SIMULTANEOUS OPTICAL AND ELECTROCHEMICAL MONITORING
OF THE PROTECTIVE EFFECT OF FUNCTIONAL SURFACE
HEALING AGENTS

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Keywords: corrosion protection, capsules, coating, silane, hydrophobicity, optical analysis

ABSTRACT

Encapsulation of reactive agents embedded within a matrix is the most studied concept to develop self-healing materials. The most common approaches employ either a single component with catalyst dispersed in the matrix or a single environment-reactive component for corrosion protection [1].

Recently an approach for corrosion protection based on a single reactive healing agent that combines wetting, reactivity with ambient humidity and the underlying metallic surface, hydrophobicity and densification in time was proposed [2]. Following this idea of using silyl esters, Huang et al. developed a similar system where 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) was used in place of a silyl ester [3]. Despite the good results offered by the octyldimethylsilyl ester and the POTS, there is room for improvement in the design of the healing agents employed for corrosion protection.

The goal of this research is to better understand the wetting, barrier and densification properties of silane based healing agents to be able to develop efficient single reactive healing agents. Therefore a selection of silanes with different chemical backbone structure and surface-reactive end group is evaluated. The barrier properties and the hydrophobicity of the agents is investigated to gain insight into the relationship between chemical structure and final thin film properties. Moreover, in order to evaluate the time dependent corrosion protection performance of the different healing agents a novel optical-electrochemical analysis technique has been developed.

1. INTRODUCTION

Self-healing coatings is a rapidly growing research field. Concepts such as encapsulation of single reactive agents allow the integration of the healing functionality into existing coating technology. The research focuses mainly on new carrier systems, new release concepts, and new protective agents. This research aims at investigating the abilities of silane based healing agents to prevent corrosion of an underlying aluminium alloy exposed to a sodium chloride solution. Additionally, a simultaneous optical and electrochemical technique was developed. This technique allowed monitoring the time dependent corrosion protection performance of functional surface healing agents.
2. EXPERIMENTAL

An aluminium alloy AA2024-T3 sheet was employed as a substrate due to its frequent use in the aerospace and automotive industry and for its low corrosion resistance when compared to other aluminium alloys [4]. Several different silane chemistries were chose as surface healing agents. In this work, three silanes with a trimethoxysilane end group and an alkyl chain of varying lengths of 6, 8 and 10 carbons long for hexyltrimethoxysilane, octyltrimethoxysilane and decyltrimethoxysilane respectively were evaluated. These systems allow a direct correlation between the alkyl chain length and the hydrophobicity and corrosion protection properties. The metallic samples were cut in small coupons of 2x2cm and grinded using 1000 grit followed by sonication in acetone for 15min and air drying before exposure to the silanes. After the surface treatment a single droplet of 2.5µl of undiluted silane was deposited over the substrate using a micro-pipette. The strong wetting capabilities of silanes allowed a rapid coverage. The samples were left at open air to allow hydrolysis and condensation for 24h, leading to the formation of a thin film coating on the metal. The hydrophobicity of the coatings was characterized using a goniometer with 5µl drops of ionized water. Finally, corrosion protection was characterized by potentiodynamic polarization scans in a conventional three electrode set-up at a scanning rate of 1mV/s, and by a self-developed corrosion imaging analysis technique for the immersion prior to the potentiodynamic polarization test. The tests were performed under 0.5M NaCl solution in deionized water. The analysis procedure uses image processing software to quantify the number of pits forming during the total immersion time (120 min) followed by the quantification of the corrosion current density by polarization tests.

3. RESULTS

Table 1 shows that the addition of silanes on the surface does not increase the hydrophobicity of the AA2024 in a significant grade. Moreover, the results show a reduction of the contact angle for the longest carbon chain silane (decyltrimethoxysilane (C10)) compared to the other samples.

Table 1: Contact angle (CA) values for the bare substrate and alkyltrimethoxysilanes with three different alkyl chain lengths as indicated by the number of carbons. The values are averages of 4 different measurements and measured between 10 and 30 seconds after deposition of a 5µl deionized water drop.

<table>
<thead>
<tr>
<th></th>
<th>Bare</th>
<th>C6</th>
<th>C8</th>
<th>C10</th>
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<tbody>
<tr>
<td>CA (°)</td>
<td>83±1.0</td>
<td>84±0.6</td>
<td>85±0.5</td>
<td>77±0.3</td>
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Figure 1 shows the potentiodynamic polarization curves of the four studied samples performed after the first 120min immersion. It can be seen that the hexyltrimethoxysilane, octyltrimethoxysilane and decyltrimethoxysilane coated samples show higher corrosion potentials than the bare aluminium sample, indicating a protective effect. Despite the minor difference in alkyl chain length, the corrosion current density of the octyltrimethoxysilane covered sample shows an increase compared to the other samples and even to the bare aluminium.
Figure 1: Potentiodynamic polarization scans of the bare aluminium alloy (bare) and the three trimethoxysilanes (C6, C8 and C10) after exposure to a 0.5M NaCl solution for 120min.

Figure 2 shows the optical analysis of the samples immersed in 0.5M NaCl during 120 min prior to the potentiodynamic polarization test. The area covered by pitting (quantified as area of pitting / total exposed area x 100) for hexyltrimethoxysilane and octyltrimethoxysilane is similar and always below that of the reference sample for the same immersion time. Nevertheless, this value is significantly higher when decyltrimethoxysilane is used compared to the other two silanes. This result is in agreement with the potentiodynamic polarization results although more tests need to be performed to confirm the technique works properly.

Figure 2: Corrosion image analysis showing the area covered by pitting (quantified as area of pitting / total exposed area x 100) with the exposure time to a 0.5M NaCl solution for the bare sample and the three different silane surface modifications (C6, C8, and C10).
4. CONCLUSIONS

From potentiodynamic polarization scans and optical analysis it was confirmed that the chain length of the silane has a strong influence on the corrosion protection of aluminium substrates. It was found that C6 and C8 show similar protecting results while C10 leads to higher corrosion. Interestingly the contact angles measured with a goniometer showed that the same C10 had the lowest contact angle suggesting a link between the two characteristics. The findings are valuable for the further development of surface reactive healing agents for encapsulated systems. The novel methodology employed to optically monitor corrosion during exposure to a corrosive environment delivered satisfactory preliminary results which are in agreement with the electrochemical analysis. The results open the path to the development of a technique for the simultaneous optical and electrochemical monitoring of corrosion and corrosion protection.

REFERENCES