



# pH-controlled self-healing polymer coatings with cellulose nanofibers providing an effective release of corrosion inhibitor



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## ABSTRACT

Polymer coatings with various pH values and containing cellulose nanofibers and a corrosion inhibitor were applied to carbon steels for corrosion inhibition. The polarization resistance of scratches made to the prepared coatings was measured in a corrosive solution. The resistance of the scratched coatings was largely dependent on the pH of the polymer. The scratched polymer coating prepared at pH 11.4 showed a drastic increase in polarization resistance just after immersion, and was the highest measured after a 24 h corrosion test. A corrosion-protective film was formed on the scratched portion.

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## 1. Introduction

Polymer coatings are widely applied to prevent corrosion on the surface of metals exposed to a corrosive environment. These types of coatings are the most common because they are cost-effective and environmentally friendly. One of the important requirements of these coatings is the ability to self-heal after suffering mechanical damage, which initiates the corrosion process of a bare metal surface by corrosive substances in the environment. The ability to self-heal can be obtained by adding corrosion inhibition substances to the coating system.

The addition of several substances such as phosphate, phosphoric acid, molybdic acid, colloidal silica, and cerium to coating solutions have reportedly been effective in enhancing self-healing performance [1–12]. The encapsulation of inhibiting compounds before their addition to corrosion-protection systems has been used to promote self-healing [13–20]. The level of active corrosion-protection ability can be increased by introducing a porous surface or porous interlayer doped with a corrosion inhibitor [21,22]. Nanocarriers of oxide particles and polymer with corrosion inhibitor have been used in corrosion inhibition systems [23–28]. A method whereby nanocontainers are assembled layer-by-layer has exhibited excellent self-healing performance, because the multiple layers of the nanocontainer were able to accommodate large

amounts of corrosion inhibitor [29–35]. A large container for corrosion inhibitor can also be created through the use of 3D network film and electrospun coaxial fiber [36,37,38]. However, these methods have not dealt with the controlled- or triggered-release aspects of the corrosion inhibitor, and, therefore, the release of inhibitor from the container has not been optimum.

The optimal way to enhance the performance of a self-healing coating would be to control or trigger the corrosion inhibitor release. The release of inhibitor from a container could be optimized if it was controlled or triggered. The controlled release of a corrosion inhibitor such as vanadate ions from nanocrystalline layered double hydroxides (LDH) has been obtained by introducing a novel nanocontainer that is double-hydroxide-based [39]. A hybrid sol-gel matrix can be triggered by changing the pH of the polymer coatings [33,40,41] via a pH-dependent release mechanism to release organic inhibitors: polymers and metal powders [42,43], titanate matrices [44], a fluoro-organic compound [45], a organic casein [46], a titanium oxide particle-polymer composite [47], mesoporous silica powder [48], a porous polymer film with a corrosion inhibitor [49], and superabsorbent polymers [50]. However, no method has been able to sustain an amount of corrosion inhibition sufficient to promote long and continuous self-healing. Therefore, the key to the development of self-healing coatings lies not only in the ability to control the release of added inhibitors but also in providing a container that will sufficiently accommodate the corrosion inhibitor.

A bio mimic network structure is versatile in the development of self-healing coatings, because it provides much more of

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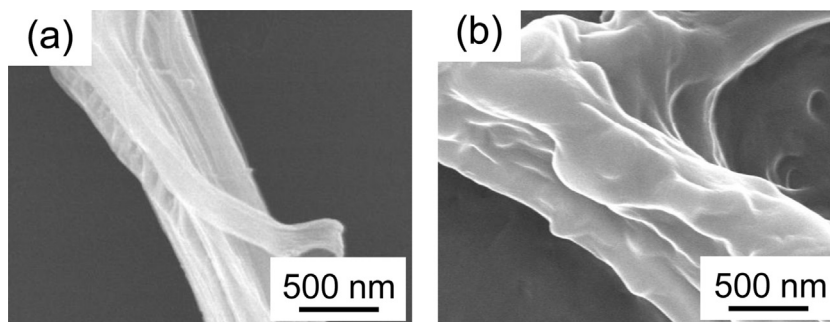


Fig. 1. SEM images of the condition of cellulose nanofibers: CNF alone (a), and CNF mixed with oleic acid (OA) (b).

the healing substances [49,51,52]. The network can be obtained from a bio-degradable polymer such as cellulose nanofibers due to the environmental appeal, and flexibility. Coating systems using cellulose nanofibers with a corrosion inhibitor have shown good self-healing performance. With this method, the cellulose nanofibers network worked well as a pathway for the release of the corrosion inhibitor [53]. However, the release of inhibitor was not optimal due to the inability to control the release mechanism. In order to improve the self-healing ability of the coating, control of the adsorption and desorption of the corrosion inhibitor on the cellulose nanofibers is a key factor. Cellulose nanofibers have an –OH terminal on the molecular chain [54], so we proposed that the pH change of the polymer in the coating must control the adsorption and desorption of the corrosion inhibitor on the nanofibers.

In the present study, cellulose nanofibers with a corrosion inhibitor at various pHs were mixed with a polymer, and this was coated onto carbon steels for corrosion inhibition. The pH values of the polymer coatings were varied in order to control the adsorption and desorption of the corrosion inhibitor from the cellulose nanofibers. The self-healing ability was evaluated by scratching the coatings, and then the polarization resistance was measured in a sodium chloride solution. The zeta potential of the cellulose nanofibers with corrosion inhibitor was measured to elucidate the behavior of the corrosion inhibitor on cellulose nanofibers when the polymer pH is changed.

## 2. Experimental

### 2.1. Preparation of the polymer coatings

The substrate consisted of a cold-rolled steel plate (wt.%, C 0.5, Si 0.02, Mn 0.2, P 0.1, S 0.1 and balance Fe, JIS G 3141, SPCC-SD, Nippon Testpanel Co., Ltd.) with a thickness of 0.8 mm. The substrate was degreased in an alkaline solution at 50 °C for 2 min and thoroughly rinsed with water. Zinc phosphate pretreatment of 2.0 g/m<sup>2</sup> on the substrate was carried out [53], and then samples were cut to 12 × 12 mm. Three epoxy-based layers that made up the primer, middle and top coats, were coated onto a pretreated substrate. As a

primer coat, cationic epoxy resin (clear type, modified epoxy resin, Nippon Paint Co., Ltd.) was coated by electrodeposition for 150 sec at 200 V at 30 °C. Next, the specimen was rinsed with water, dried under air, and baked at 170 °C for 20 min. As a base polymer for the middle and top coats, epoxy resin (Hi-Pon 20 Fine, bisphenol-A epoxy resin, organic solvent type, Nippon Paint Co., Ltd.) was used. Oleic acid (OA, Kanto Chemical Co., Inc.) was used as a corrosion inhibitor, and was mixed with sodium hydroxide (NaOH) as a pH adjuster. After the mixing, this was further mixed with cellulose nanofibers with a diameter of 100–500 nm (CNF, CELISH KY-100G, Daicel Chemical Industries, Ltd.). The mixed materials were dispersed in the base polymer, and were then applied as various middle coats. The pH of the middle coat was measured before drying using a pH meter (CyberScan pH 110, Eutech Instruments) equipped with a pH electrode (EC-620-131, Eutech Instruments). Thymol Blue was mixed into the middle coat to confirm its pH. The top coat of a plain epoxy resin was also applied with a bar-coater. The middle- and top-coat resins were dried at room temperature for 1 day, and then baked at 80 °C for 1 h. The concentrations of CNF and OA that were mixed for the middle coat were 1 and 8 wt.%, respectively. The pH of the coatings ranged from 8.1 to 12.8. For comparison, a coating of only polymer was prepared. These 3-layered coatings were defined according to their respective pH, as shown in Table 1. The thicknesses of the primer, middle and top coats were approximately 15, 35 and 15 μm, respectively.

### 2.2. Evaluation of the self-healing properties of polymer coatings

Polymer-coated specimens were scratched with the knife-edge of a scratch tester (IMC-1552, Imoto Machinery Co., Ltd.). A scratch load of 300 g was applied to expose the substrate, and the scratch length was approximately 7 mm. The scratched specimens were immersed in a 0.05 wt.% sodium chloride solution. The solution was 35 °C and was air-saturated. The pH of the solution was maintained approximately at 6.0. The self-healing properties of the scratched specimens were evaluated based on the conditions at the scratched portion of the specimens.

Table 1  
Composition and thickness of coatings.

Symbol	Polymer coating			
	Primer coat(15 μm by electrodeposition)	Middle coat	(35 μm by bar-coater)	Top coat(15 μm by bar-coater)
CNF + OA coating (pH 8.1)	Cationic epoxy resin (alone)	Epoxy resin mixed CNF and OA adjusted pH 8.4		Epoxy resin (alone)
CNF + OA coating (pH 10.4)	↑	Epoxy resin mixed CNF and OA adjusted pH 10.4		↑
CNF + OA coating (pH 10.9)	↑	Epoxy resin mixed CNF and OA adjusted pH 10.9		↑
CNF + OA coating (pH 11.4)	↑	Epoxy resin mixed CNF and OA adjusted pH 11.4		↑
CNF + OA coating (pH 11.9)	↑	Epoxy resin mixed CNF and OA adjusted pH 11.9		↑
CNF + OA coating (pH 12.2)	↑	Epoxy resin mixed CNF and OA adjusted pH 12.2		↑
CNF + OA coating (pH 12.8)	↑	Epoxy resin mixed CNF and OA adjusted pH 12.8		↑
Plain coating	↑	Epoxy resin (alone)		↑

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