Fluoride-releasing materials for orthodontic appliances
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A fluoride-releasing composite for dental applications

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Abstract

Objectives. The aim of this work was to attempt formulation of a dental composite, for investigational purposes, which will release fluoride at a rate comparable to glass ionomer materials, while retaining physical properties adequate for potential use in a number of dental applications.

Methods. An organic fluoride material, tetrabutylammonium tetrafluoroborate (TBATFB), was incorporated into a hydrophilic monomer system made of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (BisGMA) and 2-hydroxyethyl methacrylate (HEMA). This fluoride-containing monomer system was filled with silane treated quartz to 81% by weight. The resultant material was tested for fluoride release, physical strength properties and bond strength to enamel, each in comparison to control materials.

Results. Cumulative fluoride release from the experimental composite was approximately linear over time and comparable to glass ionomer materials. The long term rate of release exceeded several of the glass ionomer materials tested. Diametral tensile strength was comparable to resin-modified glass ionomer (RMGI) materials. Bond strength to etched enamel was statistically equivalent to a commercially available hybrid composite control.

Significance. The experimental resin-based composite material could potentially be used as an alternative to glass ionomer materials in non-stress bearing restorative applications and for orthodontic bracket bonding, where high fluoride release is desirable.
Introduction

Fluoride release is a desirable attribute for a material used in some dental applications. In general, materials that release greater amounts of fluoride have greater caries preventive potential and are desirable, so long as physical and mechanical properties are not adversely affected. Glass ionomers have long been accepted as materials that satisfy these requirements for a number of dental applications [1]. They, however, have disadvantages such as requiring mixing and relatively low fracture strength, so are of limited use in stress bearing areas [1]. Resin-modified glass ionomer materials (RMGI’s) have largely addressed the limitation of fracture strength [2], but still require the mixing of two components. Because of this, there is interest in a material, such as a resin-based composite, which would eliminate the need for mixing, would have acceptable physical strength properties and fluoride release comparable to glass ionomers.

One approach to accomplishing this is to incorporate an inorganic fluoride, such as NaF, into the monomer system [3,4]. This method depends upon water diffusion through the polymer matrix for dissolution of the fluoride compound with subsequent outward migration of the fluoride, but which may over time result in voids in the matrix and thus weakening of the material structure. A second approach is that of dispersion of agents, which are sparingly soluble in water, into a polymer matrix. Water diffusion into the polymer matrix results in some fluoride release, but due to the low solubility, minimal volume loss will occur, and though porosity may be avoided, fluoride release is relatively low. Examples of this method are the use of leachable glasses [5,6,7], or sparingly soluble salts such as YbF$_3$ [7,8,9]. In the referenced studies, fluoride release was found to be substantially less than for glass ionomer materials. A similar approach used fluoride encapsulated in an insoluble material as a filler in a polymer matrix [10]. For one such material, an early burst of fluoride release was observed, but over time, considerably less fluoride was released than from a glass ionomer [11].

Organic fluorides have also been examined as additives to polymer matrices. Kadoma et al. [12] described the use of methacryloyl fluoride (MF) - methyl methacrylate (MMA) copolymers in which the hydrolysis of acid fluoride groups results in the release of fluoride. Tanaka et al. [13] showed uptake of fluoride in
enamel from a light cured sealant made from this material, and estimated fluoride delivery lasting for over 2 years.

Yet a different approach is described by Kwan and O'Connell [14], where a complex of a Lewis acid, such as BF$_3$, and a Lewis base, such as diethylaminoethyl methacrylate (DEAEMA), provide a polymerizable monomer which can be incorporated into a dental resin system. Fluoride is released by hydrolysis of the Lewis acid. They describe an orthodontic adhesive capable of releasing fluoride at a rate of 2-5 μg/cm$^2$/day for a period of over one year.

A fluoride-exchanging material was described by Rawls and Zimmerman [15]. This fluoride-releasing monomer is based on an acrylic-amine-HF salt from which fluoride can be released by replacement by another negatively charged ion from the surrounding fluids. Linear fluoride release rates in the range of 6-9 μg/g/day were found for composites containing t-butylamino ethyl methacrylate hydrogen fluoride (t-BAEMA:HF), and were comparable to silicates [16]. Hamer and Suh [17] extended the work of Rawls to make a fluoride-exchanging material using morpholinoethyl methacrylate hyrofluoride (MEM:HF) as the fluoride releasing comonomer. They found that this monomer resulted in approximately twice the fluoride release as the one described by Rawls.

Another organic fluoride source that can be incorporated into a polymer matrix was described by Aasen and co-workers [18]. One of their suggested fluoride sources, tetrabutylammonium tetrafluoroborate (TBATFB), was used in this study to attempt formulation of a composite that might release fluoride comparable to glass ionomer materials, while maintaining adequate physical properties. Aasen et al. explored relatively low concentrations of the added fluoride compound in monomer systems, resulting in fluoride release well below that of glass ionomer materials. The current study used higher levels of the fluoride compound with two different monomer formulations.

**Methods and materials**

Two polymerizable monomer systems were used in formulating the fluoride-releasing composite and their compositions are shown in Table 1. Monomer
system B is more hydrophilic than system A, and these two were chosen to examine the effect that this difference might have on fluoride release, with the expectation that system B might facilitate fluoride transport more readily.

**Table 1**
Composition of monomer systems investigated for use in formulating a fluoride-releasing composite (wt %).

<table>
<thead>
<tr>
<th>System A</th>
<th>System B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA 49%</td>
<td>Bis-GMA 62%</td>
</tr>
<tr>
<td>TEGDMA 50%</td>
<td>HEMA 37%</td>
</tr>
<tr>
<td>Initiators 1%</td>
<td>Initiators 1%</td>
</tr>
</tbody>
</table>

In order to obtain an approximation of the solubility limit of the organic fluoride in the two monomer systems, amounts of 7.5, 15.0, 30.0 and 45.0 weight percent of the organic fluoride were chosen to be added to the monomers. For each monomer system, the fluoride additions were examined sequentially, beginning with the 7.5 weight percent addition. The monomer systems and fluoride were mixed at room temperature in a light protective polyethylene container. The sealed bottles were then placed into a 60°C oven for one hour, with removal and hand agitation at 15-minute intervals. If the amount of fluoride could not be incorporated even at the elevated temperature, no further additions were attempted. Those that did dissolve at the 60°C temperature were allowed to stand at room temperature and checked daily over a 3-day period for evidence of precipitation of the fluoride.

From the above experimentation, it was found that the maximum level of the organic fluoride that could be incorporated into system A was 15% by weight, while for system B, the maximum was 30% by weight.

Fluoride release rates from the two monomer systems were compared for the materials, each with 15% by weight organic fluoride added. Four discs of each material were made by light polymerizing the materials in a Teflon mold with polyester lined glass plates on either side. Light polymerization was for a total of 90
60 seconds, 30 seconds from each side. Immediately thereafter, these discs, which measured 22 mm in diameter and 1.2 mm in height, were individually suspended in polyethylene vials containing 25 mls of deionized water and stored at 37°C until the time of each measurement. To measure the fluoride concentration in water, a 10 ml aliquot was removed from the vial and added to 10 ml of TISAB (Orion Research, Boston, MA, USA). A fluoride selective electrode (Orion 96-09, Orion Research, Boston, MA, USA) was used to measure concentration of fluoride in parts per million. The discs were returned to their respective containers with fresh deionized water and again placed into 37°C storage until the next measurement. Fluoride release for each time period was recorded in μg of measured fluoride per cm² of disc surface area (μg/cm²), after the appropriate calculation was performed. Cumulative fluoride release was determined by adding the individual fluoride release measurements from each time period. Statistical differences between the groups were evaluated by t-test.

Fluoride release was greater for system B, thus a fluoride-releasing resin was made by adding 30% by weight TBATFB (Aldrich Chemical Co., Milwaukee, WI, USA) to monomer system B. Two hundred grams of a composite was formulated with this fluoride-releasing monomer system and a silane treated quartz filler at a ratio of 19% monomer to 81% filler by weight. (Table 2). These were hand mixed at room temperature until a uniform consistency was obtained. This composite material was characterized by testing for fluoride release, diametral tensile strength, compressive strength, Barcol hardness and bond strength to enamel.

**Table 2**  
Composition of an experimental fluoride-releasing composite.

<table>
<thead>
<tr>
<th></th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA</td>
<td>8.25</td>
</tr>
<tr>
<td>HEMA</td>
<td>4.92</td>
</tr>
<tr>
<td>Initiators</td>
<td>0.13</td>
</tr>
<tr>
<td>TBATFB</td>
<td>5.7</td>
</tr>
<tr>
<td>Quartz Filler</td>
<td>81.0</td>
</tr>
</tbody>
</table>
Fluoride release from the 30% by weight TBATFB containing resin and from the experimental composite was measured as described above for the monomer systems. Four glass ionomer materials were also measured, by the same method, for comparative purposes. These included two conventional glass ionomer materials, Ketac-Fil (ESPE, Seefeld, Germany, Batch 045/23) and Fuji II (GC Corporation, Tokyo, Japan, Batch 930928A/930929B) and two resin-modified glass ionomers, Vitremer (3M Dental Products, St. Paul, MN, USA, Batch 315R/320) and Fuji II LC (GC Corporation, Tokyo, Japan, Batch 071234/291132). However, both the conventional glass ionomers and the resin-modified glass ionomers were stored in their respective molds at 95% relative humidity at 37°C for one hour prior to placement in deionized water.

Multiple cylindrical samples of the cured experimental composite (n=6) were prepared for diametral tensile and compressive strength testing. These were prepared by placing the composite material into glass tubes and inserting silicone rubber plugs above and below the composite. The sample tubes were individually placed into a pressure curing fixture such that the applied pressure on the sample material between the rubber stoppers was between 35 and 40 psi for 5 minutes prior to light curing, for the purpose of eliminating entrapped air bubbles. The specimens were then cured with rotational movement for 80 seconds with two opposing Visilux™ 2 Visible Light Curing Units (3M Dental Products, St. Paul, MN, USA). After light curing, the glass tubes with composite samples inside, were cut to size with a diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) and inspected visually for apparent flaws. For diametral tensile strength, the samples were approximately 2.3 mm in height and 4 mm in diameter; for compressive strength, they were about 7.3 mm in height and 4 mm in diameter. After storage in deionized water at 37°C for 24 hours, height and diameter of the samples was accurately measured with a micrometer, prior to measuring the force required to break each sample on an Instron™ Universal testing machine (Instron Corp., Canton, MA, USA) at a cross-head speed of 1 mm/min. Values for other materials using the same measuring technique were obtained from unpublished internal data.

Barcol hardness measurements were obtained on 1.2 mm thick discs of the experimental composite, immediately after light curing for 120 seconds, again
after water storage at room temperature for 24 hours and finally, after water storage for 18 months.

The bond strength of the experimental composite to etched enamel was measured compared to a control composite, Z100 (3M Dental Products, St. Paul, MN, USA, Batch 6LC). Twenty extracted bovine teeth with no obvious flaws were embedded in self-curing acrylic, (Quickmount, Fulton Metallurgical Products Corp., Saxonburg, PA, USA) and an area of flattened enamel was exposed using 120, 320 and 600 grit silicon carbide paper. The specimens were individually acid etched with 35% phosphoric acid gel (3M Dental Products, St. Paul, MN, USA) for 15 seconds, rinsed and air dried, after which a thin layer of bonding agent, (Scotchbond Multi-Purpose Adhesive, 3M Dental Products, St. Paul, MN, USA, Batch 41-5300-4747-5, JE), was applied, gently air-thinned and light cured for 10 seconds. A 2 mm thick Teflon mold with a hole, 4 mm in diameter was clamped over the treated area and filled with the appropriate restorative material prior to light curing for 30 seconds. The samples were stored in deionized water at 37°C for 24 hours, after which the shear bond strength between the composite and enamel was measured using a wire loop on an Instron Universal testing machine at a cross-head speed of 2 mm/min. Statistical differences between groups were determined by t-test.

Visual examination of failure mode was accomplished by viewing the bond strength samples under a light microscope at about 12x. Failure was identified as adhesive if nothing remained on the enamel surface, cohesive (in composite) if remnants of the composite remained in the bonded area and cohesive (in the tooth) if a portion of the tooth was removed. Failure mode was estimated to the nearest 5%.

Finally, degradation effects of 5 months of water storage for the specimens used in the fluoride release experiment were examined visually, using both an optical microscope and by SEM. Freshly made composite samples were used as a control. Discs of these materials were fractured and observed both on the top surface and at the fractured surface.
Results

Solubility
The solubility of TBATFB in monomer system A could not exceed 15% by weight. At this level, slight precipitation began to form after approximately three days at room temperature storage. For monomer system B, 45% by weight of the TBATFB could not be incorporated into the monomer, even at elevated temperatures, but 30% by weight was stable at room temperature over an extended period of time. When examined over one year later, this system has remained stable.

Monomer System Fluoride Release
Fluoride release from the two monomer systems, each containing 15% by weight of the organic fluoride, was measured out to thirteen days. The cumulative values at thirteen days were 3.08 µg/cm² and 4.36 µg/cm² for systems A and B respectively, and were found to be statistically different (p<< 0.01), using a t-test.

Composite Characterization
The composition of the fluoride-releasing composite based on the information from the monomer systems as stated above is shown in Table 2.

Fluoride Release
Table 3 shows the incremental and cumulative fluoride release for the experimental composite and the experimental resin for the test periods. For the composite, a linear fit to the data produced the relationship y=1.96x + 9.328 (r=0.999), which gives a linear fluoride release rate of 1.96 µg/cm²/day. The data for the cured resin alone yielded a linear relationship y=4.24x + 0.239 (r=0.995). Figure 1 shows the cumulative fluoride release for the composite material compared to the glass ionomer control materials. With the exception of the earliest time periods, where the glass ionomer materials show a burst of fluoride, the fluoride release of the experimental composite is comparable to, or exceeds several of the glass ionomer materials over the time periods investigated. Table 4 shows the approximate fluoride release rates (µg/cm²/day) at several time periods for the materials shown in Figure 1.
Table 3
Fluoride Release for the Experimental Composite and Resin containing 30% TBATFB, with linear regression relationships.

<table>
<thead>
<tr>
<th>Day</th>
<th>Composite Incremental (μg/cm²)</th>
<th>Cumulative (μg/cm²)</th>
<th>Resin Incremental (μg/cm²)</th>
<th>Cumulative (μg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9.33 (1.60)</td>
<td>9.3</td>
<td>6.88 (0.07)</td>
<td>6.9</td>
</tr>
<tr>
<td>4</td>
<td>4.30 (0.41)</td>
<td>13.6</td>
<td>3.09 (0.24)</td>
<td>10.0</td>
</tr>
<tr>
<td>7</td>
<td>7.27 (0.32)</td>
<td>20.9</td>
<td>8.57 (0.35)</td>
<td>18.5</td>
</tr>
<tr>
<td>14</td>
<td>18.96 (0.63)</td>
<td>39.9</td>
<td>32.14 (1.57)</td>
<td>50.7</td>
</tr>
<tr>
<td>21</td>
<td>14.33 (0.19)</td>
<td>54.2</td>
<td>32.34 (1.20)</td>
<td>83.0</td>
</tr>
<tr>
<td>28</td>
<td>11.06 (0.23)</td>
<td>65.3</td>
<td>27.45 (3.63)</td>
<td>110.5</td>
</tr>
<tr>
<td>43</td>
<td>31.35 (0.91)</td>
<td>96.6</td>
<td>85.42 (3.90)</td>
<td>195.9</td>
</tr>
<tr>
<td>56</td>
<td>24.18 (2.99)</td>
<td>120.8</td>
<td>65.87 (5.07)</td>
<td>261.8</td>
</tr>
<tr>
<td>71</td>
<td>23.72 (0.42)</td>
<td>144.5</td>
<td>56.15 (4.48)</td>
<td>317.9</td>
</tr>
<tr>
<td>98</td>
<td>58.11 (5.26)</td>
<td>202.6</td>
<td>124.50 (8.19)</td>
<td>442.4</td>
</tr>
<tr>
<td>140</td>
<td>78.27 (7.98)</td>
<td>280.9</td>
<td>115.08 (3.49)</td>
<td>557.5</td>
</tr>
</tbody>
</table>

\[ y = 1.96x + 9.328 \]  
\( (r = 0.999) \)

\[ y = 4.24x + 0.239 \]  
\( (r = 0.995) \)

Figure 1. Cumulative fluoride release for the experimental composite and several glass ionomer materials.
Table 4
Estimated Fluoride Release Rates at Several Time Periods for Tested Materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fluoride Release Rates (μg/cm²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 days</td>
</tr>
<tr>
<td>Ketac-Fil</td>
<td>15.5</td>
</tr>
<tr>
<td>Fuji II</td>
<td>5.0</td>
</tr>
<tr>
<td>Fuji II LC</td>
<td>4.0</td>
</tr>
<tr>
<td>Vitremer</td>
<td>5.0</td>
</tr>
<tr>
<td>Exp Composite</td>
<td>3.3</td>
</tr>
</tbody>
</table>

_Diametral Tensile Strength / Compressive Strength_
Values for diametral tensile and compressive strength compared to several glass ionomer and composite materials are shown in Table 5. The experimental composite had a diametral tensile strength that was similar to the resin-modified glass ionomer materials and a microfilled composite, but greater than the conventional glass ionomers. The compressive strength of the experimental material was comparable to the conventional glass ionomer materials and slightly less than the resin-modified glass ionomer materials.

The mean Barcol hardness (with standard deviation) of the experimental material immediately after curing was 55 (0.2). After 24 hours of room temperature water storage, it was 57 (1.2), and after 18 months of water storage, the mean Barcol hardness measured was 58 (0.7).

_Bond Strength to Enamel / Failure Mode_
The results of bond strength to enamel measurements are shown in Table 6. There is no significant difference between the mean bond strengths of the experimental composite and the Z100 control material (p=0.05), as determined by t-test. The failure mode for the two materials is also shown in Table 6. Failure is primarily adhesive for both systems, with somewhat higher failure within the enamel for the experimental composite.
Table 5
Diametral Tensile and Compressive Strength for Various Materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Diametral Tensile (MPa)</th>
<th>Compressive (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketac-Fil</td>
<td>15.4 (1.7)</td>
<td>172 (6.0)</td>
</tr>
<tr>
<td>Fuji II</td>
<td>7.9 (1.6)</td>
<td>156 (21.2)</td>
</tr>
<tr>
<td>Fuji II LC</td>
<td>30.4 (4.3)</td>
<td>216 (4.8)</td>
</tr>
<tr>
<td>Vitremer</td>
<td>40.3 (8.4)</td>
<td>219 (7.1)</td>
</tr>
<tr>
<td>Exp Composite</td>
<td>34.7 (0.5)</td>
<td>168 (1.9)</td>
</tr>
<tr>
<td>Silux Plus</td>
<td>44 (11)</td>
<td>385 (25)</td>
</tr>
<tr>
<td>Z100</td>
<td>93 (10)</td>
<td>477 (34)</td>
</tr>
</tbody>
</table>

Table 6
Mean Bond Strength to Enamel, MPa (sd) and Failure Mode Summary for Experimental Composite compared to a Composite Control.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bond Strength (MPa)</th>
<th>Failure Mode (%)</th>
<th>Adhesive</th>
<th>Cohesive (comp)</th>
<th>Cohesive (tooth)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBMP/Z100</td>
<td>22.0 (3.3)</td>
<td>98</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SBMP/Exp Composite</td>
<td>20.8 (1.4)</td>
<td>79</td>
<td>5</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>
Water Aging Effects
Examination with an optical microscope revealed no differences on the outer surface or the fractured internal surface of the experimental composite specimens after long-term storage in water compared to freshly made specimens. SEM examination of the samples showed similar fractured surfaces (Figure 2).

**Figure 2a.** SEM micrograph of a fractured surface of the experimental composite immediately after being made. Marker equals 10μm.

**Figure 2b.** SEM micrograph of a fractured surface of the experimental composite after 18 months of water storage. Marker equals 10μm.
Discussion

The initial solubility and fluoride release testing indicated clear advantages for the more hydrophilic BisGMA/HEMA monomer system over the BisGMA/TEGDMA system. The advantages were in the ability to incorporate more of the organic fluoride and an increased fluoride release rate. This approach might be expected to result in a reduction in physical strength properties due to the lack of an efficient crosslinking agent such as the TEGDMA. However, it was hoped that physical properties would be adequate for some dental applications.

Measured properties for the formulated composite having an 81% by weight filler loading are shown in Table 5. The experimental material has diametral tensile strength properties intermediate between conventional glass ionomer materials, such as Ketac-Fil and GC Fuji II, and a universal hybrid composite, Z100, which has relatively high strength properties. It is similar to resin-modified glass ionomer materials and a microfilled composite. The compressive strength was comparable to the conventional glass ionomer materials, but lower than the other materials. The diametral tensile strength is of greater clinical importance than the compressive strength, because this material in its clinical application will more likely be loaded in tensile or shear than in compression. Based on the comparisons in Table 5, it seems that this experimental composite could find use in a number of dental applications, such as orthodontic bracket bonding, Class III and V restorations and primary molar restorations.

The experimental composite had similar bonding to etched enamel characteristics compared to the control composite Z100. The mean bond strengths were statistically equivalent and the failure modes were only slightly different, with adhesive failure at the bonding site being the dominant mode of failure. The small increase in cohesive failure within the enamel for the experimental composite is most likely related to test methodology, where differences in crack propagation might be caused by differences in physical properties of the two composites [19].

The critical aim of producing a material with fluoride release comparable to a glass ionomer material appears to be satisfied as shown by the data in Figure 1. The primary difference between the experimental composite and the glass
ionomers is that the composite has a linear release rate, whereas the glass ionomers show a high early fluoride release rate which diminishes over time. The longer term release rate of glass ionomers typically follows a $t^{1/2}$ relationship [20,21]. Linear release rates have, however, been described previously for polymer systems utilizing organic fluoride additives [16], as well as for a fluoroaluminosilicate glass added to a resin matrix [7].

The fluoride release for the experimental resin and composite is shown in Table 3, along with the linear relationships derived from the curve fitting. From these relationships, the rate of fluoride release of the resin is $4.24 \, \mu g/cm^2/day$ and the rate for the composite is $1.96 \, \mu g/cm^2/day$. Calculating for the theoretical filler dilution, the volume percent of the resin in the composite is about 54%. Ignoring any effects other than dilution, it would be expected that the rate of release of the composite should be about $2.3 \, \mu g/cm^2/day$. This is in reasonable agreement to what was measured, given the simplicity of the calculation.

Cumulative fluoride release may not be the best measure of effectiveness for a fluoride-releasing material, rather fluoride release rates may be a better indicator. Table 4 shows approximate fluoride release rates, for the materials studied, at several times, as determined by dividing incremental fluoride release by the number of days in that measurement period. For the first two weeks, the fluoride release rate for the glass ionomer materials exceeds that of the experimental composite. Beyond two weeks, the experimental composite shows comparable or greater fluoride release than the glass ionomer materials studied. Therefore, for long term protection against demineralization, the experimental composite may provide comparable or greater protection to that shown by glass ionomer materials. On the other hand, in vitro studies of the effect of fluoride on demineralization often have experimental time durations of less than two weeks, so glass ionomers have an advantage in these types of studies. The early burst of fluoride release from glass ionomers may also provide a long-term benefit if it results in a reservoir of fluoride, which can be maintained by the slower release thereafter. The relative effectiveness of steady fluoride release versus a sudden early burst of fluoride requires further clinical verification.

The fluoride release rate of the experimental composite was substantially greater
than some of the other fluoride-releasing composites that have been studied. Dijkman et al. [7] looked at Heliomolar® which had a fluoride release rate of about 0.2 µg/cm²/day after seven days and dropped to 0.02 µg/cm²/day after 100 days. They also examined an experimental composite which contained 65% by weight of a fluoroalumino silicate glass, which resulted in 12.4% by weight of fluoride in the composite. Here they observed a linear rate of fluoride release after about five days, and that release rate was 0.3 µg/cm²/day.

A different composite, FluorEver, which contained encapsulated fluoride [10], demonstrated a large initial fluoride “burst”, followed by a declining rate of release [11]. The fluoride release rate at 8 days was approximately 5 µg/cm²/day, but by 100 days was reduced to about 0.4 µg/cm²/day. In another study of the same material [22], the fluoride release profile was similar, but the measured release rates were about one-half of that shown above.

A single paste orthodontic bonding material, Direct® was investigated by Fox [23]. This material uses a fluoride-containing glass filler as the fluoride source. The fluoride release rate at 7 days was 0.75 µg/cm²/day and at 100 days it was 0.1 µg/cm²/day.

In general, all of the above examples had lower fluoride release rates than the 1.96 µg/cm²/day rate for the experimental composite material. Assuming this linear release rate, the fluoride present in the experimental composite would be depleted in about two years. Realistically, one could expect a year of fluoride release at this rate before experiencing a declining rate of release.

For the 20 weeks that the fluoride release specimens were stored in water at 37°C, there were no signs of degradation to the composite as viewed by both optical microscopy and electron microscopy. Figure 2 shows a fractured surface of a freshly made composite disc and one stored for 20 weeks in water. No discernible differences were noted between the two that would suggest breakdown of the material. Furthermore, the mean Barcol hardness of the experimental composite after 24 hours of water aging was 57, while after 18 months of water aging it was 58. This also would indicate that the material was not deteriorating over time, however, additional testing would be required to prove long-term durability.
This investigation was a feasibility effort aimed at demonstrating that a composite formulation could be achieved that would have fluoride release similar to glass ionomer materials and have moderate physical properties. While the results of this study are promising, much could be done to optimize such a composite formulation for specific dental applications. However, for the purposes of the investigators, this material is adequate for use in future investigations of its potential for protection against demineralization. One application to be considered is that of using this material to bond orthodontic brackets with the purpose of controlling demineralization surrounding the brackets. The relatively high rate of fluoride release over a period of one year or more fits well into the time frame of orthodontic treatment, and the physical properties should be sufficient for such an application.
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