Does the Acidity of Self-etching Primers Affect Bond Strength and Surface Morphology of Enamel?

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Purpose: This study examined the ultrastructure and microtensile bond strengths (TBS) of self-etching (with different acidity) and conventional adhesive systems bonded to unground enamel.

Materials and Methods: Resin composite (Filtek Z250) buildups were bonded to unground enamel surfaces of third molars after adhesive application with the following materials: Clearfil SE Bond (CSE); Optibond Solo Plus Self-Etch (OP); Tyrian Self Priming Etching (TY), and the controls Scotchbond Multi-Purpose Plus (SBMP) and Single Bond (SB). Six teeth were assigned to each material. After storage in water for 24 h at 37°C, the bonded specimens were sectioned into beams of approximately 0.8 mm^2 and subsequently subjected to μTBS testing at a crosshead speed of 0.5 mm/min. The average values were subjected to one-way ANOVA ($\alpha = 0.05$). The effect of surface conditioning of each material was observed under scanning electron microscopy (SEM).

Results: The highest resin-enamel bond strength was observed for SBMP (22.7 ± 5.2) and SB (26.7 ± 5.2 MPa). The lowest mean bond strengths were 10.9 ± 3.2 and 7.8 ± 1.5 MPa for TY and OP, respectively. CSE showed an intermediate performance (18.7 ± 4.6 MPa). An overall increase in porosity was evident along the entire enamel surface treated with the self-etching primers; however, no selective demineralization similar to that with 35% phosphoric acid was observed.

Conclusion: The highest bond strength means and the more retentive etching pattern were observed for the two-step etch-and-rinse adhesives. Among the self-etching systems studied, Clearfil SE Bond should be preferred.

Keywords: adhesive system, bonding, enamel morphology.

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Acid etching is the most accepted concept in bonding to enamel. The retentive ability of etched enamel for composite resin is assumed to be a function of the increase in surface area and in the wettability of this dental substrate.[35] Following enamel etching, the enamel surface must be rinsed off for the application of a primer and an adhesive.

In an effort to simplify the dentin/enamel bonding systems, the self-etching adhesives were developed. Some of them, called two-step self-etching adhesives or self-etching primers, have combined the tooth surface etching and priming steps into one single procedure.[37] The elimination of separate etching and rinsing steps simplifies the bonding technique and reduces the technique sensitivity associated with the etch-and-rinse approach.[37]

With the gain in popularity of the self-etching adhesives, the reliability of these new systems has become of great concern. In particular, bonding to enamel has been the focus of interest. Several factors may be responsible for the bonding efficacy of these systems to enamel, such as their demineralization ability,[1,18,20] the ground vs unground condition,[9,12] the cohesive strength of the self-etching adhesive,[18,28] and the application method employed.[7,16,17]

Morphological studies of the etched enamel surface demonstrated that the application of some self-etching adhesives did not create an enamel etching pattern as deep as did the application of 35% to 37% phosphoric acid.[18,20,31] However, it seems that as long as the prismless enamel is removed by means of diamond burs[12] or 35% phosphoric

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acid,[5,33] the bond strengths of self-etching adhesives to enamel can be significantly improved. It seems that the enamel etching pattern of the self-etching system is related to the pH of the adhesive solutions. These new adhesive systems can be classified as mild, moderate, or aggressive, depending on the pH of the priming solution,[31] which is in turn related to the composition and concentration of polymerizable acids and/or acidic resin monomers.

In most clinical scenarios, enamel is slightly ground during a bevel or cavity preparation, and this procedure provides a more receptive substrate for bonding.[12,19] There are, however, cases such as bonding of orthodontic brackets or conservative and preventive restorative procedures (diastema closures and fissure sealing), where bonding should be made on intact enamel.

This study examined the ultrastructure and microtensile bond strengths of two-step self-etching adhesives with different acidity bonded to unground enamel. The null hypothesis tested was that there was no difference between mild, moderate, and aggressive two-step self-etching adhesives when compared to etch-and-rinse adhesives in their ability to bond to unground enamel.

MATERIALS AND METHODS

Microtensile Bond Strength Evaluation

Thirty extracted human third molars were obtained under a protocol approved by the institutional review board from the University of São Paulo dental school. Buccal and lingual surfaces of these teeth were cleaned with a slurry of pumice and water and examined under a stereomicroscope (10X) to ensure that they were free of surface cracks, decalcification, or any sign of previous grinding. The occlusal third of buccal and lingual surfaces was not used for bonding due to its inclination. The teeth were then divided into 5 experimental groups, assigning 6 teeth to each adhesive tested.

Three two-step self-etching adhesives were selected according to their acidity: Clearfil SE Bond (Kuraray Medical, Tokyo, Japan) (CSE), a mild self-etching adhesive (pH 2); Opti-Bond Solo Plus Self-etching Primer (Kerr, Orange, CA, USA) (OP), a moderate self-etching adhesive (1 < pH < 2), and Tyrian Self Priming Etchant (Bisco, Schaumburg, IL, USA) (TY), an acidic self-etching system (pH < 1). As controls, one three- and one two-step etch-and-rinse adhesive were selected: Scotchbond Multi-Purpose Plus (SBMP) and Single Bond (SB) (3M ESPE, St Paul, MN, USA), respectively. All adhesives were applied in a controlled environment (24°C/75% relative humidity) by a single operator using the bonding protocols summarized in Table 1.

Special care was taken to ensure that the enamel surfaces were adequately covered by monomers after evaporation of the solvents. In the event matte enamel was encountered, an additional coat of adhesive was applied to produce shiny surfaces prior to light curing with a VIP unit (600 mW/cm^2, Bisco).

Bonded buccal and lingual enamel surfaces were coupled to a hybrid composite (Filtek Z250, 3M ESPE) that was light activated in three 1-mm-thick increments. After storage in distilled water at 37°C for 24 h, the specimens were longitudinally sectioned in both "x" and "y" directions across the bonded interface with a diamond saw in a Labcut 1010 machine (Extec, Enfield, CT, USA) to obtain approximately 10 bonded beams per tooth, each with a cross-sectional area of about 0.8 mm^2. The number of prematurely debonded beams (PD) per tooth during specimen preparation was recorded. Each stick was examined under a stereomicroscope (10X) in order to check the inclination of the bonding interfaces on the four sides of each stick. Sticks with bent bonding interfaces were not tested in tension. The cross-sectional area of each stick was measured with the digital caliper to the nearest 0.01 mm and recorded for the calculation of the bond strength.

The beams from each adhesive group were stressed to failure using a universal testing machine (Emic, São José dos Pinhais, PR, Brazil) at a crosshead speed of 0.5 mm/min. The bond failure modes were evaluated at 100X under a light stereomicroscope (HMV-2, Shimadzu, Tokyo, Japan) and classified as cohesive (failure exclusively within enamel or resin composite) or adhesive/mixed (failure at resin/enamel interface or mixed with cohesive failure of the neighboring substrates).

A bond strength index (BS) was calculated for each hemitooth used per group.[22] The BS index is a weighted mean assuming the relative contribution of the possible mode of failures, according to the following formula (values in MPa):

Bond strength index:

$$I_t = (B_{A/M} \times \%_{A/M}) + (C_D \times \%_D) + (C_R \times \%_R) + (B_{DS} \times \%_{DS})/100$$

Where:

- B_{AM} Average bond strength of sticks with adhesive/mixed fracture pattern
- $\%_{AM}$ Percentage of sticks with adhesive/mixed fracture pattern
- C_D Cohesive strength of enamel
- $\%_D$ Percentage of sticks that failed cohesively in enamel
- C_R Cohesive strength of resin
- $\%_R$ Percentage of sticks that failed cohesively in resin
- B_{DS} Bond strength attributed to spontaneously debonded sticks during preparation
- $\%_{DS}$ Percentage of sticks debonded during preparation

The cohesive strength of the resin composite and the cohesive strength of enamel are considered as the average value of all the specimens (from a single tooth) that failed in that manner. The average value attributed to specimens that failed prematurely during preparation is arbitrary, and corresponds to approximately half of the minimum bond strength value that could be measured in this study. The microtensile BS indexes were subjected to a one-way ANOVA and a post-hoc test (Tukey's test at α=0.05) for pairwise comparisons. Friedman repeated measures ANOVA by rank and Wilcoxon sign-ranked test for pairwise comparisons (α=0.05) were used to compare the frequency of prematurely debonded specimens between the materials (α=0.05).

Scanning Electron Microscopy

The effect of conditioning with 35% phosphoric acid and the self-etching primers on the unground buccal or lingual

Table 1 Adhesive systems: composition and application mode

Adhesive system	Composition	Application mode	Batch number
Clearfil SE Bond - CSE (Kuraray)	1. Primer: water, MDP, HEMA, camphoroquinone, hydrophilic dimethacrylate 2. Adhesive: MDP, bis-GMA, HEMA, camphoroquinone, hydrophobic dimethacrylate, N,N-diethanol p-toluidine bond, silanated colloidal silica	1. Application of two coats of the primer with slight agitation (20 s) 2. Air dry (10 s at 20 cm) 3. Application of one coat of the adhesive (15 s) 4. Air dry (10 s at 20 cm) 5. Light activation (10 s, 600 mW/cm^2)	00176A 001185A
Optibond Solo Self-Etch Primer and Optibond Solo Plus – OP (Kerr)	1. Primer: alkyl dimethacrylate resins, barium aluminoborosilicate glass, fumed silica (silicon dioxide), sodium hexafluorosilicate and ethyl alcohol 2. Adhesive: alkyl dimethacrylate resins (25-28%), ethyl alcohol, water, stabilizers and activators	1. Application of 1 coat of the primer with slight agitation (15 s) 2. Air dry for 10 s at a distance of 20 cm 3. Application of 1 coat of the adhesive (15 s with slight agitation) 4. Air dry (10 s at 20 cm) 5. Application of 1 coat of the adhesive (15 s with slight agitation) 6. Air dry (10 s at 20 cm) 7. Light activation (20 s, 600 mW/cm^2)	205187, 203D20
Tyrian SPE and One Step Plus - TY (Bisco)	1. Primer: 2-acrylamido-2-methyl propane sulfonic acid (2-15%); bis-GMA; ethanol (25-50%) 2. Adhesive: bis-GMA, BPDM, HEMA, glass frit initiator and acetone (40-70%)	1. Mixture of Tyrian SPE (A and B) and application of 2 coats with slight agitation (10 s) 2. Air dry (10 s at 20 cm) 3. Application of 2 consecutive coats of the adhesive, brushing for 10 s each 4. Air dry (10 s at20 cm) 5. Light activation (10 s, 600 mW/cm^2)	200002694, 200004295
Single Bond - SB (3M ESPE)	1. 37% phosphoric acid 2. Adhesive: bis-GMA, HEMA, dimethacrylates, polyalkenoic acid copolymer, initiators, water and ethanol	1. Acid etching (15 s), rinsing (15 s) and air drying (10 s) 2. Application of 1 coat of the adhesive (10s with slight agitation) 3. Air dry (10 s at 20 cm) 4. Application of 1 coat of the adhesive (10 s with slight agitation) 5. Air dry (10 s at 20 cm) 6. Light activation (10 s, 600 mW/cm^2)	2GM
ScotchBond Multi Purpose Plus – SBMP (3M ESPE)	1. 37% phosphoric acid 2. Primer: aqueous solution of HEMA, polyalkenoic acid copolymer (Vitrebond) 3. Adhesive: bis-GMA, HEMA, dimethacrylates and initiators	1. Acid etching (15 s), rinsing (15 s) and air drying (10 s) 2. Application of 2 coats of the primer(10 s with slight agitation) 3. Air dry (10 s at 20 cm) 4. Application of 1 coat of the adhesive (10 s with slight agitation) 5. Air dry (10 s at 20 cm) 6. Light activation (10 s, 600 mW/cm^2) 7. Light activation (10s, 600 mW/cm^2)	3008,7543

Abbreviations: MDP (10-methacryloyloxydecyl dihydrogen phosphate); HEMA (2-hydroxyethyl methacrylate); bis-GMA (bisphenolglycidyl methacrylate); BPDM (biphenyl dimethacrylate).

Table 2 Percentage of specimens (%) according to the fracture pattern or premature debonding for each experimental condition

	A/M	E	R	D
CSE	65.7	6.2	12.5	15.6
OP	63.1	6.2	6.2	24.5
TY	67.7	0.0	0.0	32.3
SBMP	64.4	29.5	0.0	6.1
SB	65.8	23.7	10.5	0.0

A/M = adhesive/mixed failure; E = cohesive failure in enamel; R = cohesive failure in resin; D = prematurely debonded sticks.

Table 3 Mean, standard deviation (MPa) and statistical significance of bond strength indices for each experimental condition (*)

CSE	18.7 ± 4.6 [b]
OP	7.8 ± 1.5 [c]
TY	10.9 ± 3.2 [c]
SBMP	22.7 ± 5.2 [a,b]
SB	26.7 ± 4.6 [a]

(*) Same letters indicate no significant difference ($p > 0.05$).

enamel surfaces was analyzed. Enamel surfaces not treated with the conditioners were also observed for comparison purposes.

Teeth (n=2 for each treatment) were longitudinally sectioned in a mesial to distal direction into halves. A deep lingual slit was prepared with a diamond bur to facilitate subsequent fracture of the etched surfaces. Free enamel surfaces were cleaned with a rotating brush with pumice slurry and water.

Enamel surfaces were treated with 35% phosphoric acid and self-etching primers as described in Table 1. Phosphoric acid-etched enamel was rinsed with water spray for 15 s. Enamel etched with self-etching primers was rinsed with ethanol and acetone to remove the monomers.[3] After that, the same specimens were gently split with a hammer and scapel blade along the preformed slits to provide a sagittal view of the etched enamel. Specimens were stored in a desiccator containing silica gel for 12 h. After that, they were mounted on aluminum stubs with colloidal silver and gold sputter-coated (Balzers SCD 050 Sputter Coater, Bal-Tec, Balzers, Liechtenstein) to be observed under an SEM (Philips XL30, Eindhoven, Netherlands) at 15 kV of accelerating voltage. Both the etched buccal and lingual surfaces as well as the sagittally fractured surfaces of the same tooth were examined.

RESULTS

Resin-Enamel Bond Strength

The mean cross-sectional area ranged from 0.72 to 0.78 mm^2 and no difference among the treatment groups was detected ($p > 0.05$). The percentage of sticks that had a premature failure during specimen preparation and the frequency of each fracture pattern in each group are shown in Table 2. The two etch-and-rinse adhesives performed equally in terms of prematurely debonded specimens. Both systems had no or just a few sticks lost during preparation. All other systems showed a higher percentage of premature debonding ($p < 0.05$) when compared to the etch-and-rinse adhesives. TY and OP showed the highest percentage of debonded specimens ($p < 0.05$), while CSE had an intermediate percentage between the etch-and-rinse adhesives and TY and OP systems.

The means and standard deviations (MPa) of the bond strength indices are given in Table 3. The statistical analysis detected significant differences among the adhesives tested ($p < 0.01$). The highest resin-enamel bond strength was observed for the two total-etch adhesives. The lowest mean bond strengths were observed for the self-etching adhesives TY and OP, which were statistically different from all others (Table 3).

Scanning Electron Microscopy

Scanning electron microscope photomicrographs of unground, untreated enamel surfaces, and the enamel surfaces treated with phosphoric acid and the self-etching primers are shown in Figs 1 to 5.

Figure 1 presents the enamel surface after cleaning with pumice slurry and water. Only a very smooth surface and some grooves could be observed (Fig 1a); no selective demineralization was noted. The sagittal view of the same specimen (Fig 1c) shows the presence of aprismatic enamel in some areas.

Figure 2 presents the enamel surface following treatment with 35% phosphoric acid. Different morphological findings could be observed in the same specimen: the selective etching of prism cores (type 1 pattern) and prism peripheries (type 2 pattern), also areas of no selective demineralization (Fig 2a); intraprismatic demineralization (Fig 2b); areas of aprismatic enamel (Fig 2c).

The enamel surface etched with CSE showed some shallow depressions along the enamel surface (Fig 3a) but was predominantly smooth (Fig 3b). The sagittal view of the same specimen (Fig 3c) shows areas of prismatic and aprismatic enamel.

The etching appearance of OP was predominantly unetched and smooth (Fig 4b), intercalated with some deep, large grooves on enamel surface (Fig 4a). Like other specimens, Fig 4c also shows areas of aprismatic enamel in the same specimen.

Unlike the two previous two-step self-etching adhesives, an overall increase in porosity was evident along the entire enamel surface treated with TY (Fig 5a). In contrast to the

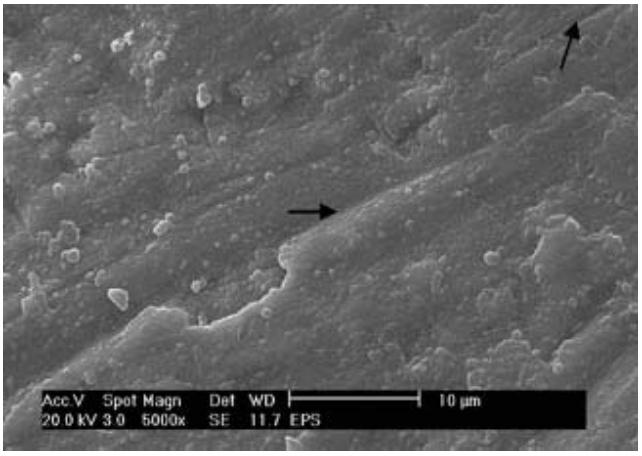

Fig 1a SEM micrograph of unground enamel following cleaning with slurry of pumice and water. The surface is very smooth. Surface view (5000X): grooves (black arrow) from the cleaning procedure.

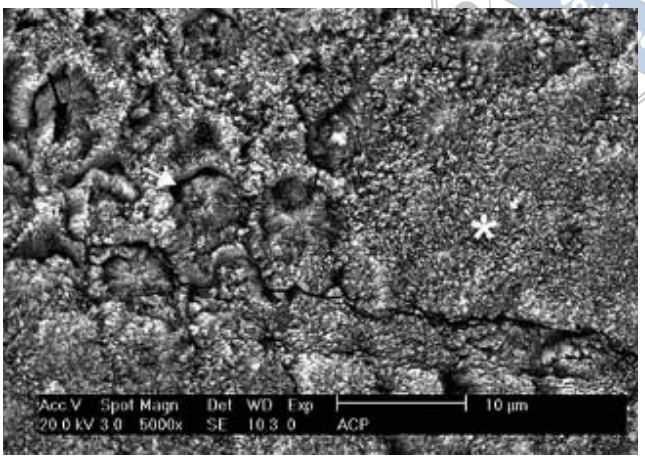

Fig 2a SEM micrograph of unground enamel following treatment with 35% phosphoric acid. Surface view (5000X): note interprismatic demineralization (black arrow – type 1 pattern; white arrow – type 2 pattern) and no uniform (white *) pattern.

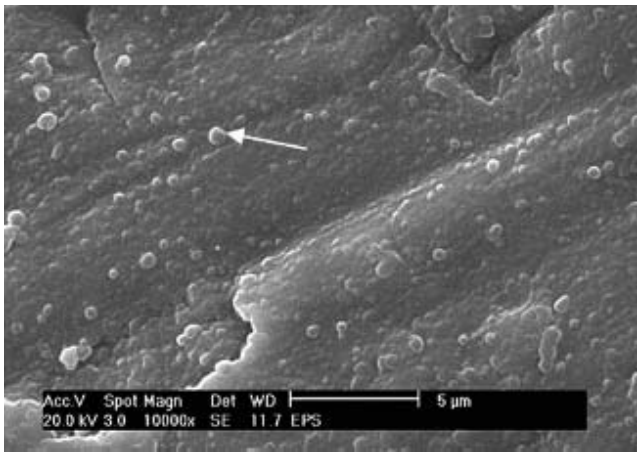

Fig 1b SEM micrograph of unground enamel following cleaning with slurry of pumice and water. Surface view (10,000X): slurry of pumice and water (white arrows).

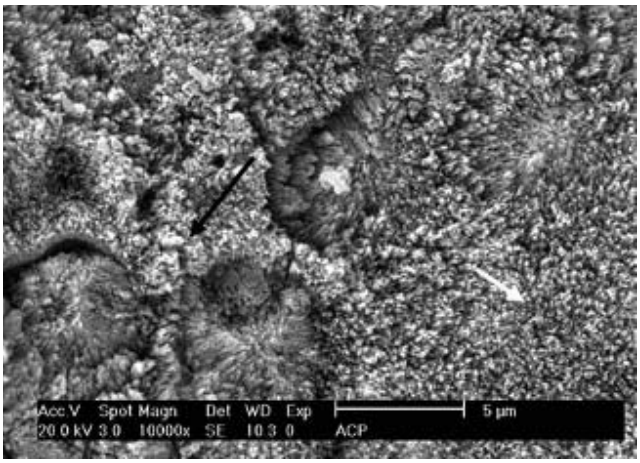

Fig 2b SEM micrograph of unground enamel following treatment with 35% phosphoric acid. Surface view (10,000X): note intraprismatic demineralization (black arrow) and no uniform pattern (white arrow).

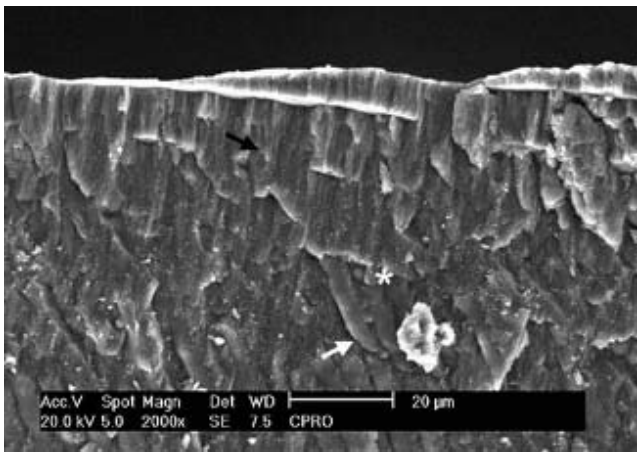

Fig 1c SEM micrograph of unground enamel following cleaning with slurry of pumice and water. Sagittal view (3000X): note aprismatic enamel layer (black arrow); prismatic enamel (white arrow) and transition between prismatic and aprismatic enamel (white *).

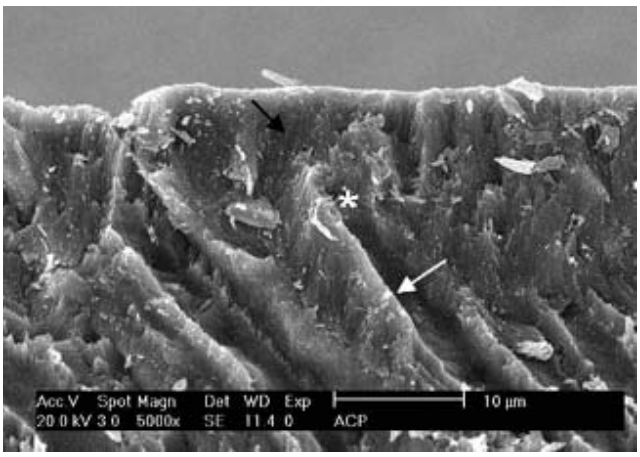

Fig 2c SEM micrograph of unground enamel following treatment with 35% phosphoric acid. Sagittal view (5000X): note aprismatic enamel layer (black arrow); prismatic enamel (white arrow) and transition between prismatic and aprismatic enamel (white *).

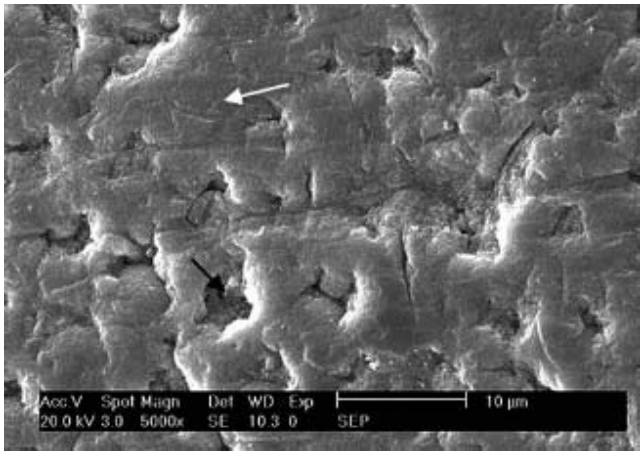

Fig 3a SEM micrograph of unground enamel etching observed following treatment with Clearfil SE primer. Surface view (5000X): note grooves from brushing with slurry of pumice and water (white arrow) and shallow depressions (black arrow) representing some prisms that could reach the surface.

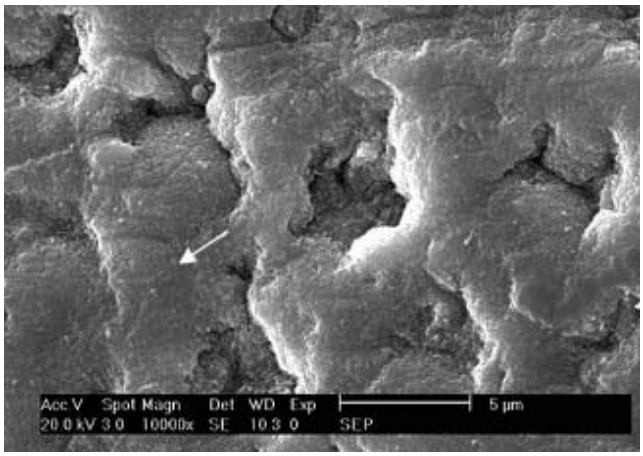

Fig 3b SEM micrograph of unground enamel etching observed following treatment with Clearfil SE primer. Surface view (10,000X): white arrow indicates predominantly flat surface.

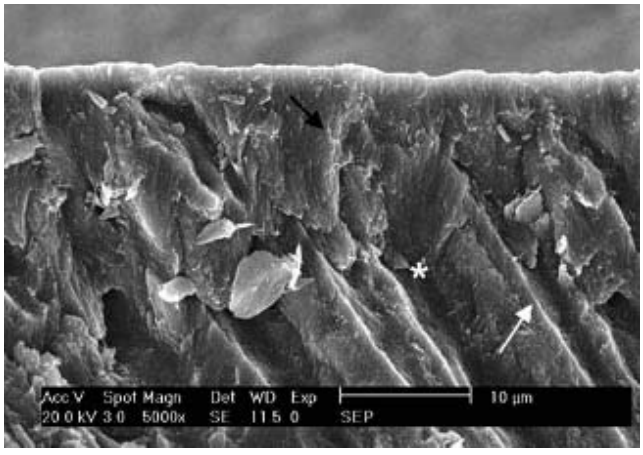

Fig 3c SEM micrograph of unground enamel etching observed following treatment with Clearfil SE primer. Sagittal view (5000X): note aprismatic enamel (black arrow), prismatic enamel (white arrow) and transition between prismatic and aprismatic enamel (white *).

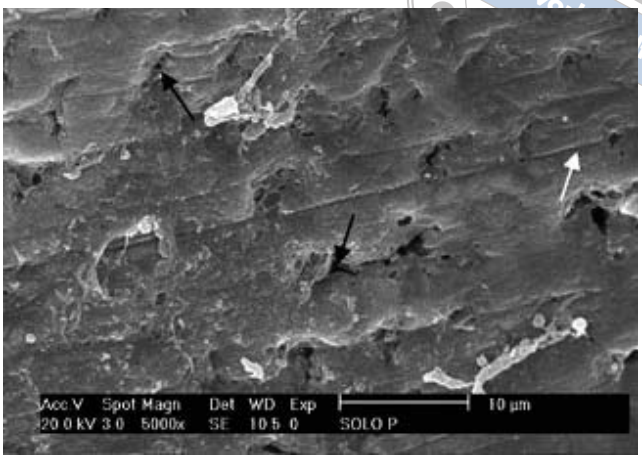

Fig 4a SEM micrograph of unground enamel observed following treatment with OptiBond Self-etching primer. Surface view (5000X): note the shallow grooves (white arrow) from brushing with slurry of pumice and water and some demineralization sites (black arrow).

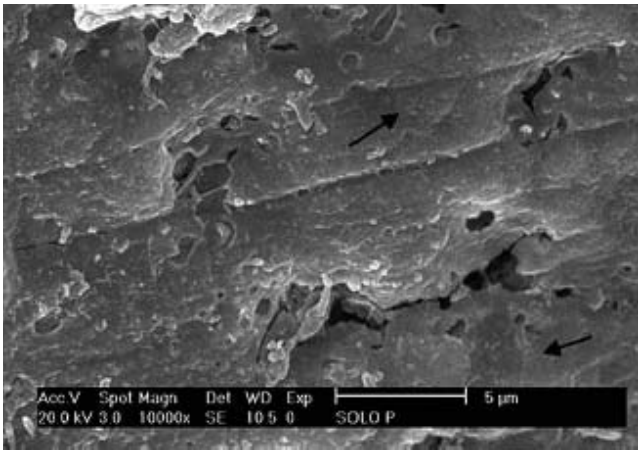

Fig 4b SEM micrograph of unground enamel observed following treatment with OptiBond Self-etching primer. Surface view (10,000X): note the predominantly flat and unetched pattern (black arrow).

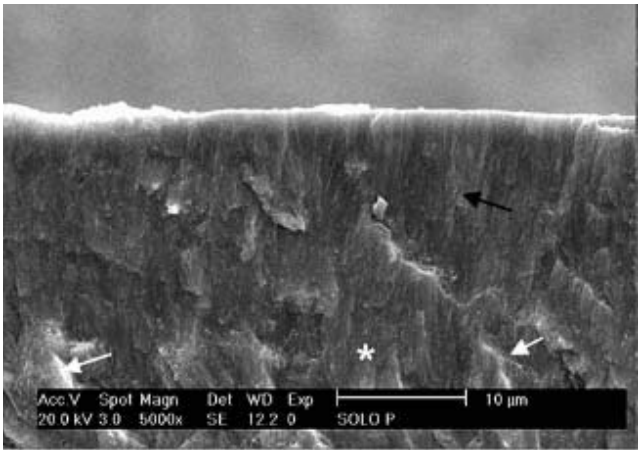

Fig 4c SEM micrograph of unground enamel observed following treatment with OptiBond Self-etching primer. Sagittal view (5000X): note aprismatic enamel layer (black arrow), the prismatic enamel (white arrow) and the transition between prismatic and aprismatic enamel (white *).

enamel microporosities produced by 35% phosphoric acid (Fig 1a), the porosities produced by the self-etching TY were less numerous, deeper, and larger. In Fig 5b, the presence of fine surface roughening on the enamel surface with an uneven conditioning pattern is evident. Areas of aprismatic enamel were also observed in the same specimen (Fig 5c).

DISCUSSION

The existence of a surface aprismatic layer in both deciduous and permanent teeth has been well documented in the literature.[7,23] Such a layer was reported to be less conducive to bonding via acid conditioning in comparison to prismatic enamel. The latter shows a preferential dissolution in which rod patterns are well delineated. In contrast, the aprismatic enamel layer exhibits a porous and potentially retentive surface with smooth surface areas intercalated with areas of well-defined etching pattern.[26] These earlier findings were confirmed in the present and in another recent publication by the SEM evaluation of phosphoric acid-treated enamel.[18]

It is known that the enamel surfaces are not homogeneous regarding the presence or absence of aprismatic enamel.[9] This means that, in the present study, not all bonding procedures were exclusively performed in the aprismatic enamel layer. The SEM analysis revealed that the bonding substrate most often encountered was aprismatic, although a few regions of prismatic enamel surface were also seen. Kodata et al[14] investigated the structural and distribution patterns of the prismless enamel on permanent teeth and found three shapes: the step-like, occurring in midcoronal enamel; the band-like, frequently observed in occlusal and fissure enamel; and the island-like shape, found in occlusal and occlusal-coronal enamel. This means that the bonding procedure is performed on a heterogeneous enamel surface.

Another recent study has attempted to evaluate the role of aprismatic enamel on bond strengths.[25] Lower bond strengths to cervical than to midcoronal enamel with both a mild self-etching system and a two-step etch-and-rinse system[19] were observed using the microshear bond strength test. This finding was attributed to the fact that aprismatic enamel is found more frequently in the cervical enamel, which is a substrate not as easily dissolved in acids as areas with a reduced amount of aprismatic enamel, such as mid- to coronal regions.[8]

It is known that the etching patterns of enamel may be dependent on the acids used and/or etching time.[20] Less aggressive acids such as 50% citric or 50% formic acids produce an almost imperceptible etch on the order of 5 µm, while strong acids such as 0.5 N hydrochloric acid produce more dramatic changes, with tissue loss exceeding 25 µm.[6] The differences in acidity among the four conditioning treatments were expressed in terms of the enamel demineralization. The dissolution produced by the 35% phosphoric acid was not uniform in the same tooth, and different morphological findings were observed; however, no other two-step self-etching system produced an etching pattern as retentive as the one produced by this conventional acid-etching treatment. Thus, the null hypothesis of this study should be rejected. Etching with phosphoric acid resulted in a

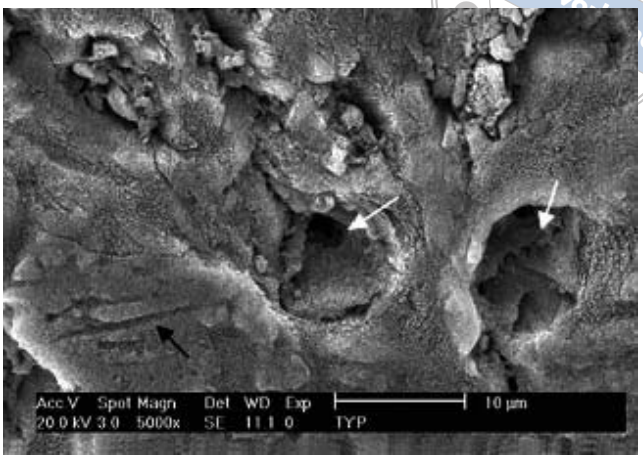

Fig 5a SEM micrograph of unground enamel observed following treatment with Tyrian SPE. Surface view (5000X): note some holes (white arrows), characteristic of no selective enamel dissolution, and grooves (black arrow).

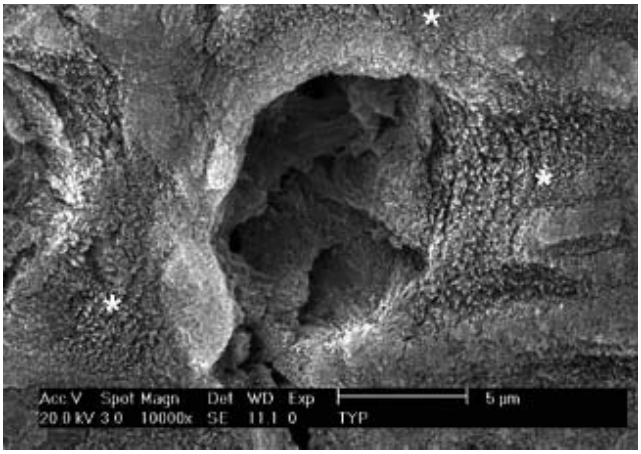

Fig 5b SEM micrograph of unground enamel observed following treatment with Tyrian SPE. Surface view (10,000X): note fine surface roughening (white *).

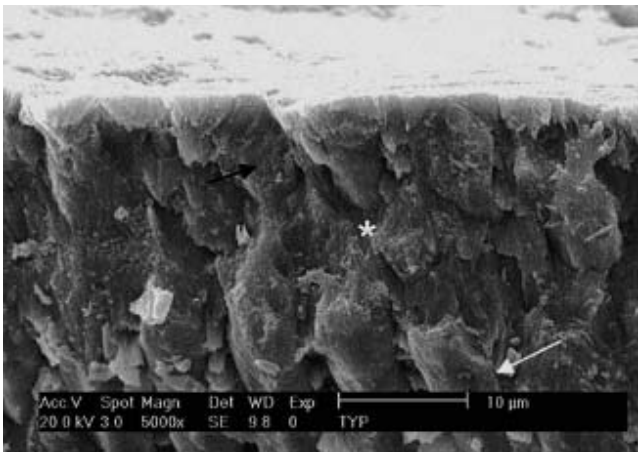

Fig 5c SEM micrograph of unground enamel observed following treatment with Tyrian SPE. Sagittal view (5000X): note aprismatic enamel layer (black arrow), prismatic enamel (white arrow) and transition between prismatic and aprismatic enamel (white *).

porous and potentially retentive structure via differential dissolution of some underlying enamel prisms.

The moderate and the more acidic two-step self-etching adhesives employed (OP and TY, respectively) produced an etching pattern more retentive than the one produced by the mild two-step self-etching adhesive (CSE), but did not resemble that of 35% phosphoric acid etching. The porosities formed by TY were larger, deeper, and less numerous than the microporosities of phosphoric acid treatment, and no preferential dissolution capable of delineating rod patterns was seen on the enamel surface. Contrary to the above findings, other studies have demonstrated that moderate and more acidic self-etching systems are able to produce an extremely defined pattern of enamel etching, similar to phosphoric acid enamel conditioning.[1,24] These differences might rely on the pretreatment of the enamel substrate. While the cited authors removed the superficial enamel, this layer was maintained in the current study, reducing the ability of the acidic monomers to demineralize enamel in a more defined etching pattern.

SEM examination of the enamel surface treated with CSE showed that this self-etching primer produced a very mild etching pattern in some areas. This could lead to the conclusion that among the adhesives tested, CSE interacts only superficially with enamel and has a reduced potential for micromechanical interlocking. Despite these morphological findings, CSE achieved the highest bond strength values among the self-etching systems. Indeed, this finding is in accordance with previous studies which demonstrated that mild self-etching systems perform well when compared to more acidic self-etching systems either in intact enamel or dentin.[4,10,11,15]

In spite of the more retentive etching pattern, the low-pH two-step self-etching adhesives tested (TY and OP) showed very low resin-enamel bond strengths and a high number of prematurely debonded specimens in the present investigation (Table 2). This result has often been documented when low-pH self-etching systems were evaluated under the microtensile bond strength approach.[4,10,34]

Although the results from the demineralization pattern and strength of bonds produced by the more aggressive self-etching on unground enamel seem to be unintelligible, this finding is consistent with previous works,[9,18,20,30] and means that other factors, apart from the etching pattern, may play a role in the bond strength values. For instance, CSE is a self-etching primer that contains 10-methacryloxydecyl dihydrogen phosphate (10-MDP) as functional monomer dissolved in water. The excellent performance of this system in in vitro[4,11,14] and in vivo investigations[36] may be partially attributed to the additional chemical interaction of hydroxyapatite with the functional monomer 10-MDP. In recent research, 10-MDP has been shown to chemically interact with hydroxyapatite.[35] Among three monomers investigated (10-MDP, 4-MET, and phenyl-P), 10-MDP revealed not only the most intense chemical interaction with hydroxyapatite, but the resultant bond with calcium also appeared the most hydrolytically stable.[38] The resulting micromechanical and chemical bonding mechanisms may have been responsible for the better performance of CSE in this and in other studies.[4,11,15]

The low initial pH of the two-step self-etching systems (TY and OP) studied appears to dramatically weaken the bonding performance via the presence of solvents within the polymer, rendering the adhesive layer thinner, possibly weakening the polymer formed,[2,27] and thus compromising their bond strength to enamel. The retention of unbound water, incompletely evaporated from the adhesive, creates water-filled channels within the adhesive.[30] These channels can be visualized after silver penetration and have been termed "water trees". Although these water-filled channels were first described in dentin,[32] similar pathways for water movement within the polymerized adhesive were seen in enamel for some one-step self-etching systems.[29] These silver impregnated areas, which represent areas of hydrophilic resin domains or entrapped water/solvent, can function as stress-raising areas, reducing the ultimate strength of the adhesive layer[21] and causing detachment of the adhesive interface, since the ultimate tensile strength of the adhesive resins is well correlated with their resin-dentin bond strengths.[28] These concerns are alleviated in two-step self-etching adhesives that utilize non-solvent-containing resin coatings, such as the mild self-etching Clearfil SE Bond. Instead, some two-step self-etching systems (eg, TY and OP, evaluated in this study) possess a solvent-rich hydrophilic resin layer, which is placed over the self-etching primer and makes them somewhat more similar to one-step self-etching systems in terms of ultimate strength.

A possible approach to improving the performance of these low-pH self-etching systems would be the application of one coat of non-solvent-containing resin to replace the subsequent coat of the hydrophilic adhesives supplied by the manufacturer.[13] This approach improved the performance of one-step self-etching systems when bonded to auto-cured composites[13] and reduced the entrapment of water when solvent-rich adhesives layers were used. However, further studies should be conducted in order to confirm the hypothesis presented in this study.

In summary, there are a large number of self-etching systems available on the dental market, but they cannot be considered as a group due to substantial differences in their mechanical properties and their modes of interaction with enamel and dentin. Before selecting a specific self-etching adhesive, clinicians should be aware of their composition, and whether or not they employ a non-solvent-containing resin after the priming step.

CONCLUSION

Based on the results of the present investigation, it was concluded that the two-step etch-and-rinse adhesives performed better on unground enamel than the most acidic two-step self-etching adhesives studied. Among the self-etching systems, the mild two-step self-etching system provided the best performance on unground enamel when compared to the other moderate and low-pH self-etching adhesives.

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Clinical relevance: Clinicians should exercise caution when selecting a self-etching adhesive system. The bonding effectiveness to enamel may be affected by the material's composition.