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The Effect of Phosphoric Acid Pre-etching Times on Bonding Performance and Surface Free Energy with Single-step Self-etch Adhesives

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Clinical Relevance

The use of shortened phosphoric acid pre-etching times of enamel less than 15 seconds improves the bonding performance of single-step self-etch adhesive systems.

SUMMARY

Objective: The purpose of this study was to evaluate the effect of phosphoric acid pre-etching times on shear bond strength (SBS) and surface free energy (SFE) with single-step self-etch adhesives.

Methods: The three single-step self-etch adhesives used were: 1) Scotchbond Universal Adhesive (3M ESPE), 2) Clearfil tri-S Bond (Kuraray Noritake Dental), and 3) G-Bond Plus (GC). Two no pre-etching groups, 1) untreated enamel and 2) enamel surfaces after ultrasonic cleaning with distilled water for 30 seconds to remove the smear layer, were prepared. There were four pre-etching groups: 1) enamel surfaces were pre-etched with phosphoric acid (Etchant, 3M ESPE) for 3 seconds, 2) enamel surfaces were pre-etched for 5 seconds, 3) enamel surfaces were pre-etched for 10 sec-

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onds, and 4) enamel surfaces were pre-etched for 15 seconds. Resin composite was bonded to the treated enamel surface to determine SBS. The SFEs of treated enamel surfaces were determined by measuring the contact angles of three test liquids. Scanning electron microscopy was used to examine the enamel surfaces and enamel-adhesive interface.

Results: The specimens with phosphoric acid pre-etching showed significantly higher SBS and SFEs than the specimens without phosphoric acid pre-etching regardless of the adhesive system used. SBS and SFEs did not increase for phosphoric acid pre-etching times over 3 seconds. There were no significant differences in SBS and SFEs between the specimens with and without a smear layer.

Conclusion: The data suggest that phosphoric acid pre-etching of ground enamel improves the bonding performance of single-step self-etch adhesives, but these bonding properties do not increase for phosphoric acid pre-etching times over 3 seconds.

INTRODUCTION

The introduction of new generation adhesive systems has aimed to reduce technique sensitivity and the number of clinical steps.[1] There has been a trend toward less time-consuming options such as single-step self-etch adhesives.[2] Further, some single-step self-etch adhesives have recently been introduced as universal adhesives, which can be used with self-etch, total-etch, and selective-etch techniques.[3] This type of adhesive is expected to adhere through monomer penetration into the tooth substrate and through chemical interaction with the tooth surface.[4] However, weak enamel bond strengths have been reported for single-step self-etch adhesives compared with those for two-step self-etch and total-etch adhesives, and this may be related to their lower etching capability.[5] A previous study demonstrated that the application of single-step self-etch adhesives did not create the typical enamel etching seen after the application of phosphoric acid.[6] Therefore, the use of phosphoric acid pre-etching to modify the enamel structure has become a standard procedure for conditioning enamel prior to the application of single-step self-etch adhesives.[7,8]

However, some previous studies have failed to find any correlation between enamel morphology and enamel bond strength.[9,10] It has also been reported that increasing phosphoric acid pre-etching times produces greater surface roughness but does not significantly increase bond strength.[11] Therefore, it may be that the bond strength of single-step self-etch adhesives depends less on mechanical interlocking than on changes to the wettability of enamel and the chemical bonding efficiency between acidic functional monomers and hydroxyapatite.

The wettability of an adherend surface is important to establish adhesion.[12] There are two potential obstacles when bonding to enamel. First, the ground enamel surface is covered by a hydrophobic smear layer of 1- to 2-μm thickness, which decreases wettability.[13] Second, the normal surface of enamel is itself hydrophobic in comparison to dentin.[14] Phosphoric acid pre-etching removes the smear layer completely and increases the enamel wettability, changing the surface characteristics from hydrophobic to hydrophilic by exposing the hydroxyl groups of the enamel.[15] Single-step self-etch adhesives are more hydrophilic than their two-step self-etch and total-etch adhesives.[2,16] Thus, the hydrophilicity of the enamel surface may also be important for compatibility between adherend and adhesive. In addition, phosphoric acid pre-etching polarizes the enamel surface, improving chemical bonding reactions between acidic functional monomers and hydroxyapatite.[15] If phosphoric acid pre-etching of enamel only needs to modify surface characteristics, rather than significantly change the morphology of the tooth substrate, shorten phosphoric acid pre-etching times less than 15 seconds may be adequate. Further, it is possible that the acidity of self-etch adhesives is capable of modifying the enamel surface sufficiently, if the smear layer is first removed so that the etching ability of the adhesive is not exhausted before the surface the enamel proper is reached.

Many of the interfacial characteristics of a surface depend on its surface free energy (SFE).[12,14,15,17] The SFE value of a solid is considered to be a useful indicator of the wettability of the surface and in the Kitazaki-Hata extension of Young-Dupré theory.[15] SFE values are composed of the dispersion force ($\gamma_S{}^d$), polarity force ($\gamma_S{}^p$), and hydrogen bond force ($\gamma_S{}^h$), where $\gamma_S{}^p$ represents the degree of polarization of surface, and $\gamma_S{}^h$ indicates the hydrophilicity of the surface.[12,15,18] Therefore, the SFE characteristics of enamel might provide insights into the influence of phosphoric acid pre-etching time on bonding performance of single-step self-etch adhesives.

The purpose of this laboratory study was to investigate the effect of phosphoric acid pre-etching times on the shear bond strength (SBS) and SFE

Table 1: *Single-step Self-etch Adhesives Used in This Study*

Adhesive	Code	Lot no.	Main components	Manufacturer
Scotchbond Universal	SU	541424	MDP, bis-GMA, HEMA, Vitrebond copolymer, polyethelene glycol, water, initiator, colloidal silica, aluminum oxide	3M ESPE
Clearfil Tri-S Bond	TS	00038B	MDP, bis-GMA, HEMA, ethanol, water, initiator, silanated colloidal silica	Kuraray Noritake Dental
G-Bond Plus	GB	1312131	MDP, 4-MET, methacrylate monomer, acetone, water, initiator, silica filler	GC

Abbreviations: bis-GMA, 2,2-bis[4-(2-hydroxyl-3-methacryloyloxypropoxy)phenyl]propane; HEMA, 2-hydroxyethyl methacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; 4-MET, 4-methacryloyloxyethyl trimellitate.

characteristics with single-step self-etch adhesives. The null hypotheses to be tested were 1) there is no difference in the enamel SBS and SFE characteristics dependent on the phosphoric acid pre-etching time and 2) the enamel SBS and SFE characteristics are not influenced by the presence or absence of a smear layer.

METHODS AND MATERIALS

Adhesive Systems

Three single-step self-etch adhesives were used in this study: 1) Scotchbond Universal Adhesive (SU) (3M ESPE, St. Paul, MN, USA), 2) Clearfil tri-S Bond (TS) (Kuraray Noritake Dental, Tokyo , Japan), and 3) G-Bond Plus (GB) (GC, Tokyo, Japan). The adhesives and associated lot numbers and components are shown in Table 1.

SBS Tests

The SBS to enamel of a resin composite using the three single-step self-etch adhesives was measured by a notched-edge test, as described by International Organization for Standardization 29022.[19] Mandibular bovine incisors extracted from two- to three-year-old cattle and stored frozen (–20°C) for up to two weeks were used in this study. The roots were removed with a diamond-impregnated disk in a slow-speed saw (Isomet, Buehler, Lake Bluff, IL, USA). Pulp tissues were then removed, and the pulp chamber of each tooth was filled with cotton to avoid penetration of embedding media. After ultrasonic cleaning for 30 seconds in distilled water to remove excess debris, the surfaces were washed and dried with oil-free compressed air. The labial surfaces were ground with wet 240-grit silicon carbide (SiC) paper to create a flat enamel surface. Each tooth was then mounted in self-curing acrylic resin (Tray Resin II, Shofu, Kyoto, Japan) to expose the flattened area, and placed under tap water to reduce the temperature rise caused by the exothermic polymerization reaction of the acrylic resin. The final finish was created by grinding with wet 320-grit SiC paper. The enamel surfaces were dried with oil-free compressed air.

Fifteen enamel specimens were used for each study group. Two no pre-etching groups, 1) untreated enamel (with smear) and 2) enamel surfaces after ultrasonic cleaning with distilled water for 30 seconds to remove the smear layer (without smear), were prepared to determine the influence of the smear layer. There were four pre-etching groups: 1) enamel surfaces were pre-etched with phosphoric acid (Etchant, 3M ESPE) for 3 seconds, 2) enamel surfaces were pre-etched for 5 seconds, 3) enamel surfaces were pre-etched for 10 seconds, and 4) enamel surfaces were pre-etched for 15 seconds. These pre-etched enamel bonding sites were rinsed for 10 seconds with an air-water spray from a three-way syringe and air dried. An Ultradent Bonding Assembly (Ultradent Products, South Jordan, UT, USA) was used for determining SBS. The adhesives were applied to the enamel surfaces according to the manufacturers' instructions. Following the application of the adhesive to the bonding sites, the resin composite cylinders were formed on the enamel surfaces by clamping plastic molds (2.4 mm in internal diameter and approximately 2.5 mm in height) in the fixture against the tooth surfaces. The resin composite (Clearfil AP-X, Kuraray Noritake Dental) was placed into the mold using a condenser and then light cured for 30 seconds with a quartz-tungsten halogen unit (Optilux 501, Demetron, Kerr, Danbury, CT, USA) set at a light irradiance average of 800 mW/cm^2. The power density (above 800 mW/cm^2) of the quartz-tungsten halogen unit was checked using a dental radiometer (model 100, Demetron) before preparing the specimens. The plastic mold was removed, and the finished specimens were transferred to distilled water and stored at 37°C for 24 hours before SBS measurements.

SBSs were determined using a universal testing machine (Type 5500R, Instron, Canton, MA, USA) with an Ultradent shearing fixture at a crosshead speed of 1.0 mm/minute. The SBS values (MPa) were

Table 2: *SFE Values and SFE Parameters of Test Liquids*

Liquid	Lot no.	Manufacturer	γ_L, mN/m	$\gamma_L{}^d$, mN/m	$\gamma_L{}^p$, mN/m	$\gamma_L{}^h$, mN/m
Bromonaphthalene	ALH4513	Wako Pure Chemical Industries, Osaka, Japan	44.8	44.6	0.2	0.0
Diiodomethane	ALL2310	Wako Pure Chemical Industries	50.8	46.8	4.0	0.0
Distilled water	—	—	72.8	29.1	1.3	42.4

Abbreviations: SFE, surface free energy; γ_L, total surface free energy of liquid; $\gamma_L{}^d$:dispersion force; $\gamma_L{}^h$, hydrogen bonding force; $\gamma_L{}^p$: polarity force.

calculated from the peak load at failure divided by the bonding area. After testing, the specimens were examined under an optical microscope (SZH-131, Olympus, Tokyo, Japan) at a magnification of 10× to determine the type of the bond failure. The proportions of the resin composite surface with adherent enamel and visible remnants were estimated and used to classify the failure as follows: 1) adhesive failure; 2) cohesive failure in the enamel; 3) cohesive failure in the resin composite; or 4) mixed failure (combination of adhesive and cohesive failure).

SFE Measurements

The enamel surfaces were prepared as described above for the SBS test. The SFEs of the no pre-etch and pre-etch specimens were determined by measuring the contact angle formed with the surface by three test liquids: bromonaphthalen, diiodomethane, and distilled water, each of which has known SFE parameters (Table 2). For each test liquid, the equilibrium contact angle (θ) was measured in five specimens per group using the sessile-drop method at 23 ± 1°C with a contact angle measurement apparatus (Drop Master DM500, Kyowa Interface Science, Saitama, Japan). The apparatus was fitted with a charge-coupled device camera that allowed automatic measurement of the contact angle. The SFE parameters of the solids were then calculated based on the fundamental concepts of wetting.

The Young-Dupré equation describes the work of adhesion (W) between a solid (S) and a liquid (L) in contact as follows: $W_{SL} = \gamma_L + \gamma_S - \gamma_{SL} = \gamma_L (1 + \cos\theta)$. Here, γ_{SL} is the interfacial free energy between the solid and liquid, γ_L is the SFE of the liquid, and γ_S is the SFE of the solid. By extending the Fowkes equation, as developed by Kitazaki-Hata, γ_{SL} can be expressed as follows:

$$\gamma_{SL} = \gamma_L + \gamma_S - 2(\gamma_L^d\gamma_S^d)^{1/2} - 2(\gamma_L^p\gamma_S^p)^{1/2} - 2(\gamma_L^h\gamma_S^h)^{1/2}$$

$$\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h, \quad \gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h$$

where $\gamma_L{}^d$, $\gamma_L{}^p$, and $\gamma_L{}^h$ are components of the SFE arising from the dispersion force, the polar force, and the hydrogen bonding force, respectively. SFE values were first determined for the three test liquids. The SFE parameters of the enamel were then calculated based on these equations using the built in interface measurement and analysis system (FAMAS, Kyowa Interface Science).

Statistical Analysis

The SBS and SFE data obtained were analyzed using a commercial statistical software package (Sigma Stat, Version 3.1, SPSS, Chicago, IL, USA). A two-way analysis of variance (ANOVA) and Tukey post hoc test were used for analysis of SBS data, and a one-way ANOVA was used for SFE data.

Scanning Electron Microscopy Observation

Ultrastructural observation of the no pre-etching and pre-etching specimens was carried out in three specimens per group by scanning electron microscopy (SEM). The enamel surfaces were prepared as described above for SBS test specimens. All SEM specimens of enamel were dehydrated in ascending concentrations of tert-butanol and then transferred to a critical-point dryer. The surfaces were coated in a vacuum evaporator (Quick Coater Type SC-701, Sanyu Electron, Tokyo, Japan) with a thin film of gold and were analyzed using SEM (ERA-8800 FE, Elionix, Tokyo, Japan).

In addition, the enamel-adhesive interface was ultrastructurally observed in three specimens per group by SEM. Bonded specimens from each group were stored in distilled water maintained at 37°C for 24 hours, embedded in self-curing epoxy resin (Epon812, Nisshin EM, Tokyo, Japan), and stored at 37°C for an additional 12 hours. The embedded specimens were sectioned through the diameter of the composite resin post, and the surfaces of the cut halves were polished with an Ecomet 4/Automet 2 (Buehler) using SiC papers with a grit size of 600, 1200, 2400, and 4000 in succession. The surface was finally polished by a soft cloth using diamond paste (Buehler) with a grit size of 1.0 μm. All SEM specimens of enamel/adhesive interface were dehydrated in ascending concentrations of tert-butanol

Table 3: *Influence of Phosphoric Acid Pre-etching Time and Smear Layer of Enamel on SBS of Single-step Self-etch Adhesives**

Treatment	SU	TS	GB
With smear	27.4 (3.1)[a,A]	24.7 (3.5)[a,A]	25.7 (3.4)[a,A]
	[15/0/0/0]	[15/0/0/0]	[15/0/0/0]
Without smear	28.2 (3.9)[a,A]	25.9 (4.6)[a,A]	26.6 (4.1)[a,A]
	[15/0/0/0]	[15/0/0/0]	[15/0/0/0]
3 seconds	33.8 (4.0)[a,B]	31.8 (3.9)[a,B]	31.5 (3.9)[a,B]
	[13/2/0/0]	[15/0/0/0]	[14/0/1/0]
5 seconds	33.8 (4.4)[a,B]	31.7 (4.7)[a,B]	31.9 (4.6)[a,B]
	[14/1/0/0]	[15/0/0/0]	[13/0/1/1]
10 seconds	34.5 (2.8)[a,B]	31.3 (3.7)[b,B]	32.4 (3.7)[a,b,B]
	[12/1/1/1]	[14/1/0/0]	[13/1/0/1]
15 seconds	33.9 (4.1)[a,B]	32.0 (3.0)[a,B]	32.5 (3.8)[b,B]
	[13/0/1/1]	[14/0/0/1]	[14/0/1/0]

** Unit, MPa. Values in parentheses are standard deviations (n=15). The same lower case letter in a rows indicates no significant difference ($p>0.05$). The same capital letter in a column indicates no significant difference ($p>0.05$). Numbers in brackets represent failure mode [adhesive failure/cohesive failure in enamel/cohesive failure in resin/mixed failure]. Abbreviations: SBS, shear bond strength; SU, Scotchbond Universal Adhesive; TS, Clearfil tri-S Bond; GB, G-Bond Plus;.*

Table 4: *Influence of Phosphoric Acid Pre-etching Time and Smear Layer of Enamel on SFE values and SFE Parameters**

Treatment	γ_S, mN/M	γ_S^d, mN/M	γ_S^p, mN/M	γ_S^h, mN/M
With smear	56.3 (3.6)[a]	41.0 (1.1)[c]	3.9 (2.4)[d]	11.4 (2.4)[f]
Without smear	54.2 (3.2)[a]	41.0 (1.2)[c]	3.2 (2.2)[d]	10.0 (2.0)[e,f]
3 seconds	75.2 (3.3)[b]	40.4 (0.9)[c]	8.7 (2.2)[e]	26.1 (2.3)[g]
5 seconds	75.8 (3.7)[b]	40.1 (1.0)[c]	9.6 (2.7)[e]	26.1 (2.4)[g]
10 seconds	75.7 (3.6)[b]	40.3 (0.9)[c]	9.3 (2.6)[e]	26.1 (2.3)[g]
15 seconds	75.8 (3.2)[b]	40.6 (0.9)[c]	8.9 (2.1)[e]	26.3 (2.2)[g]

** Values in parentheses are standard deviations (n=5). The same lower case letter in a column indicates no significant difference ($p>0.05$). Abbreviations: SFE, surface free energy; γ_S, total surface free energy; γ_S^d, dispersion force; γ_S^h, hydrogen bond force; γ_S^p, the polarity force.*

(50% for 20 minutes, 75% for 20 minutes, 95% for 20 minutes, and 100% for 2 hours) and transferred to a critical-point dryer for 30 minutes. These surfaces were subjected to argon ion-beam etching (Type EIS-200ER, Elionix) for 30 seconds, with the ion beam (accelerating voltage, 1.0 kV; ion current density, 0.4 mA/cm^2) directed perpendicularly to the polished surface. Surfaces were coated in a vacuum evaporator (Quick Coater Type SC-701, Sanyu Electron, Tokyo, Japan) with a thin film of gold and observed by SEM (ERA 8800FE, Elionix) at an accelerating voltage of 10 kV. All of the enamel-adhesive interface specimens were observed under SEM.

RESULTS

The results for the effect of phosphoric acid pre-etching times on SBS to enamel are shown in Table 3. The SBS ranged from 27.4 to 34.5 MPa for SU; 24.7 to 32.0 for TS; and 25.7 to 32.5 MPa for GB. The specimens with phosphoric acid pre-etching showed significantly higher ($p<0.05$) SBS than the specimens without phosphoric acid pre-etching regardless of the adhesive system used. SBS did not increase for phosphoric acid pre-etching times over 3 seconds. There were no significant differences ($p>0.05$) in SBS between the specimens with and without a smear layer. Failure type was not associated with bond strength, and the predominant type of failure seen was adhesive failure.

The results for the effect of phosphoric acid pre-etching time of enamel on SFE and SFE parameters are shown in Table 4. The γ_S of enamel ranged from 54.2 to 75.8 mN/m, and the specimens with phosphoric acid pre-etching showed significantly higher values ($p<0.05$) than the specimens without phosphoric acid pre-etching. There were no significant differences ($p>0.05$) in γ_S between the specimens with and without a smear layer. For all surfaces, the estimated γ_S^d remained relatively constant at 40.1-41.0 mN/m. The estimated γ_L^p (8.9-9.6 mN/m) of the specimens with phosphoric acid pre-etching for 3 seconds or more was significantly higher ($p<0.05$) than those of the specimens without phosphoric acid pre-etching (3.2-3.9 mN/m), and there were no significant differences ($p>0.05$) between the specimens with and without a smear layer. The estimated γ_S^h (26.1-26.3 mN/m) of the specimens with phosphoric acid pre-etching was significantly higher ($p<0.05$) than those of the specimens without phosphoric acid pre-etching (10.0-11.4 mN/m), and there were no significant differences ($p>0.05$) between the specimens with and without a smear layer.

Representative SEM images of enamel specimen and enamel-adhesive interface are shown in Figure 1. Enamel surfaces and enamel-adhesive interfaces pre-etched with phosphoric acid for 3, 5, 10, and 15 seconds showed a typical acid-etched enamel pattern, but there are no clear morphologic differences visible in SEM images of samples etched for 3seconds or more. Although ground enamel surfaces and ground enamel-adhesive interfaces were covered by the smear layer, enamel surfaces and the enamel-adhesive interface after ultrasonic cleaning with distilled water did not exhibit a smear layer.

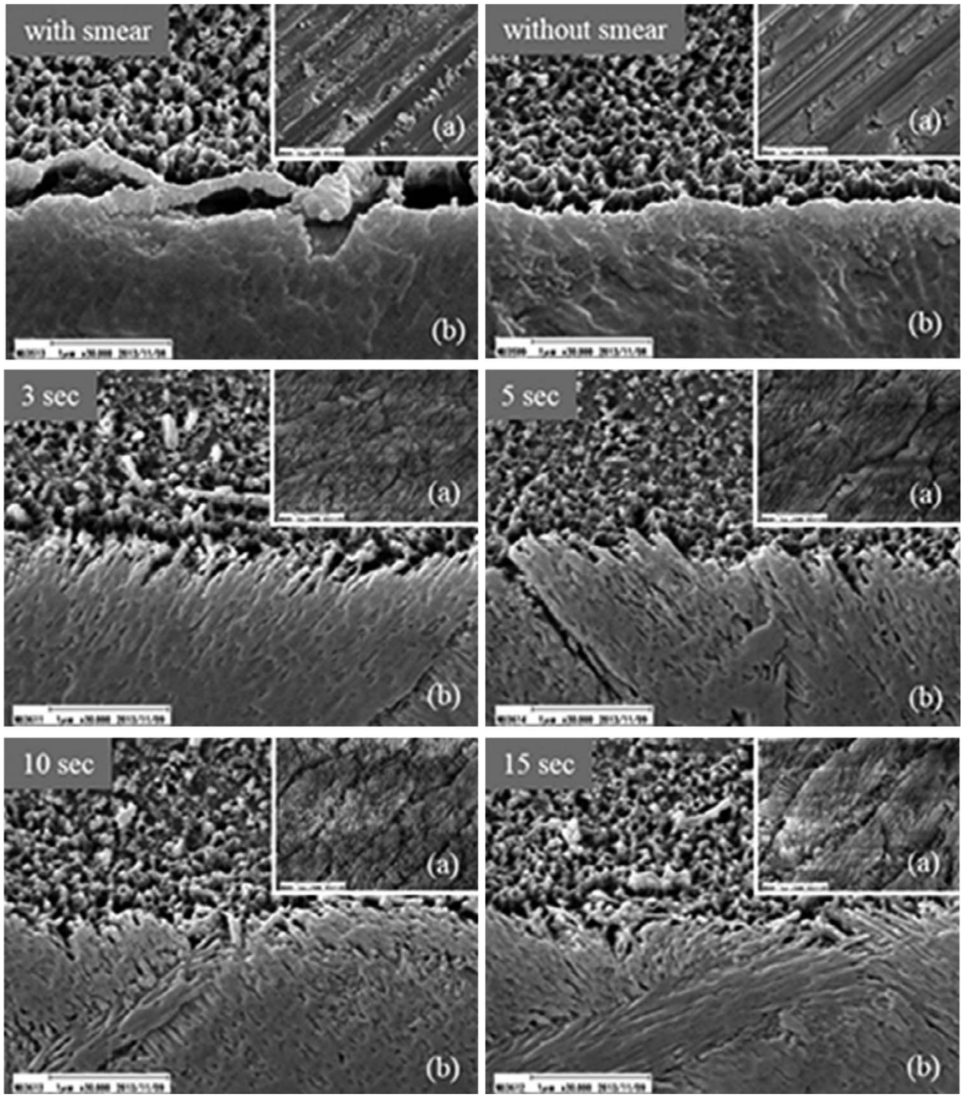

Figure 1. *Representative scanning electron microscopy (SEM) images of the enamel treated surface at 10,000 × magnification (a) and the enamel/adhesive interface at 30,000× magnification (b). Enamel-treated surfaces and enamel/adhesive interfaces pre-etched with phosphoric acid for 3, 5, 10, and 15 seconds showed a typical acid-etched enamel pattern, but there are no clear morphologic differences visible in SEM images of samples etched for three seconds or more. Although ground enamel surfaces and ground enamel/adhesive interfaces were covered by the smear layer, enamel surfaces and enamel/adhesive interface after ultrasonic cleaning with distilled water did not exhibit a smear layer.*

DISCUSSION

Although it is generally preferable to use extracted human teeth for conducting *in vitro* studies, bovine teeth were used in this study. Bovine teeth have important advantages for this study, as they have large flat surfaces and are unlikely to have undergone prior caries challenges that could affect the test results. To measure the contact angle for SFE measurement properly, a fairly large and caries-free flat surface of enamel was needed. Moreover, the mineral distribution within caries lesions in bovine teeth is reportedly similar to that found in human teeth, and the structural changes that occur in human and bovine teeth are also similar.[20]

The present study investigated the effect of phosphoric acid pre-etching times on the bonding performance of single-step self-etch adhesives. The study shows that significantly higher SBS were observed when enamel was pre-etched with phosphoric acid. However, SBS did not increase further for phosphoric acid etching times over 3 seconds. Therefore, the bonding effectiveness of single-step self-etch adhesive systems examined in this study did not improve when the phosphoric acid etching time was increased from 3 to 15 seconds. The results of this study clearly support the use of a shortened pre-etching time of enamel less than 15 seconds with single-step self-etch adhesives. This is important for clinicians who are concerned about the additional time requirement for using phosphoric acid pre-etching with single-step self-etch adhesives.

This study also examined the SBS of enamel surfaces with and without a smear layer. The results showed that there are no significant differences in SBS between the ground enamel surfaces with and without a smear layer. This indicates that the etching ability of single-step self-etch adhesives is not sufficient to condition the enamel surface, even in the absence of a smear layer.

In addition, the SBS of the specimens with and without a smear layer were significantly lower than the specimens with phosphoric acid pre-etching. It is reported that the interaction of the acidic functional monomers with enamel seems to be less than with hydroxyapatite in dentin.[21] The structure and size of enamel hydroxyapatite crystals interfere with chemical bonding to acidic functional monomers, as the crystals within dentin are considerably smaller than those within enamel.[21] Phosphoric acid pre-etching of enamel attacks the hydroxyapatite crystals, partially eroding them and creating a porous and retentive structure on the surface.[22] Therefore, the acidic functional monomers may be able to bond chemically to pre-etched enamel as effectively as to dentin.

In this study, the effect of phosphoric acid pre-etching times on the SFE characteristics of enamel was also investigated. The γ_S of the specimens with phosphoric acid pre-etching showed significantly higher values than the specimens with and without a smear layer. This finding can be explained by the increase in exposed hydroxyl sites on hydroxyapatite crystals. Although some previous studies reported that increasing pre-etching time changed the nature of the etched surface, this study does demonstrate such a change.[11] In the present study, there are no clear morphologic differences visible between SEM images of enamel specimen and enamel-adhesive interface etched for 3 seconds or more, nor was any difference in SFE measured. This suggests that shorten pre-etching times less than 15 seconds creates a micromechanical retentive enamel surface and that, although further etching may deepen the pattern, the surface properties are not markedly changed.

Optimal wettability is important to enable the adhesive materials to spread across the entire adherend surface and establish adhesion.[12,15,17,18] Theoretically, phosphoric acid pre-etching creates more porosity on enamel surfaces and increases both the bonding area and the wettability of the substrate, permitting resin to infiltrate better into the acid conditioned enamel surface.[6,7] Considering the results of the present study, a higher SFE would appear to have a strong influence on enamel bond strength, as the pre-etched specimens had a higher SBS than those with and without smear layer. This suggests that the SFE characteristics of enamel significantly influenced SBS.

In the present study, the γ_S^d of the enamel surface remained relatively constant under all of the conditions tested. It has been reported that many oxidized surfaces have a γ_S^d that is close to 40 mN/m, whereas those of surfaces coated with polytetrafluoroethylene are close to 20 mN/m.[12] This has been attributed to the so-called atmospheric contamination layer, particularly if the surface is activated chemically or mechanically.[23,24] The presence of this layer might explain why, regardless of the presence or absence of a smear layer or with and without phosphoric acid pre-etching, the enamel surfaces had similar γ_S^d. It might also explain the similarities seen in the γ_S^d of enamel surfaces with different surface roughness and surface area. The γ_S^p and γ_S^h of the specimens with phosphoric acid pre-etching for at least 3 seconds were significantly higher than those of specimens with and without smear layer. This finding can be explained by the increase in the number of hydroxyl sites on the surface of etched hydroxyapatite crystals. The γ_S^p involves the polar interaction, which is called a nondispersion force, and reflects the degree of polarization.[15] The γ_S^h is also related to the hydroxyl groups and reflects hydrophilic interaction.[12] Therefore, phosphoric acid pre-etching of enamel demineralizes the smear layer and superficial enamel and increases the number of hydroxyl sites and hydrophilicity, leading to increased γ_S^p and γ_S^h. In the present study, the SFE and SFE parameters did not show significant differences between the specimens with and without smear layer. This suggests that the SFE characteristics of enamel are not strongly influenced by pulverization.

Overall, the results of this study require acceptance of the null hypothesis that there is no difference in the enamel SBS and SFE characteristics dependent on the phosphoric acid pre-etching time, and the enamel SBS and SFE characteristics are not influenced by the presence or absence of smear layer.

In the present study, higher γ_S, γ_S^p, and γ_S^h strongly influenced the enamel SBS of single-step self-etch adhesives. Therefore, adequate enamel bonding may be achieved when optimal interfacial science characteristics are produced by phosphoric acid pre-etching of enamel. In addition, phosphoric acid pre-etching of ground enamel for 3 seconds may be sufficient to improve the enamel bonding performance of single-step self-etch adhesives in the clinic.

CONCLUSIONS

Phosphoric acid pre-etching increases the enamel SBS of single-step self-etch adhesives, but SBS did not increase for phosphoric acid etching times over 3 seconds. On the other hand, the presence of a smear layer on ground enamel does not influence the SBS of single-step self-etch adhesives. In addition, phosphoric acid pre-etching increases γ_S, γ_S^p, and γ_S^h of enamel surfaces, but those values did not increase further for phosphoric acid pre-etching times over 3 seconds. As with SBS, the presence of the smear layer did not influence the SFE characteristics of enamel. Therefore, these results indicate that ground enamel should be phosphoric acid pre-etched at least 3 seconds before the use of a single-step self-etch adhesive.

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Regulatory Statement

This study was conducted in accordance with all the provisions of the local human subjects oversight committee guidelines and policies of the ethics committee for human and animal study of Nihon University School of Dentistry. The approval code for this study is #2011-19.

Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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