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Durability of Enamel Bonding Using One-step Self-etch Systems on Ground and Unground Enamel

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Clinical Relevance

The improvement of resin-enamel bond strengths after using Si-C paper and diamond burs for enamel preparation is material dependent. No degradation of enamel bond strength could be observed for any one-step self-etch adhesive system after 12 months of water storage.

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DOI: 10.2341/08-58

SUMMARY

Objective: To examine the morphological, early and long-term microtensile bond strengths (μTBS) of one-step self-etch systems to unground and ground enamel.

Materials and Methods: Resin composite (Filtek Z250) buildups were bonded to the buccal and lingual enamel surfaces (unground, bur-cut or SiC-roughened enamel) of third molars after adhesive application using the following adhesives: Clearfil S³ Bond (CS3); Adper Prompt L-Pop (ADP); iBond (iB) and, as the control, Clearfil SE Bond (CSE). Six tooth halves were assigned for each condition. After storage in water (24 hours/37°C), the bonded specimens were sectioned into beams (0.8 mm²) and subjected to μTBS (0.5 mm/min) either immediately (IM) or after six (6M) or 12 months (12M) of water storage. The data were analyzed by three-way repeated measures ANOVA and Tukey's test (α=0.05).

Surface conditioning was observed under scanning electron microscopy (SEM).

Results: The μTBS in the Si-C paper and diamond bur groups were similar and higher than the unground group. No significant difference was observed among the different storage periods, except for CS3, which showed an increase in the μTBS after 12M. The etching pattern was more retentive on ground enamel.

Conclusions: One-step self-etch adhesives showed higher bond strengths on ground enamel and no reductions in resin-enamel bonds were observed after 12M of water storage.

INTRODUCTION

One-step self-etch systems are among the latest adhesive systems to emerge in the marketplace. The manufacturers of these products attempt to incorporate all the components of an adhesive system (etchant, primer and bonding resin) into a single solution. One-step self-etch systems (also known as all-in-one adhesives) are user-friendly, in that the number of steps required for the bonding protocol is reduced. The elimination of separate etching and rinsing steps has simplified the bonding technique and has been responsible for the increased popularity of these systems in a daily practice.[1]

The acidity of one-step self-etch systems is not as high as the phosphoric acid used with etch-and-rinse adhesives[2] and, thus, increased concern over the performance of self-etch adhesives on intact enamel has been raised. Several *in vitro* investigators have reported low resin-enamel bond strength for one-step self-etch systems.[3-6] According to some authors, grinding the enamel during a bevel or cavity preparation, for instance, results in the substrate being more receptive to bonding with one-step self-etch systems.[7] On the other hand, other authors have not detected any significant difference in the performance of self-etch systems on intact or ground enamel.[8]

It was reported that the kind of rotary instrument applied on teeth substrates could interfere with the performance of one-step self-etch materials. Diamond burs remove the superficial enamel more efficiently and also create a thick smear layer when compared with that created by SiC papers in laboratory testing.[9] In fact, studies that reported the superior performance of self-etch systems on ground enamel used diamond burs to prepare the enamel surface,[10] instead of SiC papers.[9] It is also worth mentioning that there are cases where bonding should be made on intact enamel, such as the bonding of orthodontic brackets, conservative and preventive restorative measures and enamel in the cervical margins of Class II cavities. Therefore, it is clinically important to determine the performance of such systems on unground, diamond bur- and SiC paper-roughened enamel.

Consistent information regarding the durability of self-etch adhesives when applied to dentin is available in the literature.[11-13] Although high early resin-dentin bond strength values can be achieved with self-etch adhesives, their low bonding effectiveness over time is disappointing.[12-13] Because of the high hydrophilic nature of acidic monomers and the high water content required for ionization of acidic monomers in self-etch solutions, it is likely that these materials can also have resin-enamel bonds compromised over time. However, to the extent of knowledge of the authors of the current study, there are a limited number of *in vitro* studies evaluating the durability of self-etch systems on ground versus unground enamel.

Therefore, the current study: 1) evaluated the early and long-term resin-enamel bond strength of one-step self-etch adhesives applied to unground, bur- and SiC paper-roughened enamel and 2) examined the enamel micro-morphology after the application of self-etch systems. The current study tested three null hypotheses: 1) enamel surface treatment does not affect the bonding effectiveness of one-step self-etch to enamel; 2) enamel surface treatment does not affect the etching pattern of one-step self-etch systems to enamel and 3) water storage does not affect the bonding effectiveness of one-step self-etch to enamel.

METHODS AND MATERIALS

The current study was approved by the Institutional Review Board of the Dental School, UNOESC, Joaçaba, Brazil. Fifty-one extracted human third molars were used in this study, 36 teeth for microtensile bond strength evaluation and 15 teeth for micromorphological analysis.

Microtensile Bond Strength Evaluation

Thirty-six teeth were sectioned in a mesiodistal direction in order to obtain tooth halves. The buccal and lingual surfaces obtained from these teeth were cleaned with slurry of pumice and water and examined under a 40x stereomicroscope (HMV-2, Shimadzu, Tokyo, Japan) to ensure that they were free of surface cracks, decalcification or any sign of previous grinding. The enamel surface was then demarcated to outline the flattest area for bonding. The occlusal third of the buccal and lingual surfaces was usually outside the bonding area due to its inclination. The tooth halves were then randomly divided into three groups according to the type of enamel surface preparation (Figure 1):

Group 1: no enamel preparation was performed before adhesive application, except for teeth prophylaxis with pumice slurry;

Group 2: after teeth prophylaxis, a wheel medium-grit diamond bur (#4142, particle size 100 μm, KG

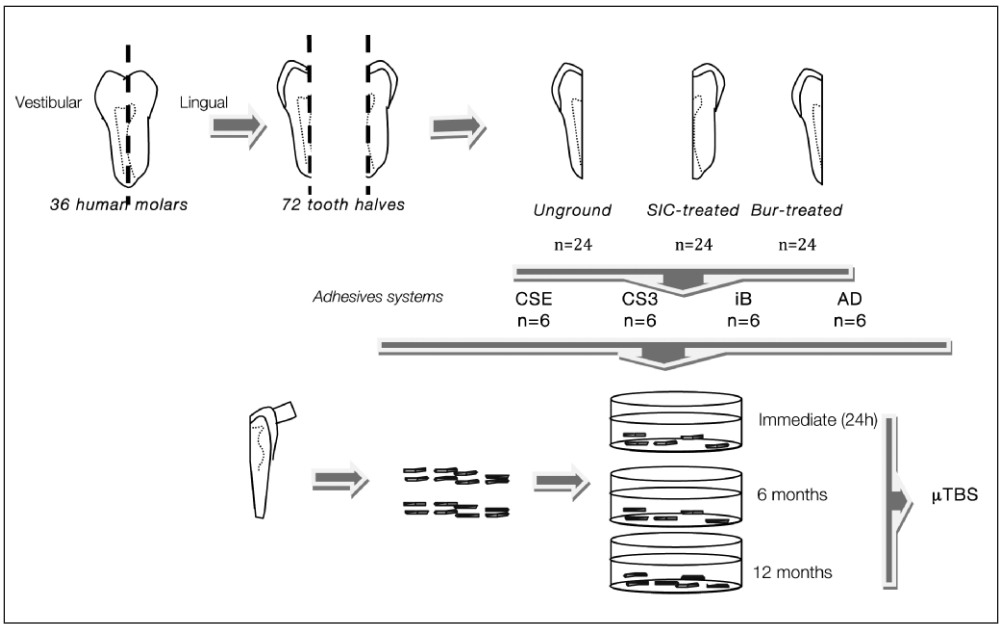

Figure 1. *Flow diagram showing distribution of teeth for microtensile testing.*

Sorensen, Barueri, São Paulo, Brazil) in a high-speed handpiece with water coolant was used in order to create 0.5-mm deep grooves on the surface. The enamel was then flattened with a tapered, rounded end fine-grit diamond bur (#4138, particle size 46 μm, KG Sorensen);

Group 3: after teeth prophylaxis, the enamel surfaces were manually ground in a 60-grit SiC under water-cooling for 60 seconds.

Each group was further subdivided into four subgroups according to the adhesive used (Figure 1). Six tooth halves were assigned to each condition. Three one-step self-etch adhesives were selected: (1) Clearfil S^3 Bond (Kuraray Medical Inc, Tokyo, Japan), (2) Adper Prompt L-Pop (3M ESPE, St Paul, MN, USA) and (3) iBond (Heraeus Kulzer, Hanau, Germany). As the control, a two-step self-etch adhesive (Clearfil SE Bond, Kuraray Medical Inc) was employed. All the adhesives were applied under 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. The light-curing procedure was performed with a VIP unit (600 mW/cm^2, BISCO Inc, Schaumburg, IL, USA). 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 hours, the specimens were longitudinally sectioned in both the "x" and "y" directions across the bonded interface with a diamond saw in a Labcut 1010 machine (Extec, Enfield, CT, USA) to obtain bonded beams with a cross-sectional area of about 0.8 mm^2. The bonded sticks that originated from the same tooth were randomly divided into three parts and assigned for testing immediately [IM] and after six [6M] or 12 months [12M] of storage in distilled water containing 0.4 % sodium azide at 37°C (Figure 1). The storage solution was not changed.[14]

The number of prematurely debonded beams (PD) per tooth during specimen preparation was recorded. Each stick was examined in a stereomicroscope (10x) in order to check the inclination of the bonding interfaces in the four sides of each stick. Sticks with bend bonding interfaces were not tested in tension. The cross-sectional area of each stick was measured with the digital caliper (Absolute Digimatic, Mitutoyo, Tokyo, Japan) to the nearest 0.01 mm and recorded for calculation of the bond strength.

The beams were fixed in a device for microtensile testing using cyanocrilate resin; they were then stressed to failure using a universal testing machine (Emic, São José dos Pinhais, PR, Brazil) at a crosshead speed of 0.5 mm/minute. The bond failure modes were evaluated at 400x under a light stereomicroscope (HMV-2, Shimadzu, Tokyo, Japan) and classified as cohesive (failure exclusively within enamel or resin composite) and adhesive/mixed (failure at resin/enamel interface or mixed with cohesive failure of the neighboring substrates).

The bond strength values from the same tooth halves were averaged for statistical purposes. Since a high number of premature debonded specimens during specimen preparation means a higher fragility of the bonding area, the authors of the current study opted to include them in the tooth-half mean. The average value attributed to specimens that failed prematurely during preparation was arbitrary and corresponded to approximately half of the minimum bond strength value that could be measured in this study.[15] The microtensile BS means were subjected to a three-way repeated measures analysis of variance (Adhesive *vs* Substrate treatment *vs* Storage period) and Tukey's test for pairwise comparisons (α=0.05). The storage period was the repeated factor.

Analysis of the Etching Pattern

Fifteen teeth were longitudinally sectioned into two halves in a mesiodistal direction. Two tooth halves were

Table 1: *Adhesive Systems: Composition and Application Use*

Adhesive Systems	Composition	Acidity Range	Application Mode
Clearfil SE Bond **CSE** (Kuraray)	1. Primer—water, MDP, HEMA, camphoroquinone, hydrophilic dimethacrylate, 2. Adhesive – MDP, Bis-GMA, HEMA, camphorquinone, hydrophobic dimethacrylate, N,N-diethanol p-toluidine bond, silanated colloidal silica	≈ 1.9–2.3	1 Application of two coats of the primer under pressure (20 seconds); 2 Gentle air stream (10 seconds at 20 cm) after application of each coat; 3 Application of one coat of the adhesive (15 seconds); 4 Gentle air stream to make the bond film uniform (3 seconds at 20 cm); 5 Light-activation (10 seconds—600 mW/cm^2).
Clearfil S^3 Bond **CS3** (Kuraray)	MDP; HEMA, Bis-GMA, water, ethanol, camphorquinone and nanofillers.	≈ 2.6–2.7	1 Application of one coat of the adhesive under pressure (20 seconds); 2 Gentle air stream (10 seconds at 20 cm); 3 Application of a second coat of the adhesive under pressure (20 seconds); 4 Gentle air stream (10 seconds at 20 cm); 5 Light-activation (10 seconds—600 mW/cm^2).
Adper Prompt L-Pop **ADP** (3M ESPE)	1. Liquid A–water, Bis-GMA, HEMA, camphorquinone and hydrophilic dimethacrylate, 2. Liquid B–water, HEMA, polyalkenoic acid, stabilizers.	≈ 0.9–1.0	1 Application of one coat of the adhesive under pressure (15 seconds); 2 Gentle air stream (10 seconds at 20 cm); 3 Application of a second coat of the adhesive under pressure (15 seconds); 4 Gentle air stream (10 seconds at 20 cm); 5 Light-activation (10 seconds—600 mW/cm^2).
iBond **iB** (Heraues Kulzer)	UDMA, 4-META, acetone, water, glutaraldehyde and camphorquinone	≈ 1.7–2.0	1 Application of one coat of the adhesive under pressure (30 seconds); 2 Gentle air stream (10 seconds at 20 cm); 3 Application of a second coat of the adhesive under pressure (30 seconds); 4 Gentle air stream (10 seconds at 20 cm); 5 Light-activation (20 seconds–600 mW/cm^2).

Abbreviations: MDP (10-methacryloxydecyl dihydrogen phosphate); HEMA (2-hydroxyethyl methacrylate); Bis-GMA (bisphenol-glycidyl methacrylate); UDMA (urethane dimethacrylate); 4-META (4-methacryloxyethyl trimellitate anhydride)

used for each condition. The enamel surfaces were cleaned with slurry of pumice and water (Group 1). After the cleaning procedure, the enamel surfaces from Group 2 were bur-cut and the enamel surfaces from Group 3 were ground with 60-grit SiC paper under water-cooling for 60 seconds, as previously described for the microtensile bond strength test.

The effect of the surface preparation was analyzed on the buccal and/or lingual surface and in the sagitally-fractured surfaces. To accomplish this goal, a deep groove with a diamond bur was placed in six tooth halves (two for each enamel treatment group) after enamel preparation in order to facilitate subsequent fracture of the enamel surfaces and visualization of the sagitally-fractured surfaces. The same specimens were then gently split with a hammer and scalpel blade along the pre-formed grooves to provide a sagittal view of the etched enamel.

The effect of conditioning with the self-etch adhesives on the unground and ground (bur-cut or Si-C paper-roughened) enamel surfaces was only analyzed in the buccal and/or lingual surfaces. Two tooth halves were employed for groups that originated from the combination of Enamel treatments x Adhesive systems. The enamel surfaces from Groups 1, 2 and 3 were treated with the adhesive systems as described in Table 1. Enamel etched with self-etching systems was rinsed with ethanol (five minutes) and acetone (five minutes) to remove the monomers.[16] The specimens were stored in desiccators containing silica gel for 12 hours. They were then mounted on aluminum stubs with colloidal silver and gold sputter-coated (Balzers SCD 050 Sputter Coater, Bal-Tec, Germany) for observation under a scanning electron microscope (Philips XL30, Eindhoven, Netherlands) at 15 kV of accelerating voltage.

RESULTS

Microtensile Bond Strengths

The mean cross-sectional area ranged from 0.82 to 0.91 mm^2 and no difference among the treatment groups was detected ($p>0.05$). The bond strength value assigned to the premature debonded specimens was 4.8 MPa, which corresponds to half of the minimum bond strength value measured. The overall means and standard deviations (MPa) of the bond strength means are shown in Table 2. The number of sticks tested and the number of premature debonded specimens are shown

Table 2: *Overall resin-enamel bond strength means and standard deviations (MPa) from the different adhesive systems under the experimental conditions of the present investigation.*

Adhesive	Unground			SiC Paper			Diamond Bur		
Systems	IM	6M	12M	IM	6M	12M	IM	6M	12M
CSE	18.7 ± 4.6	21.7 ± 1.7	17.2 ± 4.4	22.7 ± 1.8	20.7 ± 5.1	18.3 ± 2.9	19.9 ± 4.1	21.9 ± 4.0	18.2 ± 4.0
CS3	12.2 ± 4.1	22.9 ± 3.3	24.2 ± 4.2	21.2 ± 4.5	28.8 ± 5.4	20.9 ± 5.8	17.0 ± 5.2	23.2 ± 5.0	22.9 ± 4.3
ADP	16.7 ± 5.2	16.4 ± 5.6	13.7 ± 4.8	19.5 ± 4.5	20.6 ± 1.2	20.0 ± 5.2	20.3 ± 5.2	22.3 ± 4.1	21.8 ± 2.2
iB	15.3 ± 4.3	19.2 ± 4.8	19.6 ± 4.7	23.1 ± 4.9	21.1 ± 4.3	24.7 ± 4.6	19.4 ± 3.1	22.5 ± 3.1	25.2 ± 3.7

Table 3: *Number of Tested/Premature Debonded Sticks for Each Experimental Condition*

Adhesive	Unground			SiC Paper			Diamond Bur		
Systems	IM	6M	12M	IM	6M	12M	IM	6M	12M
CSE	14/05	12/02	15/04	13/00	11/01	12/02	11/02	15/02	14/02
CS3	12/03	14/04	16/02	13/04	12/02	13/01	11/03	12/00	15/04
ADP	12/03	12/02	12/01	11/00	13/00	12/02	13/03	12/00	14/01
iB	14/04	12/02	11/04	12/02	13/01	09/02	12/04	14/03	16/01

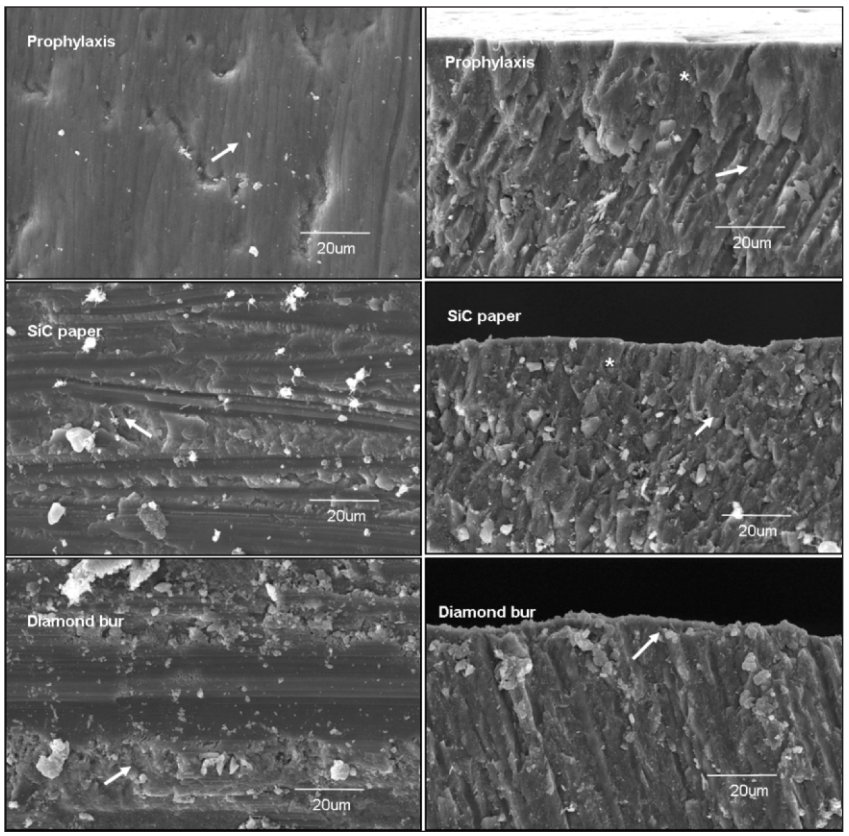

Figure 2. *Effects of the different preparation methods on the enamel surface. Intact enamel after "Prophylaxis," enamel abraded with "SIC paper" and "Diamond bur." The transversal view of enamel after tooth prophylaxis shows a very smooth surface, with small grooves (white arrow). The sagittal view of the same treatment shows the presence of the aprismatic enamel (white asterisk) and enamel prisms (white arrow). The transversal view of enamel after SiC paper treatment shows a rough surface (white arrow). Aprismatic enamel (white asterisk) and enamel prisms (white arrow) appear after SiC paper treatment. After diamond bur treatment, the enamel appears very rough, with a thick smear layer and exposure of enamel prisms (white arrow). Enamel prisms reaching the surface can be seen (white arrow).*

in Table 3. No cohesive failure in enamel or resin composite was observed in this study.

The results from the three-way ANOVA revealed that the main factors (Adhesive [p=0.039], Substrate treatment [p=0.0004] and Storage period [p=0.01]) and the interaction Adhesive *vs* Storage period (p=0.005) were statistically significant. The resin-enamel bond strength values in the Si-C paper (21.8 ± 4.1 MPa) and diamond bur (21.2 ± 3.9 MPa) groups were statistically equivalent to each other and higher than the bond strength mean observed in the unground group (18.2 ± 3.3 MPa).

Table 4 depicts the bond strength values for the interaction Adhesive vs Storage period. For each adhesive, no significant difference was observed among the different storage periods, except for CS3, which showed an increase in the resin-enamel bond strength values after six and 12 months.

Scanning Electron Microscopy

The effect of tooth prophylaxis, SiC paper and diamond bur treatments can be seen in Figure 2. SEM micrographs of ground and unground enamel surfaces treated with one-step self-etch adhesives are shown in Figures 3 to 6.

Figure 2 shows a smooth surface, with shallow grooves after prophylaxis and an apparent increase in roughness after SiC, and diamond bur treatments, with larger grooves, few exposed enamel rods and a smear layer covered with enamel. Regardless of the surface treatment, only

Table 4: *Resin-enamel bond strength means, standard deviations (MPa) and statistical analysis for the interaction Adhesive systems vs Storage period.*

Adhesive Systems	Storage Period		
	Immediate	6 Months	12 Months
CSE	20.4 ± 3.6 b	21.4 ± 3.6 b	18.9 ± 3.7 b,c
CS3	16.8 ± 4.6 c	24.9 ± 4.1 a,b	22.6 ± 4.7 a,b
ADP	18.8 ± 4.9 b,c	19.7 ± 3.6 b	18.5 ± 4.1 b,c
iB	19.2 ± 4.1 b	20.9 ± 4.1 b	23.1 ± 4.3 a,b

Means with the same superscripted letters are statistically similar (p>0.05).

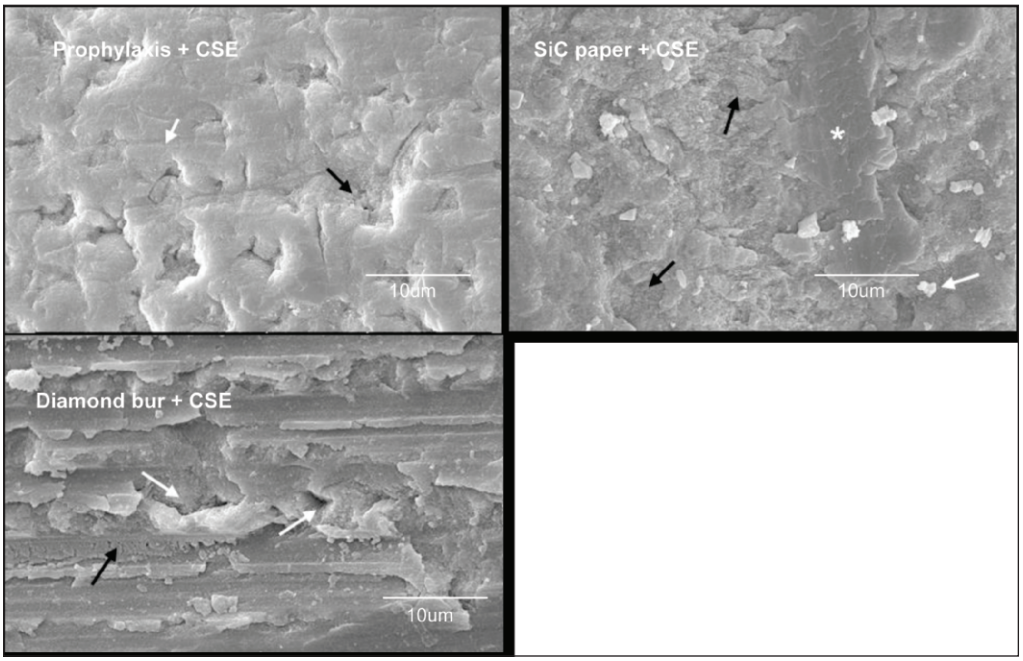

Figure 3. *SEM micrograph of different enamel-roughened groups following treatment with Clearfil SE primer. CSE applied on unground enamel created shallow depressions (black arrow) in a predominantly flat surface (white arrow). CSE applied on SiC paper-roughened enamel also created shallow depressions (black arrow) between unetched areas (white asterisk). Few enamel rods were exposed after application of CSE on diamond bur-roughened enamel.*

the diamond bur treatment removed the prismless enamel (Figure 2).

The enamel surfaces conditioned with Clearfil SE Bond (Figure 3) and Clearfil S[3] Bond (Figure 4) presented similar findings. They showed a predominant smooth surface, with shallow depressions after prophylaxis. The smear layer appeared to be only partially dissolved after the SiC and diamond bur. On ground enamel, the etching patterns created by Clearfil SE Bond were less evident, with few enamel rods exposed in the surface. iBond (Figure 6) removed the smear layer in a more effective way after the diamond bur treatment. Areas of unetched and smooth enamel were more evident after prophylaxis and SiC paper treatments. The demineralization pattern of iBond was more pronounced when applied on the diamond-bur roughened surface, that is, the prismatic enamel surface. Among the one-step self-etch adhesives studied, Adper Prompt L-Pop (Figure 5) exposed more enamel rods mainly when applied on ground enamel (SiC paper and diamond bur-treated enamel).

DISCUSSION

The current investigation has demonstrated that the two surface enamel treatments (SiC and diamond bur) were equally effective in improving the resin-enamel bond strengths of the one-step self-etch systems evaluated. This led the authors to reject the first null hypothesis. Among other factors, the investigators have attributed the lower performance of self-etch systems in enamel to the presence of a less reactive superficial enamel layer presented in unground enamel.[3,10,17-18]

When the micro-morphological findings of the same adhesive system on ground and unground enamel were compared, all one-step systems showed a deeper etching pattern when applied on SiC paper- or diamond bur-roughened enamel. This suggests that the removal of this superficial layer is essential to improving their etching potential in enamel, which was reflected in the superior performance of these materials in ground enamel. Therefore, the second null hypothesis was also rejected.

However, the literature in this matter is rather controversial. Some studies demonstrated that enamel abrasion with diamond bur can improve the bond strength of one-step self-etch adhesives to enamel.[7,19] Others, contrary to the findings of the current investigation, have reported that the bond strength on unground or ground enamel does not differ[8,20-21] or is dependent on the adhesive system evaluated.[22]

This controversy suggests that the self-etch systems' performance on enamel[3,10,18] cannot be solely attributed to the presence of the superficial enamel layer. Other factors, apart from the substrate-related ones, could be responsible for such differences. Variations in adhesive viscosity, surface tension, acidity of the self-etch sys-

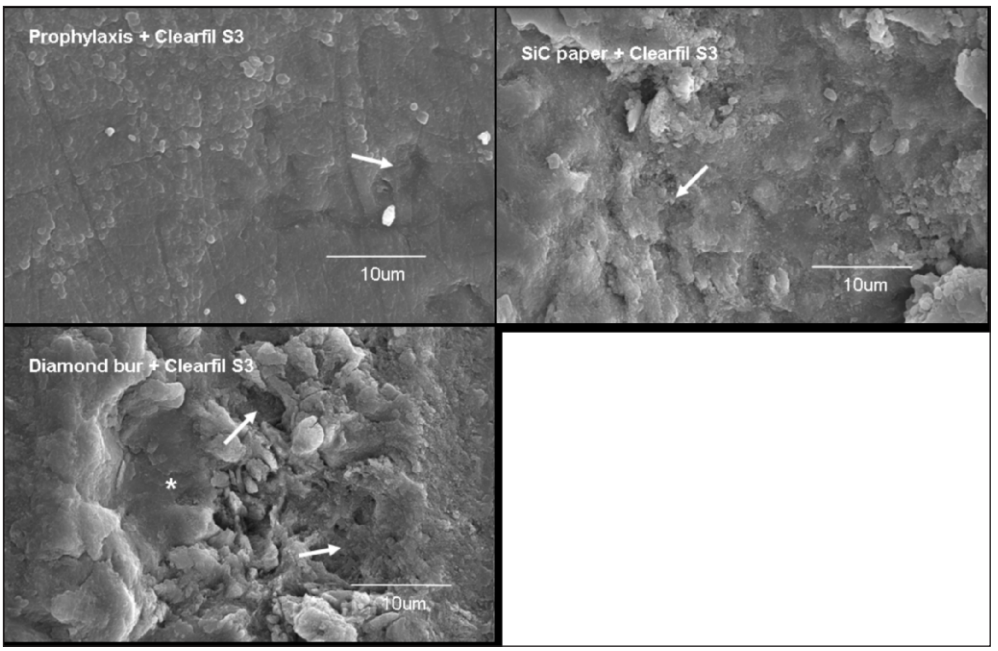

Figure 4. *SEM micrograph of the different enamel-roughened groups following treatment with Clearfil S³ Bond. On unground enamel, CS3 created an apparent flat smooth surface. Very few enamel rods can be seen reaching the surface (white arrow). A slightly more retentive and irregular etching pattern can be observed when the same adhesive was applied on SiC paper and diamond bur-roughened enamel. Some shallow depressions covered by the smear layer can be observed (white arrow) when CS3 was applied in the SiC paper-roughened enamel. Deeper depressions (white arrows) can be observed in figure "Diamond bur + Clearfil S³." The white asterisk shows an apparently unetched surface.*

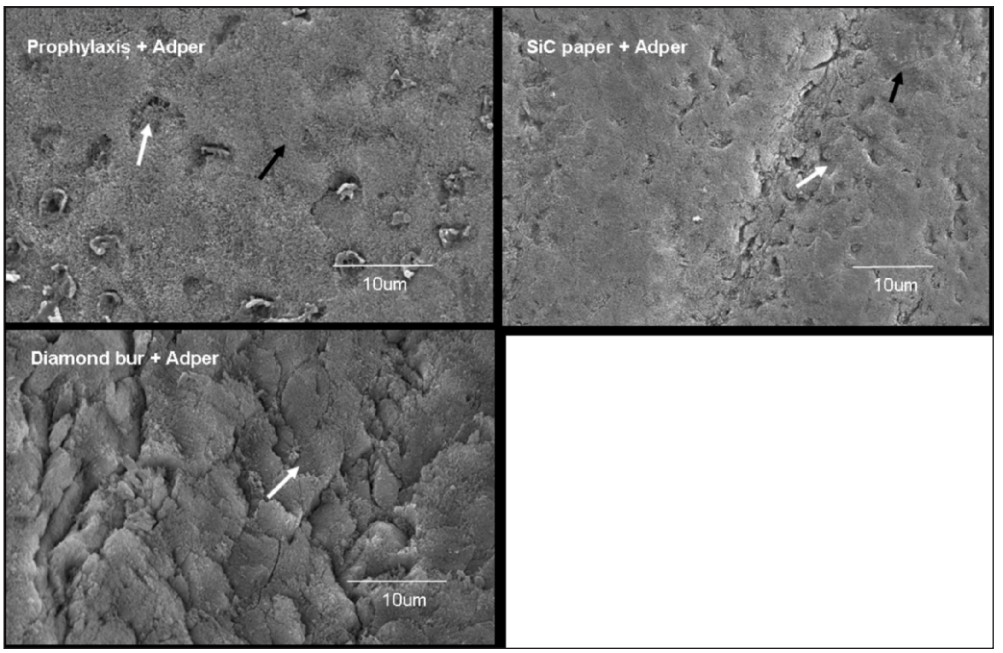

Figure 5. *SEM micrograph of different enamel roughened-groups following treatment with Adper Prompt L-Pop. Fine roughening and areas of enamel prisms exposure can be observed in the three figures. A more retentive pattern can be observed when the adhesive was applied on diamond bur-roughened enamel. White arrows show enamel prisms and black arrows show unetched areas.*

tem, chemical interaction of acidic monomers with enamel,[23] water concentration[24] and cohesive strength of the adhesives[13,25-26] are important features to be considered. It is somewhat true that, although a more retentive etching pattern was observed for Adper Prompt L-Pop and iBond when compared to Clearfil SE Bond, no significant difference in the resin-enamel bond strengths were reported among these systems in the different storage periods.

The absence of any relationship between the depth and pattern of demineralization and the strength of bonds produced by self-etch adhesives on enamel, as shown in the current investigation, is consistent with previous works.[8,9,21,27-28] As already reported, this means that other factors, apart from the etching pattern, may have a more important role in the bond strength values. For instance, CSE and CS3 are self-etch adhesives composed of a functional monomer (10-methacryloxydecyl dihydrogen phosphate [10-MDP]) dissolved in water, resulting in a pH of around 2. The excellent performance of CSE in *in vitro*[4,18,29] and *in vivo* investigations[30] may be partially attributed to the additional chemical interaction of hydroxyapatite with the functional monomer 10-MDP,[23] which can theoretically contribute to the adhesive potential to enamel that consists of nearly only mineral substance.

Surprisingly, the observable reductions in bond strength values for simplified etch-and-rinse and self-etch adhesives applied on dentin over time[6,12-13,31-33] were not observed on enamel, leading the authors of the current study to reject the third null hypothesis. The

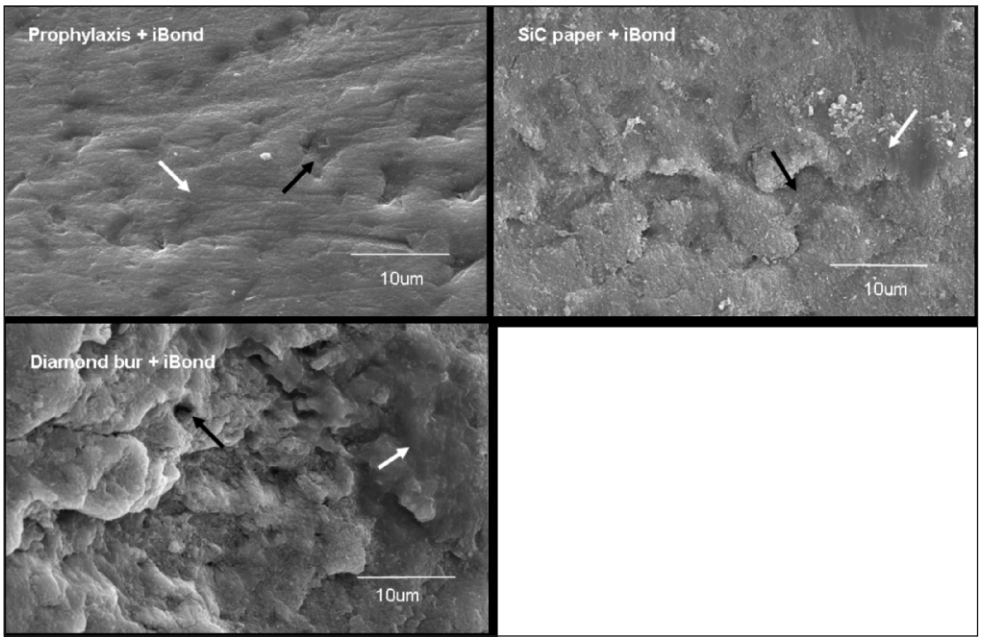

Figure 6. *SEM micrograph of different enamel-roughened groups following treatment with iBond. After tooth prophylaxis and iBond application, the surface appeared predominantly smooth (white arrow), with shallow depressions (black arrow). In "SIC paper + iBond," the black arrow indicates enamel rods exposed in a slightly rougher surface. The white arrow shows a smoother area. A more retentive pattern, with several shallow and deep depressions (black arrow), can be seen when the adhesive was applied on diamond bur-roughened enamel, but there are several unetched areas (white arrow).*

degradation of resin–dentin bonds is usually attributed to the degradation of unprotected collagen fibrils at the base of the hybrid layer or to the hydrolytic degradation that polymers are prone to after water sorption. Water can infiltrate into the resin matrix and, through swelling, can reduce the frictional forces between the polymer chains in a process known as plasticization. This water-driven process can, therefore, decrease the mechanical properties of the polymer matrix[34-35] and cause elution of uncured monomers and breakdown products.[36] More recently, evidence has demonstrated that the breakdown of unprotected collagen fibrils[12,37-38] can also occur via the activation of host-derived matrix metalloproteinases (MMPs),[39-40] even though recent evidence has shown that chlorhexidine has the potential to inhibit the activation of MMPs.[41-42]

The reported stability of the resin-enamel bonds observed could be partially explained by the enamel characteristics, which make this substrate completely different from dentin. Although copious amounts of proteins are released into the enamel matrix during amelogenesis, this secretion significantly reduces as enamel development progresses. To provide a place for enamel crystal to grow, the released proteins are degraded by proteinases, and finally, the enamel achieves its final hardened structure, where it contains less than 1% protein by weight.[44-45] This means that, compared with dentin, enamel does not contain suitable organic components to be degraded over time.

Another feature that should be considered when enamel and dentin are compared is that enamel is not an inherent wet substrate like dentin. Polymerization of the adhesive monomers in the presence of water prevents the formation of a highly cross-linked polymer.[46] It was demonstrated that the addition of as little as 20 µL/mL of water to water-free HEMA-based adhesive reduced its degree of conversion by 50%.[47] Therefore, the authors of the current study should expect an improved condition of polymerization of the adhesive in enamel compared with dentin. It is possible that the stronger polymer formed in the enamel substrate does not absorb as much water as does the polymer formed in dentin, thus making it less prone to the plasticizing effects of water over time.

In addition, it was well documented that one-step self-etch systems behave as permeable membranes after polymerization.[48-49] The lack of an additional coat of a hydrophobic bonding resin and the presence of highly hydrophilic groups in self-etch adhesive monomers draw water from the underlying hydrated dentin[50] and from the oral environment[47-51] after polymerization. This water movement from the underlying dentin through the adhesive leads to the entrapment of water droplets, known as water blisters. This phenomenon does not occur to relatively impermeable substrates, such as bonded composites[52] and to completely dehydrated dentin.[53] Based on these findings, it is fair to suppose that the adhesive layer bonded to enamel is less susceptible to work as semi-permeable membranes as long as it is covered by a composite material. Osmotic blistering was already reported for one-step self-etch systems; however, the adhesive coat was left unprotected by a composite layer.[53]

More surprising were the Clearfil S^3 Bond results. Although this system showed inferior performance in the immediate period compared with the other one-step self-etch systems, this material showed a significant increase in bond strength after six and 12 months of water storage. No obvious explanation was found for this result. According to the manufacturer, CS3 employs the molecular dispersion technology that was specifically developed to combine the functions of two-step adhesives into a one-step adhesive system. This

enables the 2-phase liquids of hydrophilic and hydrophobic monomers to be maintained in a homogeneous state at the molecular level as the solvent evaporates from the tooth substrate interfaces. As there is no reported phase separation, it is likely that a highly cross-linked polymer can be formed, allowing a superior resistance to water hydrolysis over time. It was already reported that, when one-step self-etch systems are placed on dentin/enamel and left undisturbed for a time, phase separation occurs as the solvent evaporates.[54] This phase separation phenomenon is one of the reasons for the formation of water droplets within the bonding agent frequently observed in many one-step adhesives.[54] However, this information still requires further investigation.

In agreement with the current results are the studies that demonstrate that resin-dentin bonds can be quite stable over time as long as the cavity margins are surrounded by enamel.[11] The stability of the bond strength values in specimens with an enamel border can be attributed to the protective role of the surrounding resin-enamel bond against degradation,[11,36] avoiding the water from diffusing inward.

Although no significant reductions in resin-enamel bond strengths were observed in the current study, as well as in a recent paper published by Loguercio and others,[55] several clinical trials have reported marginal discoloration around enamel margins bonded with one-step self-etch systems.[30,56] Although this information could be interpreted at first glance as inconsistent with the current findings, no study has yet demonstrated any correlation between bond strength values and marginal sealing.[2,33,57-58] Therefore, worse marginal adaptation and discoloration do not automatically mean worse retention rates. This explains why studies evaluating the retention of brackets to enamel bonded with etch-and-rinse and a self-etch system do not show higher retention rates for the former.[59-60]

The marginal discoloration observed in enamel margins when self-etch systems are employed is usually attributed to the less defined etching pattern produced by these materials on enamel. This can be somewhat improved by grinding the enamel margins with a diamond-bur[10,19] or conditioning the enamel with 35% phosphoric acid.[17,61-62] The latter approach was already shown to be effective in a clinical setting.[62]

CONCLUSIONS

One-step self-etch adhesives showed higher bond strengths on ground enamel, and no reduction in resin-enamel bonds was observed after 12 months of water storage, meaning that bonding to enamel is far more resistant to the plasticizing effects of water on bonding interfaces.

(Received 21 April 2008)

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