Effect of Acid Etching on the Human Tooth Enamel: Improvement of its Clinical Application

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The etched enamel and enamel surface after tensile bond test were observed with use of SEM. In addition, the effects of enamel etching on Ca dissolution, surface roughness and tensile bond strength were investigated.

Key Words: Enamel, Etching, Adhesion

INTRODUCTION

The acid etching of the enamel surface that produces a modified surface is an essential procedure for improvement of adhesion between tooth enamel and dental restorative materials.

Buonocore¹⁾ first reported that pretreatment of enamel with 85% phosphoric acid for 30 sec. increased adhesion of enamel to acrylic restorative materials. Subsequently, many acids such as 40%,²⁾ 50%³⁾ and 30%⁴⁾ phosphoric acid, 50% citric acid,⁵⁾ 20% lactic acid⁶⁾ and 3 mol,⁷⁾ 10%⁸⁾ pyruvic acid have been reported to produce a marked increase in the bond strength of various dental materials to tooth enamel.

Bowen⁹⁾ developed a composite resin containing Bis-GMA, and carried out many studies on surface active comonomers that improved the adhesion between composite resin and hard tooth tissue. But he could not obtain good results without pretreatment of tooth with EDTA.^{10,11)} Recently Anbar and Farley¹²⁾ and Farley, Jones and Anbar¹³⁾ found that the organic compound containing a phosphoric radical adhered strongly to enamel, when pretreatment with 30% citric acid for 15 sec. was carried out. The 4-META resin, which was developed by Takeyama et al.¹⁴⁾ and Tanaka et al.,¹⁵⁾ was found to adhere both to metal and tooth, but it required acid etching of tooth enamel with phosphoric or citric acid to obtain a stable adhesion when immersed in water for a long period. It was also reported that the new resin cement showed higher bond strength on etched enamel than on unetched enamel.¹⁶⁾

In spite of these recent developments in dental adhesive materials, acid etching of enamel is considered to be necessary to obtain a good adhesion between enamel and resin.^{17,18)} However, acid etching of tooth causes demineralization in normal enamel and may produce caries in the etched enamel not covered with a resin although a remineralization phenomenon is considered.¹⁹⁾ When the etching solution is in contact with vital dentin, damage to pulp may also occur in the recent total etching methods in which a whole cavity is etched.²⁰⁾ Therefore, the examination of etching solution that improves adhesion and the

improvement of clinical procedures are essential for successful etching without damage to tooth.

This study was carried out on the acid etching technique to obtain further information for improving its clinical application. The surface of acid etched enamel and the enamel surface after tensile bond test were observed with a scanning electron microscope (SEM). In addition, the kind and the concentration of etching solutions, the time of acid etching and the kind of resinous restorative materials were examined for their effects on Ca dissolution, surface roughness and tensile bond strength after acid etching of enamel.

MATERIALS AND METHODS

Materials

Teeth

Sound human maxillary and mandibular premolars extracted for orthodontic treatment were used. The teeth were stored in a cooled physiological saline solution until tested.

Etching solutions

Four kinds of water soluble acids were used: (1) orthophosphoric, (2) citric, (3) citraconic, (4) pyruvic acid.

Restorative resins

One filled resin (Clearfil)* in two paste forms and three unfilled resins ((1) Clearfil Bonding Agent,* (2) Concise Enamel Bond,** (3) Epobond***) in two liquid forms were used.

Methods

Preparation of the test specimen

The root and lingual cusp side of the tooth crown were cut off and the facial cusp side was fixed with cyanoacrylate on the brass block which was used as an operating table for

Figure 1 A Schematic Diagram of the Experimental Procedure

* Kurarey Co., Osaka, Japan

** 3M Co., St. Paul, U.S.A.

*** GC Co., Tokyo, Japan

preparing the tooth. The facial enamel surface was flattened with 600 grit silicon carbide paper under running water on a Wingo polishing machine* until 500–700 μm from the most projected facial enamel was removed as indicated by a gauge. A schematic diagram of the experimental procedure is shown in Figure 1.

I. Observation with SEM

1. The etched enamel

Sixteen sound maxillary and mandibular human premolars obtained from four individuals (four teeth each) were used. After surface removal as mentioned above the teeth were divided into four portions by cutting longitudinally and transversely under running tap water.

The each group of the sixteen specimens which were obtained from four teeth of one person was etched with the same concentration of each etching solution. The each group of the four specimens obtained from one tooth was etched for the same required time interval and each specimen was etched with each etching solution.

After being immersed in about 1 ml of each etching solution and gently agitated for the required time interval, the specimens were washed under a stream of distilled water for 15 sec. The etched specimens were dried with compressed air for 15 sec. and stored in a desiccator. The specimens were coated with gold in an Eiko Engineering Ioncoater Model IB-2** and examined with a Hitachi S-430 SEM*** operated at 20 KV.

2. The enamel surface after tensile bond test

After tensile bond test, the enamel surface was examined with SEM as mentioned above.

II. Measurement of the dissolved Ca, the surface roughness and the tensile bond strength

After surface removal as mentioned earlier, a square waxed paper die, which was cut out to a width of 3 mm $\times$ 3 mm, was pressed by slightly heating on the flattened enamel surface and the other denuded enamel surface was coated with a nail varnish. The square window was washed with distilled water and dried with compressed air just before the experiment.

This study was carried out based on the design of an experiment with use of the table of orthogonal arrays ($L_{64}4^{21}$) as shown in Table 1.

1. Measurement of dissolved Ca

The window was immersed in 1 ml of each etching solution and gently agitated for required time interval. The etching solutions were diluted and the Ca content was determined by the atomic absorption spectrophotometry**** with use of an acetylene N_2O flame

* Wingo Co., Osaka, Japan

** Eiko Engineering Co., Ibaragi, Japan

*** Hitachi Co., Tokyo, Japan

**** Shimadzu Co., Kyoto, Japan

Table 1 Lay Out of each Factor and Level to the Table of Orthogonal Arrays

Array Number	1 (A)	2 (B)	6 (C)	10 (D)	14 (R)
Factor	Etchant	Resin	Concentration	Etching Time	Blocks
Level	1	PHOSPHORIC ACID	COMPOSITE (CONTROL)	5 (%) W/W	15 SEC.
	2	CITRIC ACID	COMPOSITE + CONCISE	10	30
	3	CITRACONIC ACID	COMPOSITE + CLEABOND	20	60
	4	PYRUVIC ACID	COMPOSITE + EPOBOND	40	120

2. Measurement of the surface roughness of the etched enamel

After being immersed in the etching solution, the window was washed under a stream of distilled water for 15 sec. and dried with compressed air for 15 sec. Then the measurement of arithmetical average roughness was carried out with a Kosaka Surfcorder Model SE-3C.* The cut-off and sampling length used were 0.8 mm and 2 mm respectively.

3. Measurement of tensile bond strength

After the measurement of the surface roughness, the teeth were fixed on the special apparatus which was designed to obtain an exact fitness of the window with the attachment (Figure 2).

The composite resin was mixed for 30 sec. and filled in the attachment. Then the liquid resin was mixed for 10 sec. and a drop of the mixture was transferred to the exposed enamel window except control and blown off with compressed air. After being filled with the composite resin, the attachment was placed on the window with a pressure of 1.11 Kg/cm² (Figure 3). The resin was allowed to set at room temperature for 3 min. and the

Figure 2 A Schematic Diagram of the Trial Adaptation (A) and Loading (B) of the Attachment

* Kosaka Lab., Co., Tokyo, Japan

Figure 3 Loading of the Attachment

Figure 4 The Apparatus with a Universal Joint for Tensile Bond Test

Figure 5 A Schematic Relationship of Universal Joint to Tooth and Attachment

specimens were stored in distilled water at 37°C for 7 days prior to tensile bond test.

The specimens were mounted on the tensile bond test apparatus with a universal joint (Figure 4). The force needed to break a bond was automatically recorded with use of a Shimadzu Autograph Model IS-5000* at a cross head speed of 2.5 mm per min. The tensile bond strength was calculated and expressed in Kg/cm². A schematic diagram of the experimental apparatus is shown in Figure 5.

RESULTS

1. Observation of etched enamel with SEM

In case of etching with 5% phosphoric acid for 15 sec., narrow cracks were formed at the prism periphery, and deep grooves were formed at the cuspal side of the prism periphery with etching for more than 30 sec. Etching with any concentration other than 5%

Figure 6 SEM of Enamel Surface Etched with Phosphoric Acid ($\times 2000$)

* Shimadzu Co., Kyoto, Japan

for more than 15 sec. produced deep grooves at the cuspal side of the prism periphery, though the surface irregularity observed in the specimen etched with 40% phosphoric acid was small (Figure 6).

Among the etching solutions examined, citric acid showed the weakest effect on enamel, and etching time for more than 60 sec. was necessary to form wider and deeper grooves at the prism periphery with any concentration. In case of etching with 40% citric acid, the prism core became hollow and the prism periphery projected with etching for 15 sec., narrow cracks were formed at the prism periphery with etching for 30 sec., wide and deep grooves were formed at the prism periphery with etching for 60 sec. and the grooves at the prism periphery became wider and deeper with etching for 120 sec. (Figure 7).

Etching with 20% citraconic acid for more than 15 sec. produced deep grooves at the cuspal side of the prism periphery and a projection of prism core was observed. In case of etching with any concentration other than 20% for 15 sec., narrow cracks were formed at the prism periphery, whereas etching for more than 30 sec. produced deep grooves at

Figure 7 SEM of Enamel Surface Etched with Citric Acid ($\times 2000$)

Figure 8 SEM of Enamel Surface Etched with Citraconic Acid ($\times 2000$)

the cuspal side of the prism periphery (Figure 8).

In case of etching with any concentration of pyruvic acid for 15 sec., narrow cracks were formed at the prism periphery. Etching with any concentration other than 40% for more than 30 sec. produced deep grooves at the cuspal side of the prism periphery. An obscure topography of the prism, preferential loss of prism core and the formation of the narrow cracks at the prism periphery were noted after etching with 40% pyruvic acid for more than 30 sec. (Figure 9).

2. Observation of the enamel surface after tensile bond test with SEM

Resin tags were mostly fractured with few fractures of the composite resin itself or enamel.

Many scanning electron micrographs suggested the destruction between composite resin and liquid resin or the destruction of liquid resin itself in the samples applied with Concise Enamel Bond and Epobond (Figure 10).

Figure 9 SEM of Enamel Surface Etched with Pyruvic Acid ($\times 2000$)

Although the microstructure of enamel surface after tensile bond test was similar to interface failure when examined at a low power view, the fractured resin tags were observed only when examined at a high power view (Figures 11 and 12).

In some of the samples etched with citric acid for less than 30 sec. and 40% pyruvic acid, many scanning electron micrographs were similar to etched enamel surface though the fractured resin tags were observed sporadically (Figure 12).

3. Measurement of the dissolved Ca

Table 2 is the result of the analysis of variance for Ca dissolution, and shows that each of the main and the interaction effects is highly significant at the 1% level.

Figure 13 shows the estimate of the main effect of each etching solution. The confidence interval in the figure is 95% and the same interval applies correspondingly to the following figures. Among the four kinds of etching solutions, phosphoric acid showed the highest value of Ca dissolution, citraconic and pyruvic acid showed about a half of

Figure 10 (1, 1') SEM of Enamel Surface After Tensile Bond Test of Specimen Etched with 5% Phosphoric Acid for 120 sec. Using Epobond as a Liquid Resin. The Liquid Resin (B), the Fractured Resin Tag (T) and the Fractured Composite Resin (R) Can be Observed 1: ($\times 500$) 1': ($\times 2000$)
 (2, 2') SEM of Enamel Surface After Tensile Bond Test of Specimen Etched with 20% Citraconic Acid for 120 sec. Using Concise Enamel Bond as a Liquid Resin. The Liquid Resin (B), the Fractured Resin Tag (T) and the Fractured Enamel (E) Can be Observed 2: ($\times 500$) 2': ($\times 2000$)

those of phosphoric acid and citric acid showed the lowest value, about a fourth of those of phosphoric acid.

Figure 14 shows the estimate of the main effect of acid concentration. The amount of Ca dissolution increased with an increase of acid concentration to the peak at 20%, then decreased. The regression curve, calculated from this relation, $Y = 33.79 + 5.277X - 0.117X^2$, is plotted in the figure. The test of significance proved to be highly significant at the

Figure 11 (3, 3') SEM of Enamel Surface After Tensile Bond Test of Specimen Etched with 20% Citraconic Acid for 60 sec. and Applied with Only Composite Resin. The Fractured Composite Resin(R), the Fractured Resin Tag (T) and the Prism Core (C) Can be Observed 3: ($\times 500$) 3': ($\times 4000$)

(4, 4') SEM of Enamel Surface After Tensile Bond Test of Specimen Etched with 40% Phosphoric Acid for 30 sec. Using Clearfil Bonding Agent as a Liquid Resin. The Fractured Resin Tag (T) and the Periphery of Enamel Prism (P) Can be Observed 4: ($\times 1000$) 4': ($\times 4000$)

1% level. Figure 15 shows the estimate of the interaction effect of each acid concentration. Citric acid showed the maximum Ca dissolution at a concentration of 10%, though the other etching solutions showed at 20%. Pyruvic and phosphoric acid showed a significant decrease in Ca dissolution in the concentration range between 20 and 40% as compared with the other etching solutions. The regression curve of each etching solution is plotted in Figure 16. The test of significance of each etching solution proved to be highly significant at the 1% level.

Figure 12 (5, 5') SEM of Enamel Surface After Tensile Bond Test of Specimen Etched with 40% Pyruvic Acid for 60 sec. Using Concise Enamel Bond as a Liquid Resin. Similar Appearance to the Acid Etched Enamel Can be Observed but the Fractured Resin Tag (T) Can be Observed 5: ($\times 1000$) 5': ($\times 4000$)
(6, 6') SEM of Enamel Surface After Tensile Bond Test of Specimen Etched with 10% Citric Acid for 15 sec. Using Concise Enamel Bond as a Liquid Resin. The Same Observation as in 5 and 5' Can be Seen 6: ($\times 2000$) 6': ($\times 4000$)

Figure 17 shows the estimate of the main effect of etching time. The amount of dissolved Ca increased linearly with an increase of etching time. Figure 18 shows the estimate of the interaction effect of etching time of each etching solution. Phosphoric acid showed the highest increasing rate with an increase of etching time for Ca dissolution, citraconic and pyruvic acid were about a half and citric acid was about a forth of that of phosphoric acid.

Table 2 Analysis of Variance for the Ca Dissolution

Source of Variation	d.f	S.S.	M.S.	F
Etchant A	3	40.3	13.45	91.5**
Concentration C	3	5.8	1.94	13.2**
Etching Time D	3	71.8	23.93	162.8**
Blocks R	3	2.5	0.84	5.7**
A × C	9	4.8	0.53	3.6**
A × D	9	26.5	2.94	20.0**
Error	33	4.8	0.14	
Total	63	156.7		

** significant at the 1% level

Figure 13 Estimate of the Main Effect of Ca Dissolution After Etching with each Etching Solution

Figure 14 Estimate of the Main Effect of Ca Dissolution After Etching with Various Concentrations of Etching Solutions. The Solid Line Represents a Regression Curve

Figure 15 Interaction of Kinds vs. Concentrations of Etching Solutions for Ca Dissolution

Figure 16 Regression of Ca Dissolution on each Concentration of each Etching Solution Fitted to a Curve of Second Degree

Figure 17 Estimate of the Main Effect of Ca Dissolution After Etching for each Period

Figure 18 Interaction of Kinds of Etching Solutions vs. Etching Time for Ca Dissolution

Table 3 Analysis of Variance for the Arithmetical Average Roughness

Source of Variation	d.f	S.S.	M.S.	F
Etchant A	3	0.519	0.173	3.3*
Concentration C	3	0.292	0.097	1.8
Etching Time D	3	0.916	0.305	5.8**
Blocks R	3	0.378	0.126	2.4
A × C	9	0.681	0.075	1.4
A × D	9	0.293	0.032	0.6
Error	33	1.718	0.052	
Total	63	4.800		

* significant at the 5% level

** significant at the 1% level

4. Measurement of the surface roughness

Table 3 is the result of the analysis of variance for arithmetical average roughness, and shows that the main effects of kind of etching solution and etching time are significant at the 5 and 1% level respectively.

Figure 19 shows the estimate of the main effect of each etching solution. The value of arithmetical average roughness decreased in the following order of phosphoric, pyruvic, citraconic and citric acid.

Figure 20 shows the estimate of the main effect of etching time. The value of arithmetical average roughness increased linearly with an increase of etching time.

Figure 19 Estimate of the Main Effect of Arithmetical Average Roughness After Etching with each Etching Solution

Figure 20 Estimate of the Main Effect of Arithmetical Average Roughness After Etching for each Period

Table 4 Analysis of Variance for the Tensile Bond Strength

Source of Variation		d.f	S.S.	M.S.	F
Etchant	A	3	151.5	50.5	5.8**
Resin	B	3	55.0	18.3	2.1
Concentration	C	3	106.7	35.5	4.1*
Etching Time	D	3	141.7	47.2	5.4**
Blocks	R	3	29.2	9.7	1.1
A × B		9	94.7	10.5	1.2
A × C		9	137.5	15.2	1.7
A × D		9	86.7	9.6	1.1
Error		21	180.4	8.5	
Total		63	983.7		

* significant at the 5% level

** significant at the 1% level

5. Measurement of the tensile bond strength

Table 4 is the result of the analysis of variance for tensile bond strength, and shows that the main effects of kind and concentration of etching solution and etching time are significant at the 1, 5 and 1% level respectively.

Figure 21 shows the estimate of the main effect of each etching solution. Citric acid showed the lowest value though the other etching solutions showed almost the same value.

Figure 22 shows the estimate of the main effect of acid concentration. The value of tensile bond strength increased with an increase of acid concentration to the peak at 20%, then decreased. The regression curve, calculated from this relation, $Y=140.3+2.02X-0.063X^2$, is plotted in the figure. The test of significance proved to be highly significant at the 1% level.

Figure 23 shows the estimate of the main effect of etching time. The value of tensile bond strength increased with an increase of etching time.

If y symbolizes tensile bond strength, x_1 amount of Ca dissolution and x_2 arithmetical

Figure 21 Estimate of the Main Effect of Tensile Bond Strength After Etching with each Etching Solution

Figure 22 Estimate of the Main Effect of Tensile Bond Strength After Etching with Various Concentrations of Etching Solutions. The Solid Line Represents a Regression Curve

Figure 23 Estimate of the Main Effect of Tensile Bond Strength After Etching for each Period

average roughness, the partial correlation coefficient, $R_{yx_1 \cdot x_2}$ is 0.4 and $R_{yx_2 \cdot x_1}$ is -0.088 . The test of significance of $R_{yx_1 \cdot x_2}$ proved to be highly significant at the 1% level although $R_{yx_2 \cdot x_1}$ was insignificant.

The regression was used to predict the tensile bond strength (y) from Ca dissolution (x_1). The regression line of y on x_1 was estimated as $y = 128.1 + 0.234x_1$ and the test of significance proved to be highly significant at the 1% level.

DISCUSSION

1. Changes of the etching pattern of enamel surfaces

Gwinnett²¹⁾ examined the surface of tooth enamel after exposure to various kinds of etching solutions and found that three etching patterns existed in one experimental region even etched with one etching solution. Silverstone et al.²²⁾ also carried out the same observation and classified the patterns into the following three groups: a preferential loss of the prism core of tooth enamel (type I), a preferential loss of the prism periphery of tooth enamel (type II) and an indistinct surface topography of the prism of tooth enamel (type III). On the other hand, Nichol, Judd and Ansell²³⁾ explained the effects of various demineralizing treatments on human enamel with use of a two-stage model, that is, one stage is concerned with the site of initiation of attack and another stage the directionality of spread of attack.

In this study, the change of microstructure of enamel surface etched with 40% citric acid seemed to be the most typical alteration with etching time. In this change, the prism cores became hollow and the prism peripheries projected for the first time (I stage); then narrow cracks were observed between the cuspal side of the prism and the adjacent cervical side of the prism, that is, the head of the prism and the tail of adjacent prism. Such cracks were also seen at the boundary between the tails of adjacent prisms and were wider than those seen at the head of the prism (II stage). The above mentioned stages correspond to the I type as classified by Silverstone; in the next stage the cracks at the head of the prism became wider and deeper, and the head and tail of the prisms were surrounded by continuous grooves (III stage); further changes resulted in extreme dissolution at the cervical side of the prism head and the tail of the prism, where an elliptical head of the prism was seen, and wide and deep grooves were formed between the cuspal and the cervical side of the head of adjacent prism and the prism head projected (IV stage). The above mentioned stages correspond to the II type as classified by Silverstone.

As the above mentioned wider and deeper grooves are necessary for resin to flow and form a tag after polymerizing and hardening, it is easily seen that the bond strength increases with an increase of etching time.

The same changes were also observed according to the kinds of etching solutions. In case of etching with citric acid, the etching time for more than 60 sec. was necessary to show the surface microstructure of III stage with any concentration. Therefore, it is seen that the bond strength with citric acid is lower than those with the other etching solutions. However, though the surface microstructure after etching with citric acid for 120 sec. was almost the same as those after etching with the other etching solutions for 120 sec. and among the acid concentrations clearer grooves were formed than in case of etching with

the other etching solutions, the bond strength after etching with citric acid for 120 sec. had a tendency to show a lower value than those of the other etching solutions. On the other hand, though citraconic acid had a tendency to show a lower value of arithmetical average roughness than those of phosphoric and pyruvic acid, it had a tendency to show a higher bond strength than the other etching solutions. These findings suggest that the chemical properties and polarities in the acid etched surface may differ among the kinds of etching solutions.

No remarkable differences were observed when the surface microstructure was examined after treatment with various concentrations of etching solutions, except that etching with 5% citric acid for 15 sec. did not show any clear outline of the prism and the surface microstructure of stage III appeared after etching for 120 sec., the cracks formed on surface etched with 40% pyruvic acid were narrow and the surface irregularity observed in the specimen etched with 40% phosphoric acid was small. Therefore, as indicated by Chow and Brown²⁴⁾, the differences in bond strength depending on acid concentration might be affected by the formability of different re-precipitates (dicalcium phosphate dihydrate or monocalcium phosphate monohydrate).

Though the Ca dissolution from re-precipitates is considered, the amount of Ca dissolution in this study can be considered simply as the total amount of mass dissolution of enamel with parallel to enamel surface and selective dissolution of the prism core or prism periphery. As the amount of Ca dissolution increased and the cracks formed at the prism periphery became wider and deeper with etching time, both mass and selective dissolution must increase with etching time.

In case of etching with citric acid, both mass and selective dissolution must be small because a stage III surface microstructure was not observed without etching for more than 60 sec. with any concentration and the increasing rate of Ca dissolution with etching time was the smallest.

In case of etching with phosphoric acid, both mass and selective dissolution must be large because wide and deep grooves were observed with etching time for more than 15 sec. except 5%, and the increasing rate of Ca dissolution with etching time was the largest.

In case of etching with citraconic and pyruvic acid, both mass and selective dissolution might lie between those of phosphoric and citric acid because deep and wide grooves were not observed without etching for more than 30 sec. except 20% citraconic and 40% pyruvic acid, and the increasing rate of Ca dissolution with etching time was between those of phosphoric and citric acid.

The surface microstructure etched with 40% pyruvic acid was considerably peculiar, showing a topography of I and II type or III type as classified by Silverstone with different etching time. The many reasons such as crystal orientation²⁵⁾, difference in size and electric charge of radicals of etching agent²⁶⁾, re-precipitation of dissolution products²⁷⁾ and residual organic matter in enamel²⁸⁾ have been considered for the formation of such surface. In this study, this may be due to the subtle differences in the enamel structure or the change in the dynamic process of the Ca dissolution and re-precipitation of the dissolved Ca with etching time, which seems to be caused by the influence of the undissociated acid and the dissociated ion in the etching solution. The formation of these re-precipitates might

prevent Ca dissolution in case of etching with 40% pyruvic acid.

2. The amount of Ca dissolution

The amount of Ca dissolution after etching of enamel showed a marked difference depending on the kind of etching solutions, the etching time and the concentration of etching solution.

Concerning kind of etching solutions, phosphoric acid showed the highest value, and citraconic and pyruvic acid showed almost the same value which was about a half of phosphoric acid, and citric acid showed the lowest value which was about a fourth of phosphoric acid. Such differences almost agree with those reported by Ohsawa⁷⁾, and are mainly due to the difference in increasing rate of Ca dissolution depending on kind of etching solutions.

Mukai et al.^{29,30)} reported that there were no differences in the amount of Ca dissolution with respect to etching time after etching with 1 μ l of etching solution, and the amount of Ca dissolution increased with use of 2 and 3 μ l of etching solution. They also reported a negative relationship between the viscosity of etching solution and the amount of Ca dissolution.

In this study, the amount of Ca dissolution increased with an increase of etching time regardless of etching solution. This might be due to the use of 1 ml etching solution in this study. The difference in its increasing rate among etching solutions is considered to be based on the differences in pH, electrolytic dissociation constant, degree of electrolytic dissociation and structure of etching solutions.

An association between the amount of Ca dissolution and the concentration of etching solution was observed by drawing a curve of second degree with a maximum peak between 15 and 25% in any etching solution. This tendency agrees with those reported by Nakagawa³¹⁾, Yamaki, Nakazawa and Takimoto³²⁾ and Ishizaki³³⁾. The fact that the amount of Ca dissolution initially reached a certain peak then decreased out of proportion to the concentration of etching solution is probably due to the balance of decrease in pH and increase in viscosity caused by the increase in concentration. Moreover, at a low pH, the diffusion of Ca ion from enamel into solution may be prevented by the increase of free Ca ion in the solution caused by the prevention of formation of the coordination compound which is made from dissolved Ca ion and acid anion. As indicated by Chow and Brown²⁴⁾, this may also be affected by the formability of re-precipitates having different chemical structures on the etched enamel surface according to different concentration of etching solutions.

Phosphoric and pyruvic acid showed a remarkable decrease in Ca dissolution in the concentration range between 20 and 40% as compared with the others. This may be due to the considerably higher mol concentration of these etching solutions at 40% than the others. Namely, this may be due to the extreme prevention of formation of Ca-coordination compound as compared with the other acids or due to the difference in stability of coordination compound formed. Also, in case of phosphoric acid, it is possible that an abundance of phosphoric ions in the solution prevents the diffusion of the phosphoric ion from enamel into the etching solution, and as a result, the dissolution of calcium in enamel

may be prevented. This may explain the small surface irregularity observed in the specimen etched with 40% phosphoric acid.

3. Bond strength

Buonocore¹⁾ reported first that treatment of enamel with 85% phosphoric acid increased adhesion of enamel to acrylic filling materials. The following studies proved that there was a great difference in the bond strength of resins to enamel depending on the kind and concentration of etching solutions. Ohsawa⁷⁾ examined the bond strength between a sealant containing ethyl-2-cyanoacrylate and enamel etched with 15 kinds of pretreating agents for 30 sec. at seven different mol concentrations respectively, and found that the high bond strength of the sealant was obtained on enamel etched with 3 mol of pyruvic and phosphoric acid. Soetopo, Beech and Hardwick³⁴⁾ reported that 16% phosphoric acid showed the highest bond strength between the composite resin and enamel etched with various concentrations of phosphoric acid for 1 min. Furthermore, Retief, Bischoff and van der Merwe⁸⁾ reported that 10% pyruvic acid showed the highest bond strength between the composite resin and enamel etched with 5 to 30% pyruvic acid for 90 sec. as high as that of 37% phosphoric acid. In this study, it was found that the bond strength to enamel etched with phosphoric, pyruvic and citraconic acid was almost the same value and was significantly higher than that of citric acid, showing an increasing tendency as etching time increased. The regression curve on the bond strength with all etching solutions depending on the concentration showed a curve of second degree having a maximum peak around 16% as in the case of the Ca dissolution. These differences in the bond strength may largely depend on the nature of the surface of acid etched enamel, and its relation to the bond strength was discussed previously.

The reasons for choice of citraconic acid in this study are that it is relative strong acid and highly soluble in water and it has not been employed in the systematic acid etching study and does not form specific precipitates.

Fuse³⁵⁾ compared with bond strength of the natural surface of tooth enamel with that of the enamel which was mechanically removed to a depth of 200 μ m, and found that the removed enamel had a higher and more stable bond strength than the natural surface after a long period. According to the recent study of Schneider, Messer and Douglas³⁶⁾, mechanical removal of 0.1 or 0.6 mm of the tooth enamel significantly increased the bond strength between etched enamel and composite resin. In this study, the experiment was performed on the flat surface of tooth enamel which was removed to the depth of 500 to 700 μ m from the most projected part of tooth enamel on the facial side, and if the same experiment was made on the natural surface of tooth enamel, the mean of the data obtained might be lower than in this study. However, the comparison made on each bond strength depending on the kind and concentration of etching solutions and the etching time may be applicable to that of the natural surface of enamel.

Resin tags, in which resin penetrates into the irregularity formed on tooth enamel after acid etching and polymerizes to harden, are considered to be an important factor in improving the adhesion between etched tooth enamel and resin.^{37,38,39,40,41)} Jørgensen and Shimokobe⁴²⁾ reported that there were no differences in the adaptation between com-

posite and liquid resin to acid etched enamel surfaces. Also, Rider, Kenny and Tanner⁴³⁾ and Fuse³⁵⁾ and Hormati, Denehy and Fuller⁴⁴⁾ reported that the use of liquid resin did not improve the bond strength. But, Satoh et al.⁴⁵⁾ reported that the bond strength between etched enamel and resin might increase according to the combination of composite resin and liquid resin used. Kasakura, Satoh and Hosoda⁴⁶⁾ reported that the liquid resin, which was an appendix of the composite resin, increased the bond strength after immersing in water for a long period and thermal cycling.

Among the liquid resins used in this study, Clearfil Bonding Agent, which is applied with methacrylate containing a phosphoric radical dissolved with alcohol, is different from Concise Enamel Bond and Epobond which are applied with diluted Bis-GMA⁴⁷⁾. Polymeric compounds containing a phosphoric radical are considered to be chemically adsorbed in enamel¹³⁾. In this study, though the use of liquid resin did not increase the bond strength statistically, the use of Clearfil Bonding Agent tended to increase the bond strength. Dogon⁴⁸⁾ and the author et al.⁴⁹⁾ reported that the sealing property at the cavity margin was improved with use of liquid resin. Moreover, Prévost, Fuller and Peterson⁵⁰⁾ suggested that the liquid resin was not any disadvantageous to the bond strength and microleakage. The filling technique in the mouth is so vexatious that it is necessary to apply liquid resin before filling the composite resin.

Fuse³⁵⁾, Kurosaki et al.⁵¹⁾ and Takahashi et al.⁵²⁾ reported that the bond strength between composite resin and etched enamel did not decrease after a long period. Satoh et al.⁴⁵⁾ found that the bond strength between composite resin made from Bis-GMA and etched enamel tended to increase and that of resin made from MMA tended to decrease when immersed in water for a long period. In referring to these reports, assuming that the immersion in water was carried out for a longer period than in this study, the bond strength might be the same as obtained in this study.

4. Relationship between the amount of Ca dissolution, the surface roughness and the bond strength

Nakagawa³¹⁾ reported that the maximum peak of the Ca dissolution was around 20% and the bond strength reached a constant value at a concentration of more than 20% when the bovine enamel was etched with 1, 5, 10, 20, 50 and 65% phosphoric acid for 30, 60 and 180 sec. On the other hand, Ohsawa⁷⁾ examined the Ca dissolution using enamel tablet and the bond strength using human central incisor, and found that the Ca dissolution and bond strength showed a relatively similar tendency among the same kinds of etching solutions but there was no tendency between them among the different kinds of etching solutions, and the bond strength showed a marked difference among the different kinds of etching solutions when the same amount of Ca dissolution was obtained.

It is difficult to compare directly the relationship between the Ca dissolution, the arithmetical average roughness and the bond strength obtained from each experiment because the experimental materials and methods are different from each other. But in this study, there was a statistically significant relationship between the bond strength and the Ca dissolution though not between the bond strength and the arithmetical average roughness.

It is said that the rougher the surface becomes, the smaller the contact angle becomes

and the easier the adhesive wets the surface if the contact angle which the adhesive has originally is smaller than 90° ⁵³⁾. As mentioned earlier, the bond strength is considered to mainly depend on resin tags which are formed in fine irregularity of the acid etched enamel. Therefore, it seems that the reasons for the absence of a statistically significant relationship between the bond strength and the arithmetical average roughness are due to the following facts. The exact measurement of fine irregularity in acid etched enamel was difficult to achieve under a pressure of more than 2 tons pre 1 cm^2 regarding the stylus of Surfcorde as a flat of diameter of $2\text{ }\mu\text{m}$, and as the true interface failure did not occur in the measurement of bond strength, many factors participated in the value obtained for bond strength. However, the measurement of the bond strength and the arithmetical average roughness used in this study can be compared to some extent because two or three factors showed statistically significant differences.

5. Observation of the enamel surface after tensile bond test

In the tensile bond test, the places where the destruction occurs between enamel and resin are considered as follows: 1. the interface failure between resin and enamel; 2. the cohesive failure within resin; 3. the cohesive failure in enamel and 4. the mixed type failure listed in 1, 2 and 3.

In this study, there were four cases in which the enamel was peeled off from the dentin and destroyed, and two cases in which the composite resin was destroyed and covered the enamel completely, and in other cases the destruction left more or less fragments of resin within enamel. In the last case, the subtle destruction in enamel was considered where the fractured resin tags remaining in the cracks that were formed in acid etched enamel and enamel around them were observed at the same time. In this study, the microstructure of the enamel surface after tensile bond test showing a bond strength of $60\text{--}70\text{ Kg/cm}^2$ was very similar to the surface of acid etched enamel and suggested the interface failure by the examination at a low power view but the scattering fragments of fractured resin tags were observed only when the examination was made at a high power view. As the number of sample which showed such a microstructure of enamel surface after tensile bond test became fewer with an increase in bond strength, the bond strength is considered to owe mainly to the resin tag.

A considerable amount of resin remnants like an island in enamel was observed on the enamel surface after tensile bond test of samples applied with Concise Enamel Bond and Epobond. In this study, after applying liquid resin the excess was blown off with an air gun to make it thin layer. But as compared with Clearfil Bonding Agent in which the solvent is pre-evaporated, it seems that these liquid resin layers are of uneven thickness. Also, there seems to be a difference in the affinity between composite resin and liquid resin as pointed out by Satoh et al.⁴⁵⁾ From these reasons, the remnants like an island may occur, suggesting the destruction between composite resin and liquid resin or of liquid resin itself. But the high bond strength was obtained even in the sample in which the above mentioned microstructure was observed. The bond strength of 212 Kg/cm^2 was obtained with Epobond (Figure 10).

6. Clinical consideration

Comparison of four kinds of etching solutions used in this study will be described as follows for the clinical application. Phosphoric acid showed a high bond strength though it dissolved a large amount of tooth Ca. Though citric acid dissolved a small amount of tooth Ca, it showed a smaller bond strength than the other three etching solutions. Consequently, the good adhesion is attained in short time with relatively smaller damage to enamel when the etching is carried out with 15 to 25% of citraconic and pyruvic acid for 30 sec. Though the acid etching time of 15 sec. seems to be sufficient for the cavity which is surrounded by cavity walls and hardly receives the external forces such as occlusal force, the prompt decision cannot be made due to the problem of marginal sealing in cavity⁵⁴⁾. Moreover, as compared with pyruvic acid, citraconic acid is more suitable for the use in oral cavity because pyruvic acid has a strong smell.

CONCLUSIONS

In this study, the acid etched enamel surface and enamel surface after tensile bond test were observed with use of SEM and, as a newly designed experimental procedure, measurements of dissolved Ca, surface roughness and tensile bond strength were carried out on one tooth. The following results were obtained.

1. The observation of the acid etched enamel surface with use of SEM revealed that the prism core became hollow at first. Then narrow cracks were formed at the prism periphery and became wider and deeper. Consequently, the irregularity of etched enamel surface increased with an increase of etching time. Citric acid showed the weakest effect on the enamel surface among four etching solutions examined, wide and deep grooves were not observed without etching for more than 60 sec. with any concentration of the etching solution. Morphology which was caused by treatment with 40% pyruvic acid for more than 30 sec. showed various appearances.

2. Among four kinds of acid etching solutions, phosphoric acid showed the high value for all of Ca dissolution, arithmetical average roughness and tensile bond strength. Citraconic and pyruvic acid showed almost the same value as phosphoric acid for tensile bond strength and arithmetical average roughness though the value for Ca dissolution was about a half of phosphoric acid. Citric acid showed the lowest value for Ca dissolution, arithmetical average roughness and tensile bond strength.

3. For Ca dissolution and tensile bond strength, all etching solutions showed a tendency drawing a curve of second degree with a maximum value at a concentration of about 20%. Pyruvic and phosphoric acid showed a remarkable decrease in Ca dissolution in concentration range between 20–40% as compared with the other etching solutions.

4. The value for Ca dissolution, arithmetical average roughness and tensile bond strength increased with an increase of etching time in all etching solutions examined. For Ca dissolution, phosphoric acid showed the highest increasing rate with an increase of etching time, citraconic and pyruvic acid showed about a half and citric acid about a forth of that of phosphoric acid.

5. For tensile bond strength, no statistically significant differences were observed in the resinous restorative materials used.

6. There was a statistically significant relationship between tensile bond strength and Ca dissolution but not between tensile bond strength and arithmetical average roughness.
7. The examination of the enamel surface after tensile bond test with SEM revealed the destruction in resin and enamel. Even if the enamel surface after tensile bond test was very similar to acid etched enamel surface at a low power view, the fractured resin tags remaining in enamel were observed at a high power view.
8. Citraconic acid is thought to be useful for clinical application.

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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速やかに形成された。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の原因であった。

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) の配合されたカルボ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、カルボキシレートセメントの場合には HY 剤配合による影響など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ボ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、吸水率も硬化後の早期からわずかながら増加した。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方が収縮も吸水率も逆にわずかながら減少した。

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 観察および赤外吸光分析により検討した。

各酸の陰イオンと Al 又は Ca との錯体の安定度定数が大きい程あるいは、酸溶液の pH が低い程、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解することが分かった。0.01 M クエン酸および塩酸中では、セメント浸漬後に白色沈殿が生成した。その沈殿は、水和ケイ酸質ゲルであることが 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、まず小柱中心部が窪み、次に小柱辺縁に狭い溝が形成され、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折が観察された。リン酸はすべての測定値において大きな値を示した。シトラコン酸とピルビ

ン酸は、Ca の溶出量はリン酸の約半分であったが、それ以外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は増加するが、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。