SELF-HEALING COATING HEALED WITH A VISCOELASTIC SUBSTANCE

Y. K. Song¹ and C. M. Chung¹

¹ Department of Chemistry, Yonsei University, Wonju, Gangwon-do 220-710, South Korea – e-mail: ssong-a@yonsei.ac.kr; cmchung@yonsei.ac.kr

Keywords: self-healing, protective coating, capsule type, viscoelastic substance, secondary crack free

ABSTRACT

A protective coating is used to protect surface of a material from various deterioration factors. When cracks form and propagate in the coating, water, chloride ion, and carbon dioxide would penetrate through the cracks. This results in the deterioration of the material, leading to reduction in its serviceability. If the protective coating has self-healing ability, it would effectively protect the materials from the deterioration.

In this work a capsule-type self-healing protective coating has been developed using vegetable oils as healing agent. Healing-agent-loaded microcapsules are embedded in a coating matrix to obtain a self-healing protective coating. Upon damage-induced cracking, the microcapsules are ruptured by the propagating crack fronts, resulting in release of the healing agent into the crack by capillary action. A healing reaction occurs by atmospheric oxygen, generating a viscoelastic substance. The self-healing coating was evaluated as protective coating for steel, and it was demonstrated that our system has good self-healing capability.

In conventional capsule-type self-healing systems, healing reactions generally produce hard solids, so the systems are considered to be vulnerable to regeneration of cracks in the healed region. Furthermore, the regenerated cracks can not be healed because healing agent is consumed in the first healing process. It should be noted that our new system can effectively prevent the coating from regeneration of cracks in the healed region (Figure 1).

Figure 1: The concept of this study
1. INTRODUCTION

A protective coating is used to protect surface of a material from various deterioration factors. Several reports of microcapsule-type self-healing coatings for metal protection have appeared [1~5]. The conventional extrinsic self-healing coatings have employed healing agents that harden by healing reaction. This type of self-healing systems are limited to single local self-healing event: when the healed region is damaged again, self-healing cannot be repeated due to the depletion of healing agent-filled microcapsule, and the conversion of the released healing agent into a hard solid having no intrinsic self-healing ability. We thought that, if a healing agent has an intrinsic self-healing function after the release and reaction, repeatable self-healing can be accomplished. In this work a novel repeatable self-healing coating has been developed by combination of the extrinsic and intrinsic healing concept, using reactive vegetable oils as healing agent. When vegetable oil-loaded microcapsules are ruptured, the healing agent is released and fills damaged region, generating a viscoelastic substance by oxidation reaction that has intrinsic self-healing ability. It is expected that, if the secondary damage occurs in the healed area, repeated self-healing events would be possible due to the viscoelastic recovery. Although this approach has difficulty in recovery of mechanical property, the recovery of corrosion protection function would be more important than that of mechanical performance in the case of protective coating. In addition to the repeatable self-healing ability, our system also offers the advantages of environment-friendly self-healing because the healing reaction occurs by atmospheric oxygen. This system would be more useful than our previous repeatable self-healing system that only functions in the presence of light [6].

2. MATERIALS

Vegetable oil used as core material was purchased from CJ Cheiljedang. Urea, aqueous formaldehyde solution (37wt%) used as shell materials were purchased from Sigma-Aldrich. Poly(ethylene-alt-maleic anhydride) (EMA) used as surfactant was purchased from Sigma-Aldrich. Resorcinol used as chain extender and 1-octanol used as defoamer were purchased from Sigma-Aldrich. Ammonium chloride and sodium hydroxide, used to control the pH of solution, was purchased from Duksan Pharmaceutical. Soybean oil and olive oil as vegetable oils were purchased from CJ Cheiljedang. Cobalt (II) 2-ethylhexanoate, 65 wt% solution in mineral spirits as dryer was purchased from Sigma-Aldrich. An enamel paint (KCI 7200, white) was purchased from Kunsul Chemical Industrial Co. Silicone sealant (SL 907) was purchased from KCC. All the materials are commercial products and were used without purification.

3. METHODS

A healing agent was prepared by mixing soybean oil, olive oil and the dryer with mass ratio of 1 :0.594 :0.006. The healing agent was coated on a KBr disk and stored under ambient conditions. The reaction of the coating to atmosphere was performed at 20℃. The conversion was measured by FT-IR spectroscopy. We have performed microencapsulation of soybean oil using urea-formaldehyde (UF) polymer as shell material. The UF microcapsules were prepared by in situ
polymerization in an oil-in-water emulsion at an agitation rate of 800 rpm. Microcapsules filled with dryer-containing olive oil were prepared in a similar fashion. The enamel paint and microcapsules (soybean oil microcapsules and olive oil microcapsules were mixed with a ratio of 1:0.6) were mixed to give a self-healing coating formulation. A control coating was prepared in a similar fashion using the enamel paint without microcapsule.

Cross scribes were applied manually on the prepared self-healing and control coatings with a cutter blade. The scribed coatings were stored under ambient conditions for 3 days. The scribed specimens were then immersed in 10 wt% NaCl solution for 48 h to evaluate the accelerated corrosion process. After washing with distilled water and removal of residual water, the coating were observed by optical photography. The first scribed and healed region in the coatings was re-scribed and the resultant coatings were kept for 20 min under ambient conditions. The second anticorrosion test was carried out by immersion of the coatings in the NaCl solution and subsequent photography according the method described above.

4. RESULTS

Figure 2: Infrared spectra of healing agent (left): (a) before and (b) after oxidation reaction for 10 h. A plot of conversion of C=C vs. oxidation reaction time (right).

The reaction behavior of the soybean oil/olive oil/dryer healing agent was investigated. The healing agent was coated on a KBr disk and stored under ambient conditions to induce oxidation reaction of the soybean oil. The reaction conversion was measured by FT-IR spectroscopy: the ratios of calculated area of the two absorption bands (C=C and C=O as an internal standard) before and after exposure were compared to determine the degree of conversion of the C=C bond using the following formula. The conversion increases with increasing reaction time and 92% conversion was reached after 10 h (Figure 2).

Figure 3: Size distribution of microcapsules obtained at an agitation rate of 800 rpm. The inset shows the microcapsules.
The scribed vegetable oil-based coatings were stored under ambient conditions to induce cross-linking reaction of the released healing agents. Control coatings without microcapsule were also scribed. The scribed and healed self-healing coatings and control coatings were immersed in 10wt% aqueous NaCl solution for 48 h. All control samples corrode, but the self-healing coatings showed no visual evidence of corrosion (Figure 4b). The scribe area in the self-healing coatings was subjected to second scribing to evaluate their repeatable self-healing capability. After 20 min storing under ambient conditions, the coating samples were immersed again in the NaCl solution for 48 h. As shown in Figure 4a, the control coatings showed further corrosion. It is apparent that the vegetable oil-based coatings are nearly free of corrosion despite of the secondary damage (Figure 4c). This result clearly demonstrates the repeatable self-healing capability of the vegetable oil-based coating system. It is considered that the repeatable self-healing can be accomplished based on the viscoelastic property of the cross-linked vegetable oil.

5. CONCLUSIONS

It was successfully demonstrated by anticorrosion test that the vegetable oil-based self-healing coating system has repeatable self-healing capability. This coating system offers the advantages of simple, inexpensive, practical self-healing.

REFERENCES