Controlling the Corrosion of Metals with Polyphenolic Proteins

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Introduction

When metal surfaces are prepared for repainting, some form of surface preparation is necessary to remove old coatings and leave a clean surface for new coatings to adhere to. Common surface preparation techniques include grit-blasting or ultra-high pressure (UHP) water jetting. Unfortunately, these treatments can leave exposed metal surfaces vulnerable to rapid atmospheric corrosion during the time between surface treatment and coating application. The ultimate objective of this research is to develop a bio-inspired flash rust inhibitor that is water-soluble, environmentally friendly, and able to promote the adhesion of subsequent coating systems.

Several proteins from the mussel species Mytilus edulis and polypeptides from the tunicates Molgula manhattensis and Styela plicata have been investigated as a possible inspiration for such a coating. The amino acid L-3,4 dihydroxyphenylalanine (L-Dopa) is present in varying amounts in these biomolecules, and it is primarily responsible for the adhesive and anticorrosive properties that they exhibit. The catechol functional group on L-dopa can form strong bidentate complexes with metal ions, allowing biopolymers containing L-dopa to adsorb strongly to metal surfaces and inhibit corrosion by forming stable complexes with a metal surface[1]. Furthermore, catechols can participate in crosslinking reactions with other functional groups in a biopolymer facilitating cover metal substrates more complete substrate coverage as well as multi-layer adsorption, which also reduces corrosion[2]. A family of proteins from the mussel species Mytilus edulis is perhaps the most widely studied group of L-dopa containing proteins. These proteins are referred to as Mussel Adhesive Proteins (MAPs) and are numbered in the order of their discovery. Their L-dopa content ranges from 3-27%, and they vary in size from 6-115kDa[3]. The two tunicate polypeptides are smaller than the proteins derived from Mytilus edulis, but their L-dopa content is greater[4].

The goal of this research is to investigate the effect of various mixtures of biomolecules containing L-dopa on the corrosion properties of HY80 steel, a high strength low alloy steel vulnerable to flash rusting. In addition, this work will examine the effect of cross linking on coating performance for each of the proteins and polypeptides.

Materials and Methods

To assess the effectiveness of the biopolymers under relevant conditions, HY80 samples were tested in a Q-Fog CCT1100 exposure chamber operating at 100% humidity and 40°C. Samples were prepared by grinding to a rough 60 grit finish, then cleaning by sonication in organic solvents and allowing to dry in air for at least 24 hours. Samples were then masked with electroplating tape, leaving an exposed an area of 0.5cm^2 onto which protein was applied. Samples were monitored in the exposure chamber and removed for photographs at regular intervals. The performance of the exposure chamber samples was evaluated based on the time elapsed before visible corrosion was observed, total mass loss, and pit density. Electrochemical experiments were also undertaken to quantify inhibitor performance. For these tests, the open circuit voltage of the metal samples exposed to a seawater electrolyte was monitored until equilibrium was reached, after which an electrochemical impedance spectroscopy (EIS) experiment was performed, followed by cyclic polarization. The resulting dataset includes the polarization resistance, total charge passed during cyclic polarization, mass loss, and corrosion current.

Results and Discussion

Preliminary electrochemical tests with MAP-1show a modest corrosion-inhibiting effect, based on the reduction in mass loss and total charge passed during cyclic polarization compared with a buffer control. EIS measurements made after three hours of immersion in seawater showed that the protein did not increase the polarization resistance, which is in agreement with another study in which an MAP-1 layer adsorbed onto carbon steel did not begin to have a dramatic effect on the polarization resistance until after 1-3 days of exposure to 0.1M NaCl[2].

The performance in the exposure chamber of triplicate samples of 0.2mg/cm^2 of MAP-1 in a pH 7.0 buffer were compared with a protein-free buffer control. Another triplicate set of protein samples was additionally treated with 10µL of 1mg/mL mushroom tyrosinase to facilitate enzymatic crosslinking of the protein. The buffer used was 0.87M in acetate and 0.05M in borate. The protein-treated samples outperformed the buffer-only controls on average: they lasted longer in the exposure chamber before corroding, had roughly half the mass loss after 30 days of exposure, and showed a reduced tendency toward localized attack. The mass loss of the protein-treated samples were similar to samples treated with a commercial flash rust inhibitor, Halox® 900, applied at the same mass concentration. At the pH and protein concentration tested, protein crosslinking did not have a demonstrable effect on overall protein performance.

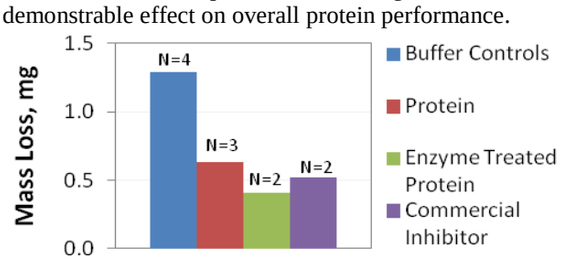

Figure 1- The mass loss of the treated samples after 30 days of exposure

More recently, efforts have been focused on determining what conditions of buffer chemistry, pH, and protein concentration will lead to inhibition of flash rusting that is as effective as a commercial inhibitor in humidity chamber experiments. Electrochemical and exposure chamber data comparing the effectiveness of different proteins from Mytilus edulis as well as one of the tunicate polypeptides will be presented.

References

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