Change in Physical Properties of Tannin Fluoride-containing Luting Cements following Immersion in Water up to 12 Months

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Examination was made on the physical properties of commercially available tannin-fluoride incorporated polycarboxylate and zinc phosphate cements for luting, following immersion in distilled water for up to 12 months. Same cements, containing no fluoride, were used as controls.

Key Words: Fluoride incorporated luting cements, Tannin-fluoride preparation, Physical properties.

INTRODUCTION

Tannin-fluoride preparation (HY-agent) is a recently developed caries preventive material that reinforces both crystal and collagen of tooth structure. At present, dental cements into which HY-agent has been incorporated are commercially available with zinc phosphate, polycarboxylate, zinc oxide-eugenol and glass-ionomer products and the characteristics of these cements have been examined by several investigators. In our previous investigation, a decrease in compressive and diametral tensile strength was observed following 12 months immersion in distilled water with zinc phosphate, polycarboxylate and glass ionomer cements for luting, containing no fluoride. Because the release of fluoride from the cement is an essential factor for the reinforcement of tooth structure, we examined the influence of prolonged water immersion on the physical properties of polycarboxylate and zinc phosphate cements into which tannin-fluoride was incorporated.

MATERIALS AND METHODS

Commercially available polycarboxylate and zinc phosphate cements, with or without HY-agent, were examined (Table 1). Five specimens were prepared according to A.D.A. Specification No. 87, for each experiment. Compressive and diametral tensile strength, changes in specimen’s size and water sorption during storage were determined periodically up to 12 months. Specimens were prepared in a constant-temperature and humidity room, maintained at 22±1°C and 50±10%RH. Specimens were stored in distilled water at 37°C.

A universal testing machine* with a cross-head speed of 0.5 mm/min. was used for determination of compressive and diametral tensile strength. The height of cylindrical specimen was measured with a micrometer** and the changes in specimen’s dimension during storage was observed. Water sorption was examined by a microbalancer***.

* Autograph IS-5000, Shimadzu Seisakusho Co., Japan
** Mitsutoyo Seisakusho Co., Japan
*** Type L-200, Shimadzu Seisakusho Co., Japan
Table 1 Materials used

<table>
<thead>
<tr>
<th>Cement</th>
<th>Manufacturer</th>
<th>Batch No.</th>
<th>Hy-agent</th>
<th>Mixing time (sec.)</th>
<th>P/L ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarboxylate</td>
<td>Shofu</td>
<td>P: 127889</td>
<td>–</td>
<td>30</td>
<td>1.8 g/1.0 g</td>
</tr>
<tr>
<td>Carbo Cement</td>
<td></td>
<td>L: 127804</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HY-BOND Polycarboxylate</td>
<td>Shofu</td>
<td>P: 028213</td>
<td>+</td>
<td>30</td>
<td>2.2 g/1.0 g</td>
</tr>
<tr>
<td>cement</td>
<td></td>
<td>L: 028205</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc phosphate</td>
<td>Shofu</td>
<td>P: 097986</td>
<td>–</td>
<td>60</td>
<td>1.5 g/0.5 ml</td>
</tr>
<tr>
<td>Micro Cement</td>
<td></td>
<td>L: 087916</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HY-BOND</td>
<td>Shofu</td>
<td>P: 018138</td>
<td>+</td>
<td>60</td>
<td>1.5 g/0.5 ml</td>
</tr>
<tr>
<td>Zinc phosphate cement</td>
<td></td>
<td>L: 068135</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In each test, examination was made at 1 day, 1, 2, 4, 8, and 12 months after the mixing.

RESULTS

1. Compressive strength

The results are shown in Fig. 1. In regard to the incorporation of HY-agent to polycarboxylate cement, little influence was observed on the strength of resultant specimens. Decrease in compressive strength following water immersion was not apparent even at the end of 12 months, satisfying the requirement (50 MPa) of A.D.A. Specification No. 618).

On the other hand, in the case of zinc phosphate cement, a considerable increase in strength was seen at the end of 12 months following the incorporation of HY-agent. Regardless of the incorporation, compressive strength of cements satisfied the requirement (75 MPa) of A.D.A. Specification No. 87).
2. Diametral tensile strength

The results are shown in Fig. 2. For polycarboxylate cement, the incorporation of HY-agent had little influence on strength, although a slight increase was observed at 4 months. However, regardless of the incorporation, a considerable decrease in strength was observed at the end of 12 months.

On the other hand, with zinc phosphate cement, an increase in strength was observed after 8 or 12 months immersion, following the incorporation of HY-agent.

3. Change of specimen's dimension

A considerable shrinkage, approximately twice that of the control, was observed with polycarboxylate cement following the incorporation of HY-agent at the end of 12 months (Fig. 3).

In contrast, only slight contraction was noted with the incorporation.

4. Water sorption

The result are shown in Fig. 4. Polycarboxylate cement containing HY-agent exhibited an increase in water sorption at the initial stage and this continued for 12 months.

On the other hand, the increase in water sorption was negligible with zinc phosphate cement.

![Figure 2](image-url)  
Figure 2  Effect of water immersion on the diametral tensile strength

![Figure 3](image-url)  
Figure 3  Effect of water immersion on the change in dimension
DISCUSSION

It has been reported\(^1\) that, reinforcement of tooth structure with HY-agent occurs by the reaction of fluoride to tooth apatite or tannin to tooth collagen. Therefore, the solubility of incorporated HY-agent is of primary importance for the reinforcement. Apparently, one of the most interesting aspects in the incorporation of such fluorides to dental cement is the alteration in physical properties following its long-term release.

In this investigation, although the influence of incorporation of HY-agent was not as apparent as previously expected, contraction of cements reached nearly twice that of control and although slight, water sorption also increased, in the case of polycarboxylate cement. In some investigations\(^2,3,5\), reinforcement in the manipulative characteristics and physical properties of polycarboxylate cement following the incorporation of HY-agent were reported, assuming an improvement in reactivity of powder to liquid.

In the case of zinc phosphate cement, on the other hand, these alterations were negligible. Besides, considerable reinforcement in strength and water sorption was apparent. Although this phenomenon remains to be clarified, it is considered to be favourable to clinical practice.

In the case of polycarboxylate cement, the benefits of addition of HY-agent been demonstrated both experimentally\(^2,9,10\) and clinically\(^11\). However, as these studies were made in a relatively limited periods, further investigation is needed on the alteration of physical properties of the resultant dental cements following the incorporation of fluoride.

CONCLUSION

Physical properties of polycarboxylate and zinc phosphate cement into which HY-agent was incorporated for caries prevention, were examined in relation to long-term water immersion. The following results were obtained:

1. Regarding either compressive or diametral tensile strengths, little reinforcement was observed with HY-agent containing polycarboxylate cement.

On the other hand, an apparent increase in strength was obtained with zinc phosphate cement.
2. Reduction in dimension of HY-agent incorporated polycarboxylate cement at the end of 12 months was that of cements lacking fluorides. Water sorption increased during the initial stage of immersion with the addition of HY-agent, however the differences from the control gradually became small.

With zinc phosphate cement, in contrast, reduction in dimension and water sorption was noted following incorporation of HY-agent.

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REFERENCES
0.87より大きい合金では、AuCu I型規則格子の微細なドメインが粒内に連かやに形成された。この反応により引き起こされる弾性ひずみ場が時効硬化的原因であった。

タンニン・フッ化物合剤（HY 剤）の配合された
合着用セメントの長期浸水による物性の変化

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タンニン・フッ化物合剤（HY 剤）の配合されたカルポキシレートセメントとリン酸セメントについて長期間の浸水に伴う物理的性質の変化を検討し、フッ化物の配合されていない同種セメントと比較した。

圧縮、引張り強さについてみると、カルポキシレートセメントの場合には HY 剤配合による影響はほとんどみられないが、リン酸セメントの場合には、強さが明らかに増加した。寸法変化、吸水性についてみると、HY 剤の配合されたカルポキシレートセメントの場合、12ヶ月の浸水後では配合されていないものの約2倍の収縮を示し、吸水率も硬化後の期待からわずかがら増加した。一方、リン酸セメントの場合にも、HY 剤を配合されたものの収縮も吸水率も逆にわずかから減少した。

有機酸中におけるグラスアイオノマーセメントの侵食過程

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酢酸、乳酸、クエン酸および塩酸中におけるグラスアイオノマーセメントの侵食過程を化学分析、SEM 観察および赤外吸収光分析により検討した。

各酸の濃度と Al 又は C との錆体の安定度定数が大きい程あるいは、酸溶液の pH が低くなる程、Al、Ca、Na、Si および F の溶出量が多くなった。SEM 観察により、0.01 M クエン酸および塩酸中ではセメントマトリックスが溶脱することが分かった。0.01 M クエン酸および塩酸中では、セメント液渇後に白色沈殿が生成した。その沈殿は、水和ケイ酸ゲルであることが IR スペクトルによりわかった。

人エナメル質に対する酸処理法の効果
（酸処理法の臨床応用の改善）

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エナメル質酸処理法に関する研究として、エナメル質の酸処理面や接着破壊面を SEM を用いて観察した。また、酸処理に伴う Ca の溶出量、中心線平均アラサ、接着強さの測定を行った。その結果、まず小径中心部が溶かし、次に小径辺縁部に細かい溝が形成され、酸処理時間が長くなる程溝は広く深くなった。接着破壊面には、レジンとエナメル質の破壊が観察された。リン酸はすべての測定面において大きな値を示した。シトラコン酸とビリビン酸は、Ca の溶出量はリン酸の約半分であったが、それ以上の測定値はリン酸とほぼ等しかった。クエン酸はすべての測定値で最小の値を示した。Ca の溶出量と接着強さは、酸の濃度が増加するにしたがい一定の値まで増加するが、その後減少した。すべての測定値は、酸処理時間が長くなる程増加した。シトラコン酸の臨床使用の可能性が示唆された。