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Self-healing capability of inhibitor-encapsulating polyvinyl alcohol/polyvinylidene fluoride coaxial nanofibers loaded in epoxy resin coatings

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ABSTRACT

The self–healing capability of epoxy coatings modified with coaxial core–shell nanofibers loaded with the corrosion inhibitor 2–mercaptobenzothiazole (MBT) was investigated using electrochemical techniques. The polyvinyl alcohol/polyvinylidene fluoride core–shell nanofibers were prepared by coaxial electrospinning. Electrochemical impedance results showed that the MBT–loaded coaxial nanofibers improved the barrier properties and decreased the corrosion activity of the coatings. Results of the Scanning Kelvin Probe technique revealed that the MBT–loaded coaxial nanofibers healed corrosion over artificial defects exposed to NaCl electrolytes. These results indicate that adding MBT–loaded coaxial nanofibers to epoxy coatings is a promising strategy toward the development of self–healing epoxy coatings.

1. Introduction

Damage of internal organic coatings in oil and gas gathering pipelines due to scouring of fluids and impurities in the transporting medium causes local corrosion at the naked location. In addition, pipeline joints are broken easily when the pipelines are equipped, thereby affecting the corrosion prevention property of coatings. Resolving local corrosion in damaged coatings inevitably causes huge economic losses for pipeline digging, replacing, or local mending. Therefore, improvement and upgrading are necessary to meet industrial requirements for ordinary coatings. Coatings should serve other functions aside from physical barriers and cathodic protection. Self–healing allows the automatic repair of coating surface during mechanical damage and during degradation caused by corrosive species in the environment.

The coating can realize capability of self-healing by releasing corrosion inhibitor encapsulated by micro/nanocontainers that are incorporated into a polymer matrix. Micro/nanocontainers that store and release the inhibitor have been built by different methods; examples of such materials include nanocapsules [1,2], layered double hydroxides [3,4], halloysite nanotubes [5,6], and mesoporous silica nanoparticles [7–10]. Micro/nanocontainers can be triggered to release corrosion inhibitor through different mechanisms, such as mechanical rupture [1,2], ion exchange [3,4], pH [9,10], and desorption. The mentioned self–healing coatings exhibit much better protection performance than ordinary coatings, and provide long–term service life [1–4].

Using of fibers is another promising strategy for storing healing agents in a material. One versatile method for producing fibers is electrospinning. Several studies demonstrated that the development of self–healing coatings was based on coaxial electrospun core–shell nanofibers [11–18]. Park [11] electrospun both resin and cure materials as a core by using a coaxial nozzle and showed that the self–healing agents can be encapsulated into beaded fibers. When damage, the healing agents in the fibers released into the crack plane. Lee et al. [13,14] prepared core–shell nanofiber coatings with the self–healing agent dimethyl siloxane and dimethyl–methyl hydrogen–siloxane (cure) separately in the cores by using dual emulsion electrospinning. Once the coating was damaged, the self-healing agents (DMS resin and cure) were released separately from the nanofiber cores and polymerized inside a scratch or a micro-crack, and the surrounding PDMS matrix was self-healed. Similarly, An et al. [15] used coaxial electrospinning technique to form dual mutually-entangled nanofiber mats, which was comprised of core–shell nanofibers with healing agents with either liquid dimethylvinyl-terminated dimethyl siloxane (resin monomer), or methylhydrogen dimethyl siloxane cure in the core. Being embedded in transparent matrices, the core–shell nanofiber mats formed flexible transparent self-healing composites with self-healing properties by releasing the resin monomer and cure from the fiber cores to the scratched area. Sinha–Ray et al. [16] and Wu et al. [17] coaxially electrospun bead–free nanofibers containing the polymer monomers of interest for self–healing in the range of a few hundred nanometers. Doan et al. utilized electrospun fibers containing liquid healing agents to achieve a crosslinking reaction of poly(dimethylsiloxane) (PDMS) to a crosslinking agent poly(diethoxysiloxane) (PDES), initiated by the catalyst dibutyltindilaurate (DBTL), to fill a damaged region [18].

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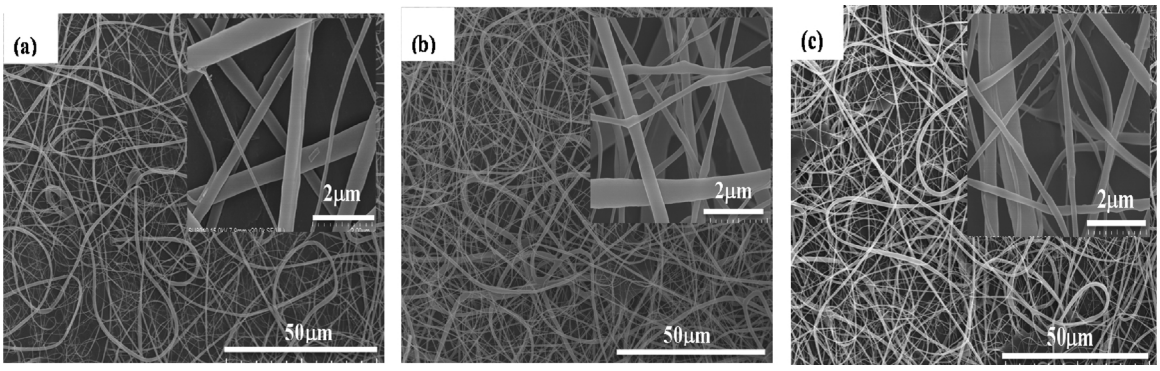

Fig. 1. SEM images of coaxial electrospun nanofiber with different feed rates (inset: local magnification of the nanofiber) (a) 1.2 mL/h, (b) 1.5 mL/h, (c) 1.8 mL/h.

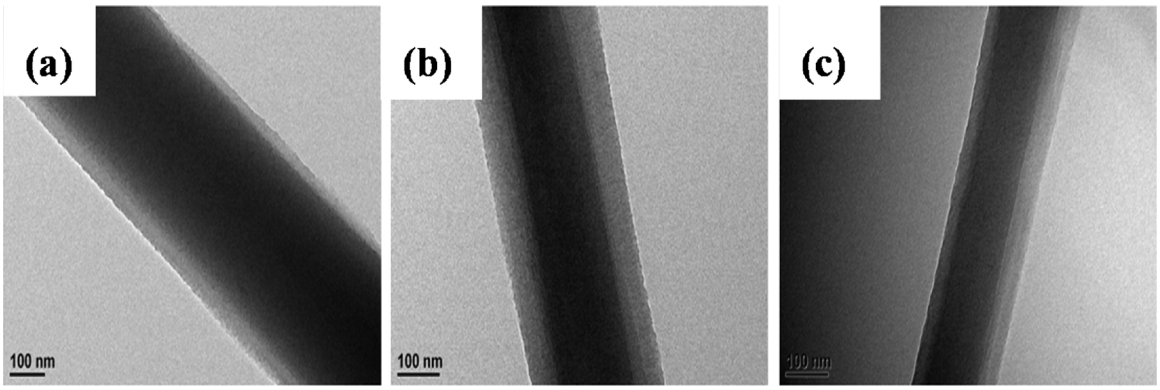

Fig. 2. TEM images for coaxial electrospun fiber with different feed rates (a) 1.2 mL/h, (b) 1.5 mL/h, (c) 1.8 mL/h.

However, none of the above coaxial electrospun core–shell nanofibers were loaded with the corrosion inhibitor and investigated the self-healing performance of the coatings. Yabuki et al. prepared pH-controlled self-healing polymer coatings with cellulose nanofibers served as pathways for the release of a corrosion inhibitor [19]. Nanofibers display numerous excellent properties, such as good mechanical strength, high degree of flexibility, and large surface area–to–volume ratio, and they were extensively used in many fields [20,21]. Nowadays, they have also been used to protect metals [22–26]. Moreover, embedding nanofibers in the resin could improve the mechanical properties of coatings [27,28].

In the present study, a self–healing corrosion-protective coating for Q345 steel was developed by coaxial electrospinning polyvinylidene fluoride (PVDF) and polyvinyl alcohol (PVA) solutions. PVDF was chosen as the shell structure because it is a hydrophobic fluoropolymer with low surface energy, high chemical resistance and moderate mechanical robustness [29]. The inhibitor 2–mercaptobenzothiazole (MBT) was blended with the PVA solutions to serve as the core structure. The PVA@PVDF nanofiber membrane was coaxial electrospun on the surface of Q345 steel at different feeding rates. Then, the epoxy resin was spun on the nanofiber membrane to prepare self–healing coatings. An electrochemical workstation was used to investigate its corrosion prevention property. The Scanning Kelvin Probe (SKP) technique was used to evaluate the corrosion potential in the scratched area of the coatings.

2. Experimental

2.1. Electrode preparation

Q345 steel (0.12%–0.20% C, 0.20%–0.60% Si, 1.20%–1.60% Mn, 0.030% S, and ≤ 0.030% P; in mass%) was used to prepare the working electrode. The working surface had an area of 1.13 cm^2. The electrodes were ground using emery paper (1000 grit).

2.2. Preparation of PVA@PVDF nanofiber membrane

In the present study, PVDF (Kynar Flex 2801, Arkema, France) and PVA (PVA1797, hydrolysis degree 96.0–98.0% (mol/mol), molecular weight 74,900 g/mol, Aladdin,China) solutions were used as the shell and core liquids in coaxial electrospinning, respectively. PVDF solution at 0.17 g/mL was prepared by dissolving PVDF powder in a mixture of dimethyl formamide and acetone (7:3, *v/v*), which were magnetically stirred for 5–6 h at 60 °C. PVA at 0.15 g/mL and MBT at 0.1 g/mL were dissolved in a mixture of dimethyl sulfoxide and ethanol (9:1, *v/v*) at 70–80 °C until a clear solution was obtained.

The coaxial electrospinning setup included two syringes to feed PVDF and PVA solutions independently. The coaxial tip consisted of two concentric needles. The exterior and interior needles had inner diameters of 1.45 and 0.5 mm, respectively. Coaxial electrospinning was performed with varied shell feeding rates. The feed rate of the shell solution was varied (1.2, 1.5, and 1.8 mL/h), and the core feed rate was kept constant depending on its own weight. The applied voltage was kept constant at 10 kV for the shell solution and 12 kV for the core solution with a 15 cm needle–to–collector distance.

The electrospun fibers were accumulated on Al foil for 30 min to observe the morphologies by scanning electron microscopy (SEM) and on electrode surfaces for 10 min to test the corrosion resistance by electrochemical impedance spectroscopy (EIS). The resultant fibrous membranes were dried under vacuum at 60 °C for 1 h to remove the residual solvent before further use. All experiments were operated at room temperature with 20% relative humidity.

2.3. Preparation of epoxy resin composite coating

Different nanofiber membranes (PVDF, PVA@PVDF, and (MBT + PVA)@PVDF) were first electrospun directly onto a 1.13 cm^2 surface of the working electrode. Bisphenol–A with an epoxy value of 0.51 mol/(100 g) was chosen (Fenghuang Epoxy Resin Factory, Wuxi,

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