Effect of Curing Method and Storage Condition on Fluoride Ion Release from a Fluoride-releasing Resin Cement

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The purpose of this study was to evaluate fluoride ion release from a resin-modified glass ionomer cement (Fuji IILC improved, FLC) and a fluoridated resin cement (Panavia F, PF) following different curing methods and storage conditions. The specimens, which were either light-cured (LC) or chemical-cured (CC), were stored in either distilled water (DW) or demineralizing solution (DS; pH 4.5) for 1, 3, 7, 15, 30, 60, and 90 days. Fluoride ion release was measured using a fluoride ion-specific electrode. Data (n=5) were statistically analyzed using one- and three-way ANOVA (p=0.05). A "burst effect" was observed in the first week from both materials. However, fluoride ion release from FLC was seven times higher than that from PF. Storage in demineralizing solution accelerated the amount of fluoride release from both materials. In addition, LC yielded a lower amount of fluoride ion release from both materials, as compared to CC. It was concluded that both curing mode and storage medium influenced the amount of fluoride release from the tested materials.

Key words : Fluoride release, Resin cement, Ion-specific electrode

INTRODUCTION

Fluoride-containing restorative materials have been developed in a bid to prevent recurrent caries. Glass ionomer cements (GICs) are considered to be bioactive materials with a therapeutic action due to continuous fluoride release over extended periods of time. The caries prophylactic effect of GIC is attributed to the latter’s discharge of fluoride ions and the subsequent fluoride uptake by enamel and dentin. It is also known that fluoride ions can inhibit the adherence of bacteria or bacterial growth. Recently, fluoride has been incorporated into resin composites and adhesive systems – which have shown secondary caries inhibition in in vitro and in vivo studies.

A research study on fluoride release from conventional GIC, resin-modified GIC, compomer, and composite resin materials has been published. It has been found that the quantity of fluoride ions released from fluoride-releasing resin composites is significantly lower than that from GICs and compomers. Likewise, fluoridated adhesives have demonstrated a capacity for fluoride release, although the amount of fluoride release is significantly less than that of resin-modified glass ionomer cements. Further, several studies have reported that acidic solutions enhanced the amount of fluoride release from these materials.

Riding on the increased use of esthetic restorations, resin cements are also extensively used and marketed because of their esthetic advantage. Recently, a fluoride-releasing resin cement has been developed and marketed, which is expected to inhibit secondary caries formation around indirect restorations. However, there is little information on the amount of fluoride release from a fluoride-releasing resin cement under different solutions and curing methods.

The purpose of this study, therefore, was to measure the amount of fluoride released from a fluoride-releasing resin cement under different conditions. The hypothesis was that both curing method and storage condition would affect the amount of fluoride release from the resin cement.

MATERIALS AND METHODS

Materials used in this study

The materials, manufacturers, and batch numbers used in this study are listed in Table 1. A resin-modified glass ionomer cement, Fuji II LC improved (FLC, GC, Tokyo, Japan), was used as a positive control. With FLC, fluoride source was from the fluoroaluminosilicate glass powder.
The other material was a fluoride-releasing dual-cure resin cement, Panavia F (PF, Kuraray Medical, Tokyo, Japan). It was composed of two pastes, which were mixed together just before use. With PF, source of fluoride was the special surface-treated sodium fluoride.

**Specimen preparation**

Fig. 1 illustrates the methodology of specimen preparation. The materials were placed in a vinyl mold (Yamato, Tokyo, Japan), through which a hole of 3 mm diameter × 0.36 mm height was made. The materials were mixed in accordance with the manufacturers’ instructions prior to application. Following this, the mold was covered with a plastic matrix strip (Lumi Strip, Inoue Attachment Co., Tokyo, Japan) and pressed flat with a glass slide. They were cured by one of the two different curing modes: light-curing mode (LC) or chemical-curing mode (CC). For the LC group, specimens were light-cured for 20 seconds from the top and bottom surfaces using a halogen light curing unit (OPTLUX500, Demetron Research, Danbury, CT, USA). For the CC group, specimens were kept in the dark at 37 °C for 20 minutes. After curing, the disk-shaped specimens were removed from the vinyl molds and stored in a bottle containing 3 ml of either deionized water (DW) or demineralizing solution (DS; pH 4.5) at 37 °C. The demineralizing solution (DS; pH 4.5) was formulated according to van Dijk and ten Cate and Duijsters, whereby composition was 2.2 mmol/L CaCl₂, 2.2 mmol/L NaH₂PO₄, and 50 mmol/L acetic acid adjusted to a pH value of 4.5 with NaOH.

In the pilot study, the amount of fluoride release from one disk was too small to be measured for Panavia F. Therefore, five disks were put together in one bottle in this study. Care was taken to avoid the disks overlapping each other during storage in both media. The amount of fluoride released from one disk was calculated after measuring the amount of fluoride released from five disks. Therefore, 25 disks were prepared in total to obtain five specimens for each group.

**Measurement of fluoride release**

Prior to measurement of fluoride release from both FLC and PF, the five disks stored in one bottle were rinsed with 1 ml of DW or DS, which was added to the 3 ml of storage solution. The specimens were then placed in a new solution of either DW or DS. One milliliter of TISAB (Total Ions Strengths Adjustment Buffer) was added to the 3 ml of old storage solution and 1 ml of rinse solution, making a total volume of 5 ml, which was measured for the concentration of F ions. Fluoride ions were measured with an ion-specific electrode (combination electrode fluoride 960900, Orion Research, Boston, MA 02129, USA) and calculated in parts per million.

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**Table 1 Materials used in this study.**

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>Batch</th>
<th>Composition</th>
<th>Manufacturer</th>
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<tr>
<td>FLC</td>
<td>Fuji II LC improved</td>
<td>108271</td>
<td>Powder Florosilicate glass, Pigments</td>
<td>GC Corp., Tokyo, Japan</td>
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<tr>
<td></td>
<td></td>
<td>310391</td>
<td>Liquid Acrylic-maleic acid copolymer, HEMA, Water, etc.</td>
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<tr>
<td>PF</td>
<td>Panavia F</td>
<td>000129A</td>
<td>A-Paste Quartz-glass, Microfiller, MDP, Methacrylate, Photoinitiator</td>
<td>Kuraray Medical, Tokyo, Japan</td>
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<tr>
<td></td>
<td></td>
<td>000071A</td>
<td>B-Paste Barium glass, NaF, Methacrylate, Chemical initiator</td>
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HEMA: 2-hydroxyethyl methacrylate; MDP: 10-methacryloxydecyl dihydrogen phosphate; NaF: sodium fluoride

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**Fig. 1 Methodology of specimen preparation.**
Theoretically, the limit of F ion measurement is 0.02 ppm with this ion-specific electrode. Measurements were taken at intervals of 1, 3, 7, 15, 30, 60, and 90 days.

**Statistical analysis**
The means and standard deviations for the five samples of each group were calculated for each interval. Statistical analysis of the total fluoride release from each material was performed using one- and three-way ANOVA and Dunnett’s T3 test at a 95% level of confidence. The factors analyzed were material, solution, and period. Data were analyzed using the Statistical Package for Medical Science (Dr. SPSS II for Windows) for statistical procedures.

**RESULTS**
Three-way ANOVA is summarized in Table 2. Amount of fluoride release was significantly influenced by material ($F=8617.454$, $p=0.0001$), immersion solution ($F=1977.744$, $p=0.0001$), and period ($F=168.918$, $p=0.0001$) (Table 2).

The amounts of fluoride ions released from FLC and PF at each period are shown in Figs. 2 and 3 respectively. A dot and a vertical bar indicated the mean and standard deviation of the amount of fluoride ion release at each period, respectively. However, the standard deviations were so small that the vertical bars were hidden under the dots except for CC/DS and CC/DW groups in FLC. A burst effect was observed after one day of storage for both FLC and PF.

The cumulative amounts of fluoride ions released from FLC and PF up to three months are shown in Figs. 4 and 5 respectively. Constant fluoride release from each group was observed in both FLC and PF after 30 days. Total fluoride ion release from FLC was more than seven times higher than that of PF in every condition ($p<0.05$). As for the highest amount of fluoride release, it was obtained in the CC/DS group for both FLC and PF. Regarding curing mode, the CC group provided a significantly higher amount of fluoride ion release than the LC group ($p<0.05$). In terms of storage solution, the cumulative amounts of fluoride ions released in the DS groups were significantly higher than those of the DW groups ($p<0.05$).

To compare the rate of fluoride ion release from each group after 30 days, a linear functional formula passing through the dots of 30 and 90 days was drawn for each group. The virtual grade of each

<table>
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<th>Table 2 ANOVA table for three-way ANOVA.</th>
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<tr>
<td>Sum of squares</td>
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<tr>
<td><strong>Main factors</strong></td>
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<tr>
<td>Material</td>
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<tr>
<td>Liquid</td>
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<tr>
<td>Period</td>
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<td><strong>2-way interactions</strong></td>
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<td>Material*Liquid</td>
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<td>Material*Period</td>
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<td>Liquid*Period</td>
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<td><strong>3-way interaction</strong></td>
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<td>Material<em>Liquid</em>Period</td>
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<td>Residual</td>
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was put in Figs. 4 and 5, which was related to the rate of fluoride release at a steady state for each group. Comparing the values of the grades of each group, the rate of fluoride ion release appeared similar to that amount of fluoride ion release mentioned above.

**DISCUSSION**

Cylindrical specimens are routinely prepared for the measurement of fluoride ion release from fluoridated restorative materials. However, thick specimens are not appropriate for measuring fluoride ion release from resin cement, because resin cement forms a thin film during cementation. To simulate clinical conditions, thin-film specimens were prepared in this study. However, the thinner the sample size, the smaller the amount of fluoride ion release from the material, thereby reaching the limit of fluoride ion measurement. Therefore, five disks were put together in one bottle in this study. The amount of fluoride ions released from the five disks was measured, and then the amount of fluoride ions per disk was calculated.

For FLC, the source of fluoride ions was the fluoroaluminosilicate glass, while that of PF was the special surface-treated sodium fluoride. Fluoride ion release from FLC was higher than that from PF. However, the so-called “burst effect” — manifested through the greatest amount of fluoride release — was observed within the first 24 hours in every condition, which agreed with previous studies. This effect might be associated with the setting and maturation reactions of the materials. After an initial fluoride “burst”, constant fluoride release from the materials was observed.

Two curing methods — light curing and chemical curing — were compared in this study. Panavia F is a dual-cured resin cement, while Fuji II LC improved is a resin-modified GIC which sets by light curing and an acid-base reaction. In both FLC and PF, the LC group released fewer fluoride ions than the CC group. The differing amounts of fluoride release by the two different curing methods might be due to the density of the resin matrix. Ruggeberg and Caughman observed distinct differences in the degree of cure of dual-cure resin cements with and without light curing. They revealed that dual-cured resin cements depended on photoactivation to achieve an optimum degree of monomer conversion. As for Shimura et al., they measured the microhardness of the resin matrix of Panavia F 2.0 using a nanoindentation test. It was found that light curing resulted in higher resin matrix microhardness than chemical curing. It is believed that the hardness value of a cured resin matrix reflects the degree of conversion. Therefore, photoinitiated polymerization enhances cross-linking density and network quality, resulting in a reduction of resin matrix permeability for fluoride ion release.

The storage medium influenced the amount of fluoride release in this study. It was reported that more fluoride ions were released from GICs in acidic conditions. In particular, organic acids — such as acetic, lactic and citric acids — increased fluoride release from GICs. Water sorption of resin-based composites was responsible for the hygroscopic expansion, which was remarkably demonstrated at the first day and continued for a long time. Type and pH of storage solution likewise strongly influenced the water sorption and leachability behaviors of the materials. Therefore, storage in DS would cause the specimens to swell more than in DW, accelerating the rate of fluoride ion release in this study.

To compare the rate of fluoride ion release after demonstrating constant fluoride release, a virtual grade of the linear functional formula passing through the dots of 30 and 90 days.
through the dots of 30 and 90 days was calculated for each group. The results demonstrated that the rate of fluoride ion release was similar to the amount of fluoride ion release for each group. However, the sources of fluoride ion release from both materials are finite. It is therefore doubtful whether the rate of fluoride ion release would remain constant for a long period of time.

Secondary caries formation around fluoridated restorative materials has been evaluated by previous studies using polarized light microscopy, microradiography, microhardness measurement, confocal laser scanning microscopy, and scanning electron microscopy. An inhibition zone created adjacent to fluoride-releasing materials (such as conventional glass ionomer cement and resin-modified glass ionomer cement) has been accepted in these studies. However, this property is not convincingly collaborated by in vivo findings. This could be because secondary caries prevention around a restoration involves many factors: physical properties of the restorative and adhesive materials, quality of the hybrid layer, and fluoride release.

Based on the results of the current study, the hypothesis was accepted. Curing mode and storage medium influenced the amount and rate of fluoride release from fluoridated restorative materials. Light curing of the dual-cure resin cement was essential to enhance the mechanical properties of the resin cement and increase immediate bonding to tooth structures. However, light intensity may not always be sufficient to reach resin cements in the clinical situation, where the main curing method employed is chemical curing. In such a circumstance where curing is chemically activated, an increased release of fluoride may be beneficial in preventing secondary caries formation clinically. In addition, it must be highlighted that pH-selective fluoride release is necessary to ensure prevention of secondary caries formation in an acidic environment around restorations.

However, the relationship between pH value of storage solution and rate of fluoride release from fluoridated restorative material was still unclear in this study. Therefore, further studies should be carried out to clarify this relationship. In addition, clinical studies are required on the secondary caries inhibition effect of fluoride-releasing resin cement in indirect restorations.

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REFERENCES


