

# Biopolymers for the corrosion protection of steel

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**Abstract:** The performance of heavy metals based anti-corrosive agents in organic coatings is well known. However, due to environmental and health concerns their application is subjected to restrictions or even forbidden.

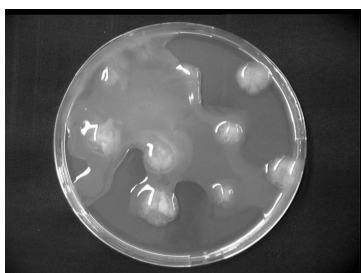
It has been shown that molecules produced by micro-organisms (exopolysaccharides, EPS's) retain anticorrosive properties. In a research programme in the Netherlands, the relation between the structure of these EPS's and their physicochemical properties is currently under investigation. The final objective of the research is to optimise the protective performance of these molecules and to incorporate them in protective organic coatings. In this paper, the electrochemical approach to study the behaviour of one of the modified EPS built in model coatings is given.

The results support the possibility to use the EPS as anti-corrosive agent in organic coatings. Moreover, in combination with previous publications and literature, hypotheses for the protection mechanism of EPS's are given.

**Keywords:** exopolysaccharides, biopolymers, anti-corrosive agents, organic coatings.

## 1. Introduction

The corrosion of iron and its alloys causes severe economical loss resulting, in a yearly loss of billions of dollars. The use of heavy metals and heavy metal containing compounds, such as chromate, has to be reduced in coatings for some are known to be very toxic, even carcinogenic, and cause enormous environmental damage. Prevention of, or reduction in the rate of corrosion may be accomplished by the use of a biological, environmentally friendly anti-corrosive layer at the metal interface. From a pilot project [1] it was clear that polysaccharides produced by bacteria (Figure 1) were suitable candidates for further investigation. Polysaccharides are components of biofilms, harmless to nature.



*Figure 1. Exopolysaccharides (EPS) produced by lactic acid bacteria are large sugar molecules (50 to 50,000 sugar units), which are secreted in the culture medium [2].*

Homopolysaccharides produced by lactic acid bacteria are often synthesized by a single extra-cellular sucrose enzyme using only sucrose as substrate [2]. They can be produced in large quantities. Moreover, their structure can be modified allowing optimisation of their physicochemical properties. By means of cyclic voltammetry, impedance measurements and potential monitoring, the electrochemical behaviour of this new type of anti-corrosive biopolymers has been studied. From the results of these measurements an optimal selection has been made of biologically manufactured and chemically modified polymers. It is the intention to use representative compounds from this selection as anticorrosive pigments in organic coatings. For this objective an experimental approach to assess the corrosion protection behaviour of these bio-coatings has been realized. This approach consists of: electrochemical measurements, surface analyses techniques (SEM, FTIR, confocal laser microscopy

and accelerated corrosion tests. In this paper the experimental set up and the results of the electrochemical measurements are presented and discussed.

## 2. Experimental

A dual approach has been followed to study the protective behaviour of the bio-coatings:

1. “*Intact model*”. In this case the coating containing the EPS was applied on steel (Q-panels) and exposed to 3% NaCl solution. Up to one month of exposure, potential and impedance measurements have been performed. From the results of these measurements protective coating properties and compatibility of the primer with the EPS can be deduced.
2. “*Scribe model*”. In this case a scribe (X-shaped, 2 cm, produced with a surgical blade) has been applied. This way, the study of self-healing properties is possible. The coatings were also exposed to a 3% NaCl solution, while the corrosion potential and (linear) polarisation resistance have been determined.

The EPS given as example for this study, is a modified polysaccharide coded EPS189. Two different binders have been used for the experiments: water-based two-component epoxy (A) and water based acrylic compound (N).

### Intact model

In Figure 2 the experimental build up of these coatings is given. For reference purposes in sample I the steel panel has been coated with the binder without addition of EPS. In the case of sample II, EPS189 has been mixed with the binder. In sample III, the steel surface has been covered by a thin layer of EPS189 ( $\pm 4 \mu\text{m}$ ) and subsequently a “top layer” was applied, consisting of the binder without EPS. In all cases the dry thickness of the binder is in the order of 100  $\mu\text{m}$ .

Figure 3 shows the experimental set up.

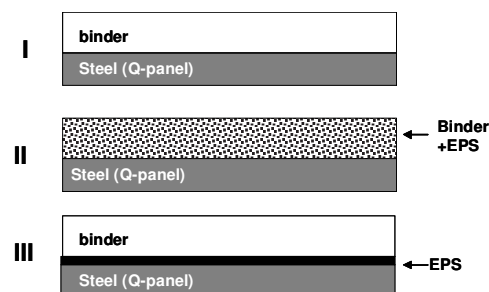


Figure 2. Schematic view of the build up of the “intact model” coating samples.

### Scribe model

For the scribe measurements, the polarisation resistance was measured at the scribe imposing a potential range of  $\pm 10 \text{ mV}$  around the open cell potential. Measurements started one minute after start of exposure to a 3% NaCl solution. The scribe was applied directly before the start of the exposure.

## 3. Results

The results of the open cell potential (OCP) measurements at steel covered by a coating containing EPS, can be divided in three different categories:

- a. Values of  $\pm 0 \text{ mV}$  (vs. sat. Ag/AgCl).
- b. Values close to the OCP of bare steel in 3% NaCl solution: circa  $-650 \text{ mV}$  (vs. sat. Ag/AgCl).
- c. Values between 0 and  $-650 \text{ mV}$  (vs. sat. Ag/AgCl).

This is demonstrated by Figure 4, obtained from a large number of acrylic coatings containing different EPS's [3].

The results of the impedance measurements are analysed qualitatively from the shape of the Nyquist plot as well as quantitatively, by using equivalent circuits as described elsewhere [2, 3]. In this paper, only the resistance representing the coating resistance ( $R_c$ ) and the charge transfer resistance ( $R_{ct}$ ) are given. The results of the OCP and impedance measurements at intact coatings are summarised in Figure 5.

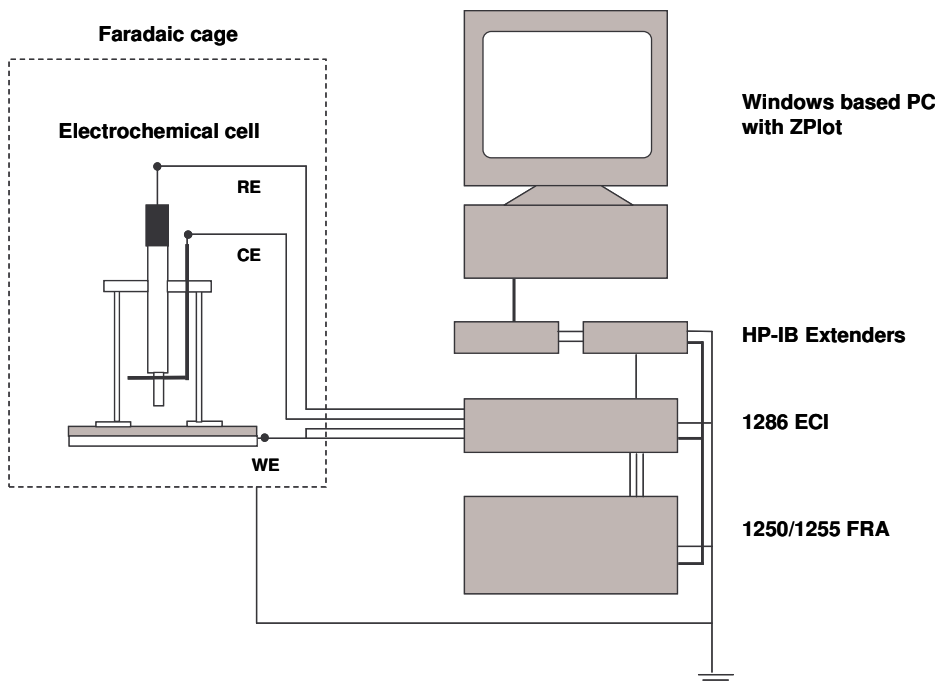


Figure 3. Overview of the set up used for electrochemical measurements at “intact model” samples.

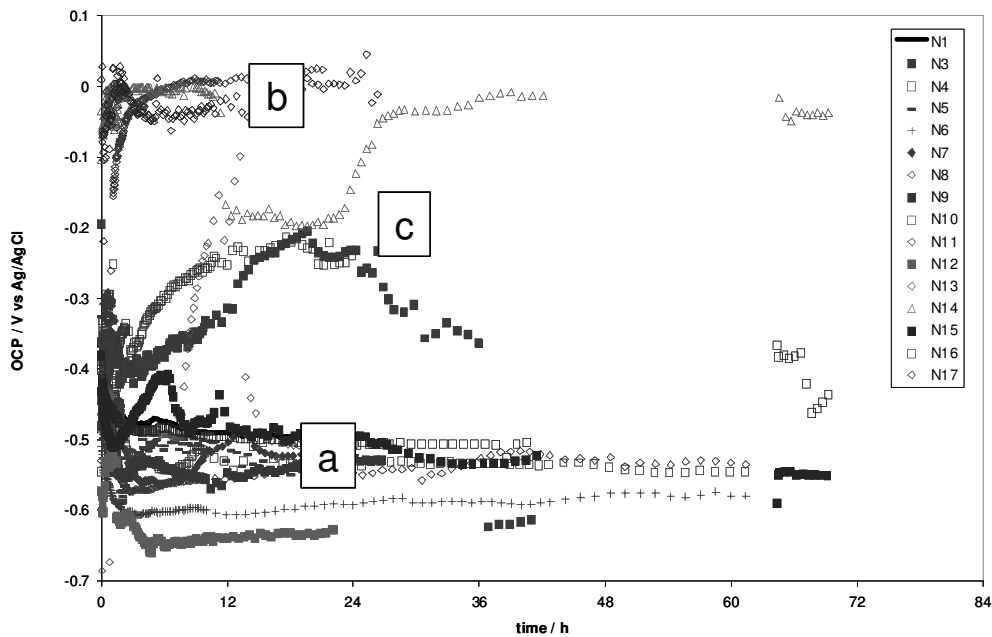


Figure 4. Open corrosion potential measured at Q-panels coated with acrylic binders containing a different EPS.

The Nyquist plots show both straight vertical lines (capacitive behaviour) as well as two semicircles with a diffusion tail. The first semicircle represents the coatings barrier properties, the second semicircle represents a system corroding on a large part of the surface.




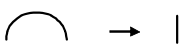
sample	OCP (V) Ag/AgCl	Layer thickness ( $\mu\text{m}$ )	qualitatively evolution of Nyquist plot during exposure	$R_c$ ( $\Omega \cdot \text{cm}^2$ )	$R_{ct}$ ( $\Omega \cdot \text{cm}^2$ )
AI	$\sim 0$	$73 \pm 7$		X	X
AII	-0.5	$66 \pm 3$	$\rightarrow$ 	$2\text{E}+07 \rightarrow 4\text{E}+06$	$1\text{E}+06 \rightarrow \text{X}$
AIII	$-0.4 \rightarrow -0.1$	$89 \pm 8$		$1\text{E}+08 \rightarrow 2\text{E}+07$	X
NI	-0.5	$60 \pm 12$	$\rightarrow$ 	$1\text{E}+08 \rightarrow 1\text{E}+05$	X
NII	-0.2	$95 \pm 12$		X	X
NIII	$-0.5 \rightarrow \sim 0$	$120 \pm 8$		$1\text{E}+06 \sim 1\text{E}+08$	X

Figure 5. Summary of potential and impedance measurements at intact model coatings performed during one month of exposure to 3% NaCl (N: acrylic; A: Epoxide; X: to high to be measured).

The epoxy without EPS (AI) shows barrier properties during exposure (up to one month): type (a) potential and capacitive behaviour in the Nyquist plot. Addition of EPS (AII) influences the barrier properties of the epoxy, after some time of exposure deviation from capacitive behaviour is found, followed by decrease of the coating resistance and of the charge transfer resistance. This last means increase of corrosion. Corrosion potential remains type (b), which means a direct contact between electrolyte and steel. However, after some time the corrosion process seems to be slowed down.

In the case of presence of a layer of EPS (AIII), a small deviation of the capacitive behaviour is directly detected, during exposure the charge transfer resistance is too high to be measured and the potential changes from type (b) to type (a), suggesting no contact with the electrolyte.

The acrylic binder without EPS shows loss of barrier properties during exposure and decrease of coating resistance. Addition of EPS appears to be beneficial in maintaining the barrier properties. This is also the effect of the presence of an EPS layer under the acrylic top layer (NIII). In this last case, from potential and impedance development, an increase in protection activity can clearly be seen.

Results of polarisation resistance measurements during the first day of exposure at scribe models samples are summarised in Figure 6 and 7. Figures show a decrease in polarisation resistance during the first hours of exposure followed by a constant value as function of time. This means that after brief corrosion propagation, stabilisation occurs. In all cases presence of EPS gives a significant higher value for the polarisation resistance, which means that the corrosion is occurring on a smaller surface area. This observation is supported by visual examination of the samples after longer exposure, Figure 8.

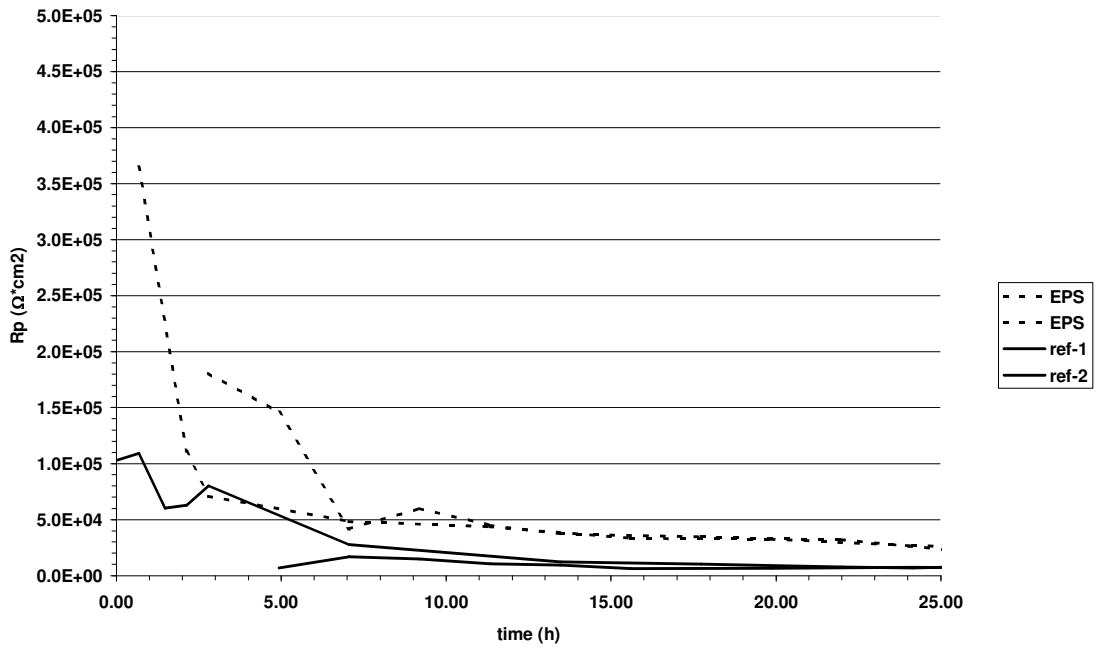


Figure 6. Polarisation resistance at scribe for waterborne acrylic binder with and without EPS.

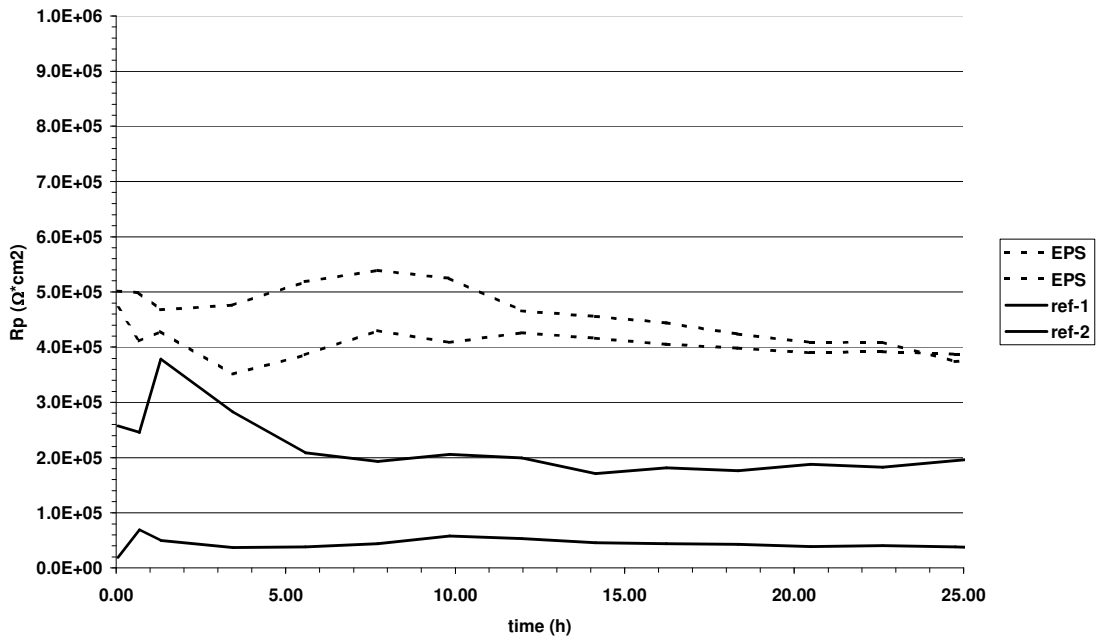


Figure 7. Polarisation resistance at scribe for waterborne epoxide binder with and without EPS.

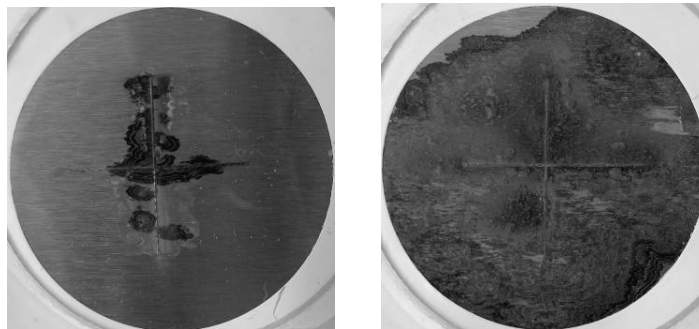


Figure 8. Pictures of scribed acrylic samples after exposure to a 3% NaCl-solution with (left) and without (right) addition of EPS189.

#### 4. Discussion

It has to be taken into account that the first objective of this study is not the development of optimal coatings but the study of the behaviour of the EPS. Therefore, model coatings have been based on a binder, without the necessary additions to give to the coatings the required properties. In any case from the results it has been found that acrylic binder suffers more from the omission of necessary additives than the epoxy binder. In addition, it can be expected that EPS negatively influences the basis properties of the model coatings. In the case of the “intact model” coatings the EPS seems to be able to “repair” these coating defects. Results from “scribe model” support this mechanism of protection.

All results indicate that the EPS can give an active contribution to reduce or even to stop the corrosion process. Hypotheses for several protection mechanisms can be envisaged:

- The EPS forms a barrier layer on the surface, which protects the surface when coating damage occurs.
- The EPS increases the adhesion of the coating to the steel, (partially) preventing cathodic delamination from the defect.
- The EPS is able to form complexes or to block the diffusion of iron or oxygen.
- There is evidence that, despite the large size of the molecule, EPS can diffuse through the coating to react where required for the corrosion protection.

These different mechanisms are subject of the future investigations.

#### 5. Conclusions

Based on the electrochemical experiments presented here, it is apparent that EPS shows anticorrosive effects. Both in case of intact coatings and in case the coatings were scribed, improvements in corrosion protection are found.

#### 6. Acknowledgements

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