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Short Communication

Synthesis of organic silane microcapsules for self-healing corrosion resistant polymer coatings

Mingxing Huang, He Zhang, Jinglei Yang *

School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore

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ABSTRACT

Hydrolysable organic silane, i.e. 1*H*,1*H*,2*H*,2*H*-perfluorooctyl triethoxysilane (POTS), was carefully selected and microencapsulated as healing agent via *in situ* polymerization in an oil-in-water emulsion. The microcapsule size was adjustable via changing agitation rate for various coating systems. POTS microcapsules were incorporated into epoxy resin and coated on a steel substrate to form a corrosion resistant organic coating. The corrosion test in the salt solution demonstrated the good corrosion resistance of the self-healing coating compared to the control sample. Additional analysis revealed that the corrosion prohibition functionality was realised by an autonomous self-healing mechanism of the encapsulated POTS hydrolysed with water upon scratch.

1. Introduction

Corrosion of metal is a worldwide issue and it causes huge economic loss annually in both developed and developing countries [1,2]. The most common approach for corrosion control is to apply protective coatings integrated with corrosion inhibitors on metal substrates, while the widely used inhibitors contain chromate and phosphate, whose usage is restricted or gradually reduced in many countries due to their highly environmental toxicity [3]. As the outmost layer on structures, protective coatings are always in the high risk of being damaged or scratched originally at micro-level during transportation, installation and service. Such damages are hard to detect and corrosion process gradually occurs. Self-healing concept was successfully proved to autonomously repair microcracks in the epoxy resin with incorporation of dicyclopentadiene microcapsules and Grubbs' catalyst particles [4]. In recent years various self-healing chemistries and material systems have been developed to address damaging issues in the field of materials science and engineering [5–10]. However, with the concern of compromised system integrity after introducing healing agent carriers in matrix materials, self-healing concepts have attracted more interests in the corrosion resistant coating applications where mechanical strength is not a major concern [11–21]. Among a number of approaches for self-healing materials development, microencapsulation is the most efficient and widely used way, and our group has recently reported a facile method to encapsulate a reactive liquid diisocyanate monomer to create a one-part self-healing corrosion resistant coating [22]. However, the potential environmental issue from the high toxicity of isocyanate monomer limited the wide applications of this material system.

Therefore, there is still demand to seek for diversified self-healing chemistries for various applications. Aramaki [23,24] applied sodium silicate in the preparation of a highly protective and self-healing film, which displayed good corrosion suppression effect to zinc surface. The inorganic silicate based corrosion resistant system mainly took the deposition of silicates or the interaction between silicates and metal substrates to realise the corrosion suppression function. But inorganic silicates are usually directly mixed into a matrix, and hence they may be susceptible to interact with environment, leading to compromise in corrosion protection during long term service [23–25]. Organic silane molecules tend to hydrolyse in wet environment and crosslink to form a solid film, and such a property indicates their potential as novel healing chemistry for one-part and catalyst free self-healing additive to corrosion resistant coating. To date, the research on organic silanes for self-healing materials remains largely unexplored, and only a few publications have appeared [12,18,19]. Braun and co-workers reported the polydimethylsiloxane-based silane microcapsules applied for self-healing coatings [12,18]. A mixture of hydroxyl end-functionalized polydimethylsiloxane and polydiethoxysiloxane was directly phase-separated, or encapsulated and then dispersed in epoxy matrix, and the yielding coating exhibited good self-healing ability for corrosion protection. However, organo-tin catalyst was necessary for such self-healing systems. Another study was the microencapsulation of a self-synthesized silyl ester for self-healing coatings [19].

* Corresponding author. Tel.: +65 6790 6906; fax: +65 6792 4062.
E-mail address: mjlyang@ntu.edu.sg (J. Yang).

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Octyldimethylsilyloleate, a silyl ester, was synthesized and encapsulated into poly(urea–formaldehyde) (PUF) microcapsules, which were then incorporated into epoxy to produce a self-healing coating, and the excellent corrosion- resistant property of the prepared coating was demonstrated via self-healing. But the synthesis of silyl ester increased the complexity and cost to the procedure. Here we report a novel self-healing corrosion-resistant polymer coating based on the microencapsulated novel organic silane, i.e. 1*H*,1*H*,2*H*,2*H*-perfluorooctyl triethoxysilane (POTS). There are several advantages of this coating system over the existing self-healing materials: (a) POTS is able to hydrolyse in wet environment to form a silane-based film and as mentioned, such ability indicates that the use of catalyst can be avoided in the end self-healing product. (b) The newly formed film from hydrolysis and poly-condensation of POTS and water is hydrophobic [26], indicating such a special wetting property will serve to repel aqueous electrolyte solution away from metal and to provide further corrosion protection to metal substrate. (c) POTS is commercially available and hence the preparation of self-healing coating will be more convenient and time efficient for mass production.

2. Experimental

2.1. Materials

Ethylene maleic anhydride was purchased from MP Biomedicals. Sodium hydroxide, sodium chloride, ammonium chloride, resorcinol, and formaldehyde solution were bought from Sigma–Aldrich. Two-part epoxy of Epolam 5015 resin and Epolam 5014 hardener was obtained from Axson. All chemicals in this study were used as received without further purification unless otherwise specified.

2.2. Synthesis of POTS loaded microcapsules

The preparation of microcapsules was based on an *in situ* polymerization reaction in an oil-in-water emulsion system. At ambient temperature, 50 ml of deionized water and 12.5 ml of 2.5 wt.% aqueous solution of ethylene maleic anhydride copolymer were mixed in a 500 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate with an external temperature probe. The solution was agitated with a digital mixer (Caframo) driving a three-bladed propeller. Under agitation at 800 rpm, 1.25 g urea, 0.125 g ammonium chloride and 0.125 g resorcinol were dissolved in the solution. The pH value of the solution was raised from about 2.60 to 3.50 by drop-wise addition of 1 M sodium hydroxide solution. 10 g POTS and toluene were then slowly added into the above aqueous solution to generate emulsion, followed by the addition of 3.17 g of 37 wt.% aqueous solution of formaldehyde. The emulsion was covered and heated to 55 °C at a heating rate of 1 °C/min. After 4 h of continuous agitation and reaction, the stirrer and hot plate were switched off. The resultant microcapsules were filtered and washed with distilled water. Microcapsules were collected for air-drying at room temperature for 48 h before further analysis.

2.3. Preparation of epoxy coatings

Self-healing coating was prepared by dispersing 10 wt.% of the synthesized microcapsules with diameter of 120 ± 33 μm into epoxy resin (Epolam 5015) at ambient temperature, followed by mixing hardener (Epolam 5014). The mixture was then degassed. The coating solution was applied on steel with the final coating thickness of 200–250 μm, and cured at room temperature for 24 h before testing. Prior to coating, all steel substrates were abraded by sand paper (Grain size: 400), washed by deionized water and acetone for three times and dried in open air.

Cross scratches were applied manually on the prepared self-healing epoxy coating by razor blade following ASTM D1654 standard. Scratched specimen was then immersed in 10 wt.% sodium chloride solution for 48 h to evaluate the accelerated corrosion process. Pure epoxy coating with the similar thickness was prepared as a control and treated in the same manner for comparison.

2.4. Characterization

The surface morphology and shell thickness of POTS loaded microcapsules were examined by using scanning electron microscopy (JEOL JSM 5600LV SEM).

Mean diameter of the microcapsules was determined from data sets of at least 200 measurements from SEM images and analysed in the software ImageJ.

Components of the microcapsules were analysed by using Fourier Transfer Infrared Spectroscopy (FT-IR, Nicolet 6700), and the spectrum in the range of 400–4000 cm^{-1} was used for the observation.

The thermal stability and the POTS content of the resultant microcapsules were characterised by using thermogravimetric analysis (TGA, Hi-Res Modulated TGA 2950). The peak width of the derivative of the weight loss curve of capsules was used to roughly determine the core fraction of microcapsules.

Optical photography was used to observe the different corrosion behaviour of the steel panel coated with self-healing coating and with neat epoxy control coating. SEM was employed to inspect the profile of the scratched area of the coating to provide detailed information about the corrosion effect. Energy-dispersive X-ray spectroscopy (EDX) was applied to reveal the elemental distribution in the observed areas.

Electrochemical test was performed after the corrosion test to quantitatively evaluate the corrosion situation of the scratched coatings. The test was conducted using a computer controlled potentiostat (Reference 600, Gamry) in a conventional three-electrode electrochemical cell equipped with a Pt counter electrode, a Ag/AgCl in saturated KCl aqueous solution as reference electrode, and the coated steel panel as the working electrode, respectively. The scribed regions on the specimens were exposed in 1 M NaCl aqueous electrolyte with the exposed area of 10 cm^2 for 48 h. The corroded specimens were then connected in the electrochemical cell to investigate the potential-current behaviour. In the measurement, the potential was scanned from −600 mV to +1100 mV (*vs.* Ag/AgCl) with a sweep rate of 20 mV/s at ambient temperature, and the current passing through the specimen was recorded by the Software DC 105 (Gamry).

3. Results and discussion

3.1. Properties of POTS microcapsules

PUF microcapsules containing POTS as core materials were synthesized via *in situ* polymerization in an oil-in-water emulsion following an established method [27]. The SEM image in Fig. 1a clearly shows the spherical shape of the resultant PUF microcapsules, and it is seen that the microcapsules have a rough outer surface. This shell structure of the synthesized microcapsules is in good agreement with PUF microcapsules reported before [27].

For a microcapsule-based self-healing system, the diameter of embedded capsules greatly influences the healing performance [28]. In this study, the influence of agitation rate on the diameter of the resultant microcapsules was investigated. It is found that

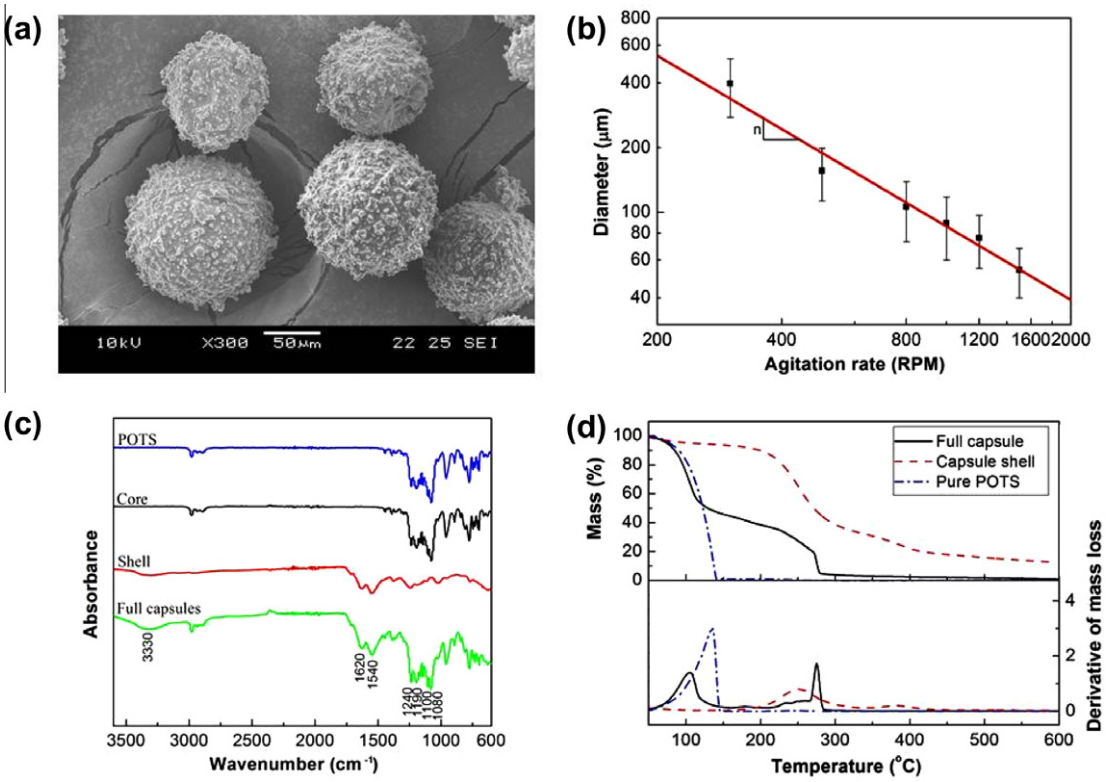

Fig. 1. Synthesis and characterization of POTS loaded microcapsules. (a) SEM image of the prepared microcapsules. (b) Average diameter of the prepared microcapsules as a function of the agitation rate ($n = -1.14$) in the double logarithm coordinates. (c) FTIR spectra of pure POTS, capsule core, capsule shell and full microcapsules. (d) TGA weight loss curves and the derivatives of the weight loss curves of pure POTS, capsule shell and full microcapsules.

the average diameter of microcapsules reduced from 400 μm to 40 μm when the agitation rate was raised from 300 rpm to 1500 rpm, respectively. This observation demonstrated that the increase of agitation rate would result in smaller microcapsules. The main reason for such a relation is that at higher agitation rate, finer oil droplets would form in the emulsion system due to stronger shear force. In the synthesis, the PUF membrane shell wall was formed surrounding the oil droplets. Therefore, the final microcapsules would accordingly be smaller at higher agitation rate. Actually, as shown in Fig. 1b, the mean diameter of the resultant microcapsules exhibited linear relation to the agitation rate in the double logarithm coordinates, and this result is in agreement with the previous research [27,29] and serves as a reference to tune capsule size for various thicknesses of coatings.

Since the synthesis of the capsule shell wall is not a strict stoichiometric reaction, and most of toluene evaporates away during the heated reaction process, the yield of the synthesis is simply calculated by the ratio of the mass of the collected microcapsules to the total mass of POTS, urea, ammonium chloride and resorcinol, while the mass of toluene is ignored. Based on this calculation, the yield of the collected microcapsules was around 60 wt.% for all batches obtained from the applied agitation rates.

The components of the prepared microcapsules were determined from FTIR analysis. As shown in Fig. 1c, the spectrum of the full capsule contains signals at 3330 cm^{-1} (O–H and N–H stretching), 1620 cm^{-1} (C=O stretching) and 1540 cm^{-1} (N–H bending), indicating the formation of PUF from the polymerization reaction between urea and formaldehyde. A simple comparison between the spectra of the full microcapsule and the capsule shell clearly shows that POTS is absent in the shell part. In the meantime, it can be seen that the spectrum of the capsule core is identical to that of pure POTS, indicating the successful encapsulation of POTS as core material.

The thermal property and the core fraction of microcapsules were characterised by using TGA method. The TGA weight loss curves of the synthesized microcapsules along with pure POTS and pure capsule shell as a function of temperature were shown in Fig. 1d. It can be seen that microcapsules experienced significant weight loss from approximately 100 °C, which is attributed to the evaporation of encapsulated POTS. The decomposition of shell started from about 200 °C. From the peak width of the derivative curve as shown in Fig. 1d, the core fraction of the microcapsules was determined to be around 60% when the agitation rate was at 800 rpm.

3.2. Corrosion protection performance of control and self-healing coatings

A self-healing corrosion resistant coating was prepared by mixing the synthesized microcapsules into epoxy resin that was coated on the steel substrate. The cured epoxy coating was manually scribed to expose the substrate and then immersed into 10 wt.% sodium chloride solution to evaluate the self-healing and corrosion protection performance. It can be seen from Fig. 2a that the scratched area of the steel panel coated with self-healing coating was nearly free of rust after 48 h immersion in the salt solution. On contrary, severe rust was seen in the control specimen (Fig. 2b). This result clearly demonstrated the good corrosion protection of the prepared coating towards steel panel under the accelerated corrosion condition.

The scratched regions of both self-healing and control coatings were inspected under SEM. It is clear that the cut of the self-healing coating was filled with newly formed materials after immersion (Fig. 2c). The cut was in this way sealed to retard the diffusion of corrosive salt solution and thus protect the substrate from corrosion. As a comparison, it could be seen that the cut of the control

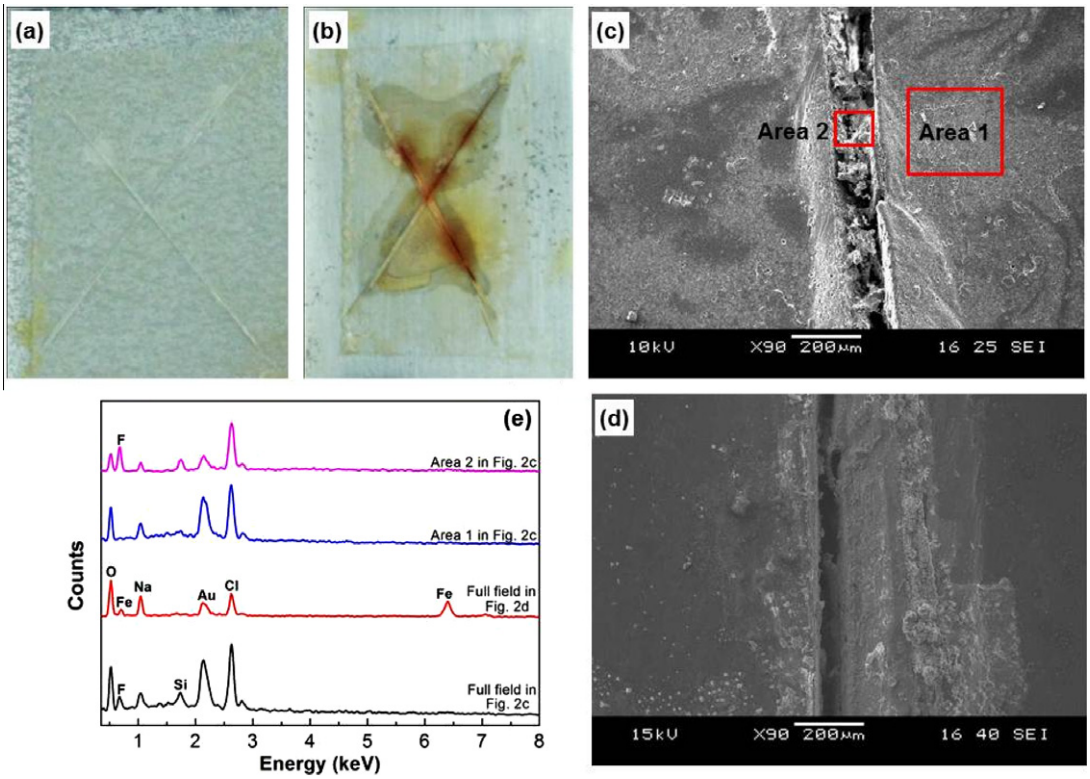

Fig. 2. Characterization of the self-healing coating with POTS microcapsules and the control coating. Optical images of the self-healing coating consisting 10 wt.% of POTS microcapsules in epoxy matrix (a) and neat epoxy control coating (b) after 48 h immersion in 10 wt.% NaCl solution. SEM images of the scribed regions of the self-healing coating (c) and control coating (d) after immersion. (e) EDX analysis of the self-healing coating as shown in (c) and control coating as shown in (d) after immersion.

specimen was still open after immersion (Fig. 2d), indicating no protection was over the exposed steel and a normal corrosion process occurred.

In order to further reveal the underlying mechanism for the corrosion protection behaviour, EDX analysis was performed to the scribed area of the coating surface to identify the elements distribution. Herein elements silicon (Si) and fluorine (F) were the focus of EDX analysis because POTS was the sole source for them in the system. If the newly formed materials in the scribes as shown in Fig. 2c were from encapsulated POTS, elements Si and F should be detected in the scribed area of the self-healing coating while absent in neat epoxy coating. From Fig. 2e, it is seen that the scribed area of the control coating afforded elements O, Na, Cl, Au and Fe. Considering that the epoxy polymeric coating itself contains O, a layer of gold was sputtered on the coating surface to perform the EDX analysis, and the specimen was immersed in sodium chloride solution, the presence of O, Na, Cl and Au is natural, while the element Fe was from the steel substrate. On the contrary, for the self-healing coating, it was seen that no detectable Fe was found in the scribed area; instead, elements Si and F were detected. It meant that the scribe of the self-healing coating was covered by a layer of material that contained elements Si and F. In the meantime, it was observed that Si and F were not detected at the intact area (Area 1 in Fig. 2c) of the self-healing coating. It suggested that elements Si and F were not detectable on the surface of the intact self-healing coating embedded with POTS-filled microcapsules. From these two aspects, it can be concluded that the elements Si and F within the scribed area were from the ruptured microcapsules. As a matter of fact, this conclusion can be further solidified by a direct analysis to the new materials generated within the scribed area (Area 2 in Fig. 2c) of the self-healing coating. As shown in Fig. 2e, the presence of Si and F is obvious in the newly formed materials within the crack when Area 2 was scanned. Hence, it can be concluded that the newly generated materials in the scribes of the self-healing coating were from the encapsulated POTS.

Electrochemical testing is able to rapidly illustrate the healing behaviour of a self-healing coating [30]. In such a testing, coated sample serves as one electrode in an electrochemical cell. An intact coating behaves as an excellent capacitor, but a scribed coating will afford high current since the underneath metal substrate directly contacts with electrolyte solution to form a circuit. If the scribes are re-sealed due to self-healing, the newly formed materials within the scribes will hinder the current flow in the circuit and therefore result in reduced current in the measurement. In the present study, the self-healing behaviour of the POTS microcapsules filled coating was further demonstrated by an electrochemical test when the immersion procedure was completed. A conventional three-electrode electrode system was used for the test, while the coated steel substrate served as the working electrode (Fig. 3a). When discrete potential swept, the current passing through the scribed coating was recorded. It should be noted that this electrochemical test is different from conventional polarisation test in corrosion study. Herein the main purpose of this study was to compare the capacitive property of the scribed coatings after a certain period of corrosion in the electrolyte solution, which was achieved by comparing the current flow through the self-healing sample to that through the control one under the same potential. Hence, a high potential sweep rate of 20 mV/s was used. As shown in Fig. 3b, for the scribed self-healing coating, the current passing through the coating was almost zero Ampere ($\sim$0.2 pA cm^{-2}) after healing process during immersion. The extremely low current density revealed the excellent capacitive or sealing property of the coating in the circuit. By comparison, current passing through the scribed control coating was 0.3 mA cm^{-2}, and the bare steel panel exhibited very high current flow. This significantly different electrochemical behaviour of the self-healing and control samples

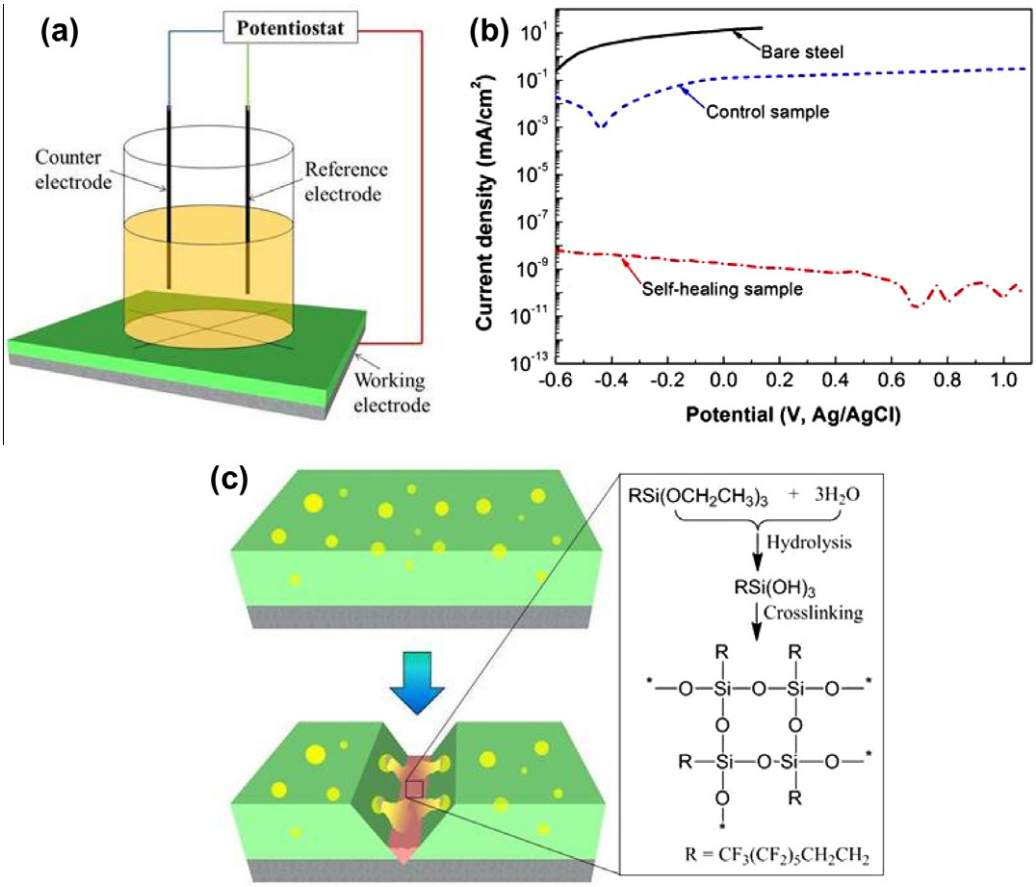

Fig. 3. Electrochemical testing and self-healing anticorrosion mechanism. (a) Schematic of electrochemical test. (b) Electrochemical results for the bare steel panel, scribed control and self-healed specimens. (c) Schematic anticorrosion mechanism of the self-healing coatings upon scratch.

clearly illustrated that the scribes in the self-healing coating were autonomously re-sealed during the immersion process, while the scribes in the control specimen were still open. However, it should be pointed out that the exact current density value of the self-healing coating as obtained from the test may not be accurate since the healed coating behaved as an excellent capacitor, which is not a suitable specimen for the electrochemical test. But as mentioned above, the recovered capacitive property undoubtedly revealed that the scribes were self-healed during the immersion.

Based on the results as discussed above, the mechanism of corrosion resistant behaviour of the prepared POTS-based coating can be hence proposed. As illustrated in Fig. 3c, when the coating was scribed, the embedded microcapsules were ruptured and the stored POTS liquid was released. Upon contact with water in solution or moisture in air, POTS initiated hydrolysis and poly-condensation reactions to produce a silane-based material depositing in the scribed areas [31]. The sealed damage separated the underneath steel substrate from external corrosive environment and thus exhibited quite good corrosion protection function. This re-sealing process occurred autonomously without any human intervention. In order to fully understand the self-healing performance and optimise the coating formulation of this system, comprehensive experiments including salt spray, electrochemical impedance spectrum analysis, and long-term corrosion in sea water are in progress.

4. Conclusion

The POTS-filled PUF microcapsules were synthesized via *in situ* polymerization reaction in an oil-in-water emulsion, and the diameter of the resultant microcapsules can be controlled by adjusting the agitation rate during the synthesis. The corrosion resistant coating was prepared based on microencapsulated POTS liquid, and it displayed quite good corrosion protection ability to steel substrate via a fully self-healing mechanism. The self-healing behaviour was realised under ambient condition, and it did not require any manual intervention such as heating or UV exposure, making it promising for the development of catalyst-free, one-part self-healing coatings, which is of considerable technical and commercial importance.

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References

[1] T.L. Metroke, R.L. Parkhill, E.T. Knobbe, Passivation of metal alloys using sol-gel-derived materials – a review, Progress in Organic Coatings 41 (2001) 233–238.
[2] D. Wang, G.P. Bierwagen, Sol-gel coatings on metals for corrosion protection, Progress in Organic Coatings 64 (2009) 327–338.
[3] R.L. Twite, G.P. Bierwagen, Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys, Progress in Organic Coatings 33 (1998) 91–100.
[4] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan, Autonomic healing of polymer composites, Nature 409 (2001) 794–797.
[5] S. van der Zwaag, Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science, Springer, Verlag, 2007.

[6] D.Y. Wu, S. Meure, D. Solomon, Self-healing polymeric materials: a review of recent developments, Progress in Polymer Science 33 (2008) 479–522.
[7] R.P. Wool, Self-healing materials: a review, Soft Matter 4 (2008) 400–418.
[8] S. Ghosh, Self-healing materials: fundamentals, design strategies, and applications, Wiley-VCH, 2009.
[9] J. Syrett, C. Becer, D. Haddleton, Self-healing and self-mendable polymers, Polymer Chemistry 1 (2010) 978–987.
[10] B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, S.R. White, Self-healing polymers and composites, Annual Review of Materials Research 40 (2010) 179–211.
[11] A.N. Khramov, N.N. Voevodin, V.N. Balbyshev, M.S. Donley, Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors, Thin Solid Films 447–448 (2004) 549–557.
[12] S. Cho, H. Andersson, S. White, N. Sottos, P. Braun, Polydimethylsiloxane-based self-healing materials, Advanced Materials 18 (2006) 997–1000.
[13] A. Kumar, L.D. Stephenson, J.N. Murray, Self-healing coatings for steel, Progress in Organic Coatings 55 (2006) 244–253.
[14] D.G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M.G.S. Ferreira, H. Mohwald, Layer-by-layer assembled nanocontainers for self-healing corrosion protection, Advanced Materials 18 (2006) 1672–1678.
[15] S.V. Lamaka, M.L. Zheludkevich, K.A. Yasakau, R. Serra, S.K. Poznyak, M.G.S. Ferreira, Nanoporous titania interlayer as reservoir of corrosion inhibitors for coatings with self-healing ability, Progress in Organic Coatings 58 (2007) 127–135.
[16] M.L. Zheludkevich, D.G. Shchukin, K.A. Yasakau, H. Mohwald, M.G.S. Ferreira, Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor, Chemistry of Materials 19 (2007) 402–411.
[17] C. Suryanarayana, K.C. Rao, D. Kumar, Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings, Progress in Organic Coatings 63 (2008) 72–78.
[18] S.H. Cho, S.R. White, P.V. Braun, Self-healing polymer coatings, Advanced Materials 21 (2009) 645–649.
[19] S.J. García, H.R. Fischer, P.A. White, J. Mardel, Y. González-García, J.M.C. Mol, A.E. Hughes, Self-healing anticorrosive organic coating based on an encapsulated water reactive silyl ester: synthesis and proof of concept, Progress in Organic Coatings 70 (2011) 142–149.
[20] I.A. Kartsonakis, A.C. Balaskas, E.P. Koumoulos, C.A. Charitidis, G.C. Kordas, Incorporation of ceramic nanocontainers into epoxy coatings for the corrosion protection of hot dip galvanized steel, Corrosion Science 57 (2012) 30–41.
[21] A. Yabuki, K. Okumura, Self-healing coatings using superabsorbent polymers for corrosion inhibition in carbon steel, Corrosion Science 59 (2012) 258–262.
[22] M. Huang, J. Yang, Facile microencapsulation of HDI for self-healing anticorrosion coatings, Journal of Materials Chemistry 21 (2011) 11123–11130.
[23] K. Aramaki, Preparation of chromate-free, self-healing polymer films containing sodium silicate on zinc pretreated in a cerium(III) nitrate solution for preventing zinc corrosion at scratches in 0.5 M NaCl, Corrosion Science 44 (2002) 1375–1389.
[24] K. Aramaki, Self-healing mechanism of an organosiloxane polymer film containing sodium silicate and cerium(III) nitrate for corrosion of scratched zinc surface in 0.5 M NaCl, Corrosion Science 44 (2002) 1621–1632.
[25] H. Gao, Q. Li, F.N. Chen, Y. Dai, F. Luo, L.Q. Li, Study of the corrosion inhibition effect of sodium silicate on AZ91D magnesium alloy, Corrosion Science 53 (2011) 1401–1407.
[26] Y. Li, L. Li, J. Sun, Bioinspired self-healing superhydrophobic coatings, Angewandte Chemie International Edition 49 (2010) 6129–6133.
[27] E. Brown, M. Kessler, N. Sottos, S. White, In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene, Journal of Microencapsulation 20 (2003) 719–730.
[28] J. Rule, N. Sottos, S. White, Effect of microcapsule size on the performance of self-healing polymers, Polymer 48 (2007) 3520–3529.
[29] J. Yang, M.W. Keller, J.S. Moore, S.R. White, N.R. Sottos, Microencapsulation of isocyanates for self-healing polymers, Macromolecules 41 (2008) 9650–9655.
[30] J.-H. Park, P.V. Braun, Coaxial electrospinning of self-healing coatings, Advanced Materials 22 (2010) 496–499.
[31] F. Zhang, S. Chen, L. Dong, Y. Lei, T. Liu, Y. Yin, Preparation of superhydrophobic films on titanium as effective corrosion barriers, Applied Surface Science 257 (2011) 2587–2591.