The Effect of pH on Fluoride Release of Glass Ionomer Based Restorative Materials

Amer A. Taqa*, Abdul-k. Abdal, Alaa I. Dawood

Department College of Dentistry, University of Mosul, Iraq
*Corresponding author: amertaqa@hotmail.com

Abstract Three Glass-ionomer based restorative materials (Conventional Glass-ionomer cement, resin-modified Glass-ionomer cement and Compomer) were used. The number of the specimens for the fluoride measurement and surface hardness test was 156 specimens. The specimens for each material were divided into four equal groups: the first group was dry stored, the second group was stored in solution pH7, the third group was stored in solution pH5 and the last group was stored in solution pH3. All the specimens were stored in an incubator at 37 °C for seven days. Fluoride release after seven days was measured with fluoride ion selective electrode. The amount of fluoride released from the three materials were significantly higher in acidic solutions than in neutral solutions. The Compomer released the highest amount of fluoride into the three storage solutions, while the least fluoride release was from the resin-modified glass-ionomer.

Keywords: fluoride release, glass ionomer, Megacem, Vivaglass, Compomer


1. Introduction

Since the observation that secondary caries formation was rarely associated with fluoride-containing silicate cement restorations [1], increasing attention has been focused on the development of various fluoride-releasing products to be used as restorative materials, lining cements, sealants and orthodontic cements. Fluoride is well documented as an anticariogenic agent. A variety of mechanisms are involved in the anticariogenic effects of fluoride, including the reduction of demineralization, the enhancement of remineralization, the interference of pellicle and plaque formation and the inhibition of microbial growth and metabolism. Fluoride released from dental restorative materials is assumed to affect caries formation through all these mechanisms and may therefore reduce or prevent demineralization and promote remineralization of dental hard tissues [1]. There are several fluoride-containing dental restoratives available in the market including glass-ionomer cement, resin-modified glass-ionomer cement, and polyacid-modified composite (Compomers) and composite resin. Due to their different matrices and setting mechanisms, the products vary in their ability to release fluoride. However, it is assumed that the antibacterial and cariostatic properties of restoratives are often associated with the amount of fluoride released [2]. A persisting concern of conventional glass-ionomers is their brittleness and low wear resistance. The acidic environment is related to the degradation of GICs according to the results of the previous studies. It is also clear that fluoride release is related to GIC degradation [3].

Restorative materials used in dentistry are required to have long term durability in the oral cavity. This is a complex environment where the material is in contact with saliva, a fluid that contains a variety of inorganic and organic species, together with a bacterial flora complex, in addition to the effect of diet. Repair of teeth is increasingly being carried out with tooth coloured restorative materials, but these materials are found to be susceptible to dietary erosive. An in vitro study on the effect of some drinks on the surface hardness of glassionomer cement found that the conventional glass-ionomers dissolved completely in apple juice and orange juice, but survived in Coca-Cola with a significantly reduced hardness after 1 year. The resin-modified glass-ionomer and the Compomer survived in apple juice and orange juice, but showed greater reductions in surface hardness in these beverages than in Coca-Cola. Fruit juices were thus shown to pose a greater erosive threat to tooth coloured materials than Coca-Cola [4]. Such findings are similar to those concerning dentine and enamel towards these drinks [5,6].

The present study aim to the study the effect of pH of the storage solutions on the fluoride release of different glass-ionomer based restorative materials.

2. Materials and Methods

Three glass-ionomer based restorative materials were used in this study Megacem (Megadenta, Germany) Restorative GIC, powder A2, Vivaglass (Ivoclar Vivadent, Liechtenstein) Restorative Resin-modified GIC, powder and liquid B3 and Glasiosite (Voco, Germany) Polyacid-modified composite resin, capsule A2.
2.1. Total Ionic Strength Adjusting Buffer (TISAB) Preparation

The TISAB was prepared according to the methods described in the previous study [7,8]. TISAB used to buffer the storage solutions to provide a constant background ionic strength, a known solution pH and decomplex fluoride.

2.2. Standard Solutions and Calibration Curve Preparation

The standard solutions were prepared according to the dilution law for solutions [9]. And according to this law we prepared the standard solution of fluoride in part per million (ppm) from sodium fluoride (NaF) in deionized water to obtain a solution with concentration 1000 ppm of F ion. Then, the other standard solution prepared by diluting this main blank. The prepared concentrations were: 0.05, 0.1, 0.5, 1, 5, 10, 20, 30, 40 and 50 ppm [8]. Three ml of each concentration buffered with equal amount of TISAB. Then the concentration of fluoride measured by the radiometer with the fluoride ion selective electrode. The millivolt (mv) readings of the device plotted against the Log concentrations of the fluoride (Log c) to obtain the standard curve (Figure 1) which was used later to convert mv readings in to fluoride concentration using the regression equation: \( mv = 39.2 + 5.91 \times \log c \) where mv is the millivolt reading and c is the concentration of fluoride ions.

2.3. Fluoride Measurement

Fluoride released was measured by using a radiometer with the fluoride ion selective electrode. The measuring unit is by millivolts (mv). Then the reading from the device was pointed to the standard solution curve and according to the calibration curve method[8], the reading was determined by the use of the regression equation to obtain the concentration of the fluoride calibration curve prepared from standard solutions (Figure 1).

2.4. Preparation of the Storage Solutions

Solution pH7 prepared by adding ready-made pH7 (pH7, buffer powder, PYE UNICAM LTD, Cambridge, England) to 200 ml of deionized water according to manufacturer instructions then the solution was treated with NaOH to reach pH5. Solution pH3 prepared by dissolving 1 gm of ascorbic acid (vitamin C) in 100 ml of deionized water to obtain a solution with pH2.7, then the solution was treated with NaOH to reach pH3. pH-meter was used during this procedure to check the pH of the storage solutions.

2.5. Specimens Preparation

The dimensions of all the specimens were 2mm in height and 5mm in diameter (Figure 2) similar to the specimens used in other studies [10,11,12].

2.5.1. The Conventional Glass-ionomer Cements

The powder mixed with distilled water on clean glass slab (powder/liquid ratio 2:1, mixing time 40 seconds according to the manufacturer instructions). The mixed material then placed in a polyethylene mold and placed between two glass slabs.

2.5.2. The Resin-modified Glass-ionomer Cements

The powder and liquid were mixed on clean glass slab (powder/liquid ratio 1.5:1, mixing time 20 seconds according to the manufacturer instructions). The mixed material then placed in the mold and placed between two glass slabs and light cured by the blue LED light (Blue LED light curing unit, Ulitra-lite 200E plus, Taiwan) curing unit for 30 seconds at 490 mw/cm\(^2\) (according to the manufacturer instructions).

2.5.3. The Polyacid-modified composite Resin

(Glasiosite, Voco, Germany,capsule shade A2): The material introduced into the mold and placed between two glass slabs and light cured by the blue LED light curing unit for 40 seconds at 490 mw/cm2 (according to the manufacturer instructions). The distance between the tip of the curing unit and the surface of the specimens was 4 mm using (Digital Caliper METR-ISO-GEW, China). The light curing unit was monitored previously with curing radiometer to check the intensity of the curing light. Stainless steel orthodontic ligature wire (gauge 0.25mm) was embedded laterally into each specimen before the setting of the material to act as a cord to suspend the specimen in the storage solution (Figure 3).

![Figure 1. calibration curve prepared from standard solutions](image1)

![Figure 2. The specimens of the Glass-ionomer based materials mounted in stone blocks for microhardness assessment](image2)
2.6. Measurement of Fluoride

The study was conducted using three types of glass-ionomer based restorative materials: conventional GIC, resin-modified GIC and polyacid-modified composite resin. For each material fifty two specimens were prepared according to the manufacturer instructions (Total specimens number was 156). The specimens for each material were divided into four groups: thirteen specimens were stored in solution pH7, thirteen specimens were stored in solution pH5 and thirteen specimens were stored in solution pH3 (n=13). The specimens were stored in the incubator at 37°C for seven days (which give the minimum reading). Each specimen was suspended inside a glass vial containing 3 ml of the storage solution. The specimens were weighed before and after the storage to assess the weight change. Fluoride release was determined at the end of the storage period. The storage solution was buffered with equal volume of TISAB and the released fluoride was measured with fluoride ion selective electrode and radiometer previously calibrated with standard solutions. The amount of fluoride released after seven days was expressed in ppm in the storage solutions. The data were subjected to an analysis of variance (ANOVA) using SPSS computer program. One-way analysis of variance ANOVA, followed by post Hoc test (Duncan) for multiple comparisons (α= 0.05) were performed to compare fluoride release values (ppm).

3. Results

3.1. Fluoride Release

Descriptive statistics include mean, standard deviation (SD), standard error (SE), minimum and maximum values of the amount of the fluoride released from the tested materials into the three storage solutions after 7 days.

Table 1. Descriptive statistics for the amount of fluoride released from the different materials into the three storage solutions

<table>
<thead>
<tr>
<th>Materials</th>
<th>Storage pH</th>
<th>N</th>
<th>Mean (ppm)</th>
<th>SD</th>
<th>SE</th>
<th>Min. (ppm)</th>
<th>Max. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GIC</td>
<td>pH7</td>
<td>13</td>
<td>48×10⁻⁴</td>
<td>12×10⁻⁴</td>
<td>3×10⁻⁴</td>
<td>30×10⁻⁴</td>
<td>67×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>pH5</td>
<td>13</td>
<td>86×10⁻⁴</td>
<td>21×10⁻⁴</td>
<td>5×10⁻⁴</td>
<td>45×10⁻⁴</td>
<td>99×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>pH3</td>
<td>13</td>
<td>130×10⁻⁴</td>
<td>31×10⁻⁴</td>
<td>8×10⁻⁴</td>
<td>99×10⁻⁴</td>
<td>210×10⁻⁴</td>
</tr>
<tr>
<td>RMGIC</td>
<td>pH7</td>
<td>13</td>
<td>32×10⁻⁴</td>
<td>4×10⁻⁴</td>
<td>1×10⁻⁴</td>
<td>30×10⁻⁴</td>
<td>45×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>pH5</td>
<td>13</td>
<td>44×10⁻⁴</td>
<td>9×10⁻⁴</td>
<td>2×10⁻⁴</td>
<td>30×10⁻⁴</td>
<td>67×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>pH3</td>
<td>13</td>
<td>47×10⁻⁴</td>
<td>6×10⁻⁴</td>
<td>1×10⁻⁴</td>
<td>45×10⁻⁴</td>
<td>67×10⁻⁴</td>
</tr>
<tr>
<td>Compomer</td>
<td>pH7</td>
<td>13</td>
<td>180×10⁻⁴</td>
<td>49×10⁻⁴</td>
<td>13×10⁻⁴</td>
<td>99×10⁻⁴</td>
<td>210×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>pH5</td>
<td>13</td>
<td>427×10⁻⁴</td>
<td>85×10⁻⁴</td>
<td>23×10⁻⁴</td>
<td>210×10⁻⁴</td>
<td>470×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>pH3</td>
<td>13</td>
<td>909×10⁻⁴</td>
<td>197×10⁻⁴</td>
<td>54×10⁻⁴</td>
<td>470×10⁻⁴</td>
<td>1030×10⁻⁴</td>
</tr>
</tbody>
</table>

N = Number of specimens, SD = Standard deviation, SE = Standard error, Min. = Minimum and Max. = Maximum.

Table 2 shows the analysis of variance results, which compares the fluoride release values (ppm) of the specimens of the same materials stored at different pH. Table (4.3) shows the analysis of variance results, which compares the fluoride release values (ppm) of the specimens of the different materials stored at same pH. The amount of the fluoride released from the three materials in the various storage solutions varied significantly (p≤0.05).

Table 2. ANOVA results of the fluoride release values (ppm) of the specimens of the same material stored at different pH

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean square</th>
<th>F</th>
<th>Sig</th>
</tr>
</thead>
<tbody>
<tr>
<td>GIC (pH7, pH5, pH3)</td>
<td>Between Gps.</td>
<td>437×10⁻⁴</td>
<td>2</td>
<td>219×10⁻⁴</td>
<td>40.658</td>
</tr>
<tr>
<td></td>
<td>Within Gps.</td>
<td>194×10⁻⁴</td>
<td>36</td>
<td>537×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>630×10⁻⁴</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMGIC (pH7, pH5, pH3)</td>
<td>Bet. groups</td>
<td>174×10⁻⁴</td>
<td>2</td>
<td>866×10⁻⁴</td>
<td>17.568</td>
</tr>
<tr>
<td></td>
<td>Within Groups</td>
<td>178×10⁻⁴</td>
<td>36</td>
<td>493×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>351×10⁻⁴</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compomer (pH7, pH5, pH3)</td>
<td>Bet. Groups</td>
<td>36×10⁻⁴</td>
<td>2</td>
<td>179×10⁻⁴</td>
<td>109.833</td>
</tr>
<tr>
<td></td>
<td>Within Groups</td>
<td>59×10⁻⁴</td>
<td>36</td>
<td>163×10⁻⁴</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>417×10⁻⁴</td>
<td>38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

df = degree of freedom, Sig. = significance
3.1.1. Fluoride Release from GIC

Table 1 shows the mean fluoride release from the GIC into the three storage solutions with Duncan’s test results. The highest amount of fluoride was released from the GIC into the pH3 storage solution followed by the pH5 storage solution, and the least amount was released into pH7 storage solution (p<0.05).

3.1.2. Fluoride Release from RMGIC

Table 1 shows the mean fluoride release from the RMGIC into the three storage solutions with Duncan’s test results. There was no significant difference between the amount of fluoride released into the pH3 and pH5 storage solutions (p>0.05) however it was higher significantly (p<0.05) than the amount of fluoride released into pH7 storage solution.

3.1.3. Fluoride Release from CompoMer

Table 1 shows the mean fluoride release from the CompoMer into the three storage solutions with Duncan’s test results. The highest amount of fluoride was released from the CompoMer into the pH3 storage solution followed by the pH5 storage solution, and the least amount was released into pH7 storage solution (p<0.05).

3.1.4. Fluoride Release from pH7 Stored Specimens

Table 1 shows the mean fluoride release from the three materials stored in the pH7 storage solution with Duncan’s test results. There was no significant difference between the amount of fluoride released from the GIC and RMGIC (p>0.05). The CompoMer released the highest amount of fluoride compared with the other tested materials (p<0.05).

3.1.5. Fluoride Release from pH5 Stored Specimens

Table 1 shows the mean fluoride release from the three materials stored in the pH5 storage solution with Duncan’s test results. The amount of fluoride released from the three materials varied significantly (p<0.05). The lowest amount of fluoride was released from the RMGIC followed by the GIC. The highest amount of fluoride was released from the CompoMer.

3.1.6. Fluoride Release from pH3 Stored Specimens

Table 1 shows the mean fluoride release from the three materials stored in the pH3 storage solution with Duncan’s test results. The amount of fluoride released from the three materials varied significantly (p<0.05). The lowest amount of fluoride was released from the RMGIC followed by the GIC. The highest amount of fluoride was released from the CompoMer.

| Table 3. ANOVA results of the fluoride release values (ppm) of the specimens of the different materials stored at the same pH |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | Sum of squares  | df              | Mean square     | Sig             |
| pH7 (GIC, RMGIC, CompoMer) | Bet. Groups | 171 x 10^4 | 2 | 853 x 10^4 |
|                  | Wit. Groups    | 32 x 10^4     | 36 | 871 x 10^3 |
|                  | Total          | 202 x 10^3    | 38 | 97.826 |
| pH5 (GIC, RMGIC, CompoMer) | Bet. Groups | 12 x 10^4     | 2 | 576 x 10^4 |
|                  | Wit. Groups    | 96 x 10^4     | 36 | 265 x 10^3 |
|                  | Total          | 125 x 10^4    | 38 | 217.463 |
| pH3 (GIC, RMGIC, CompoMer) | Bet. Groups | 58 x 10^4     | 2 | 294 x 10^4 |
|                  | Wit. Groups    | 49 x 10^4     | 36 | 14 x 10^3 |
|                  | Total          | 636 x 10^4    | 38 | 220.040 |

df = degree of freedom, Sig. = significance.

Table 4 shows the mean fluoride release (ppm) from the three Glass-ionomer based restorative materials into the different storage solutions after 7 days. The superscript letters represent the Duncan’s test results (Statistically significant differences between columns are shown by the first superscript letters A, B, C (A = lowest values), between rows by the second superscript letters a, b, c (a = lowest values), same letters are not significantly different (p>0.05).

| Table 4. Mean fluoride release (ppm) from the three tested materials into the three storage solutions |
|-------------------------------------------------------------|-----------------|-----------------|-----------------|
| Storage pH | pH7 | pH5 | pH3 |
| GIC        | 48 x 10^-4 | 86 x 10^-4 | 130 x 10^-4 |
| RMGIC      | 32 x 10^-4 | 44 x 10^-4 | 47 x 10^-4 |
| CompoMer   | 180 x 10^-4 | 427 x 10^-4 | 909 x 10^-4 |

In general, CompoMer released the highest amount of fluoride into the three storage solutions. The least fluoride release was found with the RMGIC (Figure 4). For each material, the highest amount of fluoride was released into the acidic media (Especially pH3 storage solution) compared to pH5 and pH7 storage solutions. GIC and CompoMer released the highest amount of fluoride into the pH3 storage solution, followed by pH5 and the least amount of fluoride was released into the pH7 storage solution. RMGIC released the highest amount of fluoride into the pH3 storage solution which was statistically similar to the amount of fluoride released at pH5 storage solution. The least amount of fluoride was released into the pH7 storage solution.

4. Discussion

4.1. Fluoride Release

This study investigated the effect of acidic environment on the fluoride release. Also it compared between the ability of the tested materials to release the fluoride.

Figure 4. Mean fluoride release (ppm) from the three tested materials into the three storage solutions.
4.1.1. Fluoride Release and the pH of the Storage Solutions

According to these results, there was a positive correlation between the amount of fluoride released and the acidic environment. In other words, the increased acidity of the storage solution caused greater elution of fluoride from the tested materials. Such results came in agreement with the results of other previous studies [13]-[17]. The increasing amount of fluoride in acidic media could be explained by the fact that a decrease in pH increases the dissolution of the material leading to a higher fluoride level in the acidic immersion [1]. Fluoride release may depend on GICs surface degradation caused by pH in the solution [16].

The structure of the tested materials was disintegrated at low pH that may be predominantly due to an enhanced hydrolytic degradation occurring at the matrix-filler interface [11].

4.1.2. Fluoride Release from the Different Materials

These results showed that the Compomer released the highest amount of fluoride followed by the conventional GIC. The RMGIC released the lowest amount of fluoride. These differences in the amount of fluoride release may be due to the differences in the chemical composition and the setting reaction of the various Glass-ionomer based materials used in this study. The results of this study showed that the conventional GICs released greater amount of fluoride than the amount released from the RMGICs. These results came in agreement with the results of other study [18]. This can be explained by the fact that the conventional GIC consists of an ion-leachable calcium aluminofluorosilicate glass and aqueous solution of polymers and copolymers of acrylic acid. It sets by the acid-base reaction which is the main factor responsible for the elution of fluoride ion [19,20]. The acid-base reaction represents the main setting reaction of the conventional GIC, while the Resin-modified glass-ionomer cements set through a combination of acid-base reaction and photochemical polymerization [21]. Such polymerization may lead to further cross-linking in the structure of the set material and therefore reducing the fluoride ions liberation.

The Compomers are hydrophobic resins by definition that contain poly acid side chains that are attached to one or more of their methacrylate monomers. They rely primarily on the light initiated free-radical polymerization mechanism for curing. These materials can be thought of as low-fluoride-releasing composite resins. The fillers include a reactive aluminofluorosilicate glass (used in glass-ionomers). The monomer ionizes by absorbing water during the days and weeks after it is light cured. The hydrogen ions that are released then react with the glass filler to initiate an acid-base reaction. Ionic cross-linking also occurs, and fluoride is released [22,23].

The results of this study showed that the amount of fluoride release of compomer was significantly higher than those of the other tested materials. It is a disagreement point [24,25]. This variation in the amount of fluoride released from the Compomer may be attributed to the manufacturer composition of the Compomer used in this study and the amount of glass filler responsible for the fluoride elution.

5. Conclusions

On the basis of this results, and within the limitations of the in vitro study, it may be concluded that: The fluoride release from the three tested materials increased significantly in the acidic environment. There was no relation between the amount of residual monomer released from the resin based Glass-ionomers and the pH of the storage solution.

References


