pH Determinations on the Surface of Luting Cements
I. A Test Method

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The pH changes of small amounts of distilled water in contact with the surface of samples of dental luting cement were determined by using a flat combination electrode. The results showed that the initial pH value and the neutralization rate of the water in contact with the cement surface decreased with both decreasing amounts of water and the time interval between cement mixing and contact with water. Initial pH value and the neutralization rate for polycarboxylate cement was higher than those for zinc phosphate and glass ionomer cements. This suggests that the water in contact with polycarboxylate cement is rapidly neutralized because of the relatively small release of acid from the cement after initial setting.

Key words: Luting cement, pH, Flat pH electrode, Test method

INTRODUCTION

The acidity of dental cements is well-known as a cause of pulpal irritation, and many studies have investigated the problem of acidity in order to obtain reliable data as to the true pH value of the cements. Harvey et al have directly measured the pH on the surface of dental cements by using an organic indicator. Norman et al have used an antimony electrode to measure both the surface pH and the pH of the internal mass of the cements during setting. Jyoshin has used a glass electrode for direct pH measurements on the cements. Kent et al have measured by means of a flat-headed glass electrode in direct contact with the cement paste. Both Crowell and Brune have measured the pH of water (5 ml) in contact with pellets of cement by using a glass electrode.

One side of a luting cement in the mouth is in contact with the tooth structure, in which there is no significant circulation of fluids. The cement tends to saturate the fluid in the approximating dentin with acid, and this acid can probably be removed only by diffusion, with little or no assistance from any internal circulation. To study the effect of cement acidity on pulp irritation, one must employ an indirect pH measurement method whereby little fluid and little circulation exists on the surface of the cement samples. We used a flat combination electrode which seemed to be a suitable pH electrode for this purpose, and describe here the construction of a pH measurement apparatus and also discuss the pH change of small amounts of distilled water in contact with the cement surface during setting.

MATERIALS AND METHODS

Tests were conducted on samples of three cements — zinc phosphate cement (ELITE
CEMENT 100), polycarboxylate cement (LIV CENERA), and glass ionomer cement (FUJI IONOMER type I). The codes, brand names, batch numbers, powder/liquid ratios and mixing times of the three commercial luting cements are given in Table 1. The chemical composition of these cement powders and liquids have been described previously 7).

To conduct the pH measurement of a small amount of water in contact with the cement surface, a flat combination electrode (#6210-06T, HORIBA, Kyoto, Japan) was used. The apparatus assembly is presented in Figure 1. The pH-sensitive surface of the elec-

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>(type)</th>
<th>Batch No.</th>
<th>P/L Ratio</th>
<th>Mixing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL</td>
<td>ELITE CEMENT 100</td>
<td>(zinc phosphate)</td>
<td>P: 300341</td>
<td>1.45 g</td>
<td>1'30&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L: 291141</td>
<td>0.5 ml</td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>LIV CENERA</td>
<td>(polycarboxylate)</td>
<td>P: 030531</td>
<td>2 g</td>
<td>30&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L: 260431</td>
<td>1 g</td>
<td></td>
</tr>
<tr>
<td>FI</td>
<td>FUJI IONOMER (type I)</td>
<td>(glass ionomer)</td>
<td>P: 170921</td>
<td>1.4 g</td>
<td>40&quot;</td>
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<td></td>
<td></td>
<td></td>
<td>L: 300831</td>
<td>1.0 g</td>
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*: G-C Dental Industrial Corp., Tokyo, Japan

Figure 1  Design of the apparatus for pH measurement.
trode was a flat circle, 9 mm in diameter. Calibration was accomplished by measurement of standard buffer solutions, pH 4.00 and 6.88 at 20°C. Filter paper (#6, TOYO ROSHI Co., Tokyo, Japan), 12 mm in diameter, was used to maintain water at the pH-sensitive surface of the electrode and to prevent the pH electrode from adhesion with the test specimen. Although it was feared that the cement surface might become contaminated by the filter paper and potassium chloride from the electrode, stable and reproducible values were obtained without difficulty. Therefore, pH values for each specimen were continuously measured for 24 hours by the electrode connected to a pH meter (M-5, HORIBA), coupled to a recorder (DR-1112, OHKURA ELECTRIC Co., Tokyo, Japan).

Three specimens of each cement (approximately 1 g) were prepared according to the manufacturer's instructions. Specimens were then placed in the specimen holder and were quickly transferred to the frame. The filter paper was placed on the surface of the specimens at an arbitrarily chosen time from the start of mixing, and the guide rim was clamped. A small amount of distilled water (pH 6.8–7.2) was dropped on the filter paper by a microsyringe and the pH-sensitive surface of the electrode came into contact with the filter paper within 30 seconds. The amounts of water used were 0.2, 1.0 and 2.0 ml, and the time intervals between mixing and contact with water were 3, 5, 10 and 30 minutes. The manipulation and the pH measurements were conducted at 23±2°C and 60±10% humidity.

The recording paper containing the pH change curve was then placed on the measuring table of a digitizer (MYPAD-A3 K-510, KANTO DENSHI Co., Tokyo, Japan) connected to a computer (APPLE IIe, Apple Computer Inc., Cupertino, C.A., USA). As the sensor was moved along the curve, the computer measured the pH value. It calculated the mean curve from the pH value at arbitrary elapsed time, and this curve was displayed on an X–Y plotter (7470A, HEWLETT PACKARD, San Diego, C.A., USA) by fitting the cubic spline interpolation formula.

For comparison, pH values were also measured by a conventional combination electrode (#6028, HORIBA) on 25 ml of the water after immersion of these cements during setting. These data are presented in Table 2.

<table>
<thead>
<tr>
<th>Table 2 Comparison of pH values obtained by various investigators</th>
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<tbody>
<tr>
<td><strong>Investigation</strong></td>
</tr>
<tr>
<td></td>
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<tr>
<td>Crowell(2)</td>
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<tr>
<td>*Norman et al(2)</td>
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<tr>
<td>*Jyoshin(2)</td>
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<tr>
<td>*Adaniya et al(2)</td>
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<tr>
<td>Brune et al(2)</td>
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<tr>
<td><strong>Present Investigation</strong></td>
</tr>
<tr>
<td>Conventional</td>
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<tr>
<td>(±0.35)</td>
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<tr>
<td>Flat</td>
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<td>(±0.22)</td>
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</table>

*: direct measurement  ( ): standard deviation
RESULTS

The pH changes during 24 hours with three amounts of water in contact with zinc phosphate cement (EL) are shown in Figure 2-A. The initial pH value and the slope of the pH curve decreased with decreasing amount of water. However, within an hour from the start of measurement, the pH change was independent of the amount of water. Considering the clinical situation of cement against real tooth structure, it is desirable to use the smallest amount of water possible in such a test. However, reproducibility of the pH change curves obtained in less than 0.1 ml of water was inadequate, because the volume of water was too small to be in stable contact with the electrode.

The pH changes of zinc phosphate cement (EL) over a 24 hour period for four time intervals between mixing and water contact are shown in Figure 2-B. The initial pH value and the slope of the pH curve decreased with decreasing time intervals between mixing and contact with water. Thus, the pH change of water in contact with the cement surface was affected by both the amount of water and the time interval between mixing and contact with water. The other cements also behaved similarly. As a standard test condition, the amount of water was 0.2 ml and the time interval was 3 minutes.

The pH changes of three luting cements obtained in the standard test condition are shown in Figure 3-A. The pattern of the pH change for polycarboxylate cement (LC) differed somewhat from those of zinc phosphate (EL) and glass ionomer cement (FI). For the polycarboxylate cement, the pH was initially higher and the slope of the curve was steeper than those for the other cements. For glass ionomer cement, the pH value was initially slightly higher than that for the zinc phosphate cement and lower than that after 24 hours. Glass ionomer cements do not cause pulp irritation clinically\(^8\), but the pH value we obtained showed an acidity nearly the same as the zinc phosphate cement. Although both the glass ionomer and polycarboxylate cements mainly contain polycarboxylic acid in the cement liquid\(^7\), the pH changes of each cement type showed a different pattern.
Figure 3-A: pH changes of 3 cements obtained by the flat electrode technique. (0.2 ml water at 3 minutes time between mixing and water contact)

Figure 3-B: pH changes of 3 cements obtained by a conventional combination electrode. (Cement immersed in 25 ml water)

The pH changes obtained by the conventional method are shown in Figure 3-B. The initial pH value in each pH change curve was higher, but the slope of the pH change curve was equal or less than that obtained by using the flat combination electrode. The lowest pH values of the polycarboxylate cement and glass ionomer cement were approximately 1.0 higher, and that of the zinc phosphate cement was approximately 0.3 higher than those obtained by the flat electrode (Fig. 3-A). Representative data are shown in Table 2, and are compared with previous data\textsuperscript{2,3,5,6,9). The flat electrode indicated a higher acidity than the conventional indirect method.

DISCUSSION

Initial Acidity

In the mouth, the acid of the cement may be neutralized by the mineral salts in the dentin, and as setting proceeds, the cement itself may take up some of the acid which is liberated in the earlier setting stages. This study has investigated only the relationship between water and the cement surface.

The pH values obtained by using the flat combination electrode were lower than those obtained by the conventional indirect method. The differences between the flat electrode method and the conventional electrode method are 1) the amount of water, and 2) the distance between the cement surface and pH-sensitive surface of the electrode. The differences in pH values obtained by the two methods can be explained by the degree of ionization of the acids and the diffusion coefficients of the acids in solution.

The initial acidity of water placed in contact with the cement surface during setting is caused by the release of acid from the unreacted cement liquid. The amount of unreacted cement liquid depends on the rate of the setting reaction\textsuperscript{10), and the pH value depends on the dissociation fraction of the acid released into the water. The cement liquid of the zinc phosphate cement contains approximately 56% phosphoric acid\textsuperscript{7). Ortho-
phosphoric acid ($\text{H}_3\text{PO}_4$) dissociates to $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$ according to the pH reactions:

\[
\begin{align*}
\text{a)} & \quad \text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^- + \text{H}^+ \\
\text{b)} & \quad \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}^+ \\
\text{c)} & \quad \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}^+
\end{align*}
\]

The dissociation depends on the well-known equation of Henderson-Hasselbalch:

\[
\text{pH} = \text{pK} - \log\left(\frac{1-\alpha}{\alpha}\right),
\]

where $\alpha$ is the dissociation fraction, $\text{pK} (=-\log\text{Ka})$ is the constant and Ka is the dissociation constant of each component; $\text{pK}$ is 2.1, 7.2 and 12.4 for $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$, respectively. At pH 3 and 4, the dissociation fractions of phosphoric acid are determined by equation (1) and were 0.89 and 0.99, respectively.

In the polycarboxylate and glass ionomer cements, the liquid contains 42%-59% polycarboxylic acid$^7)$. The pH of the solutions containing polyelectrolytes fit the generalized Henderson-Hasselbalch equation by Katchalsky$^{11})$,

\[
\text{pH} = \text{pK} - n \log\left(\frac{1-\alpha}{\alpha}\right),
\]

where $\text{pK}$ and $n$ are constants and independent of the molecular weight and concentration, and $\alpha$ is the degree of ionization. For the polyacrylic acid, $\text{pK}=6.17$ and $n=2$; the degrees of ionization at pH 3 and 4 were determined by equation (2) and were 0.025 and 0.076, respectively. The degree of ionization for polyacrylic acid at around pH 3 to 4 is lower than that of phosphoric acid, and the pH changes with polycarboxylate and glass ionomer cements were more affected by the amount of water than the pH change with the zinc phosphate cement.

The Nernst-Einstein relation for the coefficient of diffusion, employing Stokes’ law for the mobility of spherical particles in a viscous liquid, gives the relation between viscosity $\eta$ and coefficient of diffusion $D$,

\[
D = \frac{kT}{6\pi r \eta},
\]

where $r$ is the radius of the diffusing particles, considered as spheres$^{12})$, $k$ is the constant, and $T$ is the absolute temperature of the system. The molecular weight of polyacrylic acid is 5000–30000$^{10}$, while that of orthophosphoric acid is only 98. Considering this larger molecular weight and size in equation (3), the diffusion coefficient for polyacrylic acid is smaller than that of orthophosphoric acid. Furthermore, the conventional pH electrode—sample distance is larger than the flat-electrode—sample distance (i.e. the thickness of filter paper —approximately 0.25 mm). Thus, the initial measured pH value of water in contact with the cement surface may be affected by the rate of release and the diffusion of acid from the unreacted cement liquid.

**Neutralization of Surface Water**

The neutralization rate of surface water may depend upon three factors: (A) the
rates of dissolution of cement powder, (B) the rate of decomposition of the matrix, and (C) the continued release of acid from unreacted cement liquid. In our neutralization tests, dilute solutions (pH 4) of polycarboxylate cement liquid (LC) required dissolution of more cement powder (0.5 mg/ml) than did the zinc phosphate cement liquid (0.1 mg/ml) to obtain neutralization to around pH 6. However, we found that the neutralization rate of the water in contact with the polycarboxylate cement surface was faster than that of the water in contact with the zinc phosphate cement surface (Fig. 3-A).

This suggests that the neutralization rate of the water in contact with the polycarboxylate cement surface is mainly affected by the relatively slower release of acid from the unreacted liquid in the cement surface and not from dissolution of cement powder or matrix. Adaniya et al.9) reported that the pH value of polycarboxylate cement obtained by direct pH measurement was rapidly raised (i.e. the cement was neutralized) to around pH 6 within 1 hour from the start of mixing, while that of zinc phosphate cement was slowly neutralized and still showed a pH < 3 over the same period of time, due to the continuous release of acid into water from the cement surface after initial setting.

Although polycarboxylate and glass ionomer cement liquids contain polycarboxylic acids, the neutralization rate of the water in contact with the glass ionomer cement surface was nearly as slow as that in contact with the zinc phosphate cement. Infrared analysis (multiple internal reflection method) of the surface of glass ionomer cement during setting showed that the absorption band of COOH groups at around 1700 cm⁻¹ still remained after 24 hours from cement mixing. This suggests that carboxylic acid remains on the surface of the glass ionomer cement after initial setting. Thus, the slow neutralization rate of the water in contact with the glass ionomer cement is also due to the continuous release of acid into water from the cement surface.

CONCLUSIONS

The pH changes of small amounts of distilled water in contact with cement surfaces were determined by using a flat combination electrode, and the patterns of pH change for three luting cements were determined during setting. Initial pH value and the slope of the pH curves decreased with decreasing amount of water and the time interval between cement mixing and contact with water. The initial pH value of the water in contact with the cement surface seems to be affected by the release and the diffusion of acid from the unreacted cement liquid. While the rate of neutralization of the acid may depend on the rate of dissolution of the unreacted cement powder, the rate of decomposition of the matrix and/or the rate of release of acid, the water in contact with polycarboxylate cement is rapidly neutralized because very small amounts of acid are released from the cement after initial setting. Zinc phosphate and glass ionomer cements show slow neutralization due to the relatively larger amount of acid release from the unreacted cement liquid.

REFERENCES


合着用セメント表面の pH 測定

I. 測定方法と pH 変化

セメント表面に接する少量の蒸留水の pH 値をフラット型複合 pH 電極により測定し、硬化中の 3 種合着用セメントの pH 変化を測定した。初期の pH 値と中和速度は接する水量と試験から接触するまでの保有持続時間の減少に伴い低くなった。すなわち、セメント表面に接する水の初期の pH 値は未反応のセメント液の酸の溶出と拡散に影響されるためと考えられる。一方、その中和速度は未反応のセメント粉末の溶解速度、マトリックスの分解速度あるいは酸の溶出速度に依存するものと考えられる。ゆえに、ポリカルボキシレートセメントに接する水の中和が遅いのは、初期硬化後の酸の溶出が少なかったためであり、これに対し、リン酸亜鉛セメントとグラスアイオノマーセメントの中和速度が遅いのは、未反応のセメント液の酸の溶出が多いためと考えられる。

各種歯科用セメントへの Streptococcus sanguis
ATCC 10556 の付着について

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広島大学歯学部歯科保存学第一講座

修復および合着用セメントの表面は、修復材料の中でも化学的成分に多様性を持ち、反応基を多く含んでいる。さらに、顕著抑制効果を持つために、HY 材やフィッシャを添加することも試みられており、これらの含有する成分の変化により菌体の付着、ブリッジ形成に影響を及ぼすと思われる。

各種セメントへの菌付着実験を代表的口腔細菌である Streptococcus sanguis ATCC 10556 を用いて行なう、菌付着に及ぼす各種セメントの成分、表面性状の影響を検討した。

使用したセメントは、Glass Ionomer (GI), Polycarboxylate (Car), HY-Polycarboxylate (H・Car), Zinc Phosphate (Znph), HY-Zinc Phosphate (H・Znph), Zinc Oxide-EBA (EBA), Silicate (Sil), Resin Cement (ReC) の 8 種で、対照として Composite resin (CR) を用いた。菌体の付着は、pH 依存性を示し、セメントの種類によって異なり、GI が最大で H・Car, Sil が次いで多く EBA と ReC が少なかった。セメントに含有される有機成分が、菌付着に影響を及ぼすと思われる。

コンポジットレジンにおける上向き切削・研削と下向き切削・研削の仕上面の差異について

近藤誠一郎、大川昭治、塚 隆夫、菅原 敏、太田 守
北海道大学歯学部歯科理工学講座

歯科用修復材料の切削・研削の最適加工条件を検討する研究の一環として、コンポジットレジンの定荷重方式