



# Application of PEO<sub>113</sub>-b-PS<sub>218</sub> nano-aggregates for improved protective characteristics of composite zinc coatings in chloride-containing environment

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## ABSTRACT

This study reports on the influence of a very low concentration of polyethylene oxide-b-polystyrene nano-aggregates (PEO<sub>113</sub>-b-PS<sub>218</sub> micelles of 0.5 g/l in the starting electrolyte) on the corrosion behavior and surface characteristics of zinc coatings in chloride-containing environment (5% NaCl). Both zinc (Zn) and composite Zn-polymer (ZnP) coatings were electrodeposited from slightly acidic electrolytes with a coating thickness of approximately 8 μm. The involved experimental techniques were electrochemical methods (potentio-dynamic (PD) polarization, EIS and SVET) and surface analysis techniques (SEM, EDX, XRD and XRF). The morphology, distribution and size of the PEO<sub>113</sub>-b-PS<sub>218</sub> micelles were investigated in demi-water by TEM and dynamic light scattering (DLS), prior to their co-deposition within the metallic zinc matrix. The electrochemical behavior was studied on certain intervals (from initial measurements after OCP stabilization up to 480 h of immersion in 5% NaCl). The recorded parameters account for higher corrosion resistance of the nano-composite (ZnP) coating, compared to galvanic Zn, especially after prolonged periods of treatment. The superior performance of the composite ZnP coating in the very aggressive medium of 5% NaCl is denoted to the combination of increased barrier effects (in the presence of the nano-aggregates) and “self-healing” mechanisms (as a result from a reversible shrinkage and swelling of the polymer shells in the presence of chlorides).

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## 1. Introduction

The electrodeposited zinc and zinc alloy coatings on a steel substrate find practical utilization in various industrial applications, providing protection of the steel substrate as a result of impeded corrosion initiation and/or propagation [1–5]. As well known, under atmospheric conditions zinc corrodes by a factor of up to 100 times less than steel [6]. The galvanic corrosion of zinc, however, contrary to many other metals is to certain extent a desirable event [7]. The latter statement can be clarified from the view point of the main purpose of a zinc coating i.e. galvanic protection of the steel substrate or so-called sacrificial effect. In galvanic protection, zinc is less noble or anodic to steel at ambient conditions, and will predominantly corrode to protect the substrate (steel) even if some of the steel is exposed as cut edges or scratches in the coating [8]. The process leads to the formation of zinc corrosion products, which differ in composition with respect to the relevant environmental conditions, but are generally characterized with a low product of solubility value. The result is an additional

(except the sacrificial effects) influence on the corrosion characteristics of the original zinc coating i.e. increased barrier effects and thus enhanced corrosion resistance of the zinc-coated steel substrate.

To this end, although the sacrificial effects are desirable, extending the service life of a zinc coating will provide longer protection and increased service life for the protected steel. Various methods and techniques are available for improving the zinc coatings performance e.g. alloying with other metals [9–18], conversion coatings, based mainly on environmentally friendly compounds [19–21] and more recently, composite coatings, incorporating micro- or nano-sized polymeric aggregates [22–24]. Another approach is the electrodeposition of nanocrystalline coatings by using selected organic additives or pulse deposition techniques [25]. The corrosion resistance of the zinc layer is in correlation with and depending on the morphology and crystallographic orientation in the deposit [26–28]. It is also well known that electro-crystallization occurs by growth of existing crystals or formation of new nuclei [28]. These conditions and in particular grain refinement of the zinc layer, may be achieved by means of incorporating polymeric nano-sized aggregates, which on one hand act as new nucleation sites and on the other hand, increase the corrosion resistance of the zinc layers in aggressive environment, due to the amphiphilic nature of the used polymer [24,29].

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Our previous research [23,24,29–32] shows a significant improvement of the corrosion resistance of a zinc coating, with incorporated within the electrodeposition process polymeric nano-aggregates (concentration of 1 g/l in the starting electrolytes). Previously investigated were zinc coatings with: embedded stabilized micelles, formed from poly ethylene oxide–b-poly-propylene oxide–b-poly ethylene oxide (PEO–PPO–PEO) [24] and zinc coatings, incorporating polymer nano-aggregates from the amphiphilic tri-block copolymer poly(2-hydroxyethyl methacrylate)–poly (propylene oxide)–poly (2-hydroxyethyl methacrylate) (PHEMA<sub>15</sub> PPO<sub>34</sub>PHEMA<sub>15</sub>) [29]. The present study investigates composite zinc layers, incorporating poly (ethylene oxide)–block-polystyrene (PEO<sub>113</sub>–b-PS<sub>218</sub>) di-block copolymer in concentration of 0.5 g/l to the starting electrolyte. The research is part of an experimental study on the application of this type of polymer nano-aggregates for increased corrosion resistance of the steel substrate (by means of composite Zn coatings) or improved characteristics of both steel (as reinforcement) and cement-based matrix in the case of reinforced concrete.

The hereby discussed approach is based on the formation of a composite zinc coating, containing practically insoluble polymer micelles and metallic grains, which leads to an altered zinc matrix with improved characteristics [29]. Consequently, the combination of increased barrier and sacrificial effects would be more pronounced, and since this study was performed for comparatively longer investigation periods, the long term service life improvement of the composite coating will be clarified. Finally, certain phenomena, denoted to the combination of increased barrier effects (in the presence of the nano-aggregates) and a kind of “self-healing” mechanisms (as a result from a reversible shrinkage and swelling of the polymer shells in the presence of chlorides) are also discussed.

## 2. Materials and methods

### 2.1. Galvanic coatings

Both zinc (Zn) and composite zinc (ZnP) coatings were electrodeposited on a steel substrate (carbon steel, surface area of 1 cm<sup>2</sup>) from slightly acidic sulfate-chloride electrolyte with the following composition: 150 g/l ZnSO<sub>4</sub>·7H<sub>2</sub>O, 30 g/l NH<sub>4</sub>Cl, 30 g/l H<sub>3</sub>BO<sub>3</sub>, additives AZ-1 (wetting agent) 50 ml/l and AZ-2 (brightener) 10 ml/l. For the ZnP coating, the electrolyte also contains the previously dissolved in demi-water polymer micelles (concentration of the micelles in the electrolyte is 0.5 g/l, peculiarities and synthesis below). The electrodeposition conditions were realized at current density of 2 A/dm<sup>2</sup>, pH 4.5–5.0, *t*<sup>o</sup> – 22 °C, no stirring or agitation. The coating thickness for both hereby investigated Zn and ZnP layers was approximately 8 μm. The coating thickness was calculated following well known estimation/calculation procedure for coatings, electrodeposited in galvanostatic regime i.e. the coating thickness *T* (μm) can be calculated, using Eq. (1):

$$T = E_q \cdot I_{cat} \cdot C_{ef} \cdot \tau / D \quad (1)$$

where: *E<sub>q</sub>* is electrochemical equivalent, g/Ah (*E<sub>q</sub>* = *A*/*n* · *F*, where *A* is atomic mass; *n* is valence; *F* is Faraday's constant); *I<sub>cat</sub>* is the cathodic current density, A/dm<sup>2</sup>; *C<sub>ef</sub>* is the cathodic efficiency, %; *τ* is the deposition time, *h* and *D* is the density of the metal, g/cm<sup>3</sup>.

Using Eq. (1) the thickness can be obtained by varying the deposition time. For example, in the case of 8 μm, the deposition time will be:

$$\tau = D \cdot 8 / E_q \cdot I_{cat} \cdot C_{ef} \quad (2)$$

Additionally, visual evidence for the thickness of the coatings (as electrodeposited, before treatment) is given by their cross sections (Fig. 3).

Should be noted, that thinner coatings were hereby chosen for investigation (rather than the generally applied in practice deposits of ~12 μm) for two reasons: at first, a comparison was aimed with previously investigated layers of 12 μm, the latter however being composites, electrodeposited from electrolytes with twice higher concentration of different type nano-aggregates [23,24,29–32]; secondly, thinner layers will speed up the monitored phenomena. Additionally, since both Zn and ZnP coatings were with equal thickness, the comparison of derived parameters is considered reliable and accurate.

### 2.2. Polymeric micelles

Poly(ethylene oxide)–block-polystyrene (PEO<sub>113</sub>–b-PS<sub>218</sub>) di-block copolymer was synthesized by atom transfer radical polymerization (ATRP) employing the macro-initiator technique. The polymeric core-shell micelles were further formed by dissolving PEO<sub>113</sub>–b-PS<sub>218</sub> di-block copolymer in dioxane. Finally, a turbid dispersion (*c* = 0.5 g/L) was obtained, which is stable for months without any precipitation. Water is good solvent for PEO and non-solvent for PS. Thus, in aqueous media PS blocks form the micellar core, surrounded by the PEO shell. Dynamic light scattering measurements (Fig. 1a) showed an apparent

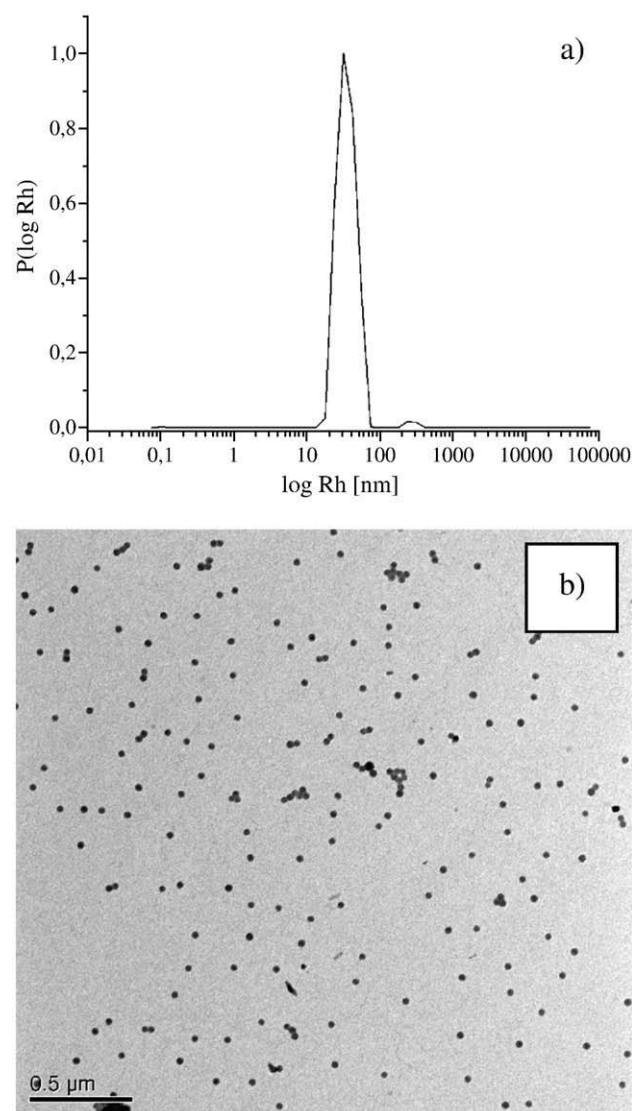


Fig. 1. DLS (a) and TEM (b) of the PEO<sub>113</sub>–b-PS<sub>218</sub> micelles in demi-water, prior to admixing with the starting electrolytes and co-deposition in the Zn metallic matrix.

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