



Superabsorbent polymer additives for repeated barrier restoration of damaged powder coatings under wet-dry cycles: A proof-of-concept

Vimal Saini^{a,b,1}, Max von Tapavicza^{a,b}, Christina Eloo^{a,*}, Katrin Braesch^a, Holger Wack^a, Anke Nellesen^a, Annette M. Schmidt^{a,b}, Santiago J. García^c

^a Fraunhofer UMSICHT, Fraunhofer Institute for Environmental, Safety, and Energy Technology, Oberhausen, Germany

^b University of Cologne, Chemistry Department, Luxemburger Str. 116, 50939, Köln, Germany

^c Novel Aerospace Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS, Delft, The Netherlands

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ABSTRACT

Superabsorbent polymers (SAPs) are well known for their ability to absorb and hold high water amounts accompanied by a high volume expansion. In this work we show the benefits of this underlying property of SAPs to induce underwater crack closure with subsequent barrier restoration in damaged protective coatings. For the proof of concept, three layer epoxy-polyester (EP) powder coating systems were developed and applied on carbon steel. In these systems the middle EP layer (also called functional layer) contained crosslinked acrylamide/acrylic acid copolymer SAPs in different amounts ranging from 0 to 40 wt%. The capability of the SAPs to close damages and extend barrier and corrosion protection was evaluated by electrochemical impedance spectroscopy (EIS), NaCl aqueous solution immersion test and optical microscopy. It was found that coatings loaded with a 20 wt% SAP led to the best overall corrosion protection for the studied systems. In order to proof the potential use of this extrinsic healing concept for multiple healing events wet-dry cycles on scratched systems were performed and the corrosion performance was followed by EIS. Although not yet optimal, the results show the potential of the concept for multiple healing events under wet-dry conditions.

1. Introduction

Corrosion protection of metal structures using self-healing concepts has attracted significant attention in the last two decades. Such attention is based on the potential of the concept to restore local protection after damage by multiple strategies [1]. Two main self-healing generic strategies have been explored in anticorrosive coatings, namely intrinsic and extrinsic self-healing. Intrinsic self-healing implies that the healing capability is given by the matrix itself. In this concept temporary mobility of the matrix (e.g. polymeric coating) leads to damage restoration such as closure of scratches or recovery of adhesion [2]. Intrinsic healing can be obtained by using various types of reversible covalent and non-covalent chemistries such as ionomers [3], disulfide bridges [4], shape memory polymers [5] and Diels Alder moieties [6]. Extrinsic self-healing is obtained by secondary reactive phases added to the main matrix. The most common approaches use capsules containing reactive liquids [7] or inorganic nanoparticles loaded with corrosion inhibitors [8–12]. Despite the multiple strategies developed, clear benefits to extend the corrosion protection at damaged sites is still

challenging due to some drawbacks. On the one hand most intrinsic healing principles require a localized energetic input which can limit future applications while extrinsic concepts using encapsulated liquids can only heal once and are technologically complex to upscale. Moreover most of the existing research has focused on solvent based coatings while the more environmentally friendly organic powder coatings [13–15] have attracted little to no attention. In this work we explore the potential of superabsorbent polymers to develop an extrinsic healing powder coating capable of repeated healing at the same damaged site with wet-dry cycles. Superabsorbent polymers (SAPs) have the ability to absorb liquids up to several thousand times of their own weight, keeping this water in the structure for long periods of time. Superabsorbent polymers are extensively used in baby diapers [16] and agriculture [17–20] but their use in self-healing coatings is limited to a handful of works. Yabuki et al. showed that a SAP could act as a self-healing agent in a vinyl-epoxy liquid coating [21] and some patents were filed showing the potential of SAPs for water blocking in optical cables [22]. SAPs have also been used to develop swellable thermo-plastic/elastomer alloys [23], water-swallowable rubbers [24] and self-

* Corresponding author.

E-mail address: christina.eloo@umsicht.fraunhofer.de (C. Eloo).

¹ Present address: Elementis GmbH, Stolberger Straße 370, 50933 Köln, Germany.

healing concrete [25–27]. In all these concepts the underlying principle is the same: when there is damage, the SAP is exposed to the environment from where the SAP absorbs humidity thereby expanding. The local expansion of the SAP leads to the blocking of the damage and protection of the underlying (metallic) structure by local barrier restoration.

In this work we show the potential use of SAPs as self-healing additives in powder coatings. To demonstrate the concept a three layered epoxy-polyester (EP) powder coating system was developed. Acrylamide/acrylic acid copolymer SAP was synthesized and incorporated in the coating system by blending it with the middle EP layer, this conforming the so called functional middle layer. Several coatings were prepared with different SAP concentrations in the middle layer ranging from 0 to 40 wt%. To evaluate the damage healing potential the coatings were manually scratched with a knife ensuring the underlying substrate was reached. The behavior of the coatings and their barrier restoration efficiencies were then evaluated by electrochemical impedance spectroscopy (EIS) and salt water immersion testing. The potential of the concept as an extrinsic healing strategy with multiple healing events at the same damaged site was evaluated by wet-dry cycles and EIS. The results are promising although more research is needed to improve the overall barrier restoration and healing repeatability at one same damaged site.

2. Materials and experimental

2.1. Synthesis of SAP

Crosslinked acrylamide/acrylic acid superabsorbent copolymers (SAPs) were synthesized in the lab by radical polymerization. Acrylic acid (99% purity; 0.02% hydroquinone monomethyl ether as stabiliser) was supplied by Sigma–Aldrich Chemie GmbH. *N,N'*-methylene bisacrylamide (> 98% purity), sodium hydroxide (> 98% purity), ammonium persulfate (> 98% purity) and sodium bisulfite (97–100% purity) were supplied by Merck KGaA and used as received.

Acrylic acid (AA) and sodium acrylate (SA) were used as functional monomers and *N,N'*-methylene bisacrylamide as a crosslinking monomer. The redox system ammonium persulfate and sodium bisulfite was used as the initiator. For the synthesis of SAP, 0.78 mol of AA was first dissolved in 16 mol of deionised water in an ice bath at 3 °C. Subsequently, this mixture was neutralized with 0.58 mol of NaOH to achieve the required 75 mol% degree of neutralization of AA. After this, 0.04 mol of crosslinker was dissolved in the solution, which was then deaerated by bubbling with nitrogen for 10 min. Thereafter, the solution was cooled down to 10 °C in an ice bath and stored for further 5 min. This monomer solution was then mixed with the initiator solution (0.01 mol of ammonium persulfate and 0.01 mol of sodium bisulfite dissolved in 10 ml of deionised water) and then transferred to a 500 ml glass bottle at 60 °C to allow the polymerization reaction to proceed. The polymerization reaction was completed after 4 h. Thereafter, the hydrogel was taken out of the glass bottle and cut into small pieces. The hydrogel pieces were stored in deionised water at ambient temperature for four days for washing out of the unreacted components, at daily water exchange. The hydrogel was then dried in vacuum oven for 24 h at 70 °C and ground in a ball mill to obtain a powder. The resulting particles had a cubically broken geometry. The powder had an unimodal distribution with a $d(0.1)$ of 15 μm , a $d(0.5)$ of 42 μm and a $d(0.9)$ of 76 μm .

2.2. Swelling degree of SAP

The tea bag method was used for the measurement of swelling degree of the synthesized SAP. About 0.2 g of SAP powder is sealed in a liquid-permeable tea bag and immersed in a bath of 5 wt% aqueous NaCl solution and kept at ambient temperature. The tea bag was then taken out at set intervals (1, 2, 5, 10, 15, 20, 30 and 60 min) and drained for one minute to remove the excess water before weighing. The equilibrated swelling (ES) was measured twice using the following equation

$$ES(\text{g/g}) = \frac{W_2 - W_1}{W_1} \quad (1)$$

After weighing the swollen gels, the swelling degree (water absorption of SAP at a given moment) was calculated according to Eq. (1).

2.3. Cyclic absorption-drying tests of the SAP

To identify any potential loss in the absorption potential of the SAPs up to four absorption-drying cycles were performed. During the absorption step the SAPs were immersed for one hour in 5 wt% aqueous NaCl solution until saturation was reached. The drying cycle consisted of exposing the saturated SAPs in an oven at 70 °C until full drying.

2.4. Coating systems preparation

Low carbon, cold rolled steel with a thickness of 0.8 mm and a size of 102 x 102 mm used as metal substrate was supplied by Q Lab Germany under the brand name R46, and used after degreasing. Epoxy-polyester powder coatings containing high performance epoxy and polyester resins were used as received from Axalta Coating Systems Germany GmbH with a particle size < 160 μm (brand name Aleasta EP). The EP powder coatings were deposited by electrostatic spraying onto the low carbon steel (at 60 kV potential difference) and cured in an oven at 170 °C for 10 min.

Based on preliminary tests it was decided to develop a three layer system in which the SAP particles are located in the middle (i.e. a functional coating as middle layer between a primer and a topcoat). It should be noted that when the SAPs were added in the primer the coatings showed a clear adhesion loss and low resistance to water exposure, thereby highlighting the need for a primer below the SAP-containing layer. When the SAP-containing layer was directly exposed to water a fast and uncontrolled leaching of the SAP was observed with its consequent loss of healing potential. This highlighted the need for a barrier topcoat to force the SAP swelling and expansion to occur only at damaged sites. To form the three-layer coating systems first the base EP layer was applied and placed in an oven at 170 °C for 3 min to ensure sufficient melting and coverage. Then the functional middle EP layer containing the SAPs was applied using different EP/SAP powder mixtures (0 up to 40 wt% SAP) and placed in an oven at 170 °C for 3 min. Finally the last EP layer was deposited and the three-layer coating system cured in an oven at 170 °C for 10 min. A schematic of the process is depicted in Fig. 1. The average coating thicknesses of all the samples was 245 μm (with a functional middle layer of approximately 104 μm thick and the base and top layers of 70 μm). To show the stability of the SAPs during the curing process at 170 °C a dedicated thermogravimetric and differential scanning calorimetry analysis of the polyacrylate-based SAPs was performed. The results showed the particles are stable until up to 230 °C, well in agreement with previously published works with

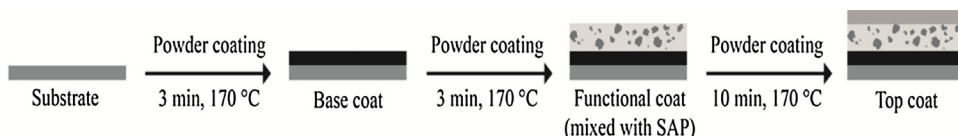


Fig. 1. Three layer coating system production.

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