



Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Self-healing polymer coatings with cellulose nanofibers served as pathways for the release of a corrosion inhibitor

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ARTICLE INFO

Article history:

Received 15 October 2013

Accepted 8 April 2014

Available online xxxx

Keywords:

A. Steel

B. EIS

B. Scratching electrode

B. SEM

C. Polymer coatings

ABSTRACT

Polymer coatings containing cellulose nanofibers were applied to carbon steel for corrosion inhibition. The specimens were scratched with a knife-edge, and then polarization resistance was monitored in a sodium chloride solution. The polarization resistance of the scratched specimen containing nanofibers and corrosion inhibitor was higher than that of a polymer coating that contained only a corrosion inhibitor. The optimal mixing ratio of corrosion inhibitor for cellulose nanofibers was 4. Empty holes were confirmed on a cross-section of the polymer coating after the corrosion test, which showed that the nanofibers served as pathways for the release of the corrosion inhibitor.

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1. Introduction

An important requirement of corrosion protective coatings is the quality of self-healing. As a coating suffers mechanical damage, which begins with the degradation of a bare metal surface by corrosive species in the environment, the damaged surface is automatically repaired by a chemical component in the coating. Recent environmental concerns about hexavalent chromate conversion coatings and chromate inhibitor pigments have necessitated a reduction and discontinuation of their use, although they have shown repairing effects.

The addition of cerium, molybdic acid, phosphoric acid and colloidal silica to coating solutions has reportedly been effective as an alternative technology for chromate conversion coatings and chromate inhibitor pigments [1–11]. Several new approaches based on the encapsulation of inhibiting compounds prior to their addition to corrosion-protection systems have been suggested [12–17]. A porous oxide interlayer doped with an organic corrosion inhibitor increased the active corrosion-protection ability of thin hybrid sol-gel films on an aluminum alloy substrate [18,19]. Inhibitor-containing oxide particles have also been used as nanocarriers of a corrosion inhibitor [20–24]. Nanocontainers that regulated the storage and release of a corrosion inhibitor were constructed with nanometer-scale precision by use of the layer-by-layer (LbL) method [25,26]. Such self-healing anti-corrosion coatings based

on LbL-assembled nanocontainers have been developed and demonstrated [27–30]. Novel nanocontainers that are layered double-hydroxide (LDH)-based carriers of a corrosion inhibitor allow the controlled release of vanadate ions from nanocrystalline LDHs [31]. Self-healing polymer coating systems based on an electrospun coaxial healing agent have been demonstrated using polysiloxane-based healing agents and an acrylate matrix [32]. The release of organic inhibitors from a hybrid sol-gel matrix can be described as a pH-dependent, triggered-release mechanism [28,33,34]. Self-healing corrosion protective coatings using polymer and metal powders [35,36], a fluoro-organic compound [37], casein as a pH-sensitive organic agent [38], a TiO₂ particle-polymer composite [39], porous polymer film with a corrosion inhibitor [40], and superabsorbent polymers [41] have also been also reported. The key to the development of self-healing coatings is the ability to control both the storage and release of the added inhibitors.

A network structure is useful in the development of the self-healing properties of coatings, because it provides much more of the corrosion inhibiting healing agent through the network [40,42]. The addition of nanofibers or nanotubes into polymer coatings was one methodology used to generate a network structure in coatings with thicknesses ranging from 10 to 20 μm, which are generally used to prevent the corrosion of metallic materials [43]. Polymer composites with a network structure of cellulose nanofibers have shown improved mechanical and thermal properties [44,45]. We selected cellulose nanofibers made from wood, because of the environmental appeal, low cost, and flexibility. Cellulose nanofibers that retain a healing agent might efficiently make

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that agent available from the inside of a polymer coating on a substrate.

In the present study, polymer coatings containing cellulose nanofibers and retaining a corrosion inhibitor were prepared for use in the corrosion prevention of carbon steel. The amounts of nanofiber and corrosion inhibitor contained by a polymer were varied in order to determine the optimal conditions for self-healing corrosion protection. Various types of specimens were scratched with a knife-edge and the polarization resistance was monitored in a sodium chloride solution. Varied amounts of nanofibers and corrosion inhibitor in the polymer were observed before and after the corrosion tests.

2. Experimental

2.1. Preparation of the coatings

A cold-rolled steel plate (C < 0.15 wt%, Mn < 0.60 wt%, P < 0.10 wt%, S < 0.05 wt%, JIS G 3141, SPCC-SD, Nippon Testpanel Co., Ltd.) with a thickness of 0.8 mm was used as a substrate. The substrate was degreased in an alkaline solution at 50 °C for 2 min and thoroughly rinsed with water. Zinc phosphate pretreatment of the substrate was carried out using SURFDAIN SD5000 (Nippon Paint Co., Ltd.) at 43 °C for 2 min, rinsing with water and drying under air at 100 °C. The amount of coating was 2.0 g/m². Samples measuring 12 × 12 mm were cut from the steel plate.

Three epoxy-based layers, which consisted of a primer, middle, and top coats, were applied to a pretreated substrate. Cationic epoxy resin (clear type, modified epoxy resin, Nippon Paint Co., Ltd.) as a primer coat was electrodeposited at 30 °C for 150 s at 200 V, followed by rinsing with water, air drying, and baking at 170 °C for 20 min. Epoxy resin (Hi-Pon 20 Fine, bisphenol-A epoxy resin, organic solvent type, Nippon Paint Co., Ltd.) was used as a base polymer for the middle and top coats. Microfibrillated cellulose nanofibers with a diameter of 100–500 nm, as shown in Fig. 1 (CNF, CELISH KY-100G, Daicel Chemical Industries, Ltd.), and calcium nitrite (CN, Kanto Chemical Co., Inc.) as a corrosion inhibitor, were mixed in the base polymer using an ultrasonic homogenizer (UH-50, SMT Co., Ltd.), then applied as various middle coats using a bar-coater. The top coat consisted of a plain epoxy resin, which also was applied via 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 following 4 types of middle coats were used for the tests: (1) CNF and CN were mixed, then mixed in polymer; (2) CNF was mixed in polymer; (3) CN was mixed in polymer; and, (4) Plain base polymer alone. The concentrations of CNF and CN that were mixed for the middle coat ranged from 0.3 to 1 wt.% and 1.2 to 8 wt.%, respectively. Thus prepared, the three

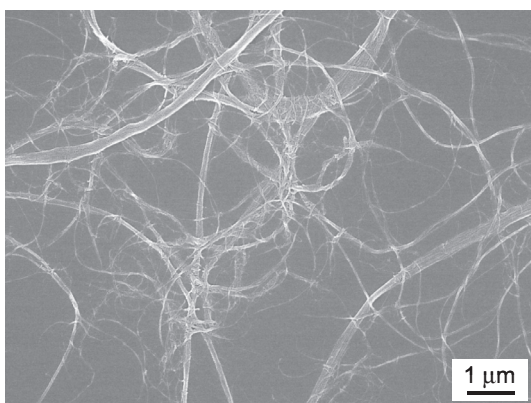


Fig. 1. Optical micrograph of cellulose nanofibers (CNF).

epoxy-based layered coatings were defined according to their respective concentrations:

- (1) CNF(1%) + CN(4%) coating: polymer alone (primer, top), 1% CNF, 4% CN and polymer (middle);
- (2) CNF(1%) coating: polymer alone (primer, top), 1% CNF and polymer (middle);
- (3) CN(4%) coating: polymer alone (primer, top), 4% CN and polymer (middle); and,
- (4) Plain coating: polymer alone (primer, middle, top).

The thicknesses of the primer, middle, and top coats were approximately 15 μm, 35 μm, and 15 μm, respectively.

2.2. Evaluation of the self-healing properties

Polymer-coated specimens with various types of additives were scratched with a knife-edge on a scratch tester (IMC-1552, Imoto Machinery Co., Ltd.). The scratch load, which was intended to expose the substrate, was 300 g. The length of each scratch was approximately 7 mm. The specimens were immersed in a 0.5 wt% sodium chloride solution that was air-saturated using an air pump and were maintained at 35 °C. The pH of the solution was 6.0. The self-healing properties of the specimens were evaluated based on the corrosion behavior at the scratched portion of the specimens.

The impedance of each specimen in the corrosive solution was measured after a 5 min immersion and at intervals of 1 h for 24 h using a platinum counter electrode and an Ag/AgCl reference electrode connected to a potentiostat (HABF-5001, Hokuto Denko Co.), a frequency response analyzer (5010A, NF Co.), and a personal computer. Sine wave voltages (10 mV rms) at frequencies ranging from 20 kHz to 100 mHz were superimposed at open circuit potential. A computer software program was used to control the measurements through a General Purpose Interface Bus (GPIB). The measured impedances data were normalized to the surface area of the scratch alone, which was calculated from the depth, the angle, and the length of the scratched portion of each specimen by using optical micrographs (VH-8000, Keyence Co.). The polarization resistance calculated from these impedances was used to evaluate the self-healing capability of the coatings.

The surface appearance of each scratched specimen after the corrosion test was observed using Field Emission-Scanning Electron Microscopy (FE-SEM, JSM-6340F).

2.3. Polarization measurement

The polarization curves of the scratched CNF + CN coatings, CN coatings and a plain coating were measured in a 0.5 wt.% sodium chloride solution using the same system as that used for the measurement of electrochemical impedance. After a 2 h immersion, the surface of the scratched portion of the coatings became almost stable, and cathodic and anodic polarization curves were measured at a sweep rate of 20 mV/min. The data were downloaded to a computer through a GPIB.

2.4. Analysis of the coatings

The solutions of CNF and CN mixed at various concentration ratios were coated on glass plates, which were dried at room temperature. The CNF and CN mixing conditions were then observed via optical micrograph and FE-SEM.

CNF and CN mixed-polymers were coated onto glass plates, which were then allowed to dry at room temperature for 1 day, and then baked at 80 °C for 1 h. A knife-edge was used to cut the film, and it was immersed in a 0.5 wt% sodium chloride solution

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