

The Effect of Immersion Time in 3.5% NaCl Upon the Adhesion and Corrosion Performance of Hybrid Epoxy/Sol-gel System

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Abstract

Adhesion property of protective coating to metallic substrate is considered to be a critical factor for achieving an excellent anticorrosion performance. Organic/inorganic coatings modified by sol-gel methods can be tailored to provide covalent bonding for strong adhesion and act as a barrier to limit the transport of water to the surface of the substrate. The adhesive strength of hybrid epoxy/sol-gel joints aged within a corrosive environment (3.5% NaCl solution) for one, two, four and eight week's was evaluated. The morphology and adhesion of hybrid epoxy/sol-gel have been examined by SEM and lap shear tests. Lap shear tests recorded a mean bonding strength larger than 25 ± 0.9 MPa for the hybrid sol-gel material in dry conditions. However, the experimental results show that the bond strength of joints decreased as the immersion times in the NaCl solution increased. This behaviour can be attributed to moisture uptake and aggressive ion ingress into the bonded area, which limits the degree of bonding at the hybrid epoxy/sol-gel/substrate interface. SEM revealed many cracks in the fracture surface of hybrid epoxy/sol-gel material. The electrochemical impedance spectroscopy (EIS) was used to illustrate the corrosion performance of the coated samples in aggressive environment. The results indicated that there is a decrease in corrosion resistance of hybrid epoxy/sol-gel adhesive with increasing the immersion time.

Keywords: Corrosion resistance; NaCl; epoxy/sol-gel; analysis.

1. Introduction

Sol-gel materials have been extensively studied for corrosion control replacements Cr(VI) based conversion coatings. The sol-gel process can be used to form nano-structured inorganic films (typically to 10 μm in overall thickness) that can be tailored to be more resistant than metals to oxidation and wear. Hybrid organic/inorganic materials modified by sol-gel processing have attracted considerable attention in the research and industrial communities for corrosion protection and adhesive structural durability [1]. The organic/ inorganic sol-gel coatings are complex matrices where the intermolecular interactions between the macromolecular existing structures and metallic surface are extremely relevant to material properties, like low porosity and rigidity and adhesion to substrate. The conjugation

of these interactions results in materials with enhanced protective properties against oxidation, corrosion, erosion, and good thermal and electrical insulation properties [2]. The tested corrosion protection processes and materials based on sol-gel technology demonstrate positive performances when several properties are considered, such as adhesion, fatigue resistance, reliability, and quality control [3, 4]. Adhesion property of hybrid sol-gel materials to metallic substrates is a key factor may affected on their corrosion performance [5]. Aluminum-based alloys are materials with a wide range of applications due to their physical and process ability properties, namely low density, easy shaping (in rolling, drawing and extrusion), high corrosion resistance in different environments, easy machining, colorless and nontoxic corrosion products, and high thermal and electrical conductivity together with low cost.

Due to their natural tendency to form a passive Al_2O_3 layer, which can also be artificially generated by anodizing the substrate, these materials are remarkable economical and industrial importance alloys [6]. However, this passivation layer deteriorates when in contact with aggressive media, such as those containing chloride ions (particularly sea side environments) resulting in pitting corrosion. To overcome this situation, aluminum substrates are usually treated by different processes to improve their effectiveness of corrosion protection [7]. In addition, electrochemical methods have found wide spread use for characterization of anti corrosive coatings, and are commonly employed to assess the performance and durability of anticorrosive coatings in the laboratory [8]. The current work evaluated the effects of different immersion times in NaCl solution on the adhesive strength and corrosion resistance of epoxy-hybrid sol-gel materials.

2. Materials and Methods

Al alloys 2024-T3 was used as the substrate materials in testing the adhesive strength of the hybrid sol-gel materials. The samples were ultrasonically cleaned by using acetone at room temperature. Hybrid epoxy/sol-gel was then applied as a thin layer (0.03-0.05 mm) on the surface of both samples and the coated substrates were left for dry for one hour at room temperature. According to ASTM D1002, the coated samples (100 X 25 X 1.5 mm) were assembled into a single lap shear joint with 12.5 mm of overlap length shown in Figure 2.1. The applied contact pressure was constant, which allowed a uniform adhesive thickness to be achieved. The specimen was then placed into an oven for heat treatment at various designated times and temperatures. Table 2.1 & 2.2 presents the composition and typical mechanical properties of Al2024-T3 used in measuring the lap shear adhesive strength of hybrid epoxy/sol-gel, respectively.

2.1. Hybrid epoxy/sol-gel adhesives

Hybrid silica-based sols were first prepared from silane-based precursors. This hybrid sol was produced by mixing tetra-ethoxysilane (TEOS), methyltrimethoxy-silane (MTMS), ethanol, and deionised water at a mole ratio of 2:3:40:60. Nitric acid (HNO_3) was added as a catalyst to promote the hydrolysis and condensation reactions. The sol-gel modified epoxy adhesives were prepared by mixing the

Table 2.1: Composition of Al2024-T3.

Composition	AA2024-T3 wt%
C	—
P	—
S	—
Mn	0.6
Fe	0.5 max
Cu	4.4
Mg	0.45
Si	0.5 max
Cr	0.1 max
Ni	0.05 max
Zn	0.2 max
Ti+Zr	0.2 max
Al	Rest

Table 2.2: Mechanical properties of Al2024-T3.

Materials	Tensile strength MPa	Brinell hardness HB500	Elongation %
AA2024-T3	485	120	18

DGEBA with the as-prepared hybrid sol and then left in an ultrasonic bath for 45 minutes at room temperature to ensure uniform dispersion. Note: the sol-gel systems were not formulated with a curing agent. The sol-gel epoxy adhesives were further modified by doping with 0.007 g multiwall carbon nano-tubes. Due to their hydrophobic properties and the formation of stabilised bundles under the action of van der Waals forces, carbon nano-tubes (CNTs) generally aggregate together after being dispersed in water, resulting in the formation of hollow ropes [9]. Thus, uniform dispersion in a sol is one of the key issues for the application of CNTs. To achieve optimum dispersion, multi-wall carbon nano-tubes (MWCNTs) and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles were first added to 2-propanol. The solution was then ultrasonically dispersed for 90 minutes at 25 °C using an ultrasonic generator. After being dispersed, it was mixed with the as-prepared sol-gel/epoxy solution and this mixture was then excited ultrasonically for 2 hours, followed by continuous stirring overnight to obtain a stabilised uniform sol.

2.2. Shear test (single lap joints)

Adhesive-bonded single lap joints were produced to measurement the adhesive strength of the joints. The joint consists of two plates of substrate joined using a simple overlay, see Figure 2.1. Under the applied load the joint will fail in shear mode as the faces of the surfaces slide relative to one another. As a result, stress distributions in the lap joint change along the bonded area. Maximum stresses are located at the edges, while the minimum stresses are normally distributed within the centre of the joint [10].

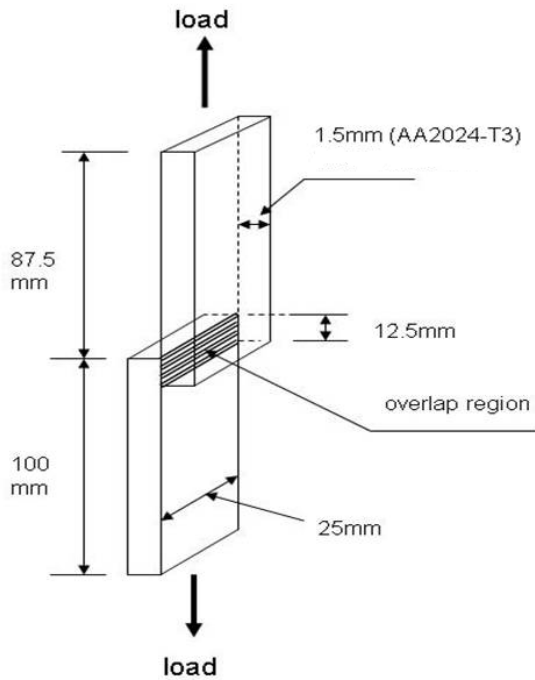


Figure 2.1: Single lap joint for adhesive strength testing.

3. Results and Discussions

3.1. Adhesive strength of hybrid epoxy/sol-gel

The adhesive strength of hybrid epoxy/sol-gel on AA2024-T3 substrates aged in 3.5% NaCl solution is shown in Figure 3.1. The maximum shear strength value of this adhesive in dry conditions was 24 ± 0.6 MPa for joints cured at 140°C for 16 hours. After eight weeks exposure the average shear strength was 7.8 MPa. The reduction in strength is relatively low initially but begins to drop rapidly after

four weeks immersion. At eight weeks about 68% of loss adhesion was recorded. The substantial reduction in the adhesion force was attributed to the increase in crack defects within the bulk adhesive. In addition, the formation of Al-O-Si covalent bonds at the adhesive/substrate interface during the polymerisation process (curing) reduced the moisture or water penetration at these region and, as a result, increased the load at failure. It has previously been reported [11] that aluminium oxide and silicon oxide may form a stable mixed oxide barrier layer at the interface, which reduces pitting corrosion on the substrate surface and increases adhesion.

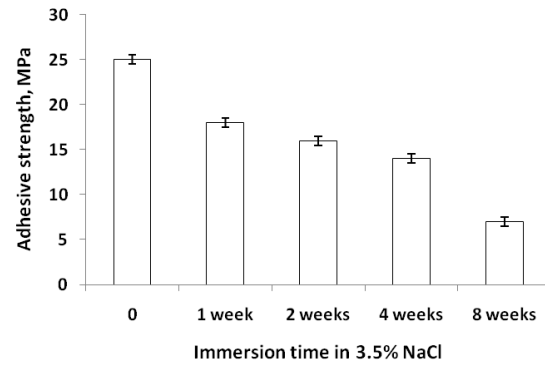


Figure 3.1: Effect of immersion times on adhesive strength of hybrid epoxy/sol-gel.

Also, the more time the lap joint was immersed in the NaCl solution the lower the adhesive strength. The percentage reduction in adhesive strength for one, two, four and eight week immersion periods was 29%, 39%, 42% and 68%, respectively, see Figure 3.2. In this case, the adhesive performance may be influenced by water penetration within the adhesive matrix (hybrid epoxy/sol-gel) which lowered the adhesive glass transition temperature " T_g ", (the temperature which the adhesive changed from rubber-like to a solid like state) by reducing the forces between adhesive molecules. Uddin et al. [12] reported that moisture effects cause a reduction in T_g and mechanical integrity of cured adhesive. As the uptake of the aggressive medium within the matrix increased with time so the degradation in cohesive bonding increased, causing a reduction in the joint's ability to carry load.

3.2. Fracture surface

The drop in strength after eight weeks immersion may indicate that the failure was governed by the

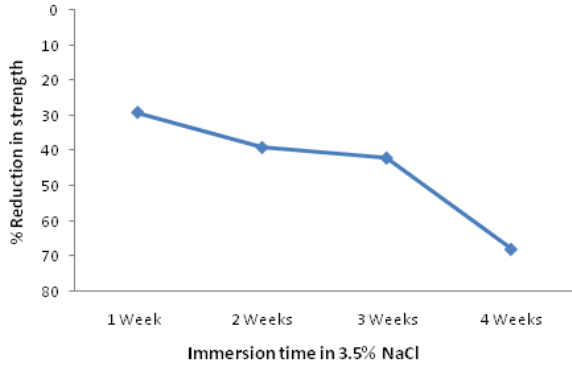


Figure 3.2: Reduction in adhesive strength of hybrid epoxy/sol-gel in 3.5% NaCl.

degree of damage within the adhesive structure as the diffusion of the aggressive NaCl solution within the matrix increased with time. This behaviour was supported by others. Comyn [13] demonstrated that the degradation in adhesive strength may be caused by diffusion of solution through the adhesive or/and along the interface or by capillary action through cracks in the adhesive. Figure 3.3 shows that adhesive material was found on both surfaces with short cracks distributed on the surface near the interface regions, indicating a mixed cohesive/adhesive failure mode.

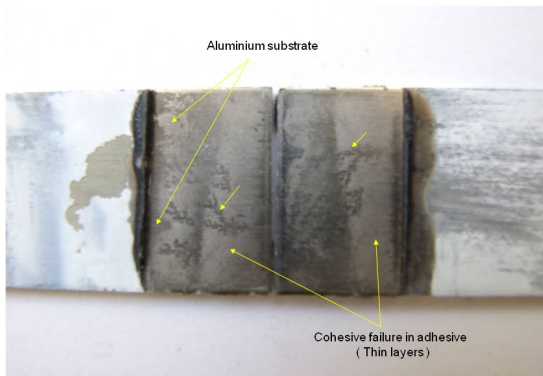
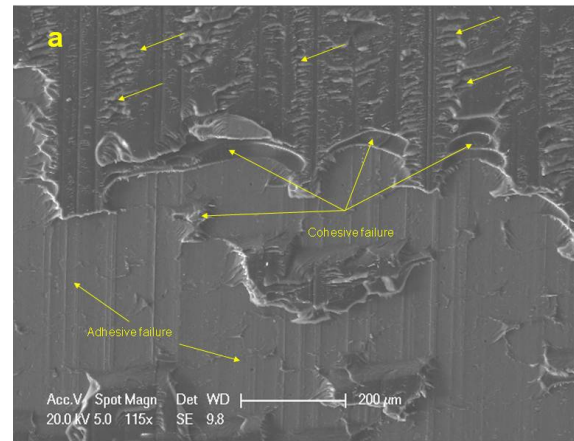


Figure 3.3: Cohesive failure mode of lap joints after eight weeks immersed in 3.5% NaCl.

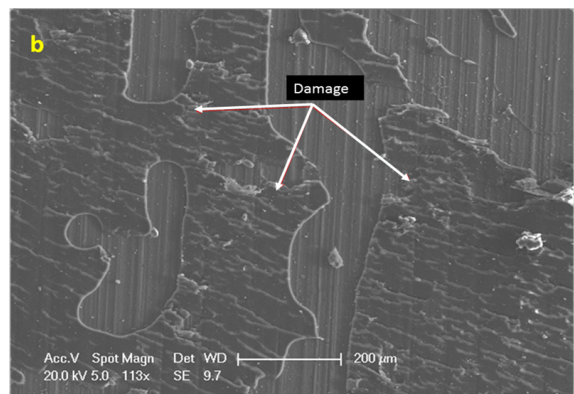
3.3. SEM observations

Figures 3.4a and b, respectively, show the fracture surface of lap joints immersed for one and eight weeks in the 3.5% NaCl solution. It can be seen that a mixed adhesive/cohesive mode was noted after one week, Figure 3.4a. Very short cracks in

the adhesive material were observed, which may be due to a decrease in cohesive force within the adhesive matrix. This behaviour may be attributed to damage or disruption of hydrogen bonding at the molecular chains of the adhesive. Soles and Yee [14] pointed out that moisture can be transported through the unoccupied volume of adhesive and access hydrogen bonds via the nanovoids, thus decreasing the cross-linking density. In addition, no corrosion products were observed after one week on the substrate surface, suggesting the diffusion rate of moisture through the interface within this period was low compared with that after eight weeks. This is supported by the data shown in Figure 3.2 which shows the percentage reduction in strength of the adhesive to the substrate in one week (i.e. ~30%) was lower than that after eight weeks (i.e. ~70%).



(a)



(b)

Figure 3.4: a) SEM image of one week immersed in 3.5%NaCl; b) SEM image of eighth weeks immersed in 3.5%NaCl.

However, with increase in immersion time, more damage in the adhesive material was observed due to the increase in cracks length, see Figure 3.4b. This led to higher stress intensity value at the crack tip, which reduced the adhesive's ability to resistance further crack propagation, resulting in a drop in strength of nearly 70%, see Figure 3.2. With increase in immersion time the fracture surface also showed mixed adhesive/cohesive mode.

3.4. Electrochemical impedance analysis

The EIS analysis involved applying an AC voltage at the open circuit potential (OCP), with sinusoidal amplitude of 10 mV, from a frequency of 10^6 Hz down to 10^{-1} Hz across the anodic layers. The film resistance to the AC signal, or impedance, varies according to the applied frequency and is graphically represented on a Bode frequency plot. From these plots, it can be derived a relationship between the electrochemical response of the anodic film and the applied potential. This technique has been widely used to determine the physical and protective properties of coated samples [15]. The corrosion behaviour of coated samples with hybrid epoxy/sol-gel material is also investigated by the electrochemical impedance spectroscopy (EIS) during the exposure to NaCl aqueous solution. The morphology and composition of the samples are examined by scanning electron microscopy. EIS data of tested samples showed a decrease in corrosion resistance of coated samples as the immersion time in NaCl increase. The impedance spectra of the test specimens were recorded in terms of bode plots as shown in Figure 3.5. It presented the variation in impedance and phase angle with respect to frequency. The electrochemical impedance diagrams obtained after different immersion times are characterized by two time constants. The first time constant [high frequency] is independent of the immersion time and the second [low frequency] one is better defined for increasing immersion times. According to literature [16] if the bar metal is considered, the time constant at high frequency is attributed to charge transfer process and the time constant at the low frequency is correlated with the redox processes taking place into the passive film. The coated samples showed high impedance (2×10^6 ohm.cm²) after 7 days of immersion; however, the impedance decreases with increasing time of immersion, see Figure 3.5a and b. High impedance of coated sample can be attributed to the hybrid coating properties: barrier effect which limits charge transfer

process. The second time constant was observed at low frequency (LF), Figure 3.5b. It is probably due to the reaction between metal substrate and the electrolyte, which diffuses into the coating. Also, this decrease in resistance correlates with the degradation in coating after 28 days of immersion. The initial high impedance of the coated sample reflects the hydrophobic nature of the coating. The hydrophobic of hybrid epoxy/sol-gel coating decreased with the increasing in immersion time.

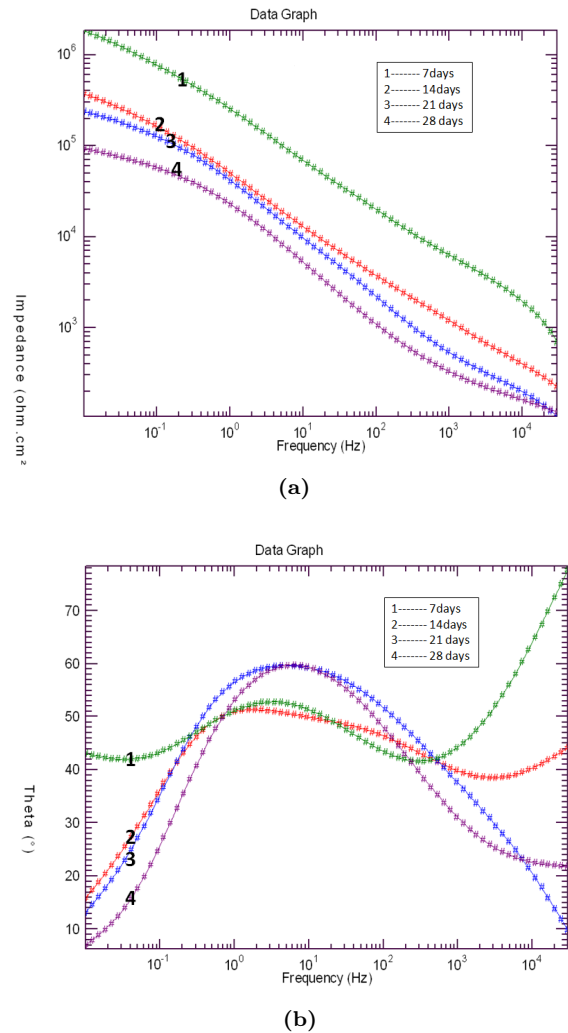


Figure 3.5: The impedance spectra of the test specimens.

4. Conclusion

1. The maximum shear strength of adhesive was 24 ± 0.6 MPa and after eight weeks immersion in 3.5% NaCl the average shear strength was 7.8 MPa. The reduction in strength was attributed to the increase in crack defects within the bulk adhesive.
2. The degradation in adhesive strength may be caused by diffusion of solution through the adhesive or/and along the interface or by capillary action through cracks in the adhesive.
3. As the immersion time increased, more damage in the adhesive and increase in crack lengths were noted. All this led to higher stress intensity value at the crack tip, which reduced the adhesive's ability to resistance further crack propagation, resulting in a drop in strength.
4. The impedance spectra indicated that there is a decrease in corrosion resistance with increasing time of immersion. The behavior may be attributed to the degradation in hybrid coating after 28 days of immersion in NaCl as the reduction in hydrophobic nature of coating.

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