Chemical Engineering Journal 315 (2017) 537–551

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

An intelligent coating doped with inhibitor-encapsulated nanocontainers for corrosion protection of pipeline steel

Yuanchao Feng, Y. Frank Cheng *

Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada

HIGHLIGHTS

- An intelligent coating is developed by doping BTA-encapsulated nanocontainers in an epoxy.
- The nanocontainers are distributed uniformly in the coating matrix.
- The encapsulated inhibitors self-release in response to the changes of solution pH.
- The intelligent coating effectively inhibits steel corrosion for a long-term immersion.

ARTICLE INFO

Article history:
Received 6 December 2016
Received in revised form 15 January 2017
Accepted 16 January 2017
Available online 18 January 2017

Keywords:
Nanocontainers
Inhibitor encapsulation
Self-releasing of inhibitors
Epoxy coating
Pipeline corrosion

ABSTRACT

In this work, an intelligent coating was developed based on encapsulation of benzotriazole (BTA) inhibitors in prepared SiO_2 nanoparticle based polyelectrolyte nanocontainers, and self-releasing of the inhibitors for corrosion inhibition to a pipeline steel in a chloride solution. Various morphological, compositional and structural characterizations demonstrate that the inhibitors BTA are effectively encapsulated in the nanocontainers, and the weight percentage of the loaded inhibitors is about 6.7 wt% in the nanocontainers. The nanocontainers can be dispersed uniformly in an industry-used epoxy coating under the testing condition, and do not change the coating properties, as shown by the identical glass-transitional temperature of the coatings containing various contents of nanocontainers. The encapsulated BTA can self-release for corrosion inhibition in response to changes of solution pH, as characterized by UV–vis spectroscopy. For the steel coated with the intelligent coating, the corrosion inhibition is time dependent upon self-releasing of the encapsulated inhibitors from the nanocontainers. With the increasing content of the nanocontainers in the coating, both the coating resistance and the corrosion resistance of the steel increase. The released inhibitors inhibit the steel corrosion by forming a layer of inhibitor-adsorptive film, which is detected on the steel surface after 30 days of immersion in the solution by elemental and structural characterizations.

1. Introduction

Corrosion has been identified as the primary mechanism causing pipeline failures and the resulting economic loss and environment problems [1]. Polymeric coatings, combined with cathodic protection (CP), provide the key means to protect transmission pipelines from corrosion attack [2]. The principle of this strategy is straightforward. The coating forms the first line of barrier to isolate the pipe steel from corrosive environments, i.e., soils. When the coating experiences degradations in service, the CP provides backup protection at the coating failures. While pipeline coatings have been developed for six decades with continuously improved performance, conventional coatings suffer from shortcomings that, upon mechanical damage caused by construction or degradation, such as disbonding from the substrate steel, during service, they are not capable of protecting pipelines in corrosive environments that develop under disbonded coating and/or at a coating defect, especially when CP is shielded from reaching the pipe steel [3–5].

Intelligent coatings, also called smart coatings, refer to coating systems with "corrosion-sensing" and "self-healing" properties, providing not only a barrier to the environment, but also a self-release of corrosion inhibitors, which are preloaded into the coating, as demanded by coating damage/degradation and the presence of a corrosive environment on metals [6–10]. In particular, benzotriazole (BTA) is an excellent choice of corrosion inhibitors encapsulated in intelligent coatings. Its derivatives are among the most

---

* Corresponding author.
E-mail address: fcheng@ucalgary.ca (Y.F. Cheng).

http://dx.doi.org/10.1016/j.cej.2017.01.064
1385-8947/

effective and commonly used inhibitors for corrosion protection of steels [11,12] and copper and its alloys [13,14]. However, if a coating is mixed directly with the corrosion inhibitors, the BTA molecules are easily dissolved in the aqueous solution, resulting in generation of micropores in the coating [14]. It was found [15–17] that encapsulation of corrosion inhibitors in micro- or nanocontainers which are inert to the host coating provides a meaningful method, where the inhibitors pre-loaded in the nanocontainers can “sense” the generation of corrosive environments and self-release to inhibit the corrosion of metals in response to certain triggering mechanisms. For example, Andreeva et al. [18] fabricated multi-layer polyelectrolyte nanocontainers encapsulating corrosion inhibitors, which are released in response to changes of solution pH for rapidly decreasing anodic activity of metals. Chen and Fu [19] prepared inhibitor-loaded capsules based on hollow mesoporous silica spheres. The pre-stored inhibitors BTA can release from the silica spheres based on the change of local pH caused by the corrosion of metals. Kopec et al. [20] also prepared inhibitor-containing nanocapsules by polyelectrolyte deposition in a water-based epoxy coating.

While the smart coatings based on encapsulation of corrosion inhibitors in micro- or nanocontainers and self-releasing of the inhibitors based on appropriate triggering mechanisms were proposed and tested as a promising coating alternative for corrosion prevention, none of them has been developed at an industrial scale, especially for pipeline corrosion control. To date, the majority of the relevant research were conducted in lab, where the host matrix coatings were not industrial ones used in the field. Moreover, the technologies to encapsulate inhibitors in the containers, such as the vacuum method, are very complicated and impractical at the industry scale, both technically and economically. With these challenges, in the previous work [21], the authors used a field-used epoxy coating as the host coating and investigated its compatibility with the prepared inhibitor capsules. It was found that doping of the nanocapsules does not affect the coating properties. This work furthers pervious one and attempts to develop an industry-feasible intelligent coating technology by encapsulation of inhibitors in fabricated nanocontainers that are uniformly doped in a field-used pipeline coating and by self-releasing of the encapsulated inhibitors on demand for pipeline corrosion control. The used materials in the work, including inhibitors BTA, epoxy coating and SiO_2 nanoparticles, are economic and available in the market. The method to fabricate nanocontainers and the inhibitor-loading process are simple and well-established. Moreover, the inhibitor-loaded nanocontainers are doped in an industry epoxy coating currently used on pipelines. All of them will contribute to develop a technically feasible and cost-effective smart coating technology for improved pipeline integrity in practice.

In this work, an intelligent coating was developed by fabrication of SiO_2 nanoparticle based polyelectrolyte nanocontainers where corrosion inhibitors BTA were pre-loaded and the doping of the nanocontainers in an industry-used epoxy coating. The morphology and structure of the prepared nanocontainers and the doped amount of the nanocontainers in the host coating were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectrum (EDS), Fourier transforms infrared (FTIR), thermal gravity analysis (TGA) and differential thermal gravity (DTG). The dispersity of the nanocontainers in the epoxy coating was characterized by SEM and EDS, and the potential influence of the nanocontainers on the coating property, i.e., glass-transitional temperature, was determined by TGA and differential scanning calorimetry (DSC). The self-releasing of the encapsulated BTA in response to changes of the solution pH was measured by UV–vis spectroscopy. The anticorrosion performance of the developed coatings and the corrosion resistance of the coated steel were measured by electrochemical impedance spectroscopy (EIS) in a chloride solution. Long-term tests were conducted to investigate the self-releasing of the pre-loaded BTA inhibitors for corrosion inhibition of the steel in the solution. The inhibitor adsorption on the steel surface was confirmed by EDS and FTIR measurements. It is expected that this work develops an intelligent coating technology with the ability to smart sense the corrosion occurrence and self-release the pre-loaded inhibitors on demand for corrosion control in practice.

2. Experimental

2.1. Materials and chemicals

Steel specimens used in this work were cut from a X65 steel pipe, with a chemical composition (wt%): C 0.04%, Si 0.2%, Mn 1.5%, P 0.011%, S 0.003%, Mo 0.02% and Fe balance. The specimens were cut into 1 cm × 1 cm area, sealed in epoxy, and subsequently ground up to 800 grit SiC emery papers. They were then washed with deionized water, degreased with ethanol and acetone, and dried in air.

The SiO_2 nanoparticles with a purity of 98+% were purchased from U.S. Research Nanomaterials, Inc., with an average diameter of 70 nm in the as-received state. They were amorphous in structure.

Corrosion inhibitors BTA were analytical grade. The BTA, i.e., $C_6H_5N_3$, is a heterocyclic chemical compound containing three nitrogen atoms, with the molecular structure shown in Fig. 1a. The protective action of BTA is attributed to formation of an adsorptive protective film on the steel surface [22,23].

Various chemicals used in this work, including sodium poly-(styrene sulfonate) (SPSS, molecular weight $M_w \sim 70{,}000$) and poly-(diallyldimethylammonium chloride) (PDDAC, $M_w \sim 100$–200 kDa), were also analytic grade. Their molecular structures are shown in Fig. 1a. The water used to prepare solutions was deionized water.

2.2. Fabrication of BTA-encapsulated nanocontainers

To fabricate BTA-encapsulated nanocontainers, 10 wt% of as-received SiO_2 nanoparticles (negatively charged) were added

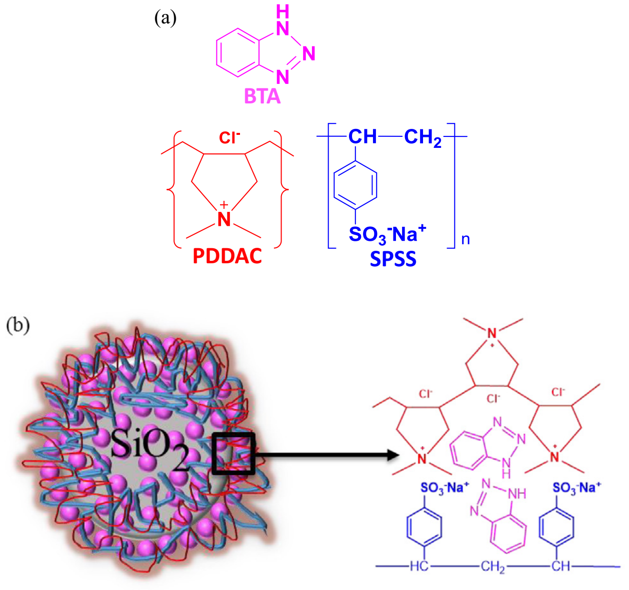

Fig. 1. Schematic diagram of (a) the molecular structure of inhibitor BTA and polyelectrolytes PDDAC and SPSS, and (b) the prepared SiO_2 nanoparticle based BTA-encapsulated polyelectrolyte nanocontainers.