Mechanical and Fluoride Release Properties of Titanium Tetrafluoride-added Glass-ionomer Cement

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The aim of this study was to determine the fluoride-release and mechanical properties of a water-hardening glass-ionomer cement (GIC) (ChemFil Superior) when titanium tetrafluoride (TiF4) was added. Three experimental groups were prepared with TiF4 added to the liquid component of the material in concentrations of 0.5, 1, and 2%. The control group was the original form of the cement and free of TiF4. After the specimens (4 mm in diameter × 6 mm in length) were prepared, their compressive strength, microhardness, modulus of elasticity, and fluoride release were measured. Data were analyzed using one-way analysis of variance (ANOVA) and post-hoc test (Bonferroni/Dunn correction). The addition of TiF4 into GIC significantly reduced fluoride release from the material with the exception of 1% TiF4 (p < 0.0083). Compressive strengths of 0.5 and 1% TiF4-added GICs were higher than that of the original GIC, but it was not statistically significant (p>0.05). The differences among modulus of elasticity values of experimental and control groups were not significant (p>0.05). Similarly, microhardness of GIC was not affected with TiF4 addition (p>0.05).

Key words : Glass-ionomer cement, Titanium tetrafluoride, Fluoride release

INTRODUCTION

Glass-ionomer cements (GICs) consist of an ion-leachable calcium fluoroaluminosilicate glass powder and an aqueous solution of polyacrylic acid, and set via an acid-base reaction1-2). In time, various improvements have been made either to the powder or solution part of the material. They were namely: using alternative polymer for the polyacid component3), incorporating the acid as a freeze-dried polymer powder blended with the glass4,5), as well as using glass particles of various types and sizes6). Despite these many modifications made to the original formulation, modern conventional GICs undergo a similar reaction. These cements offer several clinical advantages due to their physicochemical adhesion to enamel and dentin7) and their ability to release fluoride8). Previous studies have demonstrated that fluoride released from the GICs decreases enamel solubility9), inhibits the growth of microorganisms10), reduces the incidence and severity of recurrent caries11,12), and alleviates sensitivity13). Furthermore, substantial amounts of fluoride may be taken up by enamel and cementum within certain distance from GIC restoration14). Therefore, the fluoride-release behavior seems to be the primary advantage of GICs. However, it is well recognized that fluoride release severely decreases within first few days after an "initial burst". If a more stable, prolonged, and/or higher amount of fluoride release were provided, it would help to enhance the anticariogenic effect of GICs. For this purpose, various fluoride compounds have been added to GIC in several studies15-17).

The effectiveness of TiF4 has been considerably highlighted in various areas of dentistry. Superiority of TiF4 to NaF was shown in restorative dentistry such as retarding the development of carious lesion18) and preventing dental hypersensitivity and erosion19,20). Topical application of TiF4 to dentin led to deposition and long-lasting retention of fluoride in high concentrations21,22). In addition, Sen & Buyukyilmaz23) observed extremely stable structure in root canal dentin when TiF4 was applied. Therefore, it may be possible that the positive characteristics – such as fluoride abundance and firm structure – of TiF4 would help to improve the properties of GICs. Therefore, the aim of this study was to investigate the fluoride-releasing capacity of a water-hardening GIC after addition of different concentrations of TiF4 to the liquid component of the cement. Furthermore, the effect of TiF4 addition on the physical properties (compressive strength, modulus of elasticity, and microhardness) of GIC was also examined.

MATERIALS AND METHODS

This study was performed using a water-hardening conventional GIC, Chemfil Superior (Dentsply, De Trey, Konstanz, Germany, Lot Number: 0206001042). The cement powder contained freeze-dried polyacrylic acid blended with alumina silicate glass. The powder was mixed with water at a ratio of 2:2 according to manufacturer’s instructions.
Fluoride release measurement
Four groups of 10 samples each were prepared. In three test groups, the powder was mixed respectively with TiF₄ solution in concentrations of 0.5, 1, and 2 %. Samples of original cement mixed with distilled water were used as control. The mixed cement was dispensed into a cylindrical Plexiglas mold (4 mm in diameter × 6 mm in length) and kept in a 100% humid environment for one hour. Following removal from the molds, all samples were stored in individual plastic vials containing 5 ml of deionized water at 37°C. The storage water was changed at Days 1, 2, 3, 7, 14, 21, and 28. During each water replacement routine, sample was removed from the vial, rinsed with de-ionized water, and transferred to a new tube containing fresh deionized water at 37°C. A calibrated pH electrode was immersed into the solution, and 5 M NaOH was added until pH was between 5.0-5.5. This mixture was brought to room temperature, poured into a 1-liter volumetric flask, and diluted to the mark with distilled water. Fluoride release was then measured using F ion selective electrode (model 96-09, Orion Inc., Boston MA, USA). System was calibrated prior to each measurement with standard fluoride solutions.

At the end of Day 28, samples of each group were removed from immersion solution and subjected to compressive strength test. This test was performed using a universal testing machine (AG-50 kNG, Shimadzu Co., Kyoto, Japan) at a loading rate of 0.5 mm/min at room temperature. The surface of each sample was kept wet with deionized water during testing. The specimens were examined visually before and after testing.

Microhardness and modulus of elasticity measurements
Ten new samples for each group were prepared as described previously for microhardness and modulus of elasticity tests. The samples were then stored in individual vials containing deionized water at 37°C for seven days. Both microhardness and modulus of elasticity measurements were done using a dynamic ultra-microhardness tester (DUH-W201S, Shimadzu Co., Kyoto Japan). Test force and loading speed were 4 gf/s for all measurements. A Vickers diamond indenter was used in the microhardness test, and dynamic hardness values were recorded. Meanwhile, modulus of elasticity was determined by using Young’s modulus test.

Statistical analysis
One-way analysis of variance (ANOVA) with post-hoc test (Bonferroni/Dunn correction) were used to determine the significant difference between the cumulative fluoride measurements released from the original and experimental samples. Level of significance was set at p = 0.05. However, after Bonferroni correction, this level was reset to p = 0.0083.

Similarly, results of microhardness, compressive strength, and modulus of elasticity tests were statistically analyzed using one-way analysis of variance at p<0.05 significance level.

RESULTS
Cumulative fluoride release measurements are presented in Table 1. All three experimental groups released fluoride as a characteristic of original GIC (Fig. 1). Addition of TiF₄ to GIC significantly decreased fluoride release (p<0.0083) with the exception of 1 % TiF₄ (p>0.0083) (Table 1).

Results for compressive strength, microhardness, and modulus of elasticity of original and experimental GICs are also presented in Table 1. The GIC which included 1 % TiF₄ presented the highest value for compressive strength. However, there were no statistically significant differences among the original and experimental materials (p>0.05) (Fig. 2). During the compressive strength test, it was observed that cracking of experimental GIC specimens occurred in a laminar formation, whereas original GIC samples were crushed into extremely small particles. Hence, by adding TiF₄ to conventional water-

<table>
<thead>
<tr>
<th>Material</th>
<th>Cumulative fluoride release (ppm) (Mean±SD)</th>
<th>Compressive strength (MPa) (Mean±SD)</th>
<th>Modulus of elasticity (GPa) (Mean±SD)</th>
<th>Microhardness (DHV) (Mean±SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original GIC</td>
<td>10.95±1.05*</td>
<td>148.30±9.63</td>
<td>17.66±7.82</td>
<td>49.89±21.48</td>
</tr>
<tr>
<td>0.5%TiF₄-GIC</td>
<td>7.87±1.26*</td>
<td>155.95±10.5</td>
<td>14.55±5.68</td>
<td>51.94±13.99</td>
</tr>
<tr>
<td>1 %TiF₄-GIC</td>
<td>9.06±1.71</td>
<td>160.32±25.28</td>
<td>14.01±9.51</td>
<td>45.03±15.97</td>
</tr>
<tr>
<td>2 %TiF₄-GIC</td>
<td>8.38±1.62*</td>
<td>147.60±26.32</td>
<td>14.57±5.06</td>
<td>44.62±8.27</td>
</tr>
</tbody>
</table>

Same symbols indicate significant differences.
Fig. 1 Cumulative fluoride release from the materials used in this study. There were significant difference between the original and the experimental GICs except for 1% TiF₄-added group (p<0.05).

Fig. 2 The mean compressive strength values in MPa of original and experimental GICs. There were no significant differences among the groups (p>0.05).

Fig. 3 Modulus of elasticity of the original and experimental GICs used in this study. There were no significant differences among the groups (p>0.05).

Fig. 4 Dynamic hardness values (DHV) of materials tested in this study. There were no significant differences among the groups (p>0.05).

hardening GIC, a more elastic material was formed. However, differences among the moduli of elasticity of the materials were insignificant (p>0.05) (Fig. 3). Similarly, there were no significant differences among the microhardness values of all groups (p>0.05) (Fig. 4).

It is worthwhile to note that handling time of the experimental GICs seemed to be shorter than that of the original group during powder-and-liquid mixing.

DISCUSSION

Ions can be incorporated into GIC in two ways: during the mixing phase of the cement or by immersing the mixed cement into a solution which contains the ions. In this study, TiF₄ was chosen to enhance fluoride release since it was a powerful source of fluoride. However, no improvements in cumulative fluoride release were observed after 28 days. On the contrary, there was a significant reduction in fluoride release except with 1% TiF₄. One possible explanation to this could be the retention of fluoride by a complexation process. Another possible factor affecting fluoride release could be the solubility of the additive itself. When additives with different solubility levels were incorporated into GIC, fluoride release at varying amounts was observed. Previous investigations showed that NaF, with its high level of solubility, enhanced fluoride release. In this study, the low solubility of TiF₄ probably prevented increase in fluoride release.

Setting reaction of GIC based on acid-base reaction is complex and may vary with composition. Inherent acidity of the cement during setting reaction probably contributes to fluoride release. The pH values of 0.5, 1, and 2% TiF₄ are 1.90, 1.65, and 1.40 respectively – indicating a high level of acidity. When the powder and liquid components of the GIC are mixed, acidic protons rapidly attack the glass particles, from which calcium and aluminum ions are extracted. Hence, when acidity is increased by
adding TiF₄, more Al³⁺ and Ca²⁺ ions will be extracted during the initial setting reaction. These excess Al³⁺ and Ca²⁺ ions in the fresh cement will then bind more fluoride ions, leading to a decrease in fluoride release.

In this study, the fluoride release profiles of both experimental and original GICs were similar. Williams et al.²¹ showed that fluoride release profile was influenced by the method of incorporation. When ions were added in the form of a mixing liquid, they appeared to behave in a similar manner to those released from "normal" glass-ionomers.

Several attempts have been made to enhance the antimicrobial effect and fluoride-release property of GICs. However, studies on the effect of additives on the mechanical properties of restorative material are limited. Mechanical properties of a restorative material can be determined using several test methods, ranging from compressive, shear and tensile strengths to microhardness and/or modulus of elasticity. Compressive strength, although without a concrete meaning, is a mechanical strength commonly tested for in most of the studies, as it well represents the mechanical integrity of a material²⁹. It was suggested that compressive strength together with other mechanical properties of a GIC improved with time.³⁰,³¹ However, microhardness strength values between Days 7 and 30 were not significantly different²⁸. Therefore, in this study, a 7-day lead time was deemed sufficient for new samples to be prepared for modulus of elasticity and microhardness tests. On the other hand, samples were stored in distilled water for 28 days for fluoride evaluation before they were subjected to compressive test.

It has been noted that additional fluoride enhanced compressive strength.³⁰ However, such a synergistic relation between fluoride release and compressive strength was not observed in this study. On the contrary, compressive strength of experimental GICs releasing less fluoride was higher than that of the original even though it was not statistically significant.

Amongst other mechanical properties, hardness and modulus of elasticity determine the resistance of a restorative material to occlusal forces.³² Yap et al.³³ quoted that hardness has been used to predict the wear resistance of a material and that it has been related to the strength and ductility of the material. On the other hand, modulus of elasticity describes the relative stiffness of a material within its elastic range. The clinical outcome depends on how well the modulus value of the natural hard tissue matches with that of the restorative material. While high modulus of elasticity is required to withstand deformation and cuspal fracture, a low modulus allows the material to flex during tooth flexure.³⁴–³⁵

In this study, therefore, cracking in laminar formation of experimental GIC specimens during the compressive strength test could be ascribed to the flexibility of these samples with their low modulus of elasticity. More flexible restorative materials are also required for cervical lesion restorations because of the greater tooth flexure at the cervical region. Heyman et al.³⁶ reported that the retention rate of restorations with low modulus of elasticity was significantly higher than that with high modulus of elasticity. Depth-sensing microindentation approach is promising as a standardized test method for characterizing the hardness and modulus of different types of dental restorative material due to its relative simplicity and the use of size scale-appropriate specimens.³⁷ Therefore, in this study, the hardness and modulus values of both original and experimental GICs were compared using depth-sensing microindentation technique. However, no significant differences in these physical properties were observed among the test groups. According to the modulus of elasticity test results, the original GIC seemed to be a stiffer material as compared to the experimental GICs (Fig. 3).

The addition of different kinds of additive to GIC seemed to upset the intrinsic chemical equilibrium of the material even though addition was made in a simple manner. Any improvement in fluoride-releasing capacity and antimicrobial effect of GICs without compromising their physical properties would be of great value.³⁷ Thevadass et al.³⁸ reported that mixing the cement with a 4 % NaF solution increased fluoride release without changing the compressive strength of GIC significantly. On the other hand, Alkesen et al.³⁹ found that alkali metal-fluoride solution disrupted the structure of GIC significantly. Lucas et al.⁴⁰ observed that fracture toughness of GIC improved when hydroxyapatite was added to the material, but with only insignificant increase in fluoride release. Contrary to this, it was reported that the addition of zinc sulfate increased the solubility of GIC while it enhanced fluoride release and inhibited the growth of streptococcus mutans.³⁷ In our present study, certain changes in fluoride-release and mechanical properties were also observed with the addition of TiF₄. It may be suggested that one should be very careful when using additive to enhance fluoride release that it does not compromise the mechanical properties of the material.

CONCLUSION

In this study, 0.5, 1, and 2 % TiF₄ was added to conventional GIC to enhance the fluoride-release and mechanical properties of the material. It was observed that the addition of TiF₄ did not increase fluoride release. Apart from this, the improvements observed in mechanical properties were also not statistically significant.
ACKNOWLEDGEMENTS

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