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Preparation and characterization of microcapsules based self-healing coatings containing epoxy ester as healing agent

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ABSTRACT

Cracks caused by chemicals or mechanical forces would damage the performance of coatings leading to the coating failure. Microcapsules based self-healing smart coatings can provide automatic recovery and extend the durability of coatings. In this study, poly urea-formaldehyde microcapsules contained tall oil fatty acid based-epoxy ester as core materials were synthesized through in situ polymerization. The synthesized microcapsules were characterized by scanning electron microscope (SEM), optical microscope, Fourier transform infrared spectroscopy, and thermogravimetric analysis. The core content of microcapsules was 67 wt. %; the average diameter of microcapsules was 101 ± 48 μm. The self-healing coatings were prepared by embedding the poly (urea-formaldehyde)-epoxy ester (PUF-epoxy ester) microcapsules into epoxy coatings. Salt spray, SEM, and electrochemical impedance spectroscopy were examined, and the self-healing coatings exhibited satisfactory self-healing property and sufficient corrosion resistance recovery.

1. Introduction

In recent years, self-healing coatings have obtained significant attention because of their unique property of automatically repairing. The reported approaches for the fabrication of the self-healing system, include microcapsules-based, vascular, and intrinsic materials [1]. The first microcapsules-based self-healing coating was designed in 2001 by Dr. White's research group [2]. In microcapsules-based method, microcapsules containing a liquid healing agent are embedded in the coating matrix. When damage occurs, the healing agent would be released from ruptured microcapsules to fill the microcracks and form a solid layer, which is the principle of microcapsules-based self-healing systems. The new layer would be formed through the crosslinking reaction of the healing agent with oxygen [3], moisture [4], sunlight [5], or other crosslinkers [6].

After over 10 years of development, many different types of healing agents derived from petroleum resources have been developed for microcapsules-based method, including isocyanates [7], isocyanurates [8], epoxy and epoxy derivatives [9], amines [10], organic siloxanes [11], and other inhibitors [12]. However, it is predicted that the shortage of petroleum-based raw materials will occur in the future due to the global increasing usage of nonrenewable petroleum. At the same time, bio-based materials have attracted considerable attention in academia and industry to weaken the dependence of nonrenewable petroleum products [13]. Nowadays, a significant number of petroleum-based products have been replaced or modified by bio-based raw materials and their derivatives [14,15]. Among them, several vegetable oil-based materials have been developed and applied into microcapsules for self-healing coatings, such as isosorbide derivatives [16], linseed oil [17], Tung oil [18], and alkyds [19]. However, the corrosion resistance of drying oils film and alkyd coatings are not sufficient [20]. The new layer formed by these materials cannot provide enough corrosion protection. It is valuable to broaden the type of renewable bio-based healing agents to improve the performance of self-healing coatings.

To the best of our knowledge, adopting renewable bio-based epoxy ester as a healing agent for self-healing coating has not been studied. Epoxy ester is a type of fatty acid-based material synthesized from epoxy resins and fatty acids. One notable feature is that it can be cured at room temperature through auto-oxidation without additional crosslinkers. This feature ensures the epoxy ester resin to be utilized as the healing agent to repair the cracks without additional heat or catalyst. In the meanwhile, epoxy ester coatings offer more excellent adhesion property and more superior corrosion resistance compared to alkyd coatings and dry oils films, especially the ability to retain adhesion at the wet condition [20]. Based on these advantages, it is expected that epoxy ester encapsulated self-healing coating should improve the corrosion resistance over those self-healing coatings with healing agents of

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drying oils or alkyd.

This is the first time that fatty acid-based epoxy ester was developed as a novel healing agent in microcapsules for self-healing coatings. In this study, microcapsules containing epoxy ester resin were synthesized through two-step processes: (1) formation of the urea-formaldehyde prepolymer in alkaline condition and (2) encapsulation of epoxy ester in acidic condition. Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical structure of the synthesized microcapsules. Thermogravimetric analysis (TGA) was applied to examine the content of the encapsulated healing agent. Additionally, optical microscope and scanning electron microscope (SEM) were utilized to observe the surface morphology of microcapsules. Finally, SEM, salt spray, and electrochemical impedance spectroscopy (EIS) were examined to investigate the self-healing performance and anticorrosive property.

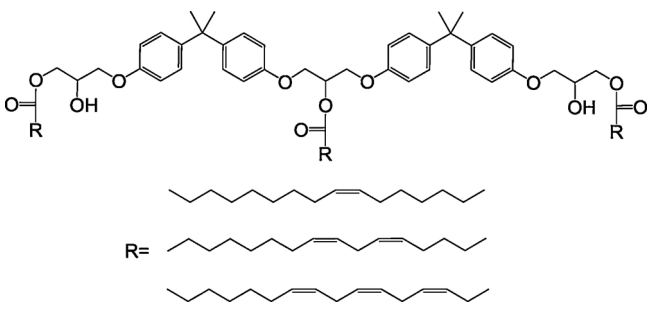
2. Experimental

2.1. Materials

Tall oil fatty acid-based epoxy ester resin 7449 (70 wt. % resin and 30 wt. % xylene) was kindly provided by OPC Polymers (Columbus, Ohio), the possible chemical structure of the epoxy ester was shown in Scheme 1. Epon 828 (epoxy resin, epoxy equivalent weight: 185 ~ 192) and Epikure 3164 (curing agent, amine hydrogen equivalent weight: 256) were kindly supplied by Hexion Specialty Chemicals (Columbus, Ohio). Ammonium chloride (≥ 99.5%), polyvinyl alcohol (PVA, Mw ~ 67,000), resorcinol (≥ 99.5%), and urea (U, ≥ 99%) were obtained from Sigma-Aldrich. Formaldehyde (F, 37 wt. % aqueous solution) was supplied by Fisher Scientific. D36 steel (bare) panels were purchased from Q-Lab (Cleveland, Ohio). All the commercial chemicals were used as received.

2.2. Synthesis of poly(urea-formaldehyde)-epoxy ester microcapsules

Poly(urea-formaldehyde)-epoxy ester (PUF-epoxy ester) microcapsules were synthesized through a typical two-step process in an oil-in-water emulsion. The urea-formaldehyde (U-F) reaction includes addition reaction and condensation reaction, as shown in Scheme 2. Under the basic condition, addition reaction occurs readily while the condensation reaction occurs hardly. As for acidic condition, both reactions can be carried out rapidly [21]. Therefore, the urea-formaldehyde addition reaction was carried out under basic condition to form the water-soluble U-F prepolymer as the first step. Fig. 1 illustrates the procedure of the formation of oil-in-water emulsion and synthesis of microcapsules. In the first step, deionized water (200 ml), urea (3.75 g), and 37 wt. % formaldehyde solutions (10.00 g) were added to a 500 ml three-neck round-bottomed reaction flask at room temperature. An overhead mechanical stirrer was utilized with a stirring rate of 800 rpm. After the urea dissolved, the pH of the solution was gradually adjusted to 9.0 by 5 wt. % KOH solution. Then the flask was slowly heated to 65 °C and maintained for 1 h to obtain the urea-formaldehyde prepolymer. In the second step, the solution of the prepolymer was cooled down to room temperature. Under agitation (800 rpm), 5 wt. % aqueous solution of PVA (15.00 g) stabilizer, ammonium chloride (0.375 g) and resorcinol (0.375 g) were added to the reaction flask, and then epoxy ester resin 7449 (15 ml) was added dropwise. After 30 min stirring, the emulsion was completely stabilized. The pH of the emulsion was carefully adjusted to 3.5 by 1 wt. % hydrochloride acid solution. Then the temperature was set at 55 °C for 4 h. The solid wall was synthesized over the epoxy ester droplets (Fig. 1). Finally, the mixture solution was rinsed with water and acetone successively. The product was under air-drying for 24 h. Pure PUF shell material was prepared by using the same procedure to compare and analyze the chemical structure and composition of the synthesized microcapsules.



Scheme 1. The structure of the tall oil fatty acid-based epoxy ester.

2.3. Fourier transform infrared spectroscopy

The FTIR spectra of PUF-epoxy ester microcapsules, pure PUF, and pure epoxy ester resin were measured by Nicolet iS10 FT-IR Spectrometer (resolution: 4 cm^{-1}; scan number: 32) to characterize their chemical structures. The range of scanning wavelength is from 400 nm^{-1} to 4000 nm^{-1}.

2.4. Morphology

The optical microscope (Olympus BX3-CBH) was used to measure the dimension and size distribution of PUF-epoxy ester microcapsules. The average diameter of microcapsules and standard deviation of size distribution were calculated by gauging the diameter of more than 200 microcapsules. Surface morphology of PUF-epoxy ester microcapsules and the surface of coatings were recorded by SEM (Hitachi TM3030). The accelerating voltage of SEM was 15.0 kV.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA, TA Q50) was used to analyze the composition of synthesized microcapsules by comparing the TGA and DTG traces of PUF-epoxy ester microcapsules, PUF shell material, and pure epoxy ester resin. Approximately 15 mg samples were slowly heated (10 °C/min) from room temperature to 800 °C. Mass loss curves were recorded under the N_2 environment with a gas purge of 40 ml/min.

2.6. Preparation of coatings containing PUF-epoxy ester microcapsules

Epoxy-amine coatings containing 10 wt. % PUF-epoxy ester microcapsules were formulated. The selected 10 wt. % was based on our previous study to ensure a reliable healing function [3,22]. The weight ratio of amine curing agent (Epikure 3164) to epoxy resin (Epon 828) is 1.35. The epoxy resin and amine curing agent were mixed and dissolved in xylene. Then the microcapsules (10 wt. %) were added to the mixture at room temperature under slow stirring. Next, the ultrasonic bath was utilized to remove the air bubble in liquid coatings. Before applying liquid coatings on metal substrates, steel panels (7.62 cm × 15.24 cm × 0.254 cm) were cleaned with acetone to remove the dust and oil. The films were coated by using a drawdown bar. The wet films were placed overnight at room temperature for solvent evaporation. Then the coatings were cured in an oven at 80 °C for 3 h. The thickness of the cured solid film was 180–210 μm, measured by digital coating thickness gauge (Elcometer 415). Neat epoxy coatings (without microcapsules) were also prepared with the same thickness as control samples. The coatings were scratched by scalpel blade to make an artificial crack for determining the self-healing performance. After making a scratch, the coatings were kept at room temperature for 72 h to make sure the healing agent was released and cured. With the completion of these steps, the coatings were ready for further evaluations.