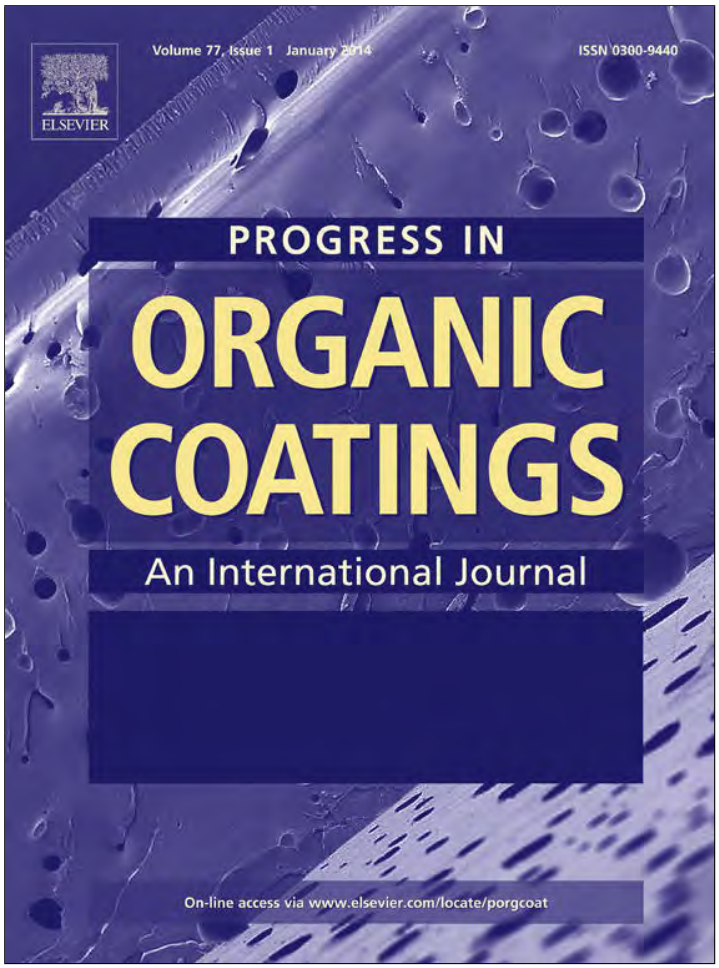

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Salt spray and EIS studies on HDI microcapsule-based self-healing anticorrosive coatings

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ABSTRACT

Anticorrosive property of hexamethylene diisocyanate microcapsule-based self-healing coatings was systematically investigated by salt spray and EIS measurements. The influences of microcapsule diameter, weight fraction and coating thickness on the anticorrosive performance of the scratched samples were studied under salt spray condition, which revealed the thicker coatings with larger microcapsules at 10 wt.% demonstrated the best anticorrosion behavior. Additionally, the kinetics of self-healing process characterized by EIS measurement was parametrically analyzed in an equivalent circuit when the scratched coating was exposed to salt solution. A simplified model was established to explain the influences of these factors with consideration of scratch dimension.

1. Introduction

Corrosion of metal is a worldwide issue in the field of materials [1,2], and corrosion inhibitors have been extensively used for corrosion control. The most widely used inhibitor is chromates, but they have been restricted in many countries due to their highly environmental toxicity [3]. Therefore, the concept of self-healing has recently been adopted as an alternative method for anticorrosion purpose. In recent years the research of self-healing materials has been well explored [4–10] since the first generation of autonomous self-healing material, which was based on encapsulated dicyclopentadiene and pre-dispersed Grubbs' catalyst particles [11], and to date, many healing species such as dicyclopentadiene [12,13], linseed oil [14], amines [15] and epoxy resins [16] have been encapsulated for self-healing applications.

For microcapsules based self-healing polymer materials, self-healing performance is influenced by factors such as the content of microcapsules in the polymer and diameter of microcapsules [17]. Rule et al. [18] pointed out that for a cracked self-healing material, the self-healing performance was directly related to the amount of healing agents that was available for delivery per unit crack area. Based on a simplified model, an equation was proposed to illustrate that the self-healing performance of a microcapsules-based self-healing material was proportional to the microcapsules weight fraction and diameter.

In our previous research, a facile method was developed to encapsulate liquid hexamethylene diisocyanate (HDI) monomer to fabricate a one-part self-healing anticorrosive coating [19]. A preliminary corrosion test was performed and the results showed excellent corrosion protection of the prepared coating to steel substrates, and it was revealed that the anticorrosion function of the coating was realized via a self-healing mechanism. In the present study, the self-healing anticorrosive property of the HDI microcapsule based coatings is evaluated by more systematical and comprehensive long-term salt spray test and quantitative electrochemical impedance spectroscopy (EIS) investigation.

2. Experimental

2.1. Materials

MDI prepolymer Suprasec 2644 was obtained from Huntsman. HDI, gum arabic, 1,4-butanediol, and sodium chloride were obtained from Sigma–Aldrich. Epoxy resin and hardener EPOLAM 5015/5014 were obtained from AXSON. All chemicals in this study were used without further purification unless otherwise specified.

2.2. Preparation of HDI based microcapsules and self-healing coatings

Polyurethane microcapsules containing HDI as core materials were synthesized through an interfacial polymerization as we reported before [19]. The agitation rate was carefully tuned so that the produced microcapsules had expected average diameter. The

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morphology and average diameter of the produced microcapsules were determined by using scanning electron microscopy (JEOL JSM 5600LV SEM).

The prepared HDI-filled microcapsules were dried at 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 × 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.

2.3. Salt spray test

Comprehensive salt spray test was performed to evaluate the corrosive protection function of the self-healing anticorrosive coating to metal substrates following standard method ASTM B117. A set of coatings with different formulations were prepared on steel substrates, and the edge and backside of the substrates were covered by water-resistant tape. The coatings were cross scratched following ASTM D1653 and then placed in salt spray chamber (QC 711, ComeTech). 5 wt.% of sodium chloride solution was used for fogging, and the temperature of the salt spray chamber was set at 35 ± 2 °C. The salt spray test lasted for 2 months.

2.4. EIS measurement

EIS measurement was also performed on the Gamry Reference 600 Potentiostat via a conventional three-electrode system as described in last section. 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).

3. Results and discussion

3.1. Overview of HDI microcapsule based self-healing anticorrosive coating

In the synthesis of HDI-filled microcapsules, an interfacial polymerization reaction occurred between Suprasec 2644 and 1,4-butanediol at the oil/water interface, while HDI was encapsulated into the created polyurethane microcapsules as core materials. As shown in Fig. 1a, the produced microcapsules have spherical shape with smooth outer surface. In our previous study, the excellent anticorrosion function of a HDI-based coating was demonstrated in an accelerated salt immersion test [19]. 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 10 wt.% salt solution for 48 h and stored in open air for 6 months at room temperature, as demonstrated in Fig. 1b, the microcapsules loaded coating was free from rust. On the contrary, as illustrated in Fig. 1c, severe corrosion was observed on the control coating that did not contain microcapsules after the same treatment. The significant difference in the extent of corrosion indicates the excellent corrosion protection property of the HDI microcapsule based self-healing coating.

3.2. Salt spray test

In order to better assess the anticorrosive performance of the HDI microcapsules incorporated epoxy coating, systematical long-term salt spray tests were performed following the standard test method ASTM B117.

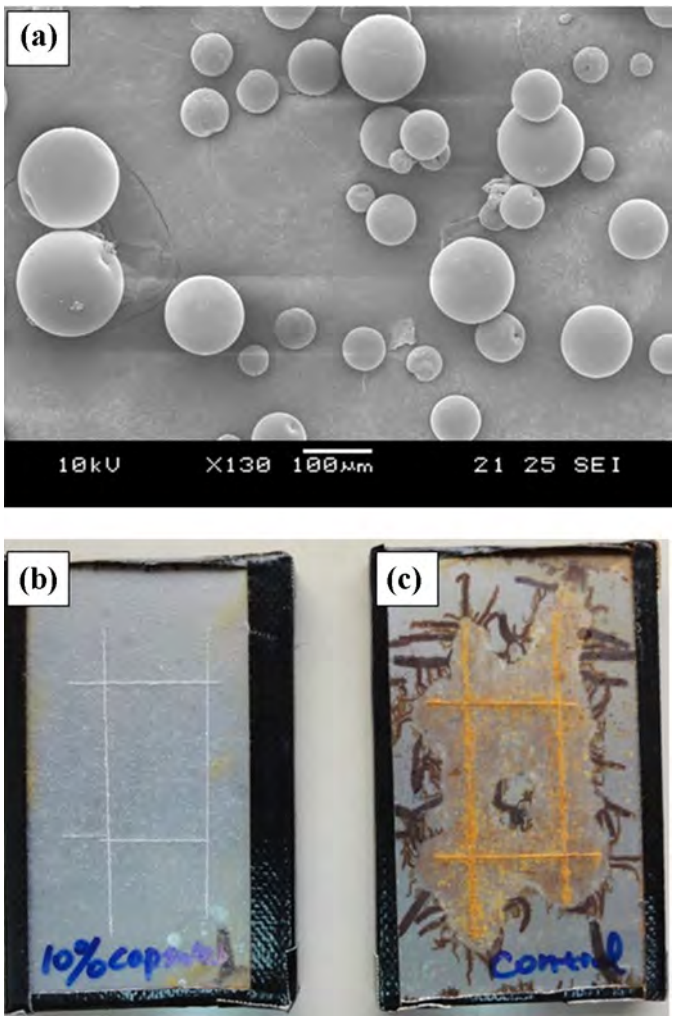

Fig. 1. (a) Morphology of HDI microcapsules, (b) steel panel coated with 10 wt.% HDI microcapsule incorporated self-healing coating and (c) steel panel coated with pure coating after immersion in 10 wt.% NaCl solution for 48 h and storage in open air for 6 months at room temperature.

The influences of three parameters, i.e. the average diameter of HDI microcapsules, weight fraction of microcapsules in coating and the thickness of final coating, on the corrosion protection ability of the coatings were investigated in the salt spray test. For each parameter three values were taken, so overall 27 formulations of coatings were prepared for the test. In addition, three pure epoxy coatings were prepared at different thicknesses as control. All the formulations of the coatings for the salt spray test are summarized in Table 1, and they are labeled in the format of SP-*D*-Φ-*H*, while three control samples were labeled as SP-Blk-*H*. Previous research has shown that the average diameter of the HDI-filled PU microcapsules synthesized through the interfacial polymerization reaction was highly dependent on agitation rate [19]. Therefore, in the present study the agitation rate was carefully tuned during the microcapsules synthesis so that microcapsules with the mean diameter of 100 μm, 50 μm and 30 μm were prepared.

The specimens coated with different HDI microcapsule based coatings were scribed and exposed to salt fog for two months in a monitored salt spray chamber. As shown in Fig. 2, it is seen that after exposure, all blank epoxy coatings (SP-Blk-400, SP-Blk-300, SP-Blk-200) with three different thicknesses were seriously corroded along the scribes, which is similar to the metal directly exposed in corrosive solution without any protection. Among the other 27 microcapsules modified coatings,

Fig. 2. Corrosion protection performance of the scratched HDI microcapsule based self-healing coatings and control coatings after exposure to salt spray for 2 months.

SP-100-10-400 and SP-100-10-300 showed no rust, indicating the excellent corrosion protection performance was achieved in the coatings with thickness not less than 300 μm and capsule content at 10 wt.%. In the meantime, slight rust was observed on the coatings SP-100-10-200, SP-100-5-400, SP-100-5-300 and SP-100-5-200, meaning the formulations with either thinner coating of 200 μm or lower capsule content at 5 wt.% could provide corrosion protection to some degree. For the rest of formulations (as shown in

Table 1
Formulations of HDI microcapsules based epoxy coating. Naming policy of samples is used as SP-*D*-Φ-*H* for self-healing samples where SP means salt spray test, *D* is average diameter of microcapsules, Φ is weight fraction of microcapsules in coating, and *H* is thickness of coating. Blk in SP-Blk-*H* for control samples means blank coating.

D (μm)	Φ (wt.%)	*H* (μm)	Name of samples
100 ± 31.6	10	400, 300, 200	SP-100-10-400; SP-100-10-300; SP-100-10-200
	5		SP-100-5-400; SP-100-5-300; SP-100-5-200
	2		SP-100-2-400; SP-100-2-300; SP-100-2-200
50 ± 17.2	10		SP-50-10-400; SP-50-10-300; SP-50-10-200
	5		SP-50-5-400; SP-50-5-300; SP-50-5-200
	2		SP-50-2-400; SP-50-2-300; SP-50-2-200
30 ± 9.4	10		SP-30-10-400; SP-30-10-300; SP-30-10-200
	5		SP-30-5-400; SP-30-5-300; SP-30-5-200
	2		SP-30-2-400; SP-30-2-300; SP-30-2-200
Control (pure epoxy)	0		SP-Blk-400; SP-Blk-300; SP-Blk-200

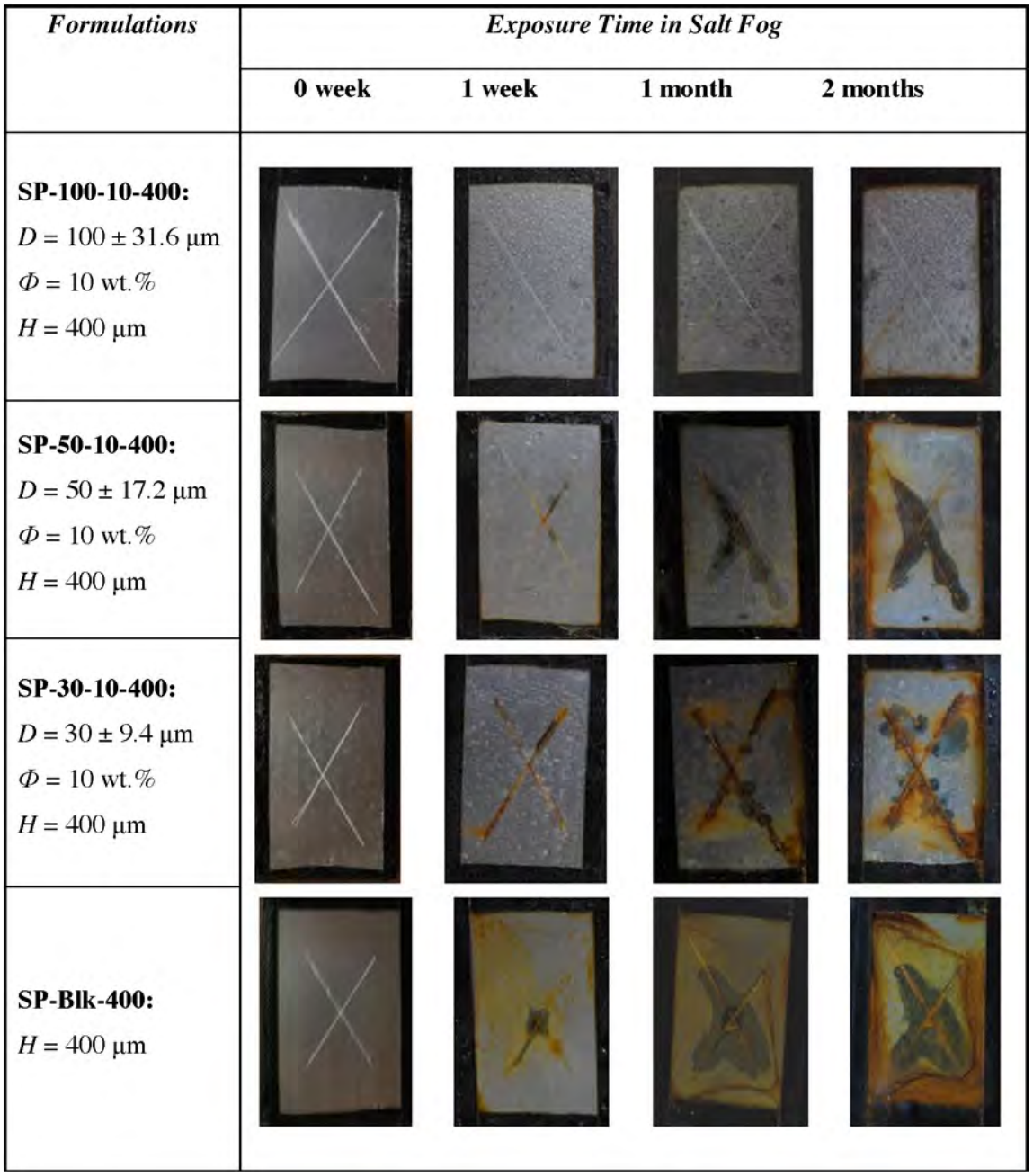

Fig. 3. Influence of exposure time and capsules diameter on the anticorrosive performance of HDI microcapsules based self-healing coatings.

Fig. S1), severe corrosion was observed along the scribes, indicating the protection of these coatings to steel substrates was quite poor. The results reveal that the HDI microcapsule based epoxy coatings exhibit good corrosion protection function to metal substrate if properly formulated.

The corrosion protection performance of the HDI microcapsules based coating was influenced by the weight fraction of microcapsules in the coating and the coating thickness. In Fig. 2, for the nine HDI microcapsules based coating, the diameter of the incorporated microcapsules remained at 100 μm, while the weight fraction of microcapsules and coating thickness varied for each formulation. If we compare the specimens in each row, in which the weight fraction of microcapsules remained, it could be seen that, generally, more rust was observed on the specimens with smaller coating thickness. If the specimens in each column, in which the coating thickness was the same, were compared, it could be found that the corrosion was more severe when the weight fraction of capsules declined. Similar trend can also be found from other specimens. The results imply that higher microcapsule content in the coating as well as larger coating thickness is favorable for the HDI based self-healing anticorrosive coating. It should be pointed out that although the edge and backside of the substrate was protected by water resistant tape during the salt spray test, some corrosion still occurred at the non-coated part. That is why much of yellowish rust was seen on the specimen although the real corrosion was much less as for specimen SP-100-5-400 in Fig. 2.

It was found from the salt spray test that the growth of corrosion was related to exposure time. Fig. 3 demonstrates the process that corrosion developed on three HDI microcapsules based coatings (SP-100-10-400, SP-50-10-400 and SP-30-10-400) and one control sample (SP-Blk-400) when the salt spray test proceeded. It is seen that corrosion started to appear on SP-50-10-400, SP-30-10-400 and SP-Blk-400 from the first week, and more and more rust was observed when the exposure time of the specimens in salt fog increased. The same dynamic effect of exposure time was also observed on other specimens during the salt spray test, as shown in Fig. S2. This is a reasonable result because corrosion is an electrochemical process, and it proceeds with time.

Fig. 3 also reveals the influence of microcapsules size on the corrosion protection ability of the microcapsules based coating. The three formulations, SP-100-10-400, SP-50-10-400 and SP-30-10-400, differed only in the average diameter of the HDI microcapsules, while the other two parameters of self-healing coatings remained. It is seen that specimen SP-100-10-400, in which the diameter of HDI microcapsules was 100 μm, was almost free from rust, while specimen SP-30-10-400, in which the diameter of microcapsules was 30 μm, showed most serious corrosion. The extent of corrosion of specimen SP-50-10-400 was between that of these two specimens. Actually the comparison of other specimens also showed similar trend, in which the coatings exhibited best corrosion resistance performance when the diameter of incorporated microcapsules was 100 μm, followed by the 50 μm specimens and the 30 μm specimens showed worst corrosion protection, as shown in Fig. S1. This results indicate that the HDI microcapsules based epoxy coating afforded better corrosion protection toward metal substrate when the diameter of microcapsules was bigger, given other parameters of the coating remained. This result is in good agreement with that reported in previous publication [18].

As discussed above, the salt spray test of the HDI based self-healing anticorrosive coating reveals that the microcapsules size, weight fraction of microcapsules in coating and the coating thickness all significantly influenced the anticorrosion performance of the prepared coating. Generally, larger microcapsules size, higher microcapsules content and thicker coating would afford better corrosion protection. In addition, In addition, from the salt spray test, it is indicated that for the HDI based self-healing coating, in order to achieve good corrosion protection performance, the diameter of HDI microcapsules should be larger than 100 μm, the weight fraction of capsules should be higher than 5 wt.% and the coating thickness should be larger than 300 μm.

The standard salt spray test provided comprehensive information about the anticorrosive performance of the HDI based self-healing coating. Nevertheless, it is noteworthy that there are also some shortcomings for this test. For example, this test affords only qualitative results, so if the corrosion protection abilities of two specimens are only slightly different, this test will be unable to differentiate them. In addition, there are also several systematic errors with the test. For example, the specimens were manually scratched before exposure to salt fogging. Although the standard method ASTM D1654 was obeyed when the scratches were made, it is still impossible to ensure that all the scribes were the same on each specimen, and this will definitely introduce some variation to the test results. Some other factors influencing the test results include the quality of prepared microcapsules, distribution of microcapsules in coating, the position of specimen in the salt spray chamber and so on. However, despite of these shortcomings, salt spray test is a valuable method to evaluate the anticorrosive function of coatings. Specifically, in our study it was confirmed from the test that by optimizing the formulation, HDI based self-healing epoxy coating could provide excellent corrosion protection to metal substrates.

3.3. EIS measurement

The self-healing performance of the HDI based coating was further characterized by EIS measurement. A conventional three-electrode system was used for the test, while the coated steel substrate served as the working electrode (Fig. 4a). The impedance modulus (Z_{mod}) and phase angle of the circuit were recorded when the frequency was swept from 10^5 Hz to 10^{-2} Hz. In order to interpret the EIS spectrum, a simplified model was constructed based on a proven model [20]. As shown in Fig. 4b, when the microcapsules loaded coating is scratched, the substrate was corroded by the corrosive electrolyte solution to form an oxide layer, i.e. rust. The scratch ruptures the embedded microcapsules to release HDI monomer, which will react with water to form a new film to cover the exposed substrate. Based on this simplified model, an equivalent circuit is established as shown in Fig. 4c. 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 is 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 ($C_{healing}$).

Fig. 5a shows the EIS spectrum of HDI-based self-healing coating after exposed to salt solution for 8 h. From the spectrum one can find the change of impedance modulus (Z_{mod}) and phase angle as a function of the frequency. The equivalent circuit was used to fit the obtained EIS data by Gamry software, and the fitted curves were plotted in Fig. 5a as well. Based on the fitted curves, the values of each component in the equivalent circuit can be obtained: $R_u = 22.01\ \Omega$; $C_{coating} = 13.79 \times 10^{-6}$ F; $R_{pore} = 269.7\ \Omega$; $C_{healing} = 7.543 \times 10^{-9}$ F; $C_{oxide} = 176.2 \times 10^{-6}$ F; $R_{oxide} = 16.55 \times 10^3\ \Omega$; $C_{dl} = 23.64 \times 10^{-6}$ F; $R_p = 21.09\ \Omega$; $R_{healing} = 2.377 \times 10^3\ \Omega$. These values stand for the properties of the equivalent circuit when the HDI microcapsules based coating was scratched and exposed to salt solution for 8 h.

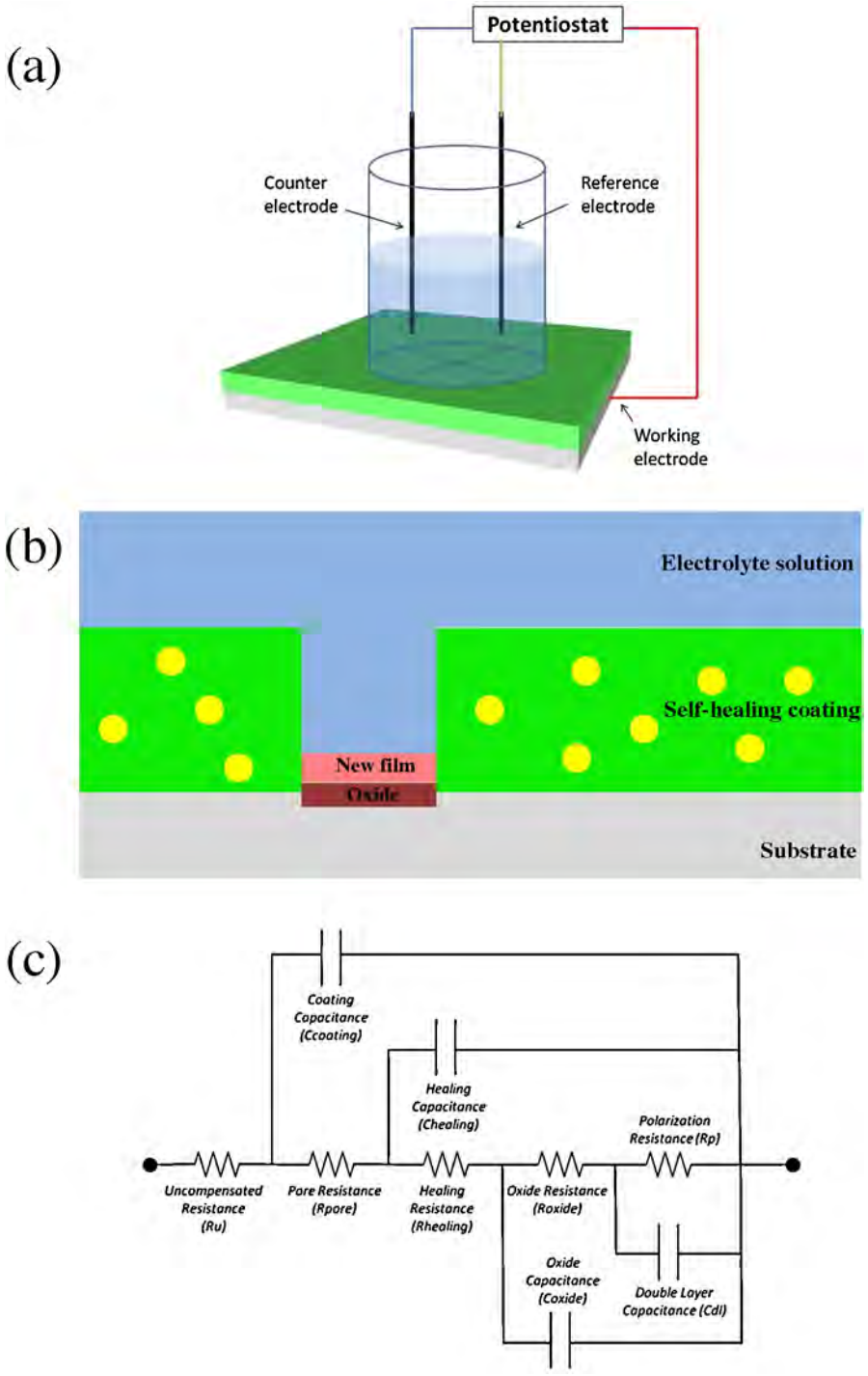

Fig. 4. EIS measurement and equivalent circuit of HDI-based self-healing coating. (a) Schematic diagram of the EIS measurement, (b) schematic diagram of a scratched self-healing coating in electrolyte solution and (c) equivalent circuit of the scratched self-healing coating in EIS measurement.

The values of each component of the equivalent circuit can be hence similarly obtained when the specimen was immersed in salt solution for different time, and the $R_{healing}$ of the HDI-based self-healing coating as a function of immersion time was plotted in Fig. 5b. It could be seen that generally the $R_{healing}$ of the self-healing coating exhibited a trend of increase with immersion time. When the immersion increased from 2 h to 24 h, the $R_{healing}$ increased from 1.90×10^3 Ω to 4.65×10^3 Ω. 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 is seen that evolution in the scribes is completely autonomous. Hence, such a change confirms the excellent self-healing behavior of the HDI-based coating during the immersion in salt solution.

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

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \quad (1)$$

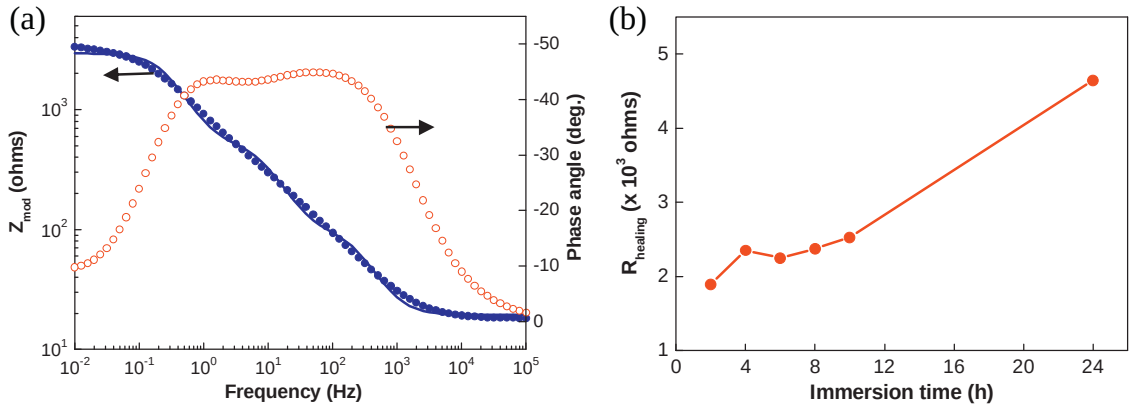

Fig. 5. (a) Bode plots (impedance module, Z_{mod}, and phase angle) and fitted curves (solid line) of scratched HDI-based coating after 8 h of immersion in 1 M salt solution. (b) Healing resistances ($R_{healing}$) of HDI-based self-healing coating when the coating was immersed in 1 M salt solution for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

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 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.

3.4. Influences of variables on anticorrosion property

The salt spray test has revealed that the anticorrosion performance of the coating was considerably influenced by the diameter of the HDI microcapsules, the weight fraction of microcapsules in coating and the coating thickness. The anticorrosive function of the scribed HDI-based coating was mainly realized though a self-healing mechanism [19]. Hence, the influences of these three factors on the anticorrosive property of the coating are discussed in terms of the self-healing behavior [18].

The discussion below is based on several assumptions: (a) the microcapsules with uniform diameter are evenly distributed in the coating matrix; (b) the fill content of each microcapsule is the same; (c) the shell of the microcapsules is negligible; (d) when a scratch forms in the coating, all of the microcapsules located at the scratch plane are ruptured; (e) all of the encapsulated healing agent of ruptured microcapsules will freely flow into the scratch; (f) the healing species will spread within the scratch.

Consider a rectangle microcapsules-based coating is penetrated by a planar scratch as shown in Fig. 6. Microcapsules with uniform diameter (d) are randomly distributed in the coating matrix. When a planar scratch penetrates the coating, all of the microcapsules lying in the scratch will be ruptured to release the healing species.

The number of microcapsules that are ruptured (n) is:

$$n = N \times P \tag{2}$$

where: N = total number of microcapsules in the coating; P = probability that a microcapsule gets ruptured.

Because the microcapsules were distributed evenly in the coating, the probability is:

$$P = \frac{Ad}{M/\rho} = \frac{\rho A d}{M} \tag{3}$$

where: A = area of the scratch plane; d = diameter of the microcapsules; M = mass of the coating; ρ = density of the coating.

The total number of microcapsules in the coating can be calculated as:

$$N = \frac{\Phi \times M}{m} \tag{4}$$

and the area of the scratch plane is:

$$A = H \times L \tag{5}$$

where: Φ = weight fraction of microcapsules in the coating; m = mass of one microcapsule; H = thickness of coating; L = length of the scratch.

Combine Eqs. (2)–(5), the number of microcapsules ruptured by the scratch is calculated as:

$$n = \frac{\rho \Phi H L d}{m} \tag{6}$$

In a typical self-healing material, the amount of the delivered healing agents has to be normalized by the area of the scratch plane since it is expected that the entire scratch plane is reconnected and re-bonded [18]. Nevertheless, for corrosion protection purpose, the basic requirement is that the exposed substrate is covered by the healing agents in the whole length of the scratch with a certain width, while the agents do not have to completely fill the entire scratch depth. Therefore, the amount of the delivered healing agents is normalized by the scratch projection area as below:

$$m_0 = \frac{n \times m}{t \times L} = \frac{\rho \Phi H d}{t} \tag{7}$$

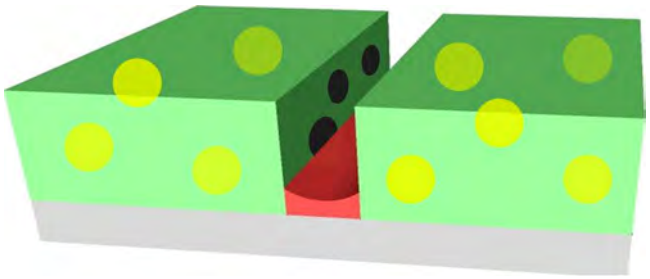

Fig. 6. Schematic diagram of a scratched microcapsules based coating.

where: t = width of the scratch.

For a given microcapsules based coating, the density of the coating (ρ) is basically determined by the coating matrix itself if the fraction of microcapsules is not too high, and hence it can be seemed as a constant. From Eq. (7), it is seen that the amount of healing species available at the scratched sites is proportional to the weight fraction of microcapsules (Φ), diameter of microcapsules (d) and thickness of coating (H). In addition, as mentioned above, the anticorrosion function is realized through a self-healing mechanism, and better self-healing property indicates better anticorrosion property. Therefore, the corrosion protection performance is accordingly also positively related to the microcapsules diameter, microcapsules weight fraction and coating thickness. This conclusion is in good consistence with the results as observed in the salt spray test, and is also in line with results reported before [18]. Furthermore, although the effect of the scratch width to the corrosion protection function of the coating was not investigated in our study, it is seen from Eq. (7) that the corrosion protection function of the microcapsules based coating should be inversely related to the width of the scratch (t). It suggests that a wider scratch is more difficult to be self-repaired by the coating itself.

As discussed above, when a microcapsules based self-healing anticorrosive coating is damaged, the corrosion protection function of the coating will be restored as long as the scratch is covered by the released healing agents, although the agents may not completely fill the entire scratch depth. Nevertheless, when the long-term corrosion protection function is considered, it is desired that the scratch depth is filled as much as possible by the healing agents since external corrosive solution may slowly diffuse through the newly formed materials within the scratch and eventually reach the underlying substrate. The extent that the released healing agents fill up the scratch can be expressed by filling efficiency (η), which is defined as the ratio of the height of the healing agents within the scratch to the depth of the scratch when a microcapsules based coating is damaged.

The volume of the healings agents flowing into the scratch is:

$$V = \frac{n \times m}{\rho_{\text{healant}}} = \frac{\rho \Phi H L d}{\rho_{\text{healant}}} \tag{8}$$

where: ρ_{healant} = density of the healing agent.

The height of the agent within the scratch is:

$$h = \frac{V}{t \times L} = \frac{\rho \Phi H d}{t \times \rho_{\text{healant}}} \tag{9}$$

Therefore, the scratch filling ratio (η) by healant can be calculated as:

$$\eta = \frac{h}{H} = \frac{\rho \Phi d}{t \times \rho_{\text{healant}}} \tag{10}$$

For a given microcapsules based coating, the density of the coating (ρ) and the healing agents (ρ_{healant}) are known and constant for the fixed formulation. It is seen from Eq. (10) that the scratch filling ratio is proportional to the diameter of incorporated microcapsules (d) and their weight fraction in the coating (Φ), but reversely related to the width of the scratch (t). Here only healant is considered without further reaction for simplified analysis. In the practical case, healant will react with water to produce the final product to seal scratch. The actual sealing efficiency or equivalent anticorrosive performance will be highly dependent on the properties of the final product, such as its bonding strength with matrix, density, thickness, water diffusivity, etc., the study on which is beyond the scope of the current work.

4. Conclusion

HDI was encapsulated into PU microcapsules through an interfacial polymerization, and the prepared capsules were used to develop self-healing anticorrosive coatings. A salt spray test was performed following the standard method of ASTM B117 to the prepared coatings to evaluate their anticorrosion property, and the results revealed that the prepared coating exhibited excellent corrosion resistant function if it was properly formulated. In order to achieve good anticorrosion property, the average diameter of the HDI-filled microcapsules should not be smaller than 100 μm, and the weight fraction of capsules should not be lower than 5%. The self-healing performance of the HDI-based coating was demonstrated by EIS measurement, and the results revealed the formation and increment of a new film formed within the scribes of the HDI-based coating. Such an evolution in the scribes indicates the self-healing behavior of the HDI-based coating when the coating was immersed in salt solution. In addition, the influences of three parameters, microcapsules diameter, microcapsules weight fraction and coating thickness, on the anticorrosion performance of the coating was investigated, and a simplified model was established to explain the influences of these parameters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.porgcoat.2013.09.002.

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