pH Determinations on the Surface of Luting Cements

II. Effects of Test Conditions

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The pH changes of small amounts of test solutions which were in contact with luting cement surfaces during setting were determined using a flat combination electrode. The effects of 1) time intervals between the start of mixing and water contact, 2) different compositions of test solutions and 3) different types of filter were examined. The results showed that the initial rate of pH change for each cement became slower as the time interval between start of mixing and water contact increased. Polycarboxylate cement was the least acidic and showed the highest neutralization rate for each test solution. For both NaHCO₃ solution and human saliva, the initial rate of pH change of each cement was lower than that for other test solutions such as distilled water, NaCl solution and albumin solution. Additionally, the pH change of the test solution varied with the type of filter placed between the cement surface and the pH-sensitive surface of the electrode.

Key words : Luting cement, pH, Test condition

INTRODUCTION

A flat pH electrode has proved to be a suitable drive for measuring the pH changes on the surface of luting cements and is able to provide information about the chemical reaction between cements and solutions in contact with them. The pH changes of small amounts of distilled water in contact with three luting cements were measured for over 24 hours¹⁾. The results suggested that the initial pH value of water in contact with the cement surface was affected by the release and the diffusion of acid from the unreacted cement liquid. The neutralization of the acid depends upon the dissolution of the unreacted cement powder, the decomposition of the matrix and/or the rate of release of acid. Although glass ionomer cement *in vitro* has strong acidity similar to zinc phosphate cement, it is only mildly irritating to the pulp *in vivo*^{2,3)}. Any pain during cementation appears within 1 minute and disappears within 5 minutes after setting of dental cements⁴⁾. Dentin is highly sensitive to various stimuli such as evaporation, scraping with a probe, temperature variations and application of hypertonic solutions, and pulpal irritation from luting cements is not limited to acidity alone. However, acidity undoubtedly plays some role in pulpal discomfort and knowledge of pH data during setting is important to interpret the pulpal response to a cement.

We describe the effects of several test conditions (time interval between mixing and contact with solutions, composition of test solutions, types of filters) on the pH changes of luting cements during the first 60 minutes after mixing, and discuss the reactions between luting cements and contacting solutions or the effects of certain filters on the acidity of the cements.

MATERIALS AND METHODS

Tests were conducted on two brands each of zinc phosphate cement (EL and HZ), polycarboxylate cement (LC and HC) and glass ionomer cement (FI and HG). Table 1 shows the codes, brand names, batch numbers, powder/liquid ratios and mixing times of the six commercial luting cements. The chemical compositions of these cement powders and liquids are as described previously⁵⁾.

To conduct pH measurements of small amounts of test solutions in contact with the cement surfaces, a flat combination electrode* was used. Figure 1 shows the apparatus assembly. The pH values for each specimen were continuously measured for 60 minutes by the electrode connected to a pH meter** coupled to a recorder***.

Specimens (approximately 1 g) were prepared according to the manufacturers' instructions. They were then placed in the specimen holder and were quickly transferred to the frame. A filter was then placed on the surface of the specimens at the arbitrarily chosen time from the start of mixing, and the guide rim was clamped. Each test solution (0.2 ml) was dropped on the filter by a microsyringe and the pH-sensitive surface of the electrode came into contact with the filter within 30 seconds. The time intervals between mixing and contact with the test solution were 2.5, 5, 10, 30, 60 and 120 minutes.

Distilled water (pH 5.6-5.8), 0.05 M NaHCO₃ solution (pH 8.0-8.4), 0.5 % egg albumin solution (pH 5.8-6.0), 0.86 % NaCl solution (pH 5.6-5.8) and human saliva (pH 6.8-7.2) were used as test solutions.

The filters used consisted of filter paper**** (15 mm in diameter, 0.25 mm in thickness), 4 layers of filter paper (15 mm in diameter, 1 mm in total thickness), a rubber ring (3.8 mm in

Table 1 Materials examined in this study

Code	Name	Manufacturer	Batch No.	P/L Ratio	Mixing Time
<i>zinc phosphate cement</i>					
EL	ELITE CEMENT 100	GC	P : 300341 L : 291141	1.45 g 0.5 ml	90"
HZ	HYBOND ZINC PHOSPHATE CEMENT	SHOFU	P : 118157 L : 078149	1.5 g 0.5 ml	60"
<i>polycarboxylate cement</i>					
LC	LIV CENERA	GC	P : 030531 L : 260431	2 g 1 g	30"
HC	HY-BOND POLYCARBOXYLATE CEMENT	SHOFU	P : 058354 L : 058365	2.2 g 1.0 g	30"
<i>glass ionomer cement</i>					
FI	FUJI IONOMER (TYPE I)	GC	P : 170921 L : 300831	1.4 g 1.0 g	40"
HG	HY-BOND GLASIONOMER-C (TYPE II)	SHOFU	P : 088440 L : 088452	1.5 g 1.0 g	60"

* # 39523 S502A, Beckman Inst. Inc., Fullerton, CA, USA

** LAB-O-MATE II, Beckman-Toshiba Ltd., Tokyo, Japan

*** DR-1112, Ohkura Electric Co., Ltd., Tokyo, Japan

**** # 6, Toyo Roshi Co., Tokyo, Japan

Fig. 1 Design of the apparatus for pH measurement.

height), and a porous hydroxyapatite disc (12 mm in diameter, 1.2 mm in thickness). Hydroxyapatite was synthesized by mixing a H_3PO_4 solution and a suspension solution of $\text{Ca}(\text{OH})_2$ while stirring at 40°C . The precipitate was dried at 105°C and calcined at 800°C as described by Fujiu and Ogino⁶. The finely ground powder, mixed with a small amount of water, was coated onto a skeletal polyurethane foam (18 mm in diameter, 2 mm in thickness). The coated foams were dried at 120°C and fired at 1200°C for 2 hours. The sintered porous hydroxyapatite discs were identified by X-ray powder diffraction. In the X-ray diffraction patterns, α - and β - $\text{Ca}_3(\text{PO}_4)_2$ phases were not detected. Before using these as test filters, the hydroxyapatite discs were stored in distilled water for 2 weeks for neutralization of the base and decomposition of any impurities.

The manipulation and the pH measurements were conducted at $23 \pm 2^\circ\text{C}$ and $60 \pm 10\%$ humidity. At least 3 specimens of each cement were measured in the same manner. Details of the pH measurement are as described previously¹⁾.

RESULTS

Effect of time interval between mixing and contact with test solutions

Figure 2 shows the pH changes of distilled water in contact with six luting cements for six time intervals using a single filter paper. For each cement, initial pH values were higher and the rate of pH change was less for the long time intervals between mixing and water contact. The distilled water in contact with polycarboxylate cement (LC and HC) was found to be neutralized 10 minutes after the start of measurement, but the water in contact with other cements was not neutralized even after 60 minutes. With a 2.5 minute time interval, the polycarboxylate cements had a pH of 3.8-3.9, while the zinc phosphate and the glass ionomer cements had a pH of 2.7-2.9 at 2 minutes after the start of measurement. Sixty minutes after

Fig. 2 pH changes of distilled water in contact with six luting cements during 60 minutes as a function of time interval. Figures stand for the time interval between mixing and contact with the test solution. A single filter paper was used.

the start of measurement the polycarboxylate cements had a pH of 4.3-5.6, while the zinc phosphate and glass ionomer cements had a pH of 2.8-3.1.

Polycarboxylate cement (HC) showed the most rapid rate of neutralization. Although the pH changes of the glass ionomer cements were initially nearly the same as those of zinc phosphate cements, the pH values of the glass ionomer increased faster than those of zinc phosphate starting 2 minutes after the start of measurement. Thus, the neutralization rates of glass ionomer cements were slightly higher than those of zinc phosphate cements.

Effect of neutralizing solutions

Figure 3 shows the pH changes of five test solutions in contact with six luting cements. The results of the distilled water correspond to those obtained with the 2.5 minute time intervals shown in Fig. 2. In the case of NaHCO_3 solution and human saliva, the initial rates of the pH changes for each cement were lower than those in the other test solutions (*i. e.* distilled water, NaCl solution and albumin solution). The highest rates of neutralization were observed in both distilled water and NaCl solution, for each cement. Of all the cements

Fig. 3 pH changes of five test solutions in contact with six luting cements during 60 minutes. A single filter paper was used, and the time interval was 2.5 minutes.

tested, HC showed the highest rate of neutralization in every test solutions. At two minutes after start of measurement, the pH value of the NaHCO_3 solution was the highest of the five test solutions, and the pH value of the NaCl solution was nearly the same as that of distilled water. However, at 60 minutes after the start of measurement, the pH values of all solutions were nearly the same for a given cement.

Effect of various filters

Figure 4 shows the pH changes of distilled water in contact with six luting cements using various filters. The results of a single filter paper was exactly the same as that of distilled water in Fig. 3. The initial rates of pH change (*i. e.* neutralization) for all test filters were less than those obtained when a single filter paper was used. For the hydroxyapatite filter, the pH change was nearly the same as the pH changes measured without contact with any luting cement. In the cases of both the 4-layer filter paper and the rubber ring, we noted that the pH of distilled water in contact with the cement surface changed in two stages. The start of the second stage of pH decrease for zinc phosphate cements was earlier than those of polycarboxylate and glass ionomer cements.

Fig. 4 pH changes of distilled water in contact with six luting cements during 60 minutes for three filters. The time interval was 2.5 minutes.

DISCUSSION

Effect of setting reaction

Both the initial pH value and the rate of pH change were a function of the time interval between mixing and contact with the test solutions, as shown in Fig. 2. The initial pH values were affected by the release and the diffusion of acid from the unreacted cement liquid¹⁾. The amount of the unreacted cement liquid depends on a rate of setting reaction and decreases as the setting reaction proceeds⁷⁾.

Judging from the result of infrared analysis (multiple internal reflection method) on the surface of the luting cements, the absorption band of acid still remained after the initial setting and disappeared with time. For polycarboxylate cement, the absorption bands of COOH⁻ groups at around 1700 cm⁻¹ disappeared at 10 minutes after the start of cement mixing, while the absorption bands of the acids on the surface of zinc phosphate and glass ionomer cements still remained after 24 hours. The slow neutralization rate of the water in contact with zinc phosphate and glass ionomer cements seems to have been due to the continuous release of acid from the cement surface into the water¹⁾, while polycarboxylate cements showed a high neutralization rate due to the rapid reduction of free COOH groups

in the setting cement.

Norman *et al.*⁽⁸⁾ have demonstrated that the internal pH of zinc phosphate cement is always higher than the surface pH, suggesting that the unreacted cement liquid remains throughout the cements. The unreacted cement liquid in the internal mass of cement diffuses to the surface because of concentration gradients caused by release from the cement surface into the water.

Shortly after mixing, unreacted cement liquid remains on the cement surface and is relatively rapidly released into water resulting in a low pH. On the other hand, with a long time interval between mixing and contact, the amount of unreacted cement liquid decreases on the cement surface. There is a smaller concentration gradient between the internal mass and the surface and diffusion is retarded. The rate of pH change therefore decreases with increasing time interval between mixing and contact.

Delaying a clinical luting procedure as long as possible should minimize the pH change in the oral environment.

Effect of contact solution

0.05 M NaHCO_3 solution is an alkaline buffer solution, with a pH of 8.0-8.4. Albumin is the main component of proteins in saliva, dental pulp fluid and dentinal fluid, and is slightly higher in viscosity than distilled water. 0.86 % NaCl is called physiological saline solution and the inorganic ions are contained in saliva and other oral fluids.

As seen in Fig. 3, the pH changes of the NaHCO_3 solution for each cement were nearly the same as those of saliva. It appears that the pH change of saliva in contact with setting cement depends mainly on its alkaline component; *i. e.* NaHCO_3 . Although the reactions between albumin and acids were not studied, it seems that the viscosity of the solution has little effect on the pH change. The pH change was independent of the existence of Na^+ and Cl^- ions, *i. e.*, the data were the same as for distilled water.

Effect of filter type

As described previously, the pH change of the solution was affected by the diffusion of acid components through it. Therefore, the measured pH change of the solutions was altered by with the type of filter placed between the cement surface and the pH-sensitive electrode.

With the 4-layer filter paper and the rubber ring, the two-stage change of pH seems to have been due to the diffusion process, and the starting time of the second reduction of pH to be the time needed for the movement of acid from the cement surface to the pH-sensitive surface of the electrode through the filter. Thus, the starting times of the second reduction of pH for polycarboxylate and glass ionomer cements were longer than those of zinc phosphate cements because of the slower rate of diffusion of polycarboxylic acid compared with phosphoric acid. (According to the Nernst-Einstein relation⁽⁹⁾, the diffusion rate of polycarboxylic acid is lower than that of phosphoric acid because of the relatively large molecular size of polycarboxylic acid⁽¹⁾.)

With the hydroxyapatite filter, the liquid that penetrated the filter was almost completely neutralized. The pH value was affected by the quality of filtration within each filter. These results suggest that dental tissue (dentin specifically) effectively filters and neutralizes the pH

of cement.

These results support the hydrodynamic hypothesis by Brännström *et al.*¹⁰⁾ that a hydrodynamic factor is responsible for transmission of pain stimuli from the dentin surface to the nerve endings in the pulpo-dentinal area and/or the pulp. It is concluded that outward movement of the tubule contents in the pulpal end of the tubule is more liable to produce pain than is a displacement in the opposite direction.

The movement of the tubule contents seems to be affected by the osmotic pressure, size of elute, and hydrophilic group. It suggested that the difference between zinc phosphate and glass ionomer cement in producing pulpal irritation is a result of reduced diffusivity of acidic components of glass ionomer cement through the "filter" of dentinal tissue in the vital tooth, and the neutralization which may occur in the process.

CONCLUSION

The pH changes of small amounts of test solutions in contact with cement surfaces were determined by using a flat electrode. The effects of the time intervals between mixing and solution contact, test solutions and filters were examined during setting. The initial rate of pH change for each cement decreased with the increase in the time interval between mixing and solution contact. Test solutions in contact with polycarboxylate cements produced the highest pH (*i. e.* least acidic) value and the highest neutralization rate. Although the pH values of test solutions placed upon the glass ionomer cements were initially nearly the same as those of zinc phosphate cements, the neutralization rates of glass ionomer cements were slightly higher than those of zinc phosphate cements. In the case of both the NaHCO₃ solution and human saliva, the initial rates of pH change for each cement were lower than those in the other test solutions (*i. e.* distilled water, NaCl solution and albumin solution). Furthermore, the pH changes of the solution varied with the type of filter placed between the cement surface and the pH-sensitive surface of the electrode. These results suggest that the measured pH value is affected by both the amount of unreacted cement liquid on the surface of the cement and the diffusivity of the acid through the solution from the cement surface to the measuring pH electrode, and that the pulpal irritation depends not only on the initial pH of the cement, but also on the ease of diffusion of its components through the dental tissues.

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て、ジミリストイル及びジバルミトイルホスファチジルコリン・リポソームを用いて、開始剤により誘起されるリポソームの相転移特性を示差走査熱量計で研究した。開始剤により相転移温度の低温シフト、エンタルピー(ΔH)の減少、ピークの高さ/半値幅の減少が生じた。照射により、この変化は著しく増大した。芳香族ケトン類は脂肪族ケトンより大きな変化を示した。増感剤と還元

剤との間に、錯体が形成され、照射により錯体が励起されると、錯体分子の一部が変化を受け表面活性を滞びる。この表面活性錯体がりん脂質の相転移特性に大きな作用をした。照射により光重合開始剤の溶血性が増大することは、この表面活性錯体の形成に関連があると考えられた。

合着用セメント表面の pH 測定 II. 測定条件の影響

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合着用セメント表面に接した少量の試験液の pH 変化をフラット型 pH 複合電極により測定した。今回は、硬化中の放置時間、試験液、フィルターの影響を検討した。初期の pH 値の減少速度は放置時間が長くなると各セメントとも減少した。ポリカルボキシレートセメントに接した試験液は最も高い pH 値と最も早い中和速度を示した。グラスアイオノマーセメントに接した試験液の pH 変化は初期段階ではリン酸亜鉛セメントとほぼ同じであったが、中和速度はリン酸亜鉛セメントより少し大きい。 NaHCO_3 溶液と人唾液はともに各セメントの pH 値

の初期の減少速度が他の試験液(蒸留水, NaCl 溶液, アルブミン溶液)よりも小さい。さらに、各液の pH 変化はセメント表面と電極の測定面との間のフィルターの種類によっても異なる。すなわち、初期の pH 変化は、セメント表面の未反応のセメント液の量と、セメント表面から電極表面にまで達する径路内の酸の拡散によって影響されるものと考えられる。このことは、セメントと歯牙組織という臨床的な環境が酸刺激を軽減するのに効果的な条件であることを示している。

合着用セメント表面の pH 測定 III. リン酸亜鉛セメントの pH 変化と硬化反応

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市販のリン酸亜鉛セメント粉末と液に種々の添加物を加えた場合の pH 変化をフラット型 pH 電極法により測定した。 CaO と $\text{Ca}(\text{OH})_2$ の市販セメント粉末への添加は、セメント表面に接する水の中和速度を増加させた。また MgO と $\text{Mg}(\text{OH})_2$ の添加はセメントの初期の pH 値を増加させた。一方、その他の無機物 (CaF_2 , $\text{Ca}_{10}(\text{PO}_4)_6 \cdot (\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Al}(\text{OH})_3$) および有機物(バラホルムアルデヒド, アルブミン, L-アスコルビン酸, タンニン酸, コラーゲン)の添加の影響はほとんど見ら

れなかった。また、正リン酸への Al イオンの添加は、無添加の場合に比べ接触する液の中和を妨げた。DSC, X 線回折, 赤外分光分析の結果から判断すると、Al イオンの添加によって硬化体中には第 3 リン酸亜鉛結晶(ホーパイト)ではなく、非晶質のりん酸塩化合物が生成されたものと考えられる。すなわち、Al イオンにより ZnO とリン酸との反応が抑制され、未反応のリン酸がセメント表面に接している水に連続的に溶出してくるため、中和を妨げる結果をもたらしたものと推察される。