Evaluation of the Breakdown Potential of Orthodontic Archwires in Acidic Soft Drinks

Anup K Holla, Sanjay Kumar, Subraya Mogra, Surendra V Shetty, Arun Urala, MB Hanu Prasad

ABSTRACT

Objective: To investigate the effect of acidic soft drinks on the breakdown potential of orthodontic archwires in comparison with artificial saliva using the electrochemical technique of anodic polarization.

Materials and methods: Five specimens each of 0.019 × 0.025 inch stainless steel, 0.018 inch Australian Special Plus and Premium Plus, 0.018 inch Nickel-Titanium (NiTi), 0.016 inch Elgiloy® and 0.017 × 0.025 inch beta-titanium, in as received form, were subjected to accelerated corrosion by the electrochemical technique of anodic polarization in an electrochemical cell containing 250 ml of artificial saliva (pH-6.7), a phosphoric acid-based beverage [Pepsi® (pH-2.46)] and a citric acid-based beverage [Limca® (pH-2.69)] at room temperature, followed by examination of wire surface under scanning electron microscope.

Results: The polarization currents and breakdown potential were seen to rise in the manner; in artificial saliva: Premium Plus > Special Plus (90 mv) > NiTi (180 mv) > stainless steel (560 mv) > Elgiloy® (8-40 mv) > beta-Titanium; in Pepsi®: Premium Plus > NiTi (310 mv) > Special Plus (410 mv) > Elgiloy® (820 mv) > stainless steel (1440 mv) > beta-titanium; in Limca®: Premium Plus > Special Plus (260 mv) > stainless steel (380 mv) > NiTi (410 mv) > Elgiloy® (710 mv) > beta-titanium. Between solutions, artificial saliva was significantly more corrosive than the beverages except with stainless steel wherein Limca® was more corrosive. Between artificial saliva and Limca®, significant differences were noted between all wires except beta-Titanium and Elgiloy®. Between Pepsi® and artificial saliva, significant differences were noted between all wires except in case of beta-Titanium. Between the two beverages, no significant differences were noted in the current densities curves except in case of stainless steel and Elgiloy®. SEM analysis revealed pitting and greater surface changes in Australian wires in all solutions and NiTi in artificial saliva.

Conclusion: Under the parameters tested, acidic beverages per se were observed to have a lesser corrosive effect over artificial saliva on orthodontic archwires.

Keywords: Corrosion, Anodic polarization, Corrosion current density, Acidic soft drinks.

INTRODUCTION

The aqueous environment of the oral cavity can be altered considerably by food and beverages, atmospheric components, temperature changes, microorganisms, as well as a plethora of organic and inorganic ions resulting in a reactive environment that can lead to the electrochemical corrosion of metals and alloys. The corrosion of orthodontic appliances has received considerable attention and the release of corrosion products has been documented by both in vitro and in vivo studies. Investigations primarily focus on the release of nickel, chromium, cobalt and iron as these metals have shown to have adverse effects. Corrosion of wires can also affect their mechanical properties, bracket archwire interactions and surface finish thereby increasing frictional resistance to sliding. The influence of low pH on the corrosion characteristics of orthodontic materials by modifying the artificial saliva with the use of organic and inorganic acids and protein have already been assessed. Low pH and higher temperature have a corrosive effect on orthodontic wires, however, Benyahia et al showed acidic pH to have a passivating effect on nickel-titanium (NiTi).

The consumption of soft drinks, primarily among young adults and teenagers is increasing worldwide and the effect of acidic soft drinks on the oral pH has been well-documented. In addition to a decrease in pH, a decrease in the redox potential and increased galvanic currents due to consumption of soft drinks has been demonstrated. Soft drinks contain acids like phosphoric acid, citric acid, malic acid, carbonic acid and other ingredients, such as sugars and artificial sweeteners and though the ionic content of soft drinks may be low, their low pH can modify the effect of even small concentrations of ions.
It has been reported that the consumption of acidic soft drinks may adversely affect orthodontic appliances as they provide a good environment of corrosive agents. Shahabi et al. reported that immersion of orthodontic brackets in artificial saliva with coca cola, lime juice and vinegar resulted in corrosion of brackets, however Parenti et al. reported that soft drinks do not affect the properties of NiTi significantly.

Potentiostatic anodic polarization measurements have been shown to be valuable in understanding and quantifying the electrochemical corrosion of metals and alloys as the technique fundamentally duplicates the electrochemistry of natural corrosion. This study was aimed at investigating the effect of phosphoric acid and citric acid-based soft drinks on the breakdown potential of orthodontic archwires in comparison to artificial saliva by the electrochemical technique of anodic polarization.

MATERIALS AND METHOD

Five specimens each of 0.019” × 0.025” inch stainless steel (3M Unitek, Monrovia, California), 0.018” Australian Special Plus and Premium Plus (AJ Wilcock, Whittlesea, Victoria, Australia), 0.018” Nickel-Titanium (3M Unitek, Monrovia, California), 0.016” Eligiloy® (RMO, Denver, Co.) and 0.017” × 0.025” beta-titanium (TMA; sdsOrmco, Glendora, California) in ‘as received’ form were subjected to accelerated corrosion by the electrochemical technique of anodic polarization in an electrochemical cell.

The cell consisted of 250 ml of electrolyte into which was immersed a reference electrode [Saturated Calomel Electrode (SCE), Elico, Hyderabad] placed in a Haber Luggin probe saturated with potassium chloride, a counter electrode (platinum) and the working electrode, i.e. the wire specimen of 5 cm length. The polarization currents were recorded by a potentiostat (Wenking LB81, Bank Elektronic, Clausthal, Germany) and plotted manually.

The electrolyte solutions used were modified Fusayama artificial saliva, the pH adjusted to 6.75 ± 0.75 with 10N sodium hydroxide or lactic acid, phosphoric acid-based [Pepsi® Lehar (pH-2.46 ± 0.2), PepsiCo India Holdings Pvt Ltd, India] and citric acid based [Limca® (pH –2.69 ± 0.2), Hindustan Coca Cola Beverages Pvt Ltd, India] soft drinks. For each specimen, fresh electrolyte solutions were used and pH was recorded separately. The solutions were used at room temperature and the soft drinks were left aside to lose their ‘fizz’ as the carbon dioxide gas was found to bubble out and get collected on the wire specimens which can lead to erroneous readings.

The electrodes were connected to the potentiostat and allowed to equilibrate, exposed to air, at room temperature for 1 hour till a constant open circuit potential value was obtained. Once stabilized, the wires were subjected to anodic polarization and the impressed potential, raised at a rate of 10 mv every 15 seconds, and the corresponding current values were recorded. The results were analyzed using the Kruskal-Wallis and Mann-Whitney U-tests using the SPSS statistical software (Version 11.5, IBM, Chicago).

The corroded specimens were examined for the type of corrosion using a scanning electron microscope (JEOL 840, JEOL Ltd, Tokyo, Japan) and compared with the ‘as received’ specimens.

RESULTS

The anodic polarization curves for the various wires tested in each solution are depicted in Figures 1 to 3. The mean...
breakdown potentials determined from the graph for the wire specimens are shown in Table 1. Statistical analysis showed very highly significant (p < 0.001) difference on evaluation of each wire among the three solutions except in case of beta-titanium (Table 2). No significant differences were noted in the current density values between citric acid (Limca®) and phosphoric acid (Pepsi®) based beverages except in case of stainless steel and Elgiloy® wires (Table 3). Between artificial saliva and Limca®, significant differences were noted in all wires except beta-titanium and Elgiloy®. Between Pepsi® and artificial saliva, significant differences were noted except in case of beta-titanium.

The polarization curves between the wires in artificial saliva were seen to increase in the manner: Premium Plus > Special Plus > NiTi > stainless steel > Elgiloy® > beta-titanium. In Pepsi®, the following trend was seen: Premium Plus > NiTi > Special Plus > Elgiloy® > Stainless steel > beta-titanium. In Limca®, the corrosion current densities varied in the order: Premium Plus > Special Plus > Stainless steel > NiTi > Elgiloy® > beta-titanium. The results of the SEM analysis are shown in Figures 4 to 7.

**DISCUSSION**

In an potentiostatic anodic polarization experiment the potentistat functions to monitor the impressed potential between the working electrode (wire specimen) and reference electrode (SCE) and accordingly alters the current between the working electrode and counter electrode to maintain the potential. When the potential is high enough leading to a breakdown in the passivating layer, termed the breakdown potential, large rise in the current densities are observed indicating a rapid increase in dissolution of metal.

Evaluation of breakdown potentials in artificial saliva showed trends similar to that noted by Kim and Johnson in 0.9% NaCl.19 No specific breakdown potential could be determined for Premium Plus and the polarization current curves of the two Australian wires were seen to increase constantly, indicating poor corrosion resistance and stability of the passive oxide layer. The difference between the two grades of wires is primarily related to hardness and resiliency attributed to the amount of carbon. The carbon content of Australian wires are seen to be higher than that of regular 18-8 stainless steel with increasing carbon content observed with higher grades of wires.22 This can potentially lead to the formation of carbides as well as a rough, irregular and excessively porous surface, hence, resulting in a decrease in the corrosion resistance. The SEM analysis showed these wires to have the roughest surface with surface defects (Figs 4A and B) and is in agreement with other studies.23

**Table 1:** The mean breakdown potential of the wires tested in artificial saliva and acidic beverages

<table>
<thead>
<tr>
<th>Wires</th>
<th>Artificial saliva</th>
<th>Phosphoric acid-based beverage (Pepsi®)</th>
<th>Citric acid-based beverage (Limca®)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.018 inch Special Plus</td>
<td>90 mv</td>
<td>410 mv</td>
<td>260 mv</td>
</tr>
<tr>
<td>0.018 inch Premium Plus</td>
<td>No specific point</td>
<td>No specific point</td>
<td>No specific point</td>
</tr>
<tr>
<td>0.019 × 0.025 inch Stainless steel</td>
<td>180 mv</td>
<td>310 mv</td>
<td>410 mv</td>
</tr>
<tr>
<td>0.017 × 0.025 inch Beta titanium</td>
<td>560 mv</td>
<td>1440 mv</td>
<td>380 mv</td>
</tr>
<tr>
<td>0.016 inch Elgiloy®</td>
<td>840 mv</td>
<td>820 mv</td>
<td>780 mv</td>
</tr>
</tbody>
</table>

**Table 2:** Statistical comparison between the three solutions for each wire tested (Kruskal-Wallis test)

<table>
<thead>
<tr>
<th>Wires tested</th>
<th>H</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.018 inch Premium Plus</td>
<td>17.9100</td>
<td>0.001**</td>
</tr>
<tr>
<td>0.018 inch Special Plus</td>
<td>25.3440</td>
<td>0.001**</td>
</tr>
<tr>
<td>0.018 inch NiTi</td>
<td>44.6300</td>
<td>0.001**</td>
</tr>
<tr>
<td>0.019 × 0.025 inch SS</td>
<td>49.27100</td>
<td>0.001**</td>
</tr>
<tr>
<td>0.017 × 0.025 inch Beta titanium</td>
<td>1.73700</td>
<td>0.42*</td>
</tr>
<tr>
<td>0.016 inch Elgiloy®</td>
<td>22.29500</td>
<td>0.001**</td>
</tr>
</tbody>
</table>

*p = 0.05 not significant; **p = 0.001 highly significant

**Table 3:** Statistical comparison of wires tested between two solutions (Mann-Whitney U-test)

<table>
<thead>
<tr>
<th></th>
<th>018 inch Premium Plus</th>
<th>018 inch Special Plus</th>
<th>0.019 × 0.025 inch Stainless steel</th>
<th>018 inch NiTi</th>
<th>0.017 × 0.025 inch Beta-titanium</th>
<th>0.016 inch Elgiloy®</th>
</tr>
</thead>
</table>

*p: 0.05 not significant; **p: 0.01 significant; ***p: 0.001 highly significant
The corrosion resistances of NiTi wires have been observed to vary considerably. The differences between various studies could be related to differences in surface roughness and defects of the wires, manufacturing process and the presence of residual stress on the wire surface and nonuniform distribution of phases within the alloy. On comparison of corrosion behavior of NiTi and stainless steel there has been considerable ambiguity, for some studies have shown NiTi alloys to have a higher corrosion resistance than stainless steel and others have shown vice versa. In the present study, the breakdown potential of NiTi was seen to be lower than that of stainless steel. This could be attributed to the difference in the surface morphology of the two wires. SEM analysis of the two wires at 150x show the presence of linear grooves due to the manufacturing process on NiTi (Fig. 4C) whereas stainless steel (Fig. 4D) showed a relatively
smoother surface. Also, since the cut ends of the wires were placed inside the solutions, as in clinical situation, the passivation may have not been stable enough to provide protection, hence, leading to corrosion as has been shown by Rondelli et al.\textsuperscript{26} using potentiostatic scratch test.

The good corrosion resistance of Elgiloy\textsuperscript{®}, a chrome-cobalt alloy, as observed in the present study can be attributed to the inherent corrosion resistance of cobalt and the passivation layer and microstructural changes caused by the addition of chromium.\textsuperscript{27} Yonekuru et al.\textsuperscript{25} reported good corrosion resistance for Co-Cr wire in 0.9% NaCl though NiTi wire and was shown to have a slightly higher breakdown potential which was attributed to a smoother surface texture of NiTi, nevertheless the Co-Cr alloy showed the maximum release of Co ions into the solution. Es-Souni et al.\textsuperscript{28} also showed good pitting corrosion resistance of Co-Cr alloy but poor repassivating potential with large increases in current density once the breakdown potential was breached. No significant surface changes were observed on SEM analysis between the ‘as received’ (Fig. 4E) and corroded Elgiloy\textsuperscript{®} wire specimens (Figs 5E, 6E, 7E).
No specific breakdown potential of beta-titanium in artificial saliva was noted within the capacity of the instrument (2000 mv) and the current density was the lowest when compared to the rest of the wires. Titanium and its alloy are known to have excellent passivation potential because of the unstable nature of the pure metal, hence, its ability to form an oxide layer (TiO₂) rapidly on exposure to air. The breakdown potential of beta-titanium was not significant between any of the solutions thereby indicating a good corrosion resistance in acidic medium as well as in artificial saliva (Figs 4F, 5F, 6F, 7F).

Decreasing the pH causes an increase in corrosion and release of metal ions and, though the acidity of the beverages was low (2.46 ± 0.2 for Pepsi® and 2.69 ± 0.2 for Limca®), the increase in corrosion rates and lowering of the breakdown potential was significantly of greater magnitude in artificial saliva at pH 6.7 than those of in acidic beverages alone. The ionic content of artificial saliva includes chlorides, phosphates and sulfides. Of these, chlorides are the most detrimental to stainless steel and, in industrial use, stainless steel is not considered corrosion resistant to chloride at any concentration or temperature. The SEM images (Figs 5A to C) of wires subjected to anodic polarization in artificial saliva show pitting indicative of chloride corrosion. The chloride content of the beverages would probably reflect the amount of chlorides present in the water used during bottling which can be assumed to be about 10 mg/Lt but vary considerably depending on the source of the water.

In Premium Plus wires, the rise in polarization currents did not vary significantly between the two beverages once past the breakdown potential, however, in Special Plus and stainless steel wires, the breakdown potential was higher in Pepsi® as compared to Limca® (Table 1). Phosphoric acid being inorganic and a mineral acid, is oxidizing and stainless steel alloys have the ability to passivate under such conditions. The disparity between the two beverages was greater in case of stainless steel as compared to Special Plus, which shows the stainless steel to have better corrosion resistance in mineral acid and a better passivating ability as noted by the passive range. Nevertheless, in an immersion experiment, Staffoloni et al showed no difference in the release of ions in either organic or inorganic acidic pH solutions after 28 days. In the present study, no significant surface changes were seen for stainless steel wires in any of the solutions tested (Figs 5D, 6D, 7D). Contrary to the trend seen among other wires in the study, stainless steel showed a reduced breakdown potential and higher rise in polarization currents in Limca® than artificial saliva. This may be because of the combined effects of the reduced pH as well as the presence of sodium citrate. It has been shown that citrate complexing agent influences the passivating layer significantly as it effects the distribution of elements within and underneath the passive layer. This effect was not observed in the Australian wires as the corrosion resistance was low in all solutions. For NiTi, a lower breakdown potential was seen in Pepsi® as compared to Limca® though the rise in polarization currents once past the breakdown potential did not vary significantly. Statistically significant differences between the corrosion currents were observed for Co-Cr wire between the two soft drinks with greater corrosion seen in Limca® though no significant surface changes were discernible on SEM analysis (Figs 6E and 7E). Once past the breakdown potential, the rise in current density was similar to that seen in artificial saliva indicating a poor repassivation potential of Co-Cr alloys.

The temperature of the medium also affects the corrosion behavior and lower the temperature, lesser will be the corrosion potential. Soft drinks are consumed at low temperature and in the present study the solutions were tested at room temperature, hence in practice the corrosion potential of soft drinks would be lower. Parent et al immersed NiTi wires for 60 minutes in acidic beverages and found no significant difference in the physical and chemical properties of the wires apart from smoothening of the surface as evidenced by the SEM analysis. A 6-week immersion test of brackets in artificial saliva with cola, limca and vinegar at 37°C by Shahabi et al showed significant weight loss though a continuous immersion time of 6 weeks could be considered as an extreme condition.

Acidic beverages do reduce the pH and redox potential of the oral cavity to levels below that required for enamel dissolution and consumption of beverages cause an increase in salivary flow bringing in more chloride ions into the oral cavity. Hence, regular consumption of acidic beverages leading to frequent reduction in oral pH can affect the corrosion behavior of orthodontic alloys. Though the possibilities of these changes have not been investigated in the present study, acidic soft drinks per se were found to have a decreased corrosive action as compared to artificial saliva except in case of stainless steel in citric acid-based beverage. As the present study investigated only the breakdown potentials, further investigation into the characteristics of the passivation layer are needed especially with regards to the effect of citric acid-based beverages on stainless steel.

CONCLUSION

Acidic beverages were seen to have a lower corrosive effect on orthodontic wires as compared to artificial saliva except for stainless steel wherein citric acid-based beverage (Limca®) was more corrosive. Between the two beverages, phosphoric acid-based beverage (Pepsi®) was seen to be less corrosive in case of the Australian wires and stainless steel whereas more corrosive in case of NiTi. Pepsi® was seen to have a passivating effect on stainless steel wires. Beta-titanium and Eligiloy® showed good corrosion resistance in all the solutions tested.

REFERENCES


