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Evaluation and failure analysis of linseed oil encapsulated self-healing anticorrosive coating

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ABSTRACT

In this study, a linseed oil encapsulated self-healing coating was developed by incorporating 10 wt% synthesized microcapsules into an epoxy-polyamine coating matrix. The linseed oil encapsulated polyurea-formaldehyde (PUF) microcapsules had ~80 wt% core content with ~80 um diameter. The influence of embedded microcapsules on the anticorrosive property of the self-healing coating had been studied by electrochemical impedance spectroscopy. The intact self-healing coating exhibited excellent anticorrosive property as the intact pure epoxy coating, although the addition of microcapsules into the epoxy matrix resulted in a higher water-uptake. The scratched self-healing coating showed excellent healing ability and corrosion inhibition function for microcracks, but it still cannot recover the barrier property as good as the intact coating. The failure of the scratched self-healing coating had been analyzed and the possible reason may be the formation of conductive pathways at the interface between the linseed oil film and the epoxy matrix and/or PUF microcapsule shell.

1. Introduction

Organic coatings have been widely applied for the protection of metals against corrosion. However, cracking caused by mechanical damage or weathering will result in the failure of organic coatings due to the formation of pathways for the diffusion of corrosive species to the metal substrate [1]. These microcracks are hard to be detected and repaired by a conventional method. Recently, microcapsule-based self-healing coatings were reported as a promising method to automatically repair microcracks [2]. Once the self-healing function is triggered by the formation of microcracks, the embedded microcapsules in the coating will rupture and the healing material will release to heal the microcracks. Various healing agents were proposed for the application of anticorrosive coatings, such as isocyanate [3,4], epoxy resin [2,5], alkyd resin [6], organic silane [7,8], and drying oil [9,10]. Among them, drying oil had received much attention due to its sustainable resource, cost effective feature, and autoxidative film forming mechanism.

Linseed oil is one of the most commonly used drying oil in coating industry. The first study on the application of linseed oil to prepare the epoxy based self-healing coating was reported by Suryanarayana C and co-workers [9]. The released linseed oil can react with the oxygen in air to generate a new barrier film to protect the microcrack region against corrosion. The healing ability and corrosion inhibition function of linseed oil had been reported [11–13], in the meanwhile, it was also found that the microcrack healed region was corroded rapidly under salt solution immersion. However, previous studies did not give much explanation and discussion on the rapid failure of the linseed oil coating at the microcrack. But we believe that understanding the reason for the rapid failure of linseed oil coating at microcracks will be helpful for designing novel linseed oil based healing materials and for improving the self-healing ability.

As with many other barrier coatings, the failure of linseed oil coating in the immersion of salt solution should start with the formation of conductive pathways within the coating [1]. But for the linseed oil coating at microcracks, the location of conductive pathways is not limited within the linseed oil film, it can also locate at the interface between linseed oil film and coating matrix or microcapsule shell. On the one hand, as the linseed oil is the triesters of glycerol and fatty acids [14], the ester bonds in its backbone is suspect to hydrolysis [15], which will result in the degradation of linseed oil coating in a severely corrosive environment and the formation of conductive pathways within the linseed oil film. On the other hand, the adhesion between linseed oil film and coating matrix or microcapsule shell should be based on the long range intermolecular interaction [16,17], which is not stable in the immersion of water since the water molecule has a strong tendency to form the hydrogen bond with the polar groups in epoxy matrix, polyurea-formaldehyde (PUF) shell, and linseed oil film.

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Table 1
Formulation of the self-healing epoxy coatings.

Sample	Epon 828 (g)	Epkiure 3164 (g)	Acetone (g)	Xylene (g)	Microcapsule (g)	Dry thickness (um)
EP0 [1]	5.00	6.80	1.57	2.36	0	197.5 ± 6.5
EP10 [2]	5.00	6.80	1.73	2.60	1.18	215.5 ± 8.5

Notes: 1: Pure epoxy coating; 2: Self-healing coating containing 10 wt% microcapsules.

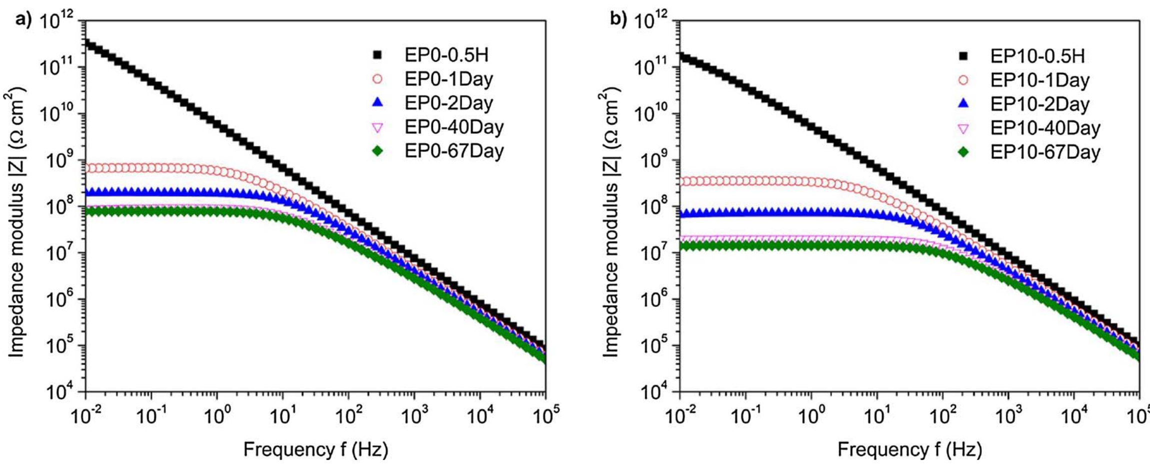

Fig. 1. Impedance modulus as a function of frequency for intact EP0 (a) and intact EP10 (b) immersed in 3.5 wt% NaCl solution. EP0 and EP10 refer to pure epoxy coating and self-healing coating as listed in Table 1.

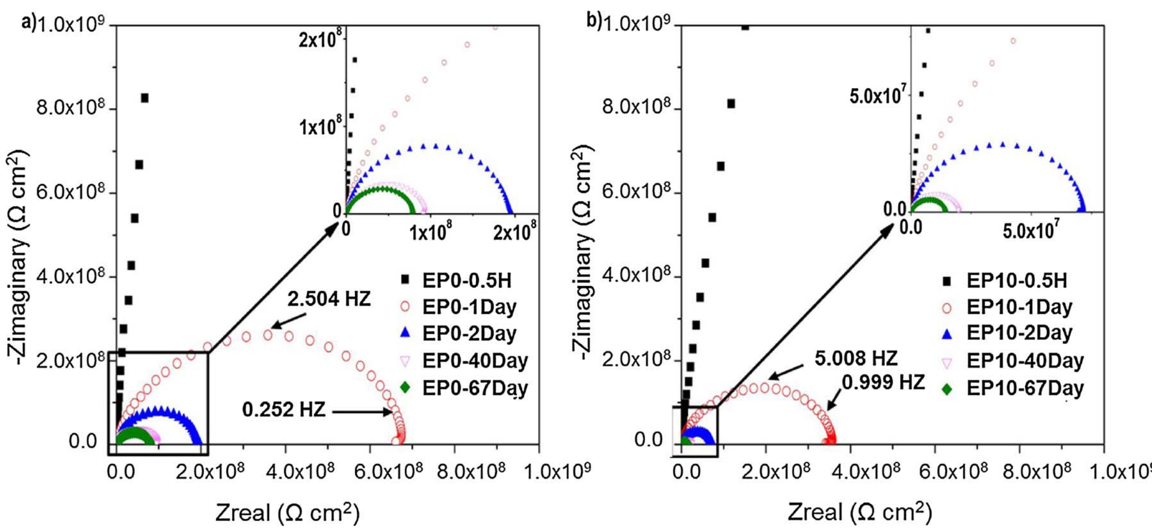

Fig. 2. Nyquist plots for intact EP0 (a) and intact EP10 (b) immersed in 3.5 wt% NaCl solution. EP0 and EP10 refer to pure epoxy coating and self-healing coating as listed in Table 1.

This strong tendency will allow water to fill in the interface between linseed oil film and epoxy matrix or PUF shell and therefore result in forming the conductive pathways.

Apart from healing performance, the anticorrosive property for the intact self-healing coating is also important. However, to our knowledge, there is not yet relevant publication that has studied the influence of linseed oil encapsulated PUF microcapsules on the anticorrosive property of intact epoxy coating. For intact barrier coating, the anticorrosive property refers to the ability of coating impeding the diffusion of corrosive species to the metal substrate [1]. The addition of linseed oil encapsulated PUF microcapsules into epoxy coating may diminish its barrier property based on two possible reasons. First, the enriched hydrophilic amino and carbonyl groups on the PUF microcapsule shell may absorb much more water than the epoxy matrix. Second, compared with the highly crosslinked epoxy matrix, the uncured liquid linseed oil encapsulated into the epoxy matrix may be the vulnerable spots for the diffusion of corrosive species to the metal substrate.

The objectives of this research are to study the influence of linseed oil encapsulated PUF microcapsules on the anticorrosive property of the intact epoxy coating and understand the failure reason for the newly formed linseed oil coating at microcracks. In this work, linseed oil encapsulated PUF microcapsule with ~80 wt% core content and ~80 um diameter was prepared according to our previous study [18]. The microcapsules were incorporated into an epoxy coating to prepare the self-healing coating. Electrochemical impedance spectroscopy (EIS) and equivalent circuit modeling were used to evaluate the anticorrosive property of the self-healing coating. Healing ability was directly characterized by an optical microscope and a scanning electron microscope (SEM). Anticorrosion performance of the linseed oil coating at microcrack was characterized by EIS. Finally, a reason for the rapid failure of the scratched self-healing coating was proposed and discussed.