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Long-term performance of *1H, 1H′, 2H, 2H′*-perfluorooctyl triethoxysilane (POTS) microcapsule-based self-healing anticorrosive coatings

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Abstract

Self-healing anticorrosive coatings were prepared based on the microencapsulation of *1H,1H′,2H,2H′*-perfluorooctyl triethoxysilane (POTS). Toluene played a critical role in the successful synthesis of POTS microcapsules although it was not contained in the resultant capsules. The excellent corrosion-resistant property of a POTS microcapsule-modified silicone elastomer coating was demonstrated by a long-term corrosion test, in which the prepared coating was unscratched and exposed to HCl solution for 1 month, and the metal substrate was inspected after peeling off the coating by scanning electron microscopy and energy dispersive X-ray spectroscopy. In addition, the self-healing behavior of a scribed POTS-based epoxy coating was characterized by an electrochemical impedance spectroscopy measurement when the prepared coating was exposed to NaCl solution. The simulated parametric study from electrochemical impedance spectroscopy equivalent circuit demonstrated the process of corrosion-healing kinetics. The anticorrosive mechanism was proposed based on the self-healing functionality of POTS microcapsules.

Keywords

Self-healing, anticorrosive coatings, silane, microencapsulation

Introduction

Development of self-healing materials has drawn considerable attention since a few decades ago (Chung et al., 2004; Jud and Kausch, 1979). However, most of early self-healing materials are not real "self" healing because manual intervention is normally required such as energy input to deliver healing agent to the damaged locations (Trask et al., 2007; Williams et al., 2008) or to activate the healing process via heating or irradiation (Jud and Kausch, 1979). It is widely accepted that the first real self-healing material was developed by White et al. (2001), which was based on the polymerization reaction of dicyclopentadiene in the presence of Grubbs' catalyst. Since then, the research of self-healing materials has achieved great progress (Blaiszik et al., 2010; Ghosh, 2009; Syrett et al., 2010; Trask et al., 2007; Van der Zwaag, 2007; Wool, 2008; Wu et al., 2008). For modern self-healing materials, healing agents are usually stored in reservoirs that are incorporated within the host matrix. When the materials experience microcracking or damage event, the healing agents flow out from the reservoirs and autonomously repair the cracks via different chemical reaction to realize the expected self-healing function. According to the type of reservoirs, self-healing materials can be generally classified into microcapsules based, hollow tube based (Uhlig, 1971), and microvascular based (Bejan et al., 2006; Toohey et al., 2007). The application of self-healing coating for anticorrosion purposes has been widely explored, and most of self-healing anticorrosive coatings are microcapsules based due to the restriction of the coating thickness. To date, many healing species such as dicyclopentadiene (Brown et al., 2003; Kessler et al., 2003; White et al., 2001), linseed oil (Suryanarayana et al., 2008), amines (McIlroy et al., 2010), epoxy resins (Yuan et al., 2006), silyl ester (García et al., 2011), and diisocyanate monomer

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(Huang and Yang, 2011) have been encapsulated for self-healing anticorrosive applications.

Many strategies have been developed to evaluate the corrosion protection property of self-healing anticorrosive coating, such as visual inspection (Cho et al., 2009; Samadzadeh et al., 2011; Suryanarayana et al., 2008) and measurement of the coating adhesion (Loveday et al., 2004). Corrosion inherently is an electrochemical process, and electrochemical test is, therefore, extensively applied to study the corrosion protection function of self-healing coatings. Electrochemical test possesses significant advantages over other measures since it is able to provide quantitative information. Sometimes direct current electrochemical measurements were used (Cho et al., 2009; Park and Braun, 2010), but alternating current (AC) electrochemical impedance measurement for corrosion study has become more common. For example, García et al. (2011) employed electrochemical impedance spectroscopy (EIS) to evaluate the anticorrosion performance of an epoxy self-healing coating. The coating was based on encapsulated silyl ester, which will experience hydrolysis and cross-linking to produce a barrier layer to realize self-healing function. García et al. (2007) also used EIS to study the corrosion process of an epoxy coated low-carbon steel substrates when the specimens were immersed in 3.5 wt.% NaCl solution. In addition, Sauvant-Moynot et al. (2008) applied EIS to characterize corrosion process during their studies on corrosion protective coatings.

We have developed a self-healing anticorrosive coating based on the microencapsulation of *1H,1H′,2H,2H′*-perfluorooctyl triethoxysilane (POTS) (Huang et al., 2012). In this study, a more comprehensive investigation was performed to study the microencapsulation process, and the long-term corrosion-resistant performance of the unscratched coating was evaluated. In addition, self-healing property of the scribed POTS-based coating was characterized by an EIS measurement with simulated parametric study to show the process of corrosion-healing kinetics. A simplified model was proposed to explain the anticorrosive performance of the coating with incorporation of POTS microcapsules.

Experimental

Materials

Ethylene maleic anhydride copolymer, ammonium chloride, urea, resorcinol, 1-octanol, toluene, sodium hydroxide, hydrochloric acid (HCl), and sodium chloride were purchased from Sigma–Aldrich. POTS was obtained from Alfa Aesar. Epoxy resin and hardener Epolam 5015/5014 were obtained from Axson. Silicone resin and hardener Sylgard 184 were supplied from Dow Corning.

Preparation of POTS microcapsule-based coating

Poly(urea-formaldehyde) (PUF) microcapsules containing POTS as core materials were synthesized via an in situ polymerization as reported before (Huang et al., 2012). The agitation rate was carefully tuned so that the produced microcapsules had expected average diameter. The morphology and average diameter of the produced microcapsules were determined with scanning electron microscopy (JEOL JSM 5600LV SEM).

To prepare POTS microcapsule-based epoxy coating, the prepared POTS-filled PUF microcapsules were dried in open air for 2 days and then mixed into epoxy resin at ambient temperature, followed by blending hardener. The mixture was degassed for 20 min and then coated on 5 cm $\times$ 8 cm steel substrate. Prior to coating, the steel substrates were abraded by sand paper (grain size: 400), washed by deionized water and acetone for three times, and dried in open air. The coating was cured at ambient temperature in open air for 24 h.

A POTS microcapsule-based silicone elastomer was prepared in a similar manner by mixing synthesized POTS microcapsules into silicone resin. The microcapsule-loaded silicone resin was applied on pretreated steel substrate and was then cured at ambient temperature in open air for 24 h.

Long-term corrosion test

The prepared POTS-based anticorrosive silicone elastomer was exposed to 1 M HCl solution for 1 month, and the exposure area was set at 10 cm^2 by using a glass cylinder, which was clamped with a rubber O-ring on the coating surface. The cylinder was covered by a Parafilm to eliminate the evaporation of HCl solution. A neat silicone elastomer without microcapsules was used as control and treated in the same manner. After 1 month exposure, the silicone elastomer was peeled away from the steel substrate. SEM was employed to inspect the corroded area on the substrate, and energy dispersive X-ray spectroscopy (EDX) was used to demonstrate the elemental distribution on the corroded substrate surface. As a comparison, prior to the corrosion test, the surface of the steel substrate was characterized by SEM and EDX for both anticorrosive and control specimens.

EIS measurement

Cross scratches were applied manually using a razor blade on the prepared POTS-based self-healing coating following the standard method of ASTM D1654. The scratched coatings were immersed in 1 M sodium chloride solution to allow for corrosion and self-healing of the specimen, and EIS measurement was performed at a certain time interval. The EIS measurement was performed on a Gamry Reference 600 Potentiostat via a conventional three-electrode system. The electrolyte

solution was 1 M sodium chloride solution. The frequency range of study was 10^{-2}–10^{5} Hz with 10 steps per decade, and the AC amplitude was 10 mV. Software EIS 300 (Gamry) was used for data collection, and the obtained impedance plots were fitted with an equivalent circuit by software Echem Analyst (Gamry) as discussed later.

Results and discussion

Overview of POTS-based self-healing anticorrosive coating

In the synthesis of POTS-filled microcapsules, an in situ polymerization reaction occurred between urea and formaldehyde in the aqueous phase to form a PUF shell surrounding the oil phase that was composed of POTS and toluene. Toluene would evaporate away during the heated process when the reaction proceeds, leaving POTS as core materials in the final microcapsules. The average diameter of the produced microcapsules was linearly related to the agitation rate in double logarithm coordinates (Huang et al., 2012).

POTS-based self-healing anticorrosive epoxy coatings were prepared by dispersing synthesized POTS-filled PUF microcapsules into epoxy resin. During the synthesis, the agitation rate was carefully tuned so that the produced microcapsules had expected diameter. The microcapsules were well mixed into epoxy resin, which was then applied on pretreated steel panels and cured at ambient temperature for 24 h.

Similarly, the synthesized POTS microcapsules were integrated into silicone resin to prepare a corrosion-resistant silicone elastomer. The prepared elastomer has much weaker adhesion to metal substrate than epoxy, and this is a quite favorable property for long-term corrosion test as discussed below since the coating will be peeled off to inspect the corrosion on the underlying substrate.

In our previous study, the excellent anticorrosion function of a POTS-based epoxy coating was demonstrated in an accelerated salt immersion test (Huang et al., 2012). A self-healing anticorrosive epoxy coating was manufactured by integrating 10 wt.% of synthesized microcapsules with the average diameter of about 100 μm into epoxy resin. When the coating was applied on steel substrate, scribed, and then exposed to salt solution, it was found that the specimen was free from rust. On the contrary, after the same treatment, severe corrosion was observed on the control sample coated with pure epoxy. The significant difference in the extent of corrosion indicates the excellent corrosion protection property of the POTS-based self-healing coating.

Role of toluene in the formation of microcapsules

For microcapsule-based self-healing system, the self-healing performance is proportional to the amount of healing agents that is available for healing (Rule et al., 2007). Hence, when the microcapsules are synthesized for self-healing applications, it is desired that the produced microcapsules contain as much healing agents as possible given that other properties of the capsules remain the same. During the microencapsulation of POTS, the oil phase was the mixture of POTS and toluene. In order to achieve higher POTS content of the synthesized PUF microcapsules, the most straightforward method is to raise the POTS content in the oil phase when the emulsion solution was created. Unfortunately, it was found that the increase of POTS content in the oil phase would compromise the quality of the final microcapsules. When the oil phase was composed of POTS and toluene with the mass ratio of about 2:1, the produced microcapsules had regular and spherical shape as shown in Figure 1(a). However, when the mass ratio was increased to 4:1, the prepared microcapsules appeared irregular in shape, as shown in Figure 1(b). It was found that if the oil phase was composed of pure POTS, the expected microcapsules would not be produced since no stable emulsion was formed. Hence, it can be tentatively concluded that toluene

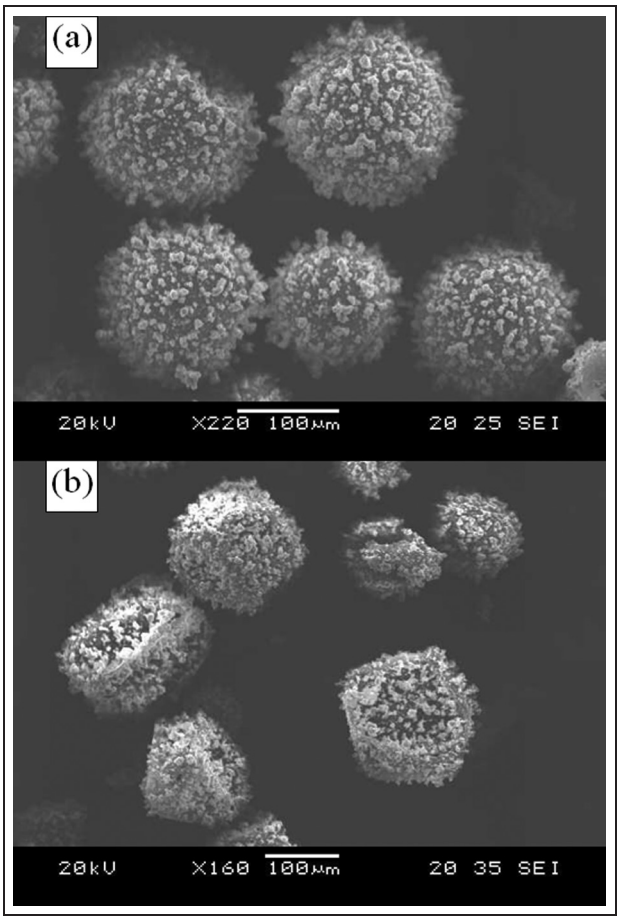

Figure 1. SEM image of POTS microcapsules with different mass ratio of POTS to toluene: (a) POTS/toluene = 2/1 and (b) POTS/toluene = 4/1.

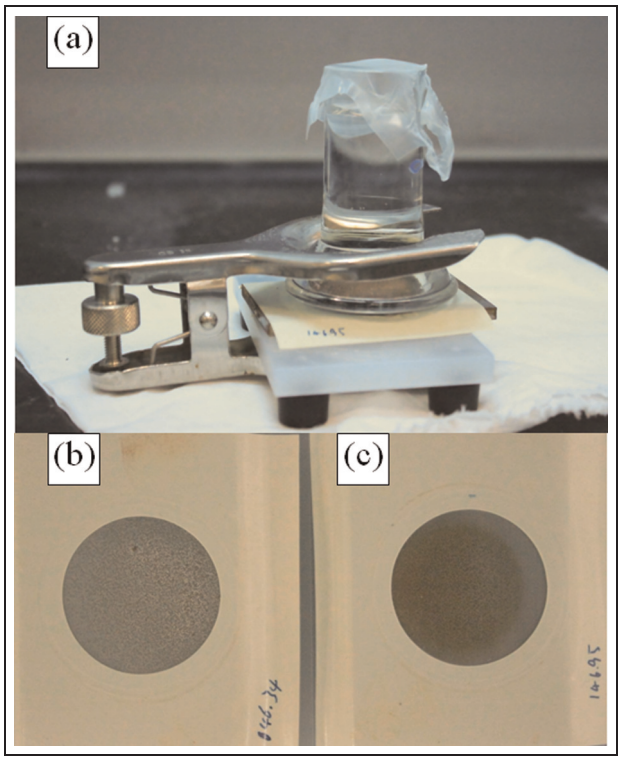

Figure 2. (a) Setup of long-term corrosion test to intact POTS-based self-healing anticorrosive coating, (b) specimen coated with POTS-based silicone coating after corrosion test, and (c) specimen coated with pure silicone coating after corrosion test.

served as a necessary auxiliary agent for stable emulsion although it would evaporate away when the synthesis proceeded. The optimal ratio of POTS to toluene in our study was determined to be 2:1. In this condition, the POTS content and quality of resultant microcapsules were optimally balanced.

Long-term corrosion test

The anticorrosion property of an intact POTS-based coating was demonstrated by a long-term corrosion test. Silicone elastomer was selected as the host matrix because it can be easily peeled away from steel substrate and hence the corrosion behavior of the steel substrates can be directly examined. POTS microcapsule-based silicone elastomer was coated on pretreated steel substrate and then exposed to 1 M HCl solution for 1 month. As shown in Figure 2(a), the area of the coating that was attacked by the corrosive acid was fixed by a glass cylinder. After 1 month of exposure, as illustrated in Figure 2(b) and (c), apparently the POTS-based anticorrosive silicone elastomer shows much less corrosion than the control specimen does. Such a difference clearly revealed that the POTS microcapsules significantly enhanced the corrosion-resistance property of the silicone elastomer.

In order to further demonstrate the anticorrosive performance of the POTS-based silicone coating to steel substrate during the exposure to HCl solution, the coating was peeled off after the corrosion test, and the underlying steel substrate was examined under SEM. It is seen that prior to exposure to the HCl solution, both steel substrates have smooth surface (Figure 3(a) and (c)). Nevertheless, after exposure, the surface of the anticorrosive specimen (Figure 3(b)) is much smoother than the control sample (Figure 3(d)). This considerable difference indicates that the steel substrate coated with POTS-based anticorrosive coating was much less corroded during the exposure to corrosive HCl acid solution.

It is known that corrosion of steel will convert iron (Fe) into rust (Fe_2O_3). Hence, for a steel panel, within a given area, the ratio of element O to Fe (O/Fe) will increase when corrosion occurs, and a higher O/Fe value in turn implies more corrosion. To compare the extent of corrosion on the steel substrate that was coated with POTS-based anticorrosive elastomer and control elastomer during exposure to the HCl solution, after the SEM inspection as discussed above, the same steel substrates were further analyzed by EDX to determine the O/Fe ratio of the substrate. As shown in Figure 3(e), before the specimens were exposed to HCl solution, the steel substrates of both anticorrosive specimen and control specimen afforded only element Fe. It means that the substrates were nearly totally free of corrosion. After exposure, elements O, Fe, and Si were detected on both specimens, but it can be seen that the O/Fe value was dramatically different between two specimens. The O/Fe of the substrate coated with POTS-based anticorrosive elastomer is 0.425 while that of the control sample is 1.148. Admittedly, the O/Fe difference between these two specimens alone is not very conclusive since the corrosion product may be quite complicated, and in the meantime, element O may come from other sources such as environment air and silicone elastomer. Nevertheless, if the influence of other factors is assumed to be at the same level for the two specimens in the test, which is a reasonable assumption, the apparently smaller O/Fe value of the anticorrosive specimen from another aspect consolidates the conclusion above that the substrate coated with the POTS-based anticorrosive coating is less corroded compared with the control specimen. From the SEM and EDX analyses, it can be concluded that the integration of POTS microcapsules enhanced the corrosion protection performance of the silicone elastomer coating.

EIS measurement and parametric study

The self-healing function of the POTS-based self-healing coating has been demonstrated in our previous study (Huang et al., 2012). The films formed on a scratched POTS-based coating were clearly shown by

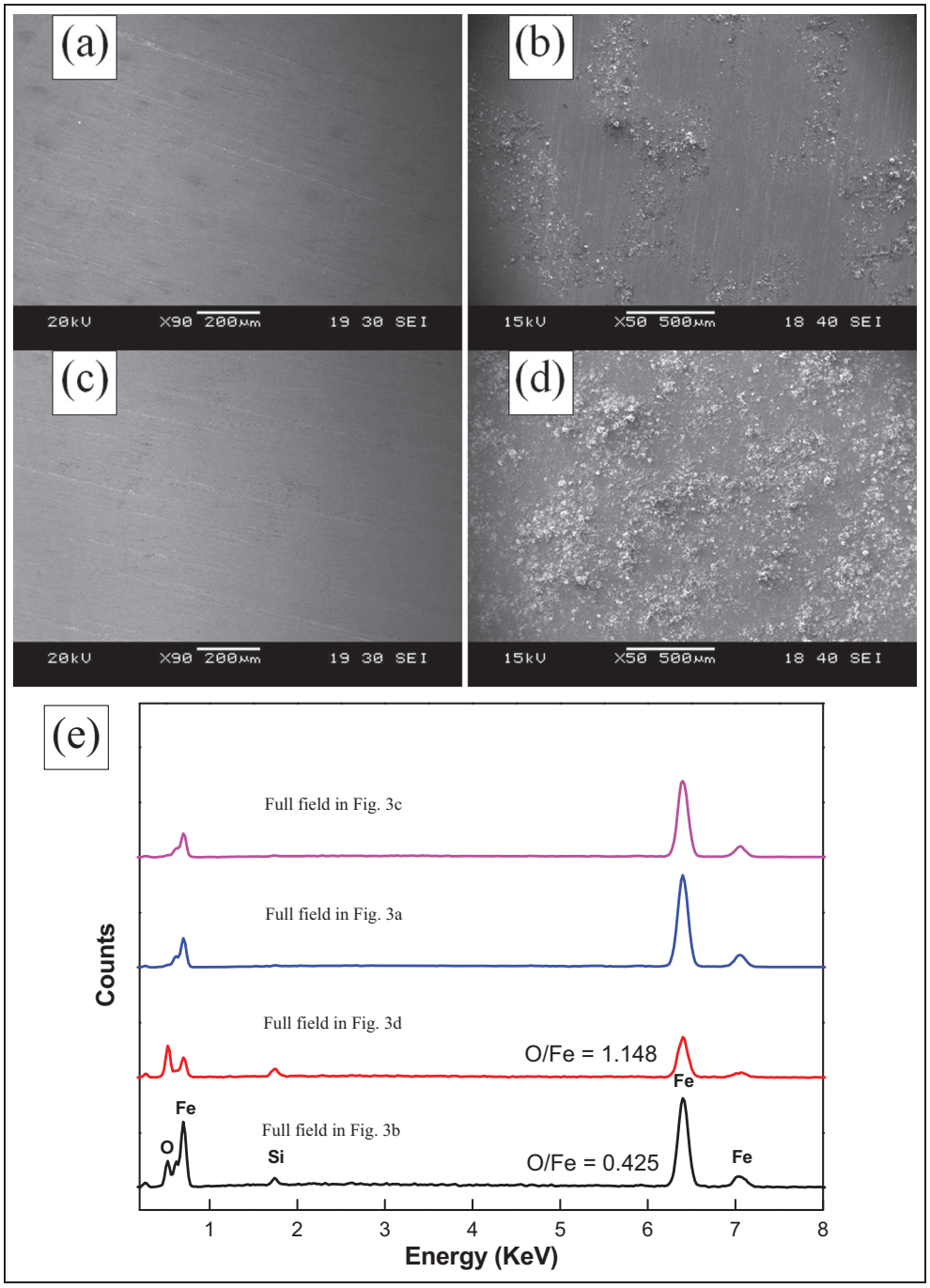

Figure 3. SEM and EDX analyses of steel substrate before and after exposure to HCl solution. Anticorrosive specimen (a) before and (b) after exposure; control specimen (c) before and (d) after exposure; (e) EDX analysis of these steel substrates.

SEM images when the scratched coating was immersed in salt solution for a period of time. The self-healing performance of the POTS-based coating was characterized by an EIS measurement. A conventional three-electrode system was used for the test, while the coated steel substrate served as the working electrode (Figure 4(a)). POTS-based self-healing epoxy coating was coated on pretreated steel substrate and then scratched manually. After that, the scratched specimen was immersed into 1 M of sodium chloride solution to allow for corrosion and self-healing. After a period of immersion, the impedance spectra of the specimen were obtained by EIS when the frequency was swept, and the change of impedance modulus (Z_{mod}) and phase angle of the circuit as a function of frequency were recorded. In order to interpret the EIS spectrum, a simplified model was constructed based on a proven model (Shchukin et al., 2006). As shown in Figure 4(b), when the microcapsule-loaded coating is scratched, the substrate was corroded by the corrosive electrolyte

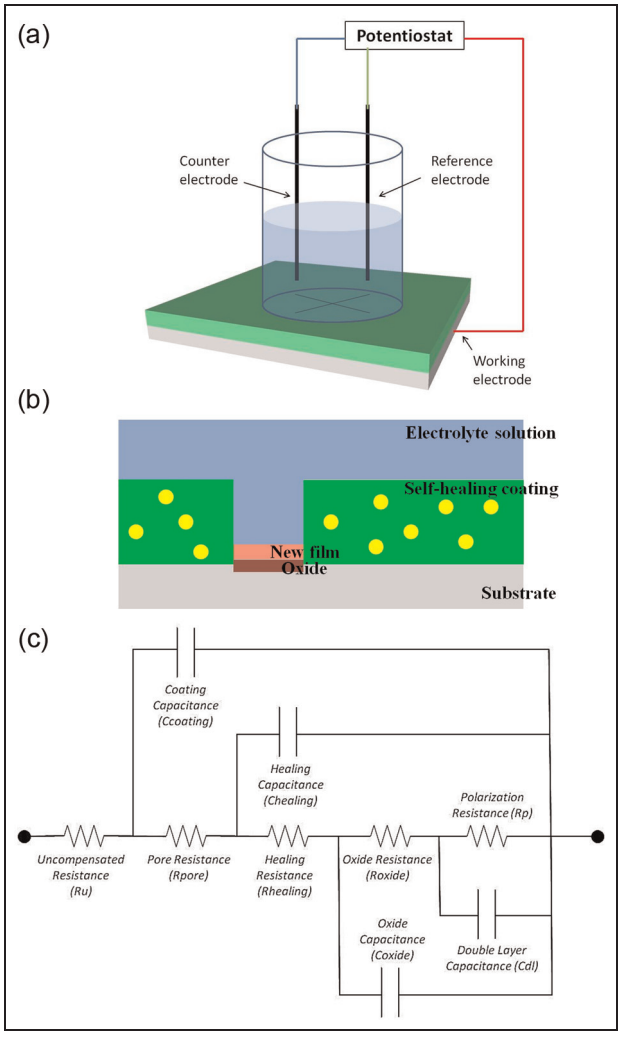

Figure 4. EIS measurement and equivalent circuit of POTS-based self-healing coating: (a) schematic diagram of the EIS measurement, (b) schematic diagram of a scratched self-healing coating in electrolyte solution, and (c) equivalent circuit of the scratched self-healing coating in EIS measurement.

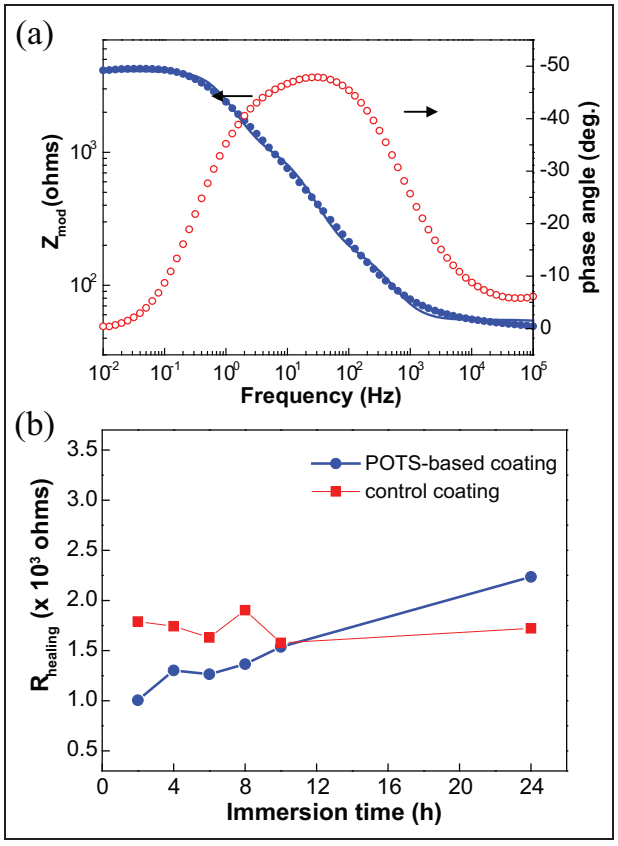

Figure 5. (a) Bode plots (impedance module, Z_{mod}, and phase angle) and fitted curve (solid line) of the scratched POTS-based coating after 8 h of immersion in 1 M salt solution. (b) Healing resistances ($R_{healing}$) of POTS-based self-healing coating and control coating when the coating was immersed in 1 M salt solution at different time durations.

solution to form an oxide layer, that is, rust. The scratch ruptures the embedded microcapsules to release POTS liquid, which will experience hydrolysis and polycondensation in moist environment to deposit a new film to cover the exposed substrate. Based on this simplified model, an equivalent circuit is established as shown in Figure 4(c). The equivalent circuit was used to fit the obtained EIS data in the data analysis. Although it is extremely complicated to assign the impedance spectra to the components of the circuit, the EIS data are able to provide some critical information regarding the self-healing behavior of the coating. If the self-healing behavior occurs at the scratched site, one of the most direct information from the EIS data will be the change of healing resistance ($R_{healing}$) and healing capacitance ($C_{healing}$).

Figure 5(a) shows the EIS spectrum of POTS-based self-healing coating after exposed to salt solution for 8 h, and the fitted curve was plotted as well. Based on the fitted curves, the values of each component in the equivalent circuit can be obtained: $R_u = 46.00\ \Omega$; $C_{coating} = 15.68 \times 10^{-6}$ F; $R_{pore} = 237.3\ \Omega$; $C_{healing} = 4.786 \times 10^{-9}$ F; $C_{oxide} = 12.56 \times 10^{-6}$ F; $R_{oxide} = 3.099 \times 10^3\ \Omega$; $C_{dl} = 62.99 \times 10^{-6}$ F; $R_p = 31.29\ \Omega$; $R_{healing} = 1.365 \times 10^3\ \Omega$. These values stand for the properties of the equivalent circuit when the POTS microcapsule-based coating was scribed and exposed to the salt solution for 8 h.

The values of each component of the equivalent circuit were similarly obtained when the specimen was immersed in salt solution for different time durations, and the $R_{healing}$ of the POTS-based self-healing coating as a function of immersion time was plotted in Figure 5(b). It was seen that generally the $R_{healing}$ of the self-healing coating exhibited an increasing trend. The $R_{healing}$ increased from about 1.0×10^3 to $2.2 \times 10^3\ \Omega$ when the immersion time increased from 2 to 24 h. Such an increase of the $R_{healing}$ is originated from the formation and increment of the new film, and it implies that the scribes of the coating were self-healed during the immersion. It was also found that the $R_{healing}$ value

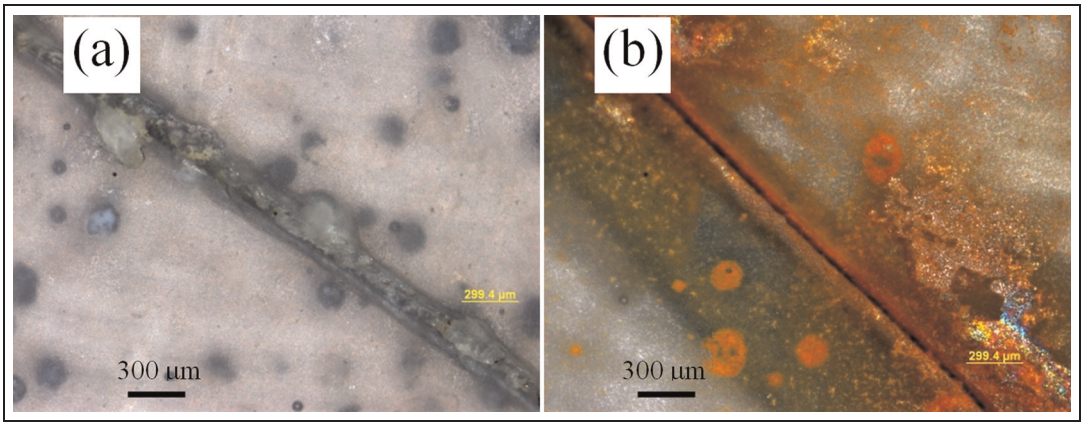

Figure 6. Microscope photographs of (a) POTS-based coating and (b) control coating after the immersion of the scratched specimens in salt solution for 48 h.

did not change too much when the immersion was extended further. On the contrary, it is seen that the $R_{healing}$ of the control coating that did not contain POTS microcapsules did not show such an increasing trend.

The new film generated in the scribes also served as a capacitor. The capacitance of a capacitor in an electric circuit is calculated as

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}$$

where A is the area of overlap of two plates, d is the distance between the plates, ε_0 is electric constant (about 8.854×10^{-12} F/m) and ε_r is the dielectric constant of the materials between the plates. In the present measurement, A was basically determined by the width and lengths of scribes and almost constant, and d is the thickness of the formed film. If the ε_r of the film within the scribes was constant, $C_{healing}$ should reduce with immersion since d was increasing due to the increment of the film. Unfortunately, the change of $C_{healing}$ did not show a clear trend in the whole process. This is reasonable since the compactness, content of moisture, and other properties of the newly formed film might vary when the healing process proceeded, and hence the change of ε_r also became very complicated. As a result, the change of the $C_{healing}$ during the immersion process was complicated and hard to predict.

A more straightforward proof of the self-healing function of the POTS-based coating is given by direct microscope examination. Figure 6 shows the microscope pictures of the POTS-based coating and control coating after the immersion process. It is clearly seen that the scratch of the POTS-based coating is sealed by a film, while that of the control coating is still open. In the meantime, the pictures revealed the similar width of the scratches on both specimens.

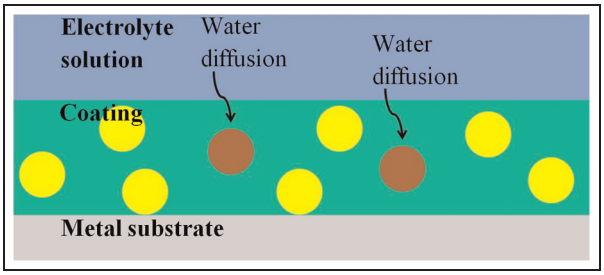

Figure 7. Schematic diagram of the corrosion-retardant effect of microcapsules in an intact POTS microcapsule-based coating.

Anticorrosive mechanism of POTS-based coatings

The self-healing mechanism has been proposed to explain the good anticorrosive performance of scratched POTS-based coating (Huang et al., 2012). The self-healing function of the coating was realized through the healing reaction of incorporated POTS liquid. As discussed above, it was observed that the intact POTS-based coating also exhibited better corrosion protection performance over blank coating when the coatings were exposed to corrosive HCl solution. The anticorrosive property of the unscratched microcapsule-based coatings can also be explained by the healing reaction of the healing agents, that is, POTS, that were prestored in the coating systems. Corrosion is an electrochemical process that requires the involvement of water. When metal is protected by a coating layer, although intact coating is able to effectively separate the substrate from corrosive environment, corrosion is still inevitable in terms of long-term effect since water may penetrate the coating via diffusion to corrode the substrate. For the POTS-based coating, the prestored POTS liquid was reactive with water. As illustrated in Figure 7, the water molecules may be trapped by POTS molecules during the

diffusion process. It means that the rate that the water passing through the coating layer will be retarded, and as a result, the corrosion of the underlying metal substrate will accordingly be retarded.

Conclusion

A novel class of self-healing anticorrosive coating was developed by incorporating POTS-filled PUF microcapsules into polymer coating matrix. During the synthesis of POTS microcapsules, toluene served as a necessary auxiliary agent for emulsion although it was not contained in the final microcapsules, and it was revealed that the optimal weight ratio of POTS to toluene is 2:1 for the microencapsulation.

The excellent corrosion-resistance property of unscratched POTS-based silicone elastomer coating was demonstrated by a long-term corrosion test. It was revealed by SEM examination that the steel substrate was less corroded when the specimen coated with the POTS-based coating was exposed to HCl solution for 1 month. The corrosion protection function of the POTS-based anticorrosive silicone coating was further solidified by EDX analysis. An anticorrosive mechanism was proposed to explain the good corrosion protection performance of intact POTS-based coating.

In addition, good self-healing performance of the POTS-based coating was demonstrated by EIS measurements. The results revealed that the scratched coating was autonomously self-healed due to the formation and increment of a new film formed within the scratches during exposure to salt solution, which was in agreement with the simulated self-healing parameter in an equivalent electrochemical circuit.

Declaration of conflicting interests

The authors declare that there is no conflict of interest.

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