Permeability of Etching Agent Constituents through Dentin

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The in vitro dentin permeability of the constituents of two types of conventional phosphoric acid etching agents which had different viscosities, and their pH changes after being permeated dentin were investigated. It was recognized that, even though the etching was for a short time (one minute) followed by rinsing, the etching agents were still detected in the dentinal tubules which had permeated through the dentin. The pH of the etching agents also increased (neutralized) after they had permeated through the dentin. The results of a qualitative and quantitative analysis of the constituents which had permeated through the dentin showed that, after one minute of etching, the concentrations of calcium, magnesium, zinc and phosphorus increased as compared with the non-etched control samples.

Key words: Acid etching, Phosphoric acid, Dentin permeability

INTRODUCTION

Dental polymolecular materials, particularly resin materials used for restorative fillings and bonding have made marked progress in recent years.

When these resin materials are applied to the tooth structure, the tooth surface is often acid-etched with phosphoric acid as a pretreatment to improve adhesive strength and marginal closure between the tooth structure and the resin material. The effect of etching on the tooth structure, particularly the morphological changes of the enamel and dentin, has been the subject of many studies. Little is known about exudation from the tooth structure after the etching agent permeates the dentin.

To clarify these changes, the present experiment was conducted using analytical methods to study the permeability of dentin to the components of zinc phosphate cement as reported by Ito et al.¹

MATERIALS AND METHODS

Materials

1. Preparation of tooth test samples

Test samples were obtained from fresh anterior teeth extracted from 4-year-old cows, these teeth had been preserved in distilled water. Bovine teeth were selected because they can make the experimental conditions more uniform.¹² The roots of the bovine teeth were sectioned at the cement-enamel junction, and the coronal pulp was removed. As shown in Fig. 1-A, the coronal portion was cut using a diamond disk so that the pulp chamber was divided labiolingually into two equal sections. Only the labial sections were used as test samples. The sections were contoured to conform to the gauge of the test tube, as shown in Fig. 1-A.
Fig. 1 Schematic illustration of the experiment.

The cavity was prepared to 5 mm in diameter, with 1 mm-thick residual dentin on the cavity floor.

After preparation, the test samples were rinsed in distilled water by ultrasonic waves for one minute, and they were wiped lightly with filter paper.

2. Preparation of glass fiber test samples

Plates of the same size as the tooth samples were made of cold cure resin* and used as control samples. A 5 mm-diameter cylindrical hole was prepared at the center of the plate. A glass fiber filter** was fixed to the floor of the hole with sticky wax, and it was used as the resin cavity floor (Fig. 1-B).

3. Fixing samples to polycarbonate test tubes

Figure 2 shows polycarbonate test tubes. They were cut to a length of 50 mm, and a hole with a diameter of 3 mm was made in the bottom. Polycarbonate test tubes were used because glass test tubes may elute calcium into distilled water, which may result in an inaccurate quantitative analysis.

Before starting the test, the test tubes were immersed in 6 N nitric acid for three days to remove any possible interference from other elements, including calcium. The test tubes were picked up, cleansed with distilled water and dried. The tooth samples were fixed to the test tubes with sticky wax.

4. Etching agents for evaluation

Two types of etching agents of different viscosities were used: One was a high viscosity paste type* and the other was a low viscosity liquid type**. Although they had different

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* Uni Fast, G C Co., Tokyo, Japan
** GA 100 m, Toyoroshi Co., Tokyo, Japan
' Panavia, Kuraray Co. Okayama, Japan
** Clearfil, Kuraray Co. Okayama, Japan
viscosities, their components were similar. The paste type was slightly viscous, because it
contained ultrafine particles of silica. The effects of the different viscosities of the two
etching agents on their permeability to the dentin was evaluated according to the experimen-
tal methods and conditions.

Experimental Methods and Conditions

A total of 36 teeth and glass fiber samples were fixed to polycarbonate test tubes, six for
each condition.

The experimental methods and conditions are shown in Table 1.

The extraction was done immediately after step 4 for condition A and one hour after step
4 for condition B. As described in step 5, the extract obtained was analyzed for pH and Ca,
P, Mg and Zn. The pH value measurement of the solution in the test tube was performed by
the glass electrode method using a pH ionmeter before and after the experiment.

To analyze the solution in the test tube, an inductively coupled argon plasma emission
spectrophotometer\textsuperscript{bb} was used to detect the constituents which had permeated through the dentin.

**RESULTS**

**pH value measurement**

Figure 3 shows the pH of the solution in the test tube. There were no significant differences in the mean pH between conditions A and C, A and E, B and D, and C and E. Regardless of the type of etching agent used, the pH of the solution, which was extracted after one hour, was higher than that of the control solution. This suggests that the solution was almost neutral. These results are comparable to those of Ito et al.\textsuperscript{1} who used zinc phosphate cement. But when a similar experiment was performed using glass-fiber samples instead of tooth samples, the pH of the solution in the test tube was 3.92 immediately after etching and 3.47 one hour after etching.

These results reflected the low pH of the etching agents, as opposed to the results obtained with tooth samples. A quantitative analysis of the solution in the test tube was made in order to investigate this phenomenon.

**Quantitative analysis of solution in the test tube**

Figures 4 through 7 show the results of an analysis of the sample solutions for the four elements using a bar graph depicting concentration (ppm) vs. experimental conditions. The height of the bars indicates the mean and the vertical lines represent the 95\% confidence limits. The results of an analysis of the glass fiber sample solutions are shown in Fig. 8.

As shown in Fig. 4, the concentrations of calcium were low, for solutions A, C and E, which were extracted immediately after completing steps 1 through 4. On the other hand, the

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{Mean pH results for each experimental condition.}
\end{figure}

\textsuperscript{bb} ICPQ-100, Shimadzu Mfg. Co., Kyoto, Japan
Fig. 4  Mean concentration of dissolved Ca.

Fig. 5  Mean concentration of dissolved Mg.
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Fig. 6 Mean concentration of dissolved Zn.

Fig. 7 Mean concentration of dissolved P.
concentrations of calcium in B, D and F after one hour were higher than those in A, C and E. The t-test showed significant differences in the mean concentrations of calcium between the etched conditions and the non-etched conditions. The concentrations of magnesium were about 1/3 of those of calcium, but, as shown in Fig. 5, the concentrations for the etched and non-etched conditions were almost the same. Compared with the former two elements, there was no appreciable zinc level detected under the various conditions. The low level was very close to the detection limit of the analyzer (Fig. 6).

The results of the phosphorus analysis are shown in Fig. 7. The concentrations were almost the same as those of calcium and magnesium.

Figure 8 shows the results of the glass fiber sample analysis. The analysis of the solution in the test tube immediately after the experiment is as follows: calcium 0.26 ppm, magnesium 0.13 ppm, zinc 0.05 ppm, and phosphorus 6.53 ppm. One hour later, the analysis yielded: calcium 0.18 ppm, magnesium 0.14 ppm, zinc 0.07 ppm, and phosphorus 10.87 ppm. The concentrations of calcium, magnesium and zinc were somewhat lower than those in the tooth samples. The concentration of phosphorus was higher than those in the tooth samples.

DISCUSSION

The entire cavities in bovine teeth were etched using two acid etching agents of different viscosities in order to evaluate the differences in their permeability to the dentinal tubules, and to evaluate their effects on the tooth structure due to the different viscosities and the
changes in the low pH of the etching agents.

After the etching agents permeated the dentin, their acidity decreased. On the contrary, their acidity increased in glass fiber samples. This may be the result of dentin's intrinsic property as a buffer, which implies that dentin is a special biological filter to acid. This phenomenon was not found in the glass fiber samples. Solutions in the test tubes were quantitatively analyzed for the four elements, P, Ca, Mg and Zn, which constitute tooth structure and for etching agents to investigate the reasons why the pH of solutions changed, after the etching agents had permeated the dentin.

Analysis of the constituents through the dentin

In both the paste (group I) and the liquid (group II) groups, the concentration of the calcium detected was about three times higher under condition B (one hour after etching) than under condition A (immediately after etching).

A similar tendency was found in the control group (group III), but the concentration of the calcium detected was lower in group III than in the paste and liquid groups, and the difference was statistically significant. This suggests that even in the control group, the calcium which had eluted from the tooth structure into distilled water could be detected. The detection of a higher concentration of calcium in groups I and II than in the control group III may be explained by the fact that the etching agent might act to decalcify hydroxyapatite, which is the main component of inorganic substances in the tooth. As a result, a calcium compound permeated the dentinal tubules and eluted into the distilled water together with free phosphoric acid. Brudevold suggested that this calcium compound was basically dibasic calcium phosphate (CaHPO$_4$ • 2H$_2$O).

There were no differences in the concentration of calcium detected between the two etching agents which had different viscosities. A study of the acid treatment of the enamel by Mukai et al. showed an almost linear correlation between viscosity and the concentration of phosphorus. They also observed a highly negative correlation: as viscosity increased, the amount of enamel decalcified was reduced. A study by Nakajima et al. showed that acid corrosion was faster in the case of etching with a 40% aqueous phosphate solution than in the case of a 40% phosphate jelly.

These studies suggest that the liquid type has a higher decalcification capability than the paste type, and a higher concentration of calcium was detected. However, this study showed no differences between the two. Comparing these acid-treating conditions to those of Mukai et al. and Nakajima et al., the etching time under these conditions is shorter, and the rinsing time is longer; so differences between the two viscosities, were hard to find.

The detection of magnesium in groups I and II is explained by the fact that since the etching agents do not contain magnesium, the magnesium in the tooth structure itself was eluted after etching, and it permeated the dentinal tubules.

Since no zinc is basically contained in the etching agents or in the tooth structure, zinc in very low concentrations close to the detection limit was detected.

In both groups I and II, a higher concentration of phosphorus was detected under conditions B and D, than under conditions A and C, as in the cases of calcium and magnesium. A similar result was observed in group III, but the concentrations of phosphorus were lower than those in groups I and II, and the difference was statistically significant. The detection
of a higher concentration of phosphorus in groups I and II may be explained by the fact that phosphorus may have eluted from the tooth structure into the distilled water, in addition to phosphorus compounds which were decalcified by the etching agents.

These results suggest that four elements permeated the dentinal tubules and eluted into the test tubes during the one minute etching, and that these elements remained in the dentinal tubules even after rinsing and continued to permeate the dentinal tubules. As a result, higher concentrations of the four elements were detected one hour after etching, than immediately after etching.

**Results of the glass fiber sample analysis**

The concentrations of the three elements detected in the solutions in the test tubes, except for phosphorus, were generally lower than those in the tooth samples. These elements are the constituent parts of glass fiber\(^6\). The phosphorus concentrations of the glass fiber samples were 20 to 100 times those of the tooth samples. This may be explained by the following facts: 1) Unlike tooth samples, phosphoric acid was not buffered when it was passed through the glass fiber filter, and 2) glass fiber samples did not react, or reacted slightly, to phosphoric acid.

Therefore, phosphoric acid permeated the dentinal tubules without a reduction in concentration, and its low pH was reflected in the solutions.

**Acidity of the eluted solutions**

It is considered that the reaction of phosphoric acid to the components of the tooth structure formed soluble hydrogen phosphates, that is, calcium dihydrogen phosphate, magnesium dihydrogen phosphate, zinc dihydrogen phosphate, and other phosphates. There may be a correlation between the four elements and the acidity of the eluted solutions.

The pH values in all conditions and the amounts of all the elements are summarized in Table 2. The calculations were made according to Ito et al.\(^1\).

As seen in Table 2, the concentrations of the elements which were eluted were almost the same in group I (A and B) and group II (C and D). This fact indicates that the viscosity of the etching agent does not affect the amount of the eluents.

For groups I and II, the pH of B and D were higher than those of A and C. In group III, the pH difference between E and F was smaller than in groups I and II. Therefore, it

<table>
<thead>
<tr>
<th>sample</th>
<th>pH</th>
<th>concentration (mol/l)/10(^{-4})</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>A</td>
<td>5.60</td>
<td>6.72</td>
</tr>
<tr>
<td>B</td>
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</tr>
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<tr>
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<td>5.70</td>
<td>4.13</td>
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<tr>
<td>F</td>
<td>6.17</td>
<td>14.5</td>
</tr>
</tbody>
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is considered that the etching agents were buffered while permeating the dentinal tubules.

CONCLUSION

Cavities prepared on the labial surfaces of extracted bovine teeth (tooth samples), and resin cavities with glass fibers on the cavity floor (glass fiber samples) were etched using two commercially available phosphate etching agents of different viscosities but with the same concentration to investigate: 1) effects of viscosity on the residual etching agent in the dentinal tubules and changes in pH, and 2) components of the tooth structure which eluted and permeated the dentin due to decalcification caused by the phosphoric acid components and by phosphoric acid that permeated the dentin. The following conclusions were obtained:

1. After etching the tooth samples, the etching agent permeated the dentin, regardless of its viscosity. The pH of the solution was higher than in the control group. The acidity of the etching agent was reduced and neutralized by its decalcification reaction to the tooth structure, which occurred when it permeated the dentinal tubules. So, it is recognized that the dentin has a buffer capacity.

2. As glass fiber samples did not react to the etching agent, phosphoric acid was eluted into the solution. Therefore, the pH was much lower than that of the other sample groups.

3. An analysis of the solution for the paste and liquid types showed no significant differences in the concentrations of the four elements detected, Ca, Mg, Zn and P. This suggests that differences in the viscosities of the etching agents do not affect the decalcification of the tooth structure.

4. The concentration of Ca, Mg and P one hour after etching was higher than that immediately after etching; the difference was significant at a level of 5%. This concentration was higher than that in the control group. This suggests that the etching agent remained in the dentinal tubules and continued to decalcify the tooth structure.

ACKNOWLEDGMENT

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REFERENCES


リン酸エッチングエージェント成分の象牙質透過性

石川恵一，伊藤成光，畑 良昭
日本歯科学会新潟歯学部歯科補綴学教室第二講座

2種類の粘稠度が異なるリン酸エッチングエージェントを用いて牛歯から製作した試料およびガラス繊維試料の審判内のトータルエッチングを行い、リン酸の象牙質透過後のpH変化と粘稠度の影響を調べた。
その結果、1分間のエッチング後、洗浄を行ってもリン酸は細管内に残留し、微弱ながらも象牙質を透過することも認められた。また、透過する際に生ずるエッチング効果によりリン酸は中和され、強酸性が減弱された。
しかしガラス繊維試料ではリン酸の強酸性は持続した。
透過成分の定量分析を行ったところ、象牙質試料の場合、
粘質成分が主なリン酸の成分を占めることが認められた。
さらに、ガラス繊維試料では
粘質成分が高いことが認められたが、他の三元素はほとんど検出されなかった。以上の結果はエッチングエージェントの粘稠度の違いによる差は認められなかった。

チタン鋳造体表面の多層構造
宫川 修，渡辺孝一，大川成剛，中野周二，小林正義*，塩川延洋
新潟大学歯学部歯科理工学教室
*新潟大学 EMX 室

硝酸塩を結合剤とし、アルミナ／シリカを耐火材とする塩ビ材の鋳造用チタンを鋳造した。鋳造体の表面構造をEPMAによって調べ、それが次の4層からなることを明らかにした。すなわち、第1層は反応層（焼き付着層）、第2層は酸素とAlで安定化したα相の層、第3層はSi、P、C及び酸素が所々に濃縮された層、そして第4層は針状または方状結晶の集合体である。鋳造体の体積が大きいほど、また鋳型温度が高いとき、各層が厚くなり、针状結晶も粗大になる。
この多層構造は鋳込みの際に塩ビ材が溶湯に巻き込まれてできたものではないことは実験結果から明らかである。塩ビ材の還元されやすい成分の分解によって生成した元素が鋳造体の内部へ拡散してきたものと考えられる。

アクリル系義歯床用レジンの衝撃特性
ー第2報ー 衝撃特性に及ぼす温度と残留モノマーの影響
奥 淳一
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PMMAレジンの粘弹性の性質は、試料の温度、試料中に含まれる残留モノマー量によって大きく変化する。本報で、PMMA レジンの衝撃特性に及ぼす温度、残留モノマーの影響を衝撃試験、クリープ試験、残留モノマー測定等を行って調べ検討した。
加熱重合レジン、常温重合レジンの衝撃特性は、温度が上昇するにつれて（23℃～60℃）明らかに減少した。また、常温重合レジンでは、重合後の時間経過とともに残留モノマー量が著しく減少した。この減少にともない衝撃特性値は変化するが、両者の間には明らかな相関関係がみられた。相関係数は衝撃強さに関しては0.92、レジリエンスに関しては－0.95であった。この結果は重合後時間経過に伴い（残留モノマーの減少に伴い）、新しい分子鎖を生じ、そのため弾性率の向上がみられたと考えられる。この変化はクリープ試験結果からも十分推測できた。