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Self-healing Ability of Smart Coating for Anticorrosion of Reinforcing Steel

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Abstract. Self-healing materials offer tremendous potential for providing long-lived structural materials. In this study, isophorone diisocyanate (IPDI) microcapsules as self-healing materials were synthesized via in situ polymerization. Thermogravimetric analysis characterized the thermal ability of IPDI, microcapsules and microcapsule shells. The morphology of microcapsules and microcapsule shells were characterized by FE-SEM. Scanning micro-reference electrode technique demonstrated that epoxy resin coatings with IPDI microcapsules on the surface of reinforcing steel Q235 could cure the scratched crevice by immersion in 0.01 M NaCl solution after the coating was scratched. The self-healing epoxy resin coating could protect Q235 from corrosion.

Introduction

Corrosion process always occurs in reinforcing steel of the buildings and metal architectures. It is estimated that corrosion destroys one quarter of the world's annual steel production, which corresponds to about 150 million tons per year, or 5 tons per second [1]. Therefore, it is necessary to inhibit the corrosion process of reinforcing steel. The coating is one of the most effective methods to protect the reinforcing steel. However, the conventional coating repair methods are not effective for healing invisible micro-cracks within the structure during its service life. In response, the concept of self-healing polymeric materials was proposed in the 1980s [2] as a means of healing invisible micro-cracks for extending the working life and safety of the polymeric components. The more recent publications in the topic by White et al. [3] in 2001 further inspired world wide interests in these materials[4]. Corrosion process of reinforcing steel always coupled by water, as water is the carrier of materials, electrons and reaction place. Thus, corrosion could be inhibited when the self-healing process inhibits the water transportation. Isocyanates are reactive with water and are thus potential catalyst-free healing agents for self-healing materials that are exposed to moist or wet environments. Yang et al.[5] first encapsulated isophorone diisocyanate (IPDI) as a healing agent via the interfacial polymerization reaction of Toluene diisocyanate prepolymer and 1,4-butanediol in an O/W emulsion. Huang et al.[6] then reported the microencapsulation of liquid isocyanate monomer. Hexamethylene diisocyanate was encapsulated by polyurethane microcapsules based on the polymerization of methylene diphenyl diisocyanate prepolymer and 1,4-butanediol via facile in-house synthesis. In this study, we prepared IPDI microcapsules using urea formaldehyde by in situ polymerization. Scanning micro-reference electrode (SMRE) technique was used to characterize the self-healing ability of epoxy resin coatings functionalized with IPDI microcapsules on the surface of reinforcing steel Q235.

Materials and Methods

All other chemicals were obtained from Sigma Aldrich and used as received. The water used in all the experiments was produced by a Millipore Milli-Q Plus 185 purification system and has a resistivity level higher than 18.2 m Ω·cm. Field Emission Scanning Electron Microscopy (FE-SEM) images of the samples were acquired with a Hitachi S-4800 FE-SEM microscope. Thermogravimetric analysis

(TGA) data were performed on a STA 409PC apparatus, NETZSCH. The measurements of the potential distribution on the steel surface were recorded with SMRE technique using model XMU-BY Being Nano-Instruments (Beijing, China).

IPDI microcapsules were synthesized using a conventional method[7] with modified parameters. In a typical procedure shown in Figure 1-a, 100 ml water and 20 ml of 3.0 wt% aqueous solution of sodium dodecyl benzene sulfonate (SDBS) were mixed at room temperature. Under agitation (600 RPM), 6.00 g urea, 1.00 g ammonium chloride and 1.00 g resorcinol were successively dissolved in water. 10 ml IPDI was slowly added into the mixture to form an oil in water (O/W) emulsion. After stirred for 30 min, the pH value of the emulsion was slowly adjusted to 3.5 by drop-wise addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl). One to two drops of 1-octanol were added to eliminate surface bubbles. Then, 10.00 g of a 37 wt% aqueous solution of formaldehyde was added. The temperature was raised to 60 °C at a rate of 1 °C min^{-1}. After 4 hours of continuous agitation the mixer and the polymerized microcapsules were obtained, they were repeatedly washed with ethanol and water to remove impurities.

Results and Discussion

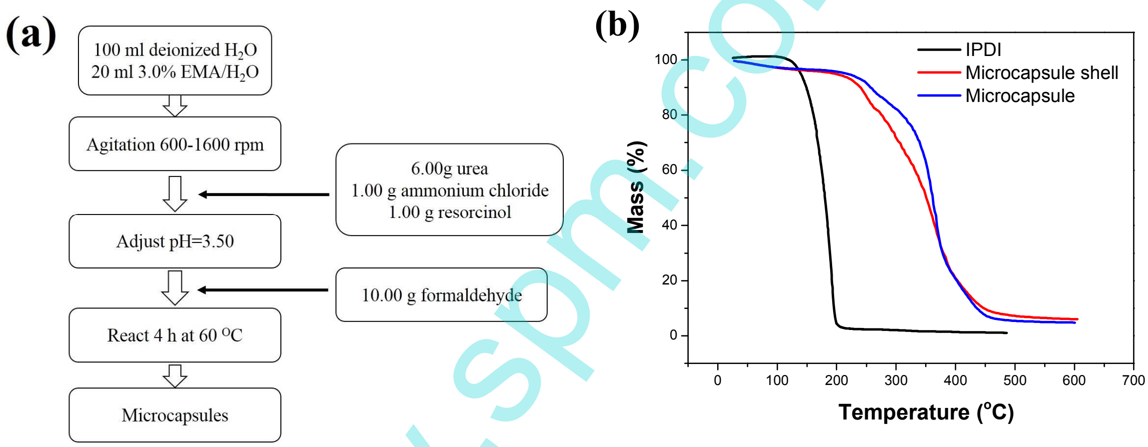

Fig. 1 (a) Microencapsulation of IPDI utilizing acid-catalyzed in situ polymerization of urea with formaldehyde to form capsule shell. (b) TGA curves of IPDI, microcapsules and microcapsule shell.

The thermal stability of IPDI microcapsules was analyzed by TGA. Fig. 1-b shows the mass loss curves of IPDI liquid, IPDI microcapsules, and the shell of the microcapsules over the temperature range of 25 to 600 °C. The start points of mass loss of the three kinds of materials are 154 °C, 245 °C and 247 °C, respectively. It seems that the shell of the microcapsules could protect the core materials (IPDI). So, IPDI microcapsules could be stable in the heating process below 240 °C. Obviously, the microcapsules shells have a role of thermal protection for core materials. And, the end points of mass loss of the three kinds of materials are 197 °C, 453 °C and 455 °C, respectively. It indicates that microcapsule materials could endure much higher temperature of mass loss than IPDI liquid.

Fig. 2-a shows the IPDI microcapsule prepared via in situ polymerization characterized by FE-SEM. IPDI microcapsules have an average diameter ~80 μm, as shown in Fig. 2-b. The microcapsules could easily separate without adhere to each other. And, the width of the microcapsule shell is nearly 582 nm in Fig. 2-c.

After preparing the IPDI microcapsules, they were added into epoxy resin for smart coating on the surface of reinforcing steel Q235. All coatings with a thickness of 100 μm were applied to 25 mm×25 mm metal substrate, and solidified at 40 °C for 24 h. Coating solutions were applied to one end of the substrate, and a micrometer-controlled doctor blade was used to spread a uniform-thickness coating.

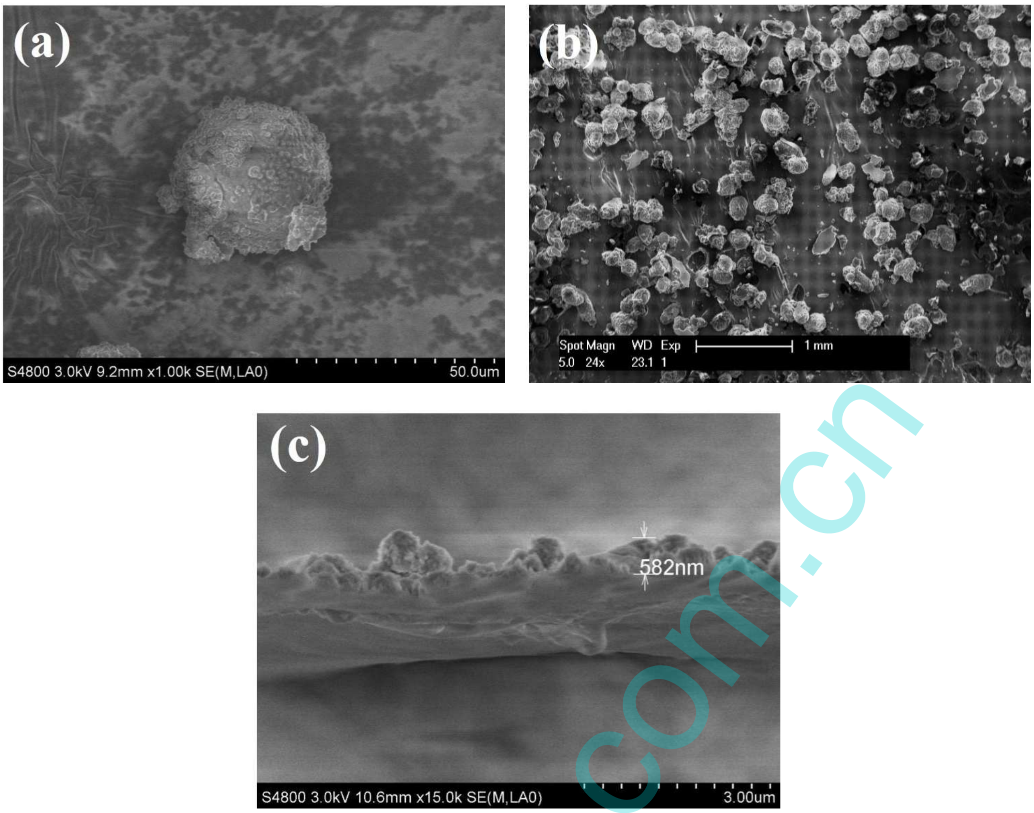

Fig. 2 (a) FE-SEM images of IPDI microcapsule prepared by in situ polymerization. (b) Low magnification FE-SEM images of IPDI microcapsules. (c) The width of the microcapsule shell.

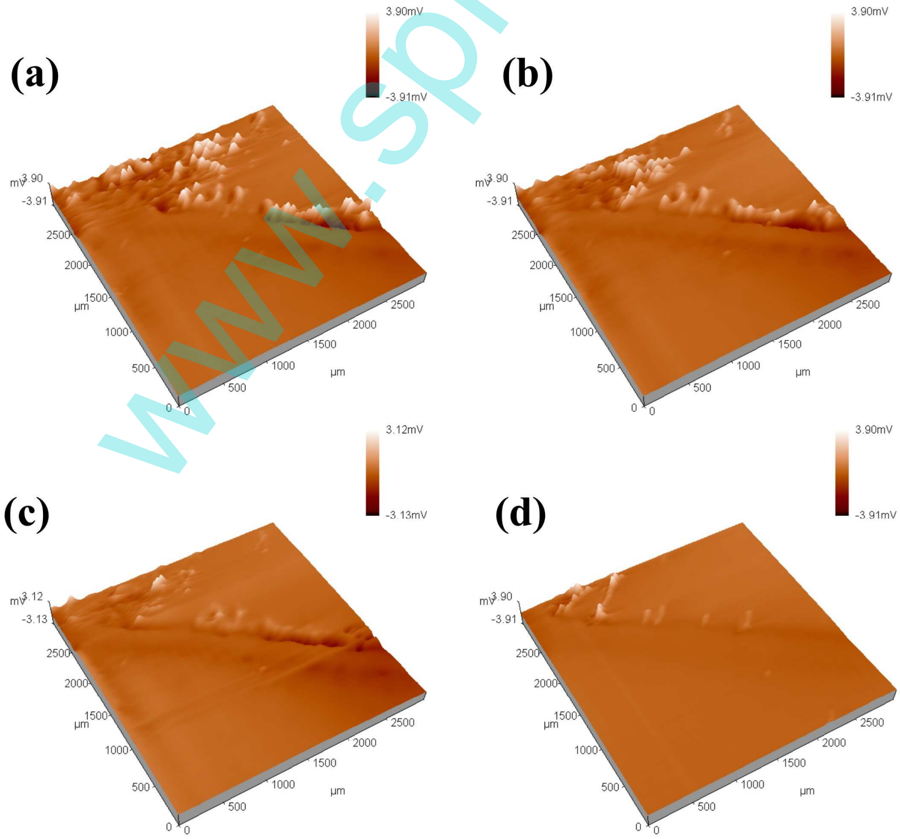

Fig. 3 Self-healing process of scratched smart coating on reinforcing steel surface for anticorrosion. The sample immersed in seawater: (a) 0.5 h; (b) 2 h; (c) 4 h; (d) 8 h.

The epoxy resin coatings with IPDI microcapsules were scratched by a doctor blade. The width of the scratched crevice is about 30 μm. Then, the samples were immersed in 0.01 M NaCl solution. The potential distribution images over the surface of reinforcing steel in NaCl solution after immersion for different time are shown in Figure 3. There obviously existed a scratched line in the SMRE figure. The potential difference along the crevice shows the corrosion process which are shown in Figure 3-a, as reinforcing steel exposed in NaCl solution. Only several small peaks (less than 3 mV) were observed indicating that no localized corrosion occurred on the steel surface. After 2 hours, the potential difference changed less (Figure 3-b). Then, the IPDI liquid in microcapsules flow out of the core, and reacted with water after 4 hours. The coating shows the self-healing ability that partly cured the scratched crevice (Figure 3-c). For 8 hours immersion, the scratched crevice was well cured, and there was nearly no potential difference along the crevice line (Figure 3-d). Under this condition, the localized corrosion did not occur. The epoxy resin coatings functionalized by IPDI microcapsules has good self-healing ability.

Conclusions

IPDI microcapsules were synthesized via in situ polymerization. IPDI microcapsules have a role of thermal protection for core materials. SMRE technique demonstrated that epoxy resin coatings with IPDI microcapsules on the surface of reinforcing steel Q235 could cure the scratched crevice by immersion in water when the coating was scratched. The self-healing epoxy resin coating could protect Q235 from corrosion.

Acknowledgements

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References

[1] R. M. Latanision, Mater. Performance, 26, 9 (1987).

[2] K. Jud, H. H. Kausch, and J. G. Williams, J. Mater. Sci., 16(1981), p:204

[3] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, et al. Nature, 409(2001), p:794

[4] D. Y. Wu, S. Meure, D. Solomon. Prog. Polym. Sci., 33 (2008), p: 479

[5] J. Yang, M. W. Keller, J. S. Moore, S. R. White and N. R. Sottos, Macromolecules, 41(2008), p: 9650

[6] M. X. Huang and J. L. Yang, J. Mater. Chem., 21(2011), p: 11123

[7] W. Wang, L. Xu, F. Liu, X. Li and L. Xing, J. Mater. Chem. A, 1(2013), p: 776