Effect of self-etch adhesives on self-sealing ability of high-copper amalgams

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Effect of Self-etch Adhesives on Self-sealing Ability of High-Copper Amalgams

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KEY WORDS
Electrochemical Test; Dental Amalgam; Corrosion; Self-etch adhesive;

ABSTRACT

Statement of the Problem: Similar to conventional amalgam, high-copper amalgam alloy may also undergo corrosion, but it takes longer time for the resulting products to reduce microleakage by sealing the micro-gap at the tooth/amalgam interface.

Purpose: The aim of this study was to evaluate the effect of self-etch adhesives with different pH levels on the interfacial corrosion behavior of high-copper amalgam restoration and its induction potential for self-sealing ability of the micro-gap in the early hours after setting by means of Electro-Chemical Tests (ECTs).

Materials and Method: Thirty cylindrical cavities of 4.5mm x 4.7mm were prepared on intact bicuspids. The samples were divided into five main groups of application of Adhesive Resin (AR)/ liner/ None (No), on the cavity floor. The first main group was left without an AR/ liner (No). In the other main groups, the types of AR/ liner used were I-Bond (IB), Clearfil S 3 (S 3 ), Single Bond (SB) and Varnish (V). Each main group (n=6) was divided into two subgroups (n=3) according to the types of the amalgams used, either admixed ANA 2000 (ANA) or spherical Tytin (Tyt). The ECTs, Open Circuit Potential (OCP), and the Linear Polarization Resistance (LPR) for each sample were performed and measured 48 hours after the completion of the samples.

Results: The Tyt-No and Tyt-IB samples showed the highest and lowest OCP values respectively. In LPR tests, the R p values of ANA-V and Tyt-V were the highest (lowest corrosion rate) and contrarily, the ANA-IB and Tyt-IB samples, with the lowest pH levels, represented the lowest R p values (highest corrosion rates).

Conclusion: Some self-etch adhesives may increase interfacial corrosion potential and self-sealing ability of high-copper amalgams.

Introduction
Dental amalgams have been widely used in dentistry for over 160 years and are still being used due to their good clinical performance, strength, durability and reasonable price. [1] In low-copper amalgams, different electrolytic potentials in various phases make it susceptible to galvanic corrosion in its most electropositive phase (γ2) especially in the interface region. [2-5] Corrosion prod-
ucts formed by the interaction of metallic ions from amalgam with chlorine and oxygen in the oral environment fill this gap. They consequently create a potential to seal the tooth/amalgam restoration interface. [6-8] On the other hand, there are less electrolytic potentials and galvanic corrosion in high-copper amalgams. Marginal microleakage due to setting contraction of high-copper amalgams has been a cause for dentists’ concern about patients’ post-operative sensitivity and secondary caries. [9-10] However, it takes some time for the microleakage of high-copper amalgams to be sealed by corrosion products. It would be advantageous if these interfacial gaps could be sealed as quickly as possible by accelerated corrosion products. [11-12] In addition to the galvanic corrosion, other types of corrosions are expected to take place in amalgam restorations, as it would be at the vicinity of some factors such as tension, [13-14] oral bacterial flora, [15-16] and pH changes. Acidic environment accelerate corrosion phenomenon. [17-18]

Applying adhesives as an intermediary layer between enamel/dentin and amalgam reduces secondary caries [19] and microleakage significantly. [20-22] It also increases bonding [23] and diminishes postoperative sensitivity. [24-26] Corrosion resistance of alloys is reduced in a lower pH environment. Due to the acidic functional monomers of Self-etched Adhesives (SEA), the resultant interfacial structure becomes more hydrophilic [27] and may create an interfacial acidic environment that would be a more efficient condition for interfacial corrosion for amalgam restorations. Electrochemical Tests (ECTs) can be considered as the testing techniques for evaluation of potential corrosion and its behavior.

The aim of this study was to evaluate the effect of SEAs with different pH levels on corrosion behavior of high-copper amalgams and its induction potential for self-sealing ability in the early post setting hours using ECT techniques.

Materials and Method
Thirty intact second mandibular bicuspid teeth extracted for the orthodontic treatment purposes were used in this study. Initially, the coronal segments of teeth were sectioned just short of the cementoenamel junction (CEJ) with a diamond disk (Drendel &Zweiling 942FDiamant GmbH; Kalletal, Germany) and using a low speed hand piece and cooling water spray. The occlusal part at the cuspal base level was removed just inside the dentinoenamel junction (DEJ) using the same instruments and technique. To standardize the samples of 5.0 mm occlusogingival thickness and make identical cylindrical cavity preparations of 4.5 mm in diameter and 4.7mm in depth with a 0.3 mm remaining dentin base at the occlusal side of the samples, attempts were made to prepare the occlusal and cervical sections parallel together within the above-mentioned dimensions. (Figures 1a and 1b)

The cavities were prepared from the pulpal toward the occlusal part (Figure 1b) with a #57-fissure bur (Brasseler USA Dental; Savannah, Georgia, USA). Each bur was replaced with a new one for each cavity preparation. Samples were then placed for two minutes in an ultrasonic device (Micro 10+Sonic; Unindent S.A. Amios International Dental Group, Genève, Switzerland) with distilled water to clean any remaining cut debris. These samples were then kept in a 37°C incubator (Thermo; Hatfield, PA 19440, USA) for 12 hours.

To leave the opposing side of the cavity floor intact for the testing purposes, a polyethylene cylinder with 4.5 mm of internal diameter and 3.0 mm length was then carefully placed and secured with cured hydrophobic resin (Margin bond®; Coltène/Whaledent AG, Altstatten, Switzerland).

To seal the none-testing surfaces, all sample surfaces except for the cavity floor and its opposing external surface were etched with 37% phosphoric acid gel (Ultra-Etch; ULTRADENT products Inc., South Jordan, Utah, USA) for 15 seconds. They were then washed and dried. One layer of mentioned hydrophobic resin was carefully applied on these surfaces and initially cured by scanning the curing light (Blue phase ® C8; Ivoclar/ Vivadent, Liechtenstein) for 20 seconds at the intensity of 600 mW/cm². The samples were post-cured using a laboratory light cure unit (TRIAD 2000; DENTSPLY International, York, PA, USA) for 15 seconds. They were then washed and dried. One layer of mentioned hydrophobic resin was carefully applied on these surfaces and initially cured by scanning the curing light (Blue phase ® C8; Ivoclar/ Vivadent, Liechtenstein) for 20 seconds at the intensity of 600 mW/cm². The samples were post-cured using a laboratory light cure unit (TRIAD 2000; DENTSPLY International, York, PA, USA) for 80 seconds. A second layer of hydrophobic resin was applied and cured in the same manner (Figure 1c). A 33 1/2 inverted cone diamond bur (DIA; F GSO10014, Italy) was used to refresh the interfacial surfaces (floor of the cavities) to guarantee the resin removal. The samples were then washed, cleaned and dried using the same procedures previously described.

The samples were randomly divided into five main
groups. The first main group was left with no AR/liner (No) as a positive control group. In other main groups, each containing of six samples was assigned to a certain AR/liner, which was applied on the cavity floor according to manufacturer’s instructions: I-Bond (IB), Clearfil S<sup>3</sup> (S<sup>3</sup>), Single Bond (SB) and Varnish (V) (Table 1). Each main group was divided into two subgroups according to the types of the used amalgams (Table 1).

Considering various electrochemical behaviors, one high-copper spherical alloy (Tytin; Kerr, USA) and one admixed alloy (ANA 2000; Nordiska Dental, Sweden) were chosen. The mixed amalgam was condensed into the assigned cavity, while a piece of copper wire of 0.7 mm diameter was inserted about 3.0 mm deep into the cavity and submerged in the condensed amalgam. Each prepared sample was then mounted in epoxy resin (ARALDIT CY219; Hardener HY5160, CIBA-GEIGY, Switzerland) in such a way to leave the opposing surface exposed (Figure 1d-1g). ECTs started 48 hours after the completion of the samples. During this time, the samples were stored in the incubator at 37°C.

The electrochemical measurements were performed using Gill AC laboratory potentiostat (ACM instrument, UK). In order to check the steady state, the prepared sample (working electrode) as the third electrode was held for 20 minutes in Fusayama-Meyer artificial saliva solution.

The Open Circuit Potential (OCP) of each sample was measured in a period of 1200 seconds. The Linear Polarization Resistance (LPR) test was performed at a constant sweep rate of 10 mV/min and in the potential range of -15 to +15 mV around the final monitored OCP value. The OCP and LPR measurements were carried out after the initial set up (20 minutes), 18 and 44 hours of immersion. For instance, figure 2 illustrates the LPR graph of ANA-IB sample. In Potentio-Dynamic Polarization (PDP) of the samples, the potential was applied by a constant sweep rate of 30 mV/min ranging from -

<table>
<thead>
<tr>
<th>Table 1: Details of the defined groups used in this study</th>
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<tr>
<td><strong>Main groups (n=6)</strong></td>
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<tr>
<td>G1 (Control)</td>
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<tr>
<td>G2</td>
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<td>G3</td>
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<td>G4</td>
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<td>G5</td>
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**Figure 1:** Schematic model of the sample preparation for the electrochemical tests. **a:** Tooth sample with a 5.0 mm thickness, **b:** Cavity with 4.5 mm diameter and 4.7mm depth, **c:** Coating the external and internal walls of the cavity with hydrophobic resin, **d:** Amalgam filling without AR/Liner, **e:** Prepared d-sample embedded in epoxy resin, **f:** Amalgam filling with AR/Liner **g:** Prepared f-sample embedded in epoxy resin.
Table 2: LPR values (R_p values) of ANA 2000 and Tytin amalgams with different AR/Liner in all tested groups

<table>
<thead>
<tr>
<th>Immersion Time (Groups)</th>
<th>LPR of ANA 2000 Groups (KΩ cm²)/pH</th>
<th>LPR of Tytin Groups (KΩ cm²)/pH</th>
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<tbody>
<tr>
<td></td>
<td>ANA-No</td>
<td>ANA-IB</td>
</tr>
<tr>
<td>Instant</td>
<td>210</td>
<td>15</td>
</tr>
<tr>
<td>18 hr</td>
<td>47</td>
<td>4.7</td>
</tr>
<tr>
<td>44 hr</td>
<td>76</td>
<td>4.2</td>
</tr>
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</table>

250 to +250 mV (with respect to the sample OCP value). A water bath was utilized to control the electrolyte temperature at 37±1°C during the entire exposure times. Three experiments were performed on each defined subgroup.

**Results**

Mean OCP values of the samples with ANA 2000 and Tytin amalgams showed (in all samples except ANA-No and Tytin-V) that the mean OCP values reached a steady state after 18 hours of immersion (Figure 3). Mean OCP values of the ANA-V and ANA-IB were the highest (least corrosion potential) and lowest (most corrosion potential) respectively (Figure 3a). Mean OCP values of the Tytin-No and Tytin-IB samples were the highest (least corrosion potential) and lowest (most corrosion potential) among the other groups (Table 2).

In LPR tests, the effect of different AR’s on polarization resistance (R_p) values (electrical resistance) of ANA 2000 and Tytin amalgams has been measured and all values are represented in Table 2. The R_p values of almost all samples have reached nearly a steady state and have diminished slightly after the 44-hour immersion time. The R_p values of ANA-V and Tyt-V were the highest (lowest corrosion rates). Contrarily, the ANA-IB and Tyt-IB samples, with the lowest pH values, represent the lowest R_p values (i.e. highest corrosion rates) among the other groups (Table 2).

Figure 4 shows the PDP curves of all tested groups in artificial saliva media. Although the values of E_corr and i_corr were different, the diagrams in each group were roughly the same. Table 3 represents the extracted parameters from these curves. According to this table, Tyt-IB had the lowest E_corr and the highest i_corr among the groups (i.e. highest corrosion rate). The highest value of E_corr was witnessed in Tyt-No and lowest value of i_corr was that of Tyt-V (i.e. lowest corrosion rate).

**Discussion**

One of the influential parameters that can affect the corrosion reactions on the amalgam surface is the pH of the aqueous environment. [17-18]

The AR/lining materials used in this study had various pH levels. The pH of the AR could influence the
**Figure 4:** PDP curves of tested groups  
(a) Tytin/ANA-No, (b) Tytin/ANA-IB, (c) Tytin/ANA-SB, (d) Tytin/ANA-S\(^3\) and (e) Tytin/ANA-V.

pH of the diffused electrolyte in AR/amalgam interface. As it was expected for AR, the lower the pH was, the lower the OCP yielded. Consequently, the lowest OCP value of the ANA-IB sample could be attributed to its lowest pH value (Table 1 and Figure 3). On the other hand, in all samples except ANA-No, the mean OCP values reached steady state after 18 hours of immersion (Figure 3). Considering this and OCP values of ANA-No and ANA-V samples, higher corrosion resistances were expected as compared to the other samples.

OCP values of the Tyt-No and Tyt-IB samples were the highest and lowest respectively (Figure 3b).

Notwithstanding the lower pH of Clearfil S\(^3\) Bond (Table 1) in comparison to Single Bond, the ANA-S\(^3\) group presented a higher OCP value. Considering the OCP values of ANA-No and Tyt-No samples, it could be stated that the ANA-No sample (with approximate OCP value of -230 mV/Sec) showed a more active corr-

<table>
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<th>Extracted parameters from PDP curves in figure four of tested groups</th>
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<tr>
<td><strong>Potentiodynamic parameters (Groups)</strong></td>
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<tr>
<td></td>
</tr>
<tr>
<td><strong>E(_{corr}) (mV)</strong></td>
</tr>
<tr>
<td><strong>i(_{corr}) (µA/cm(^2))</strong></td>
</tr>
<tr>
<td><strong>β(_a) (mV/decade)</strong></td>
</tr>
<tr>
<td><strong>β(_c) (mV/decade)</strong></td>
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osion behavior than Tyt-No (Figures 3a & 3b).

Like OCP, LPR method is a non-destructive method for evaluation of corrosion resistance. In LPR technique, a potential is applied to a freely corroding sensor element (here amalgam as a working electrode) and the resulting linear current response is measured. In samples with AR layers, the decrease in $R_p$ values can be ascribed to the water-uptake phenomenon in such polymeric layers with microleakage. [28-30] However, in the groups without AR layers, the significant $R_p$ drop after the initial immersion could be attributed to the occurrence of both the anodic and cathodic reactions at an active state leading to higher dissolution rates. As the results showed, the $R_p$ values of ANA-V and Tyt-V were the highest (i.e. lowest corrosion rates) in comparison to the other samples in other groups. Contrarily, the ANA-IB and Tyt-IB samples, with the lowest I-Bond pH values, represent the lowest $R_p$ values that mean higher corrosion rates. In other words, it can be inferred that the acidic nature of the I-Bond results in formation of higher amounts of corrosion products that can fill the gap at amalgam/dentin interface and it consequently diminishes the microleakage. A microleakage study is recommended for further substantiating the result. By comparing the $R_p$ values of the ANA-No and Tyt-No samples, it can be deduced that the corrosion rate of the ANA sample is slightly higher than the Tytin sample at longer immersion times. This superior corrosion resistance behavior of the Tytin sample can be attributed to its more homogenous microstructure. [31-32] Concerning the pH values of Clearfil S 3 sample had a lower $E_{corr}$ value in comparison with the Tyt-No sample (Table 3). Concerning their anodic and cathodic Tafel slopes, the ANA-No sample revealed a more active corrosion behavior (with a slightly higher $i_{corr}$ value) as compared to Tyt-No sample (Table 3) which could lead to lower microleakage in ANA-No sample. This can be ascribed to the ANA 2000 heterogeneous microstructure (admixed) in comparison with more homogenous spherical microstructure in Tytin. [31-32]

On the other hand, it should be considered that the corrosion rate of different groups is not only influenced by the type of amalgam and pH value [17, 31-32, 34] but also by the liner properties such as their degradability and water absorption affinity. [27-30] These factors may also be correlated with the liner porosity, the differences in the molecular structures and the densities of the polymeric chains in self-etch dentin bonding agents as well. Besides, as it has already been shown, the degree of polymerization could affect the amount of water absorption, therefore, the authors suggest evaluating the effect of AR degree of polymerization on interfacial corrosion potential and behavior of the amalgams. The application of either chlorhexidine on the dentin surface separately or a new adhesive layer with added chlorhexidine to its formula to control degradability of AR may influence the corrosion production pattern/rate at the amalgam/dentin interface. This might also require investigation.

Comparing the ANA-IB and Tyt-IB samples, both samples had almost equal $E_{corr}$ values (Figure 4b and Table 3). Besides, the Tyt-IB sample had a higher $i_{corr}$ value compared to the ANA-IB sample (Table 3), which means lower corrosion resistance or higher corrosion rate. Therefore, it can be deduced that in presence of the I-Bond (pH= 1.6), the surface activity of the Tytin amalgam was more affected as compared to ANA 2000 amalgam. On the other hand, the formation of a corrosion product layer was facilitated more, and thus, the gaps at amalgam/dentin interface have been more rapidly filled (Table 3). Comparing samples with I-Bond liners and the control groups (without any liner), a reduction in pH value resulted at higher corrosion rates.

The ANA-S 3 sample had a lower $E_{corr}$ value compared with Tyt- S 3 sample while both of them showed almost the same corrosion resistance (Figure 4c and Table 3). By comparing the $i_{corr}$ values of Clearfil S 3 samples with the control groups, it can be observed that there might have been a competition between the pH
and stability of this AR layer, which affected the overall surface activity. As a result, it can be observed that the created microleakage in ANA-S³ sample (with an acidic pH) could be restored even at a lower rate as compared to the ANA-No samples.

Both ANA-SB and Tyt-SB samples again revealed an approximately similar $i_{corr}$ values although the ANA 2000 sample value was slightly lower. Upon comparing the higher corrosion rates of SB groups with control groups, it can be deduced that the microleakage has been reduced faster.

In the Varnish groups, the corrosion rate of the ANA 2000 amalgam was higher than the Tytin. They showed almost similar corrosion behavior as compared to the control groups. Furthermore, in the presence of a more stable layer in the Varnish groups, the corrosion rates were considerably lower and hence, the sealing process would be delayed. In addition, it should be noticed that the PDP results were consistent with other previous electrochemical measurements.

Therefore, the authors believe that supplementary experiments and investigations should be performed for further confirmation of the suggested method.

**Conclusion**

Considering the limitations of this study, it can be concluded that applying some self-etch adhesives as a liner beneath the high-copper amalgam restorations may increase interfacial corrosion potential and self-sealing ability of high-copper amalgams by increasing corrosion phenomenon potential. The lowest pH level of self-etch adhesive showed the highest whilst, the highest pH level of liners revealed the lowest susceptibility to corrosion and self-sealing ability of high-copper amalgams. More specifically, I-Bond with the lowest pH value showed the highest corrosion rate whilst the Varnish with the highest pH value revealed the lowest susceptibility to corrosion. Clearfil S³ and Varnish demonstrated lower corrosion rates in comparison to the control group; therefore, these agents are not suggested for the reduction of microleakage in high copper amalgam restorations. The admixed amalgam had a higher corrosion rate in comparison with the spherical one.

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al Sciences and Mashhad Dental Research Center, Mashhad, Iran supported this study. The ECTs were done in corrosion Laboratory of Ferdowsi University, Mashhad-Iran.

**Conflict of interest**

Authors have no conflicts of interest to declare.

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