), enhanced chloride binding and “nucleation sites effect” were recorded [1,2]. An improvement was also observed in terms of steel performance in corrosive conditions: electrochemical techniques and surface analysis proved “self-healing” effects on the steel surface in addition to general barrier effects only [2]. Aiming at a cost-effective alternative (PEO-*b*-PS is a high cost material for civil engineering applications), Pluronic P123 formations were recently considered [1], targeting the above discussed superior performance. Pluronic P123 (PEO₂₀ - PPO₇₀ - PEO₂₀) is commercially available and it can self assemble into micelles/vesicles. These are, however, sensitive to ionic strength and chloride content in the medium [1]. Nevertheless, it is possible to tailor their properties in order to gain stability against dissociation and reduce their sensitivity to environmental changes. This paper reports on the stability of Pluronic micelles in model environment and briefly presents preliminary studies on steel electrochemical behaviour in the presence of stabilised and non-stabilised micelles.

2. MATERIALS AND METHODS

Polymeric micelles and stabilization: Aqueous solution of 10 wt% Pluronic P123 (Sigma Aldrich) was prepared by weighting. This stock solution was used to produce a series of 1wt.% and 0.024wt% micelles-containing test solutions with varying pH and Cl-content (pH 3, 5, 7 and 12.7 and 1%, 3.5% and 5% of NaCl). A parallel series of solutions from stabilised micelles were prepared via employing PETA monomer (pentaerythrol tetraacrylate, Sigma Aldrich) as cross-linker, added in a ratio 1:100 according to literature [3]. Polymerization of the cross-linker was achieved with γ radiation; Successful stabilization was proven by Dynamic light scattering (DLS) measurements through dissolving 1 ml of the stabilized solution in 90 ml of ethanol. Except the above test solutions, a series of model pore solutions (cement extract) was produced with analogical micelle concentration, pH and Cl-content variation.

Cement extract and electrochemical set up: Cement extract (CE) was prepared by mixing Ordinary Portland Cement (OPC) CEMI 42.5N and tap water in a ratio of 1 : 1; the suspension was rotated for 24h and then filtered. NaCl was added in 3.5 and 5 wt. % concentration to the CE. Stabilised and non-stabilised micelles (as 1wt.% and 0.024wt%) were added to the CE solutions. Steel corrosion resistance was monitored in these solutions; the difference in behaviour was expected to result from different micelle content, chloride content and possible influence of PETA stabilisation. A general 3-electrode cell arrangement was used, comprising a SCE (saturated calomel electrode) as reference, Ti mesh as counter and the steel plate (low carbon steel St37) of 4 cm² surface area as working electrode. *Impedance spectroscopy* (EIS) was carried out in the frequency range of 50 kHz to 10 mHz by superimposing and AC voltage of 10 mV; *Potential-dynamic polarization* (PDP) was performed in the range of -0.2 to + 1.2 V vs OCP at a scan rate of 0.5 mV/s.

3. RESULTS AND DISCUSSION

DLS measurements were performed on non-stabilized micelles in demi-water and cement extract at varying pH and chloride concentration. For all cases the micelles were added to the relevant solutions in a concentration of 1wt.%. The expected characteristic peak for PEO_{20} - PPO_{70} - PEO_{20} micelles can be clearly observed around 10 nm (Fig.1), which is in agreement with previous reports [1].

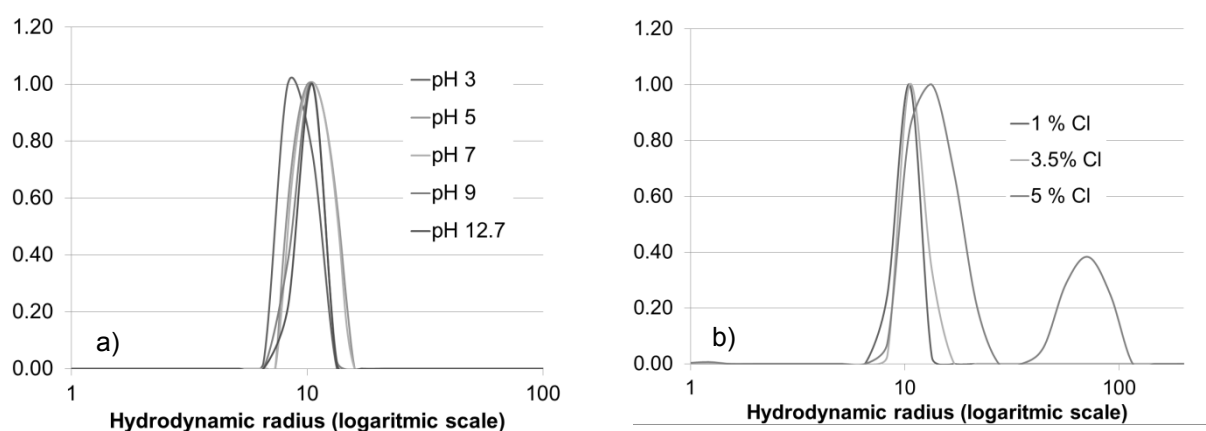


Figure 1: DLS measurements for Pluronic micelles (1%wt) in water at a) different pH and b) at pH 7 and different chloride content

There are no significant modifications of the peaks, as observed within varying pH of the demi-water solutions (Fig.1a). This result was expected to a certain extent since Pluronic is not a pH sensitive polymer [4]. Similar observations hold for the case of CE solutions, despite the complex character and composition of the latter. Non-stabilized micelles were also tested at different pH and chlorides concentrations, since salts are able to modify their properties and therefore to affect the aggregation of PEO-PPO-PEO block copolymers [3]. Chlorides have a “salting – out” effect on the PEO segment (according to the Hoffmeister series, that for this polymer in particular deviates from the original one [5]) and make it “shrink” due to an increase in its hydrophobicity. On the other hand, H^+ and OH^- ions provoke the opposite outcome (although less pronounced [5]), leading to “swelling” of the PEO co-block. The two opposite effects reach balance at more extreme pH (3 and 12.7), while at intermediate values (pH 5 and 7) the influence of chlorides prevails, particularly at the highest concentration (5%), as underlined in the DLS spectrum by a shift of the main peak to higher radius, together with the appearance of a second one (Fig. 1b). The hydrophilic/hydrophobic ratio of the PEO segment is modified due to the pronounced quantity of chlorides in the solution [6] and the micelles tend to transform into a worm – like shape [7]. DLS in CE solutions is an on-going investigation.

Electrochemical tests: PEO_{20} - PPO_{70} - PEO_{20} micelles, both stabilized and not, were added in two different concentrations (1wt.% and 0.024wt%) to CE, containing 3.5wt.% and 5%wt NaCl as corrosion medium.

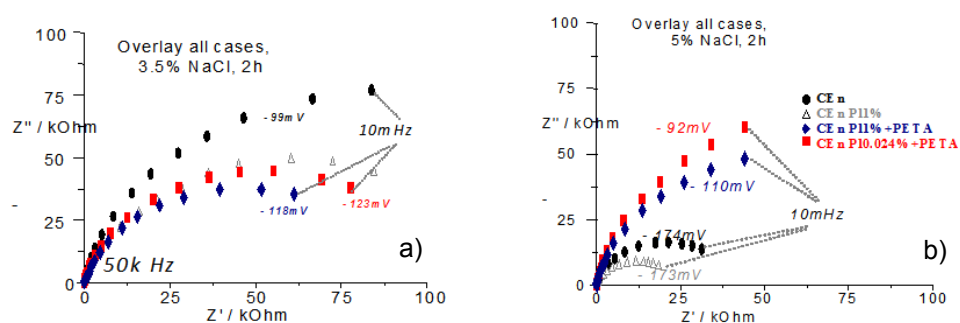


Figure 3: Experimental EIS response (Nyquist) for specimens CE, CE_PL1, CE_P1st1 and CE_P1st0 at a) 3.5 %wt and b) 5% wt chlorides respectively, after 2h of immersion

The steel electrodes were treated (immersed) in the relevant solutions for 2 and 24 h; a series of EIS and PDP measurements were performed in duplicate. The registered OCPs for all specimens show that there was no significant breakdown in steel passivity, since all values were more anodic than – 270 mV [8].

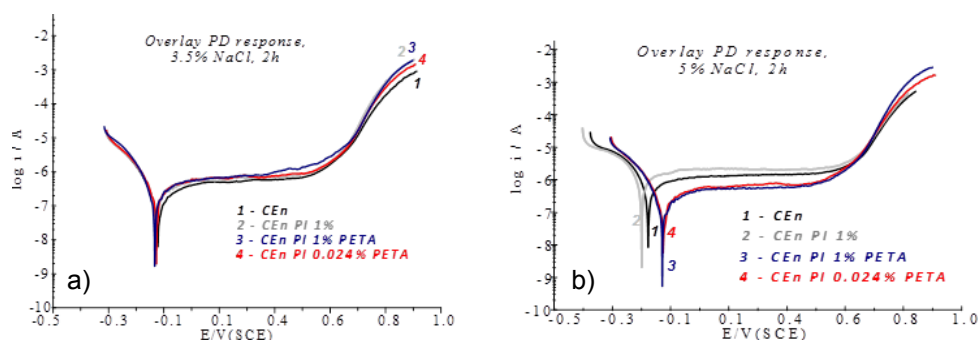


Figure 4: Polarization curves for specimens CE, CE_PL1, CE_PLst1 and CE_PLst0 at a) 3.5%wt and b) 5% wt chlorides respectively, after 2h of immersion

The so far employed Immersion intervals are thus insufficient to claim remarkable variations in corrosion performance and further investigation is on-going. However, even a 2h treatment, results in different behaviour: the EIS response (Fig. 3a) for steel in 3.5wt.% chloride-containing CE and varying micelle concentration did not show any positive effect of the micelles on corrosion resistance. For higher chloride content (5wt.%), the magnitude of impedance increased in the presence of stabilized micelles (Fig.3b), particularly for the cases at lower micelles concentration, whereas the presence of non-stabilised micelles did not improve corrosion resistance. The recorded polarization curves (Fig. 4) support the EIS results: at 3.5 wt.% chloride concentration (Fig.4a) no significant differences were observed. In contrast, steel treated in the 5 wt.% chloride-containing solutions in the presence of both 1 wt% and 0.024wt% stabilised micelles (Fig.4b) showed more anodic corrosion potentials and lower anodic and corrosion current densities, suggesting improvement in steel corrosion performance. The non-stabilised micelles at 1 wt.% did not exert any positive effects.

4. CONCLUSIONS

The Pluronic micelles' behaviour and stability with varying pH and chloride concentration was characterized via DLS analysis. At pH of 7 the effect of chloride prevails, leading to morphological changes. DLS was also employed in order to prove micelles stabilization via cross-linker polymerization. Preliminary electrochemical tests were also performed in cement extract with both stabilized and non stabilized micelles, in order to highlight their possible effect on steel corrosion resistance. The experiments show the positive effect of stabilised micelles. The on-going investigation will clarify the influence of micelle stabilisation and optimum micelle concentration for improved steel electrochemical performance.

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