©Operative Dentistry, 2015, **40-4,** 379-395

Effect of Phosphoric Acid Pre-etching on Fatigue Limits of Self-etching Adhesives

T Takamizawa • WW Barkmeier • A Tsujimoto
DD Scheidel • RL Erickson • MA Latta
M Miyazaki

Clinical Relevance

The effect of phosphoric acid pre-etching of enamel and dentin prior to the use of self-etching adhesives is dependent on the mineralized substrate and the adhesive material.

SUMMARY

The purpose of this study was to use shear bond strength (SBS) and shear fatigue limit (SFL) testing to determine the effect of phosphoric acid pre-etching of enamel and dentin prior to application of self-etch adhesives for bonding resin composite to these substrates. Three self-etch adhesives—1) G- ænial Bond (GC Corporation, Tokyo, Japan); 2) OptiBond XTR (Kerr Corp, Orange, CA, USA); and 3) Scotchbond Universal (3M ESPE Dental Products, St Paul, MN, USA)—were used to bond Z100 Restorative resin composite to enamel and dentin surfaces. A stainless-steel metal ring with an inner diameter of 2.4 mm was used to bond the resin composite to flat-ground (4000 grit) tooth surfaces for determination of both SBS and SFL. Fifteen specimens each were used to determine initial SBS to human enamel/dentin, with and without pre-etching with a 35% phosphoric acid (Ultra-Etch, Ultradent Products Inc, South Jordan, UT, USA) for 15 seconds prior to the application of the adhesives. A staircase method of fatigue testing (25 specimens for each test) was then used to determine the SFL of resin composite bonded to enamel/dentin using a frequency of 10 Hz for 50,000 cycles or until failure occurred. A two-way analysis of variance and Tukey post hoc test were used for analysis of SBS data, and a modified *t*-test with Bonferroni correction was used for the SFL

Toshiki Takamizawa, DDS, PhD, assistant professor, Operative Dentistry, Nihon University School of Dentistry, Tokyo, Japan

*Wayne W Barkmeier, DDS, MS, professor, General Dentistry, dean emeritus, Creighton University School of Dentistry, Omaha, NE, USA

Akimasa Tsujimoto, DDS, PhD, assistant professor, Operative Dentistry, Nihon University School of Dentistry, Tokyo, Japan

Donal D Scheidel, DDS, associate professor, Diagnostic Sciences, Creighton University School of Dentistry, Omaha, NE, USA

Robert L Erickson, PhD, DDS, clinical professor, General Dentistry, Creighton University School of Dentistry, Omaha, NE, USA

Mark A Latta, DMD, MS, professor, General Dentistry, dean, Creighton University School of Dentistry, Omaha, NE USA

Masashi Miyazaki, DDS, PhD, professor, Operative Dentistry, Nihon University School of Dentistry, Tokyo, Japan

*Corresponding author: Wayne W Barkmeier, DDS, MS, 2500 California Plaza, Omaha, NE 68178, USA; e-mail: wbark@creighton.edu

DOI: 10.2341/13-252-L

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

data. Scanning electron microscopy was used to examine the area of the bonded restorative/ tooth interface. For all three adhesive systems, phosphoric acid pre-etching of enamel demonstrated significantly higher ($p<0.05$) SBS and SFL with pre-etching than it did without pre-etching. The SBS and SFL of dentin bonds decreased with phosphoric acid pre-etching. The SBS and SFL of bonds using phosphoric acid prior to application of self-etching adhesives clearly demonstrated different tendencies between enamel and dentin. The effect of using phosphoric acid, prior to the application of the self-etching adhesives, on SBS and SFL was dependent on the adhesive material and tooth substrate and should be carefully considered in clinical situations.

INTRODUCTION

With the increased popularity of adhesive restorative dentistry, many dental manufacturers have introduced self-etching adhesive systems to the profession. Self-etch adhesive systems are promoted as being more efficient for bonding procedures in that they require fewer treatment steps to condition tooth surfaces for bonding resin-based materials. However, self-etching adhesive systems are not able to etch enamel as effectively as the phosphoric acid used in etch-and-rinse adhesive systems, and most published work[1-7] indicates that self-etching adhesive systems provide lower resin composite to enamel bond strengths than do etch-and-rinse adhesive systems, which may be related to their lower etching capability. In order to achieve a durable bond to enamel with self-etching adhesive systems, selective etching of enamel with phosphoric acid before the application of self-etching adhesives has been proposed.[8-13] However, it may be difficult to precisely etch only the enamel region, and there is certainly the possibility of affecting exposed dentin.

A major concern in adhesive dentistry is whether the resin monomer of a self-etching adhesive infiltrates into the entire depth of demineralized dentin. Incomplete penetration of a resin monomer into the demineralized dentin might lead to bond degradation from oral fluids and bacterial enzymes.[14-16]

The ability of adhesive agents to bond resin-based materials to tooth structures has been measured extensively in the laboratory using various methods to determine bond strengths. Common laboratory methods employed to determine shear bond strength (SBS) or microtensile bond strength (μ-TBS) use a monotonically increasing load until bond failure occurs. These standardized tests provide valuable information regarding the ability of adhesive agents to bond resin-based materials to demineralized tooth structures. However, this type of force is not the likely mode of failure for bonds in the oral cavity, where failure is considered to result from repeated loading over many months or years, and at lower force levels. Adhesive bonds to both enamel and dentin substrates in the mouth are subjected to repeated stress over long periods of time by the process of loading on tooth structure or restorations that apply compressive, flexural, or tensile stresses to the bonds.

Cyclic loading of specimens to elicit failure is often referred to as fatigue testing.[17-21] A common method of fatigue testing is the staircase method,[22] in which the load on a specimen is increased or decreased by a fixed amount depending on whether the preceding specimen survived or failed, respectively. With this type of test, a parameter called the fatigue limit, which represents the load (stress) at which half the specimens fail during the cycling period, can be calculated.

Limited information is available regarding the ability of enamel bonds produced by self-etching adhesives to resist the forces of fatigue cycling.[19-21] Further research is also needed regarding dentin bonding with self-etching adhesives and the relationship of shear fatigue limit (SFL) and SBS. The purpose of this study was to use fatigue testing to examine the effect of phosphoric acid etching of enamel and dentin, prior to the application of self-etching adhesives, for bonding resin composite, the latter group being included to test the effect of inadvertent exposure of dentin to phosphoric acid during selective enamel etching. The null hypothesis proposed was that pre-etching with phosphoric acid does not affect the SBS and SFL regardless of tooth substrate (enamel/dentin) and self-etching adhesive system (material).

METHODS AND MATERIALS

Study Materials

The materials used in this study are shown in Table 1. The self-etching adhesives used were 1) G- ænial Bond [GB]; (GC Corporation, Tokyo, Japan); 2) OptiBond XTR [OX]; (Kerr Corp, Orange, CA, USA); and 3) Scotchbond Universal [SU]; (3M ESPE Dental Products, St Paul, MN, USA). The phosphoric acid pre-etching agent was Ultra-Etch (Ultradent Products Inc, South Jordan, UT, USA). The resin composite used for the bonding procedure was Z100 Restorative (Shade A2; 3M ESPE).

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Table 1: *Study Materials*

	Manufacturer	Main Components	Code
Adhesive			
G-ænial Bond, Lot No. 1102221	GC Corporation Tokyo, Japan	4-META, UDMA, TEGDMA, phosphoric acid monomer, acetone, water, silanated colloidal silica, initiator	GB
OptiBond XTR Primer: Lot No. 4483016 Adhesive: Lot No. 4544058	Kerr Corp Orange, CA, USA	Primer: GPDM phosphate monomer, HEMA, dimethacrylate monomers, acetone, ethyl alcohol, water, initiator Adhesive: ethyl alcohol, dimethacrylate monomers, barium aluminoborosilicate glass, fumed silica, sodium hexafluorosilicate	OX
Scotchbond Universal, Lot No. 451192	3M ESPE Dental Products St Paul, MN, USA	MDP phosphate monomer, HEMA , dimethacrylate resins, Vitrebond copolymer, filler, ethanol, water, initiators, silane	SU
Pre-etching agent			
Ultra-Etch, Lot No. G017	Ultradent Products Inc South Jordan, UT, USA	35% Phosphoric acid	
Resin composite			
Z100 Restorative, Lot No. N416713 (Shade A2)	3M ESPE Dental Products St Paul, MN, USA	Zirconia/silica, 0.01-3.5 μm Filler load: 84.5% weight, 66% volume	

Abbreviations: GPDM – glycero-phosphate-dimethacrylate; HEMA – hydroxyethylmethacrylate; 4-META – 4-methacryloxyethyl trimellitate anhydride; MDP – methacryloyloxydecyl dihydrogen phosphate; TEGDMA – trietyleneglycoldimethacrylate; UDMA – urethanedimethacrylate

Specimen Preparation

The enamel/dentin bonding sites were prepared by sectioning extracted human molar teeth mesio-distally and then removing approximately two-thirds of the apical root structure. The buccal and lingual tooth sections were mounted with Triad DuaLine (DENTSPLY International, York, PA, USA) in 25-mm-diameter brass rings. The enamel/dentin bonding surfaces were ground flat to 4000 grit using a water coolant and a sequence of carbide polishing papers (Struers Inc, Cleveland, OH, USA).

Metal rings machined from 304 stainless steel with an inner diameter of 2.4 mm, an outer diameter of 4.8 mm, and a length of 2.6 mm were used to bond resin composite (Z100 Restorative) to enamel/dentin surfaces for SBS and SFL tests. The bonding procedure resulted in a resin composite cylinder inside the ring that was 2.36 mm in diameter and approximately 2.5 mm in length. The ring was left in place for the tests.

SBS Tests

Fifteen specimens each were used to determine initial SBS to enamel/dentin with and without phosphoric acid (15 seconds) pre-etching prior to the application of the adhesive. The adhesive agents were applied according to manufacturers' directions, as shown in Table 2.

Following the treatment of the enamel or dentin flat ground tooth surface with the adhesive agent, the metal ring was positioned over the bonding site and secured in place by clamping in a custom fixture. The resin composite material was placed into the ring using a condenser and polymerized for 40 seconds with a Spectrum 800 Curing Unit (DENTSPLY Caulk, Milford, DE, USA) set at 600 mW/cm^2. The bonded specimens were stored for 24 hours in distilled water at 37°C before testing. The specimens were loaded to failure at 1 mm/min using a MTS Insight machine and TestWorks 4 software (MTS Systems Corporation, Eden Prairie, MN, USA). A metal rod with a chisel-shaped end was used to apply the load on the metal ring immediately adjacent to the flat ground tooth surface. The SBS values (MPa) were calculated from the peak load at failure divided by the bonded surface area. After testing, the bonding-site tooth surfaces and resin composite cylinders were observed under an optical microscope (MZ16; Leica Microsystems Ltd, Heerbrugg, Switzerland) at a magnification of 20× to examine the bond failure site. The type of bond failure was based on the percentage of substrate area (adhesive - resin composite - enamel/dentin) observed on the de-bonded cylinders and tooth bonding sites and was recorded as 1) adhesive failure, 2) cohesive failure in composite, 3) cohesive failure in enamel or dentin, or 3) mixed failure—partial adhesive and partial cohesive.

SFL Testing

A staircase method of fatigue testing described by Draughn[22] was used for SFL testing. Test specimens were made as described above for SBS testing. The lower load limit was set near zero (0.4 N), and the initial maximum load applied was 50%-60% of the SBS

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Table 2: *Application Protocol for Pre-etching and Self-etching Adhesives*

Method code	Pre-etching Protocol	Adhesive Application Protocol
With	1. Enamel/dentin surface was phosphoric acid conditioned for 15 s. 2. Conditioned surface was rinsed with water for 15 s (three-way dental syringe) and air-dried.	
Without	Phosphoric acid pre-etching was not performed.	
Adhesive		
GB		1. Adhesive applied to air-dried enamel/dentin surface for 10 s. 2. Adhesive light-cured for 10 s.
OX		1. Primer applied to air-dried enamel/dentin surface with rubbing action for 20 s. Medium air pressure applied to surface for 5 s. 2. Adhesive applied to primed surface with rubbing action for 15 s and then air-thinned for 5 s. 3. Primer/adhesive light-cured for 10 s.
SU		1. Adhesive applied to air-dried enamel/dentin surface with rubbing action for 20 s. 2. Gentle stream of air applied over the liquid adhesive for 5 s or until adhesive no longer moved and the solvent has completely evaporated. 3. Adhesive light-cured for 10 s.

Abbreviations: GB, G- ænial *Bond; OX, OptiBond XTR; SU, Scotchbond Universal.*

determined for each of the adhesive systems tested. The load was applied at a frequency rate of 10 Hz with an ElectroPuls E1000 machine (Instron Worldwide Headquarters, Norwood, MA, USA) using a sine wave for 50,000 cycles or until failure occurred (Figure 1a,b). The load was incrementally adjusted upward or downward (depending on survival or failure) approximately 10% of the initial load. For each test condition 25 specimens were used to determine the SFL. After testing, the specimens were examined to define the location of the bond failure in the same manner as described above for SBS.

Scanning Electron Microscopy (SEM) Observations

The restorative/tooth interfaces were observed by SEM. For the ultrastructure observation of the restorative/tooth interface, bonded specimens (stored in 37°C distilled water) were embedded in epoxy resin and then longitudinally sectioned with a diamond saw (Isomet Low Speed Saw, Buehler, Lake Bluff, IL, USA).

The sectioned surfaces were polished to a high gloss with abrasive discs (Fuji Star Type DDC, Sankyo Rikagaku Co Ltd, Saitama, Japan) followed by diamond pastes down to 0.25-μm particle size (DP-Paste, Struers, Ballerup, Denmark). The specimens were dehydrated in ascending grades of *tert*-butyl alcohol (50% for 20 minutes, 75% for 20 minutes, 95% for 20 minutes, and 100% for two hours) and then transferred from the final 100% bath to a critical-point dryer (Model ID-3, Elionix, Tokyo, Japan) for 30 minutes. The polished surfaces were then subjected to argon-ion beam etching (EIS-200ER, Elionix) for 45 seconds with the ion beam (accelerating voltage 1.0 kV, ion current density 0.4 mA/cm^2) directed perpendicular to the polished surfaces. The surfaces were coated in a vacuum evaporator with a thin film of gold. Observation was done under a SEM (FE-8000, Elionix) at an operating voltage of 10 kV.

Statistical Analysis

A two-way analysis of variance (ANOVA) and Tukey post hoc test were used for analysis of SBS data, and a modified *t*-test with Bonferroni correction was used for SFL data.

RESULTS

SBS and SFL—Enamel

The study results for SBS and SFL for resin composite bonded to enamel with the three adhesive systems with and without phosphoric acid pre-etching are shown in Table 3.

The two-way ANOVA revealed that the factors (pre-etching vs no pre-etching and adhesive system) significantly influenced the SBS values ($p<0.001$). Interaction between the two factors was not statistically significant ($p=0.154$).

The SBS of resin composite to enamel produced by the three self-etching adhesives, after phosphoric

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Figure 1. *(a) ElectroPuls E1000 testing machine. (b) Test specimen mounted in custom fixture on ElectroPuls E1000 testing machine.*

acid pre-etching, ranged from 42.0 ± 3.5 to 48.1 ± 6.1 MPa. The SBS for the same adhesives for enamel surfaces that were not pre-etched with phosphoric acid ranged from 27.7 ± 3.8 to 34.2 ± 3.8 MPa. For all three of the self-etching adhesives, the SBS of resin composite to enamel was significantly higher ($p<0.05$) in the phosphoric acid pre-etching group compared to the group without pre-etching.

There appeared to be a trend toward differences in the failure mode between enamel pre-etching groups and the groups without pre-etching. All three self-etching adhesive systems exhibited more cohesive failures in enamel with pre-etching when compared to surfaces that were not pre-etched. The predominant failure mode without phosphoric acid pre-etching of enamel was adhesive failure for all the self-etching adhesives.

The SFL of self-etching adhesives was significantly higher in specimens with phosphoric acid etching of enamel (19.6-25.1 MPa) than in specimens without phosphoric acid pre-etching (12.9-17.8 MPa). The predominant failure mode for all the self-etching adhesives without phosphoric acid pre-etching was adhesive failure. However, for the groups with phosphoric acid pre-etching, mixed failures and cohesive failures in enamel were increased for all of the self-etching adhesives. OX demonstrated a higher ratio of SFL/SBS than did SU and GB, regardless of whether the enamel was pre-etched with phosphoric acid or not pre-etched.

SBS and SFL—Dentin

The results for SBS and SFL of resin composite bonded to dentin are shown in Table 4. The two-way ANOVA revealed that the factors (pre-etching vs no pre-etching and adhesive system) significantly influenced the SBS values ($p<0.001$) to dentin. Interaction between the two factors was not statistically significant ($p>0.05$).

The SBS of resin composite to dentin using GB was significantly lower in specimens with phosphoric acid pre-etching than in specimens without phosphoric acid etching. The SBS of SU and OX to dentin with phosphoric acid pre-etching tended to decrease compared to values associated with no pre-etching, but there was no significant difference ($p>0.05$) in SBS.

The failure site locations for OX and SU with phosphoric acid pre-etching tended to exhibit more mixed failures when compared to those with no pre-

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Table 3: *Influence of Phosphoric Acid Pre-etching of Enamel on Shear Bond Strength (SBS) and Shear Failure Limit (SFL), in MPa (Standard Deviation) [Failure-mode Percentages]* [a & b]

H_3PO_4	With SBS	Without SBS	With SFL
OX	48.1 (6.1) a,A [73.0/6.7/13.3/6.7]	34.2 (3.8) a,B [80.0/0.0/6.7/13.3]	25.1 (1.8) a,A [50.0/33.3/16.7/0.0]
SU	44.7 (6.1) ab,A [60.0/6.7/20.0/13.3]	27.7 (3.8) b,B [86.7/0.0/0.0/13.3]	21.7 (2.3) b,A [54.5/9.1/27.3/9.1]
GB	42.0 (3.5) b,A [80.0/0.0/13.3/6.7]	28.1 (4.0) b,B [93.3/0.0/0.0/6.7]	19.6 (4.8) b,A [83.3/0.0/8.3/8.3]

Abbreviations: GB, G- ænial Bond; OX, OptiBond XTR; SBS, shear bond strength; SFL, shear fatigue limit; SU, Scotchbond Universal.
[a] *Same lowercase letters in vertical columns are not different at the 5% significance level. Same capital letters between columns indicate no difference at the 5% significance level in H_3PO_4 pre-etching vs no pre-etching groups of the same adhesive.*
[b] *Failure mode percentages (adhesive failure/cohesive failure in resin composite/cohesive failure in enamel/mixed failure).*

etching. The predominant SBS failure mode for GB was adhesive failures for all the specimens tested regardless of phosphoric acid pre-etching or no pre-etching.

There was not a significant difference ($p>0.05$) between phosphoric acid pre-etching (20.3-25.3MPa) and no phosphoric acid pre-etching (17.6-22.6 MPa) for the SFL of SU and OX; however, the SFL tended to decrease in specimens with phosphoric acid pre-etching for these two self-etching adhesive systems. The SFL of the GB self-etching adhesive was significantly lower ($p<0.05$) with phosphoric acid pre-etching compared to values associated with no phosphoric acid pre-etching.

The predominant SFL testing failure mode with phosphoric acid pre-etching was adhesive failure for all of the self-etching adhesives. However, mixed failure and cohesive failure in dentin were increased for OX and SU without phosphoric acid pre-etching. For all the adhesives without phosphoric acid pre-etching of dentin, a higher ratio of SFL/SBS was found compared to the same adhesives with phosphoric acid pre-etching.

SEM Observations

SEM observations of the restorative-enamel interface are shown in Figures 2 through 4. The restorative-enamel interface of all adhesives showed excellent adaptation regardless of phosphoric acid pre-etching or no pre-etching. The resin tags into the enamel surfaces were longer for the groups with phosphoric acid pre-etching when compared to those associated with no pre-etching.

SEM observations of the restorative-dentin interface are shown in Figures 5 through 7. The restorative-dentin interface of all adhesives showed excellent adaptation to the dentin surface. For the groups with phosphoric acid conditioning and using SU and OX, a hybrid layer of approximately 3-5 μm was found between resin adhesive and tooth structure (Figures 5a,b and 7a,b), compared to a layer of 2-5 μm for the GB adhesive (Figure 6a,b). For the SU and GB groups without pre-etching with phosphoric acid there was formation of a thin transitional layer between the adhesive resin and tooth structure (Figures 5c,d and 6c,d). A dentin hybrid layer was observed for OX regardless of phosphoric acid pre-etching (Figure 7a,b) or no phosphoric acid pre-etching (Figure 7c,d). The thickness of the hybrid layer using OX with phosphoric acid pre-etching (Figure 7a,b) was greater (3-5 μm) when compared to dentin surfaces without pre-etching with phosphoric acid (Figure 7c,d).

DISCUSSION

Laboratory bond strength tests are a common approach to evaluating the potential effectiveness of adhesive systems. Over the years, many studies have

Table 4: *Influence of Phosphoric Acid Pre-etching of Dentin on Shear Bond Strength (SBS) and Shear Failure Limit (SFL), in MPa (Standard Deviation) [Failure-mode Percentages]*[a & b]

H_3PO_4	With SBS	Without SBS	With SFL
OX	44.8 (8.1) a,A [33.3/13.3/20.0/33.3]	50.9 (4.9) a,A [0.0/33.3/40.0/26.7]	22.2 (6.2) a,A [63.6/0.0/9.1/27.3]
SU	39.2 (6.7) b,A [33.3/6.7/40.0/20.0]	42.6 (4.0) b,A [20.0/20.0/46.7/13.3]	17.6 (1.4) b,A [81.3/0.0/0.0/18.7]
GB	24.6 (2.8) c,A [100.0/0.0/0.0/0.0]	31.1 (3.8) c,B [100.0/0.0/0.0/0.0]	11.5 (2.8) c,A [100.0/0.0/0.0/0.0]

Abbreviations: GB, G- ænial Bond; OX, OptiBond XTR; SBS, shear bond strength; SFL, shear fatigue limit; SU, Scotchbond Universal.
[a] *Same lowercase letters in vertical columns are not different at the 5% significance level. Same capital letters between columns indicate no difference at the 5% significance level in H_3PO_4 pre-etching vs no pre-etching groups of the same adhesive.*
[b] *Failure mode percentages (adhesive failure/cohesive failure in resin composite/cohesive failure in dentin/mixed failure).*

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Table 3: *Influence of Phosphoric Acid Pre-etching of Enamel on Shear Bond Strength (SBS) and Shear Failure Limit (SFL), in MPa (Standard Deviation) [Failure-mode Percentages] [a & b] (ext.)*

H_3PO_4	Without SFL	With Ratio SFL/SBS	Without Ratio SFL/SBS
OX	17.8 (1.9) a,B [90.0/0.0/0.0/10.0]	.522	.520
SU	12.9 (1.5) b,B [100.0/0.0/0.0/0.0]	.485	.466
GB	13.4 (2.5) b,B [100.0/0.0/0.0/0.0]	.467	.477

been reported in the literature regarding the bonding effectiveness of adhesive systems to mineralized tooth structures using shear bond strength tests and μ-TBS testing. These types of laboratory tests routinely use a monotonically increasing force to the bonded assembly until failure occurs, while in most clinical situations, adhesively bonded restorations are typically subjected to subcritical loading during function.[17-21,23] While repeated loads typically encountered in the oral cavity are insufficient to provoke failure, they induce damage by generating cracks that grow over time and eventually result in deterioration of adhesively bonded restorations through marginal failure or, in extreme cases, bulk fracture.

Fatigue can be defined as the degradation or failure of mechanical properties after repeated applications of stress at a level well below the ultimate fracture strength of the material or interface.[24] Consequently, fatigue tests provide not only information on the ability of a material or interface to resist the development of cracks but also information related to the endurance characteristics of a bonding system (ie, materials and technique).

A popular method of fatigue testing, referred to as the staircase method, involves selecting a starting stress of approximately one-half of the ultimate strength. The load is applied at a set frequency until the specimen survives a specific number of cycles or fails during the cycling. Draughn[22] developed an analytical approach to determining the fatigue strength of materials using the staircase method. Previous studies[19] have demonstrated that fatigue limits are much lower than the initially measured SBS and may be on the order of 40%-60% of that strength.

In the present study, SBS values were determined for two single-step self-etching adhesives (SU and GB) and a two-step self-etching adhesive (OX) to provide a relative comparison of the bonding performance to both enamel and dentin using a resin composite material. The results of these SBS tests were subsequently used as baseline values for SFL testing. The results of this study demonstrated that OX produced higher SBS and SFL to enamel ($p<0.05$), when compared to SU and GB, with the exception of the SBS of SU when the enamel was pre-etched with phosphoric acid. Additionally, regardless of phosphoric acid pre-etching or no pre-etching, OX demonstrated a higher ratio of SFL/SBS than did SU and GB. These results were consistent with those of previous studies[4,25-27] comparing multiple-step self-etching adhesives and single-step self-etching adhesives with SBS and μ-TBS testing of enamel and dentin.

Recently, single-step self-etching adhesives have been advocated to reduce the number of application steps and eliminate technique-sensitive factors that may negatively impact the ability of resin materials to bond to enamel and dentin. Single-step self-etching adhesives combine the functions of a self-etching primer (acid monomer) and a bonding agent. These types of adhesives typically contain both hydrophilic and hydrophobic monomers and require a high concentration of solvent to keep them in solution.[28,29] Additionally, most incorporate water, which is essen-

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Table 4: *Influence of Phosphoric Acid Pre-etching of Dentin on Shear Bond Strength (SBS) and Shear Failure Limit (SFL), in MPa (Standard Deviation) [Failure-mode Percentages][a & b] (ext.)*

H_3PO_4	Without SFL	With Ratio SFL/SBS	Without Ratio SFL/SBS
OX	25.3 (3.7) a,A [23.0/0.0/38.5/38.5]	.496	.497
SU	20.3 (2.7) b,A [75.0/0.0/8.3/16.7/0]	.449	.477
GB	15.9 (2.2) c,B [100.0/0.0/0.0/0.0]	.467	.511

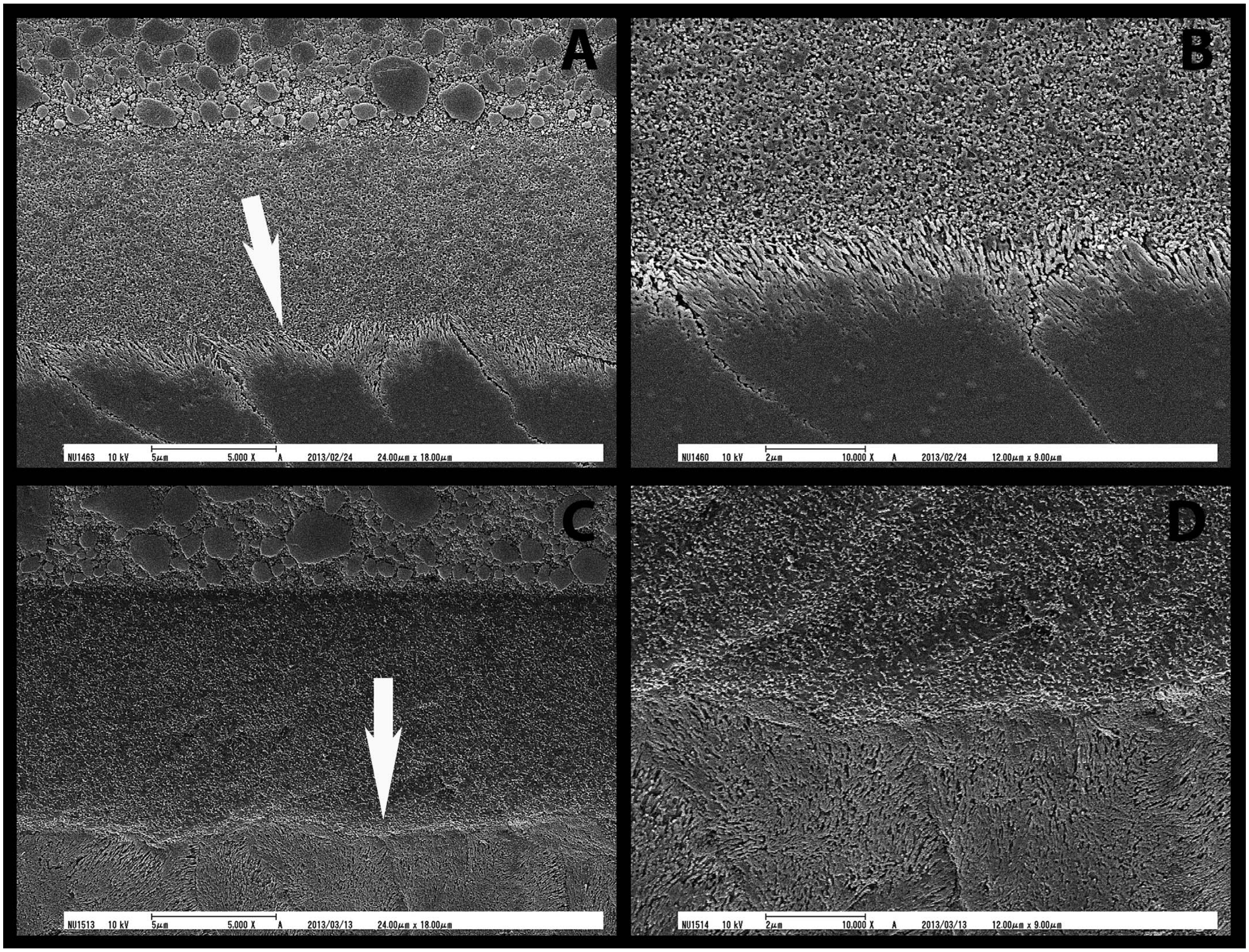

Figure 2. *(a) Scotchbond Universal—restorative/enamel interface with phosphoric acid pre-etching (5000×). (b) Scotchbond Universal—restorative/enamel interface with phosphoric acid pre-etching (10,000×). (c) Scotchbond Universal—restorative/enamel interface without phosphoric acid pre-etching (5,000×). (d) Scotchbond Universal—restorative/enamel interface without phosphoric acid pre-etching (10,000×).*

tial as an ionization medium, to enable self-etching activity to occur.[30]

Previous studies[31,32] have reported that one of the characteristics or vulnerabilities of single-step adhesives is phase separation, which may result in droplets and blisters in the adhesive layer and at the interface of the tooth substrate and the adhesive layer. In addition, single-step self-etching adhesives may contain high concentrations of water, which purportedly lower the degree of conversion.[29] These drawbacks might reduce the mechanical properties of an adhesive layer and also produce a weak point, resulting in crack initiation and propagation. The composition (Table 1) of the two-step adhesive system in this study (OX) may result in improved physical or mechanical properties when compared to the single-step adhesives (SU and GB). Improvement in physical properties may relate closely to the higher SBS and SFL exhibited by OX.

In the present study, phosphoric acid pre-etching of enamel significantly increased SBS and SFL. The range of SBS was 42.0 ± 3.5 to 48.1 ± 6.1 MPa for phosphoric acid pre-etched enamel surfaces, compared to 27.7 ± 3.8 to 34.2 ± 3.8 MPa for surfaces that were not pre-etched. The SFL ranged from 19.6 ± 4.4 to 25.1 ± 1.8 MPa for phosphoric acid pre-etched enamel surfaces, compared to a range of 12.9 ± 1.5 to 17.8 ± 1.9 MPa for surfaces without pre-etching. SEM observations also revealed that resin-tags into the enamel bonding sites were longer and more extensive for the groups with phosphoric acid pre-etching when compared to groups without

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

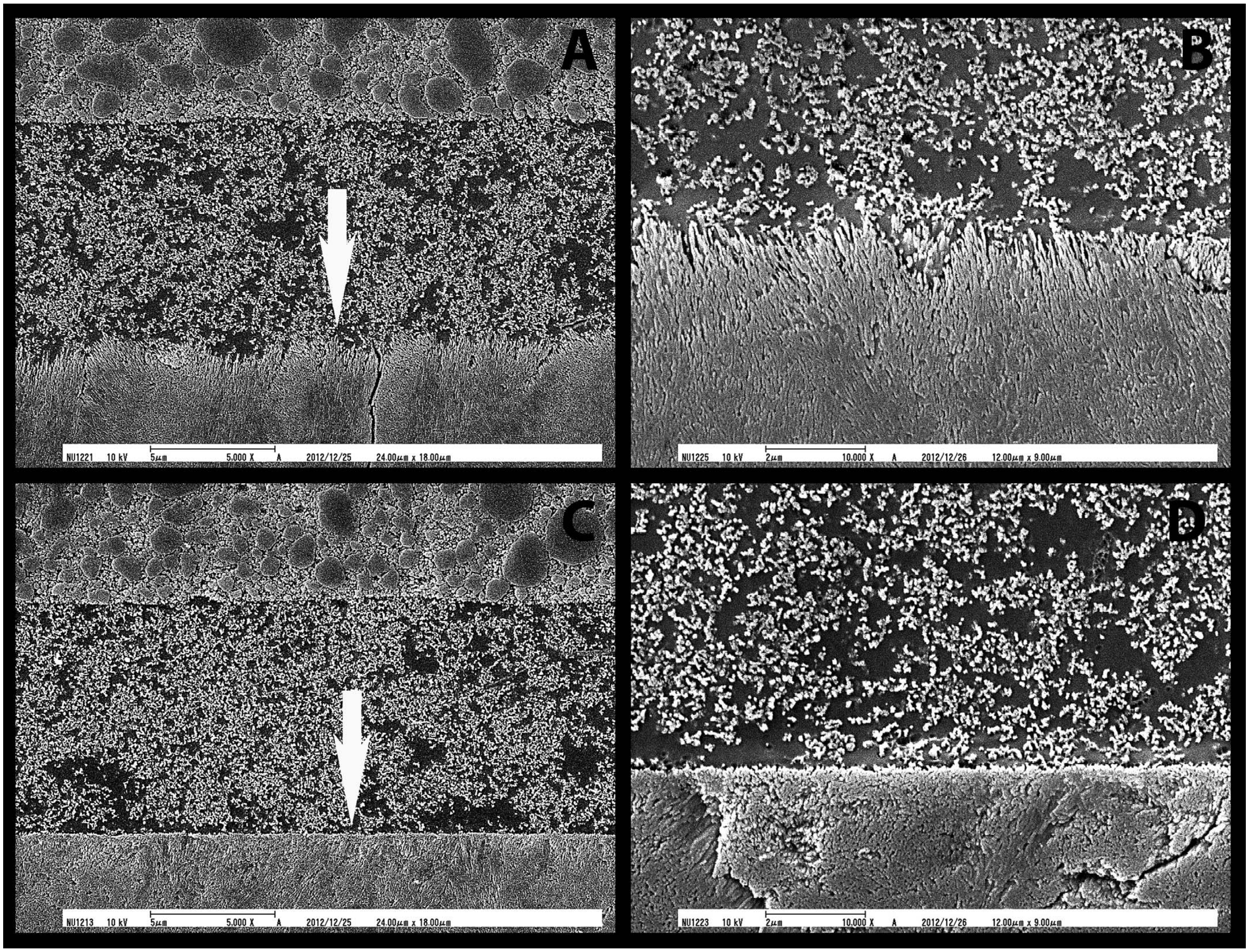

Figure 3. *(a) G-ænial Bond—restorative/enamel interface with phosphoric acid pre-etching (5000×). (b) G-ænial Bond—restorative/enamel interface with phosphoric acid pre-etching (10,000×). (c) G-ænial Bond—restorative/enamel interface without phosphoric acid pre-etching (5000×). (d) G-ænial Bond—restorative/enamel interface without phosphoric acid pre-etching (10,000×).*

phosphoric acid pre-etching (Figures 2a through 4d). Therefore, the null hypothesis that phosphoric acid pre-etching does not affect the SBS and SFL of enamel was rejected for all of the adhesive systems.

Some recent studies[1-7] on bonding to enamel have found that self-etching adhesive systems, whether two-step or one-step systems, have inferior bond strengths compared with total-etch systems. In addition, pre-etching of enamel with phosphoric acid was shown[12,33,34] to improve the bond strengths of both two-step and single-step self-etching adhesives when compared with bond strengths achieved without pre-etching. Also, SEM studies[1,7,35] examining the morphology of enamel surfaces revealed that the application of a self-etching primer and single-step adhesives did not create as deep of an enamel etching pattern as did phosphoric acid conditioning.

Over the years phosphoric acid has become the standard procedure for conditioning to modify the enamel structure prior to the application of adhesive bonding agents. The infiltration of an adhesive resin monomer into the porous zone results in the formation of resin-tags, thereby establishing micromechanical retention to the etched enamel. Phosphoric acid treatment of enamel increases the bonding area and wettability of the adherent surface. Treating enamel with phosphoric acid improves the surface free energy by about 30% compared with treating with a silica-carbide paper (grit #180, #600, and #2000) ground enamel surface without phosphoric acid treatment.[36]

With the introduction of self-etching dental adhesives to the profession, phosphoric acid pre-etching

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

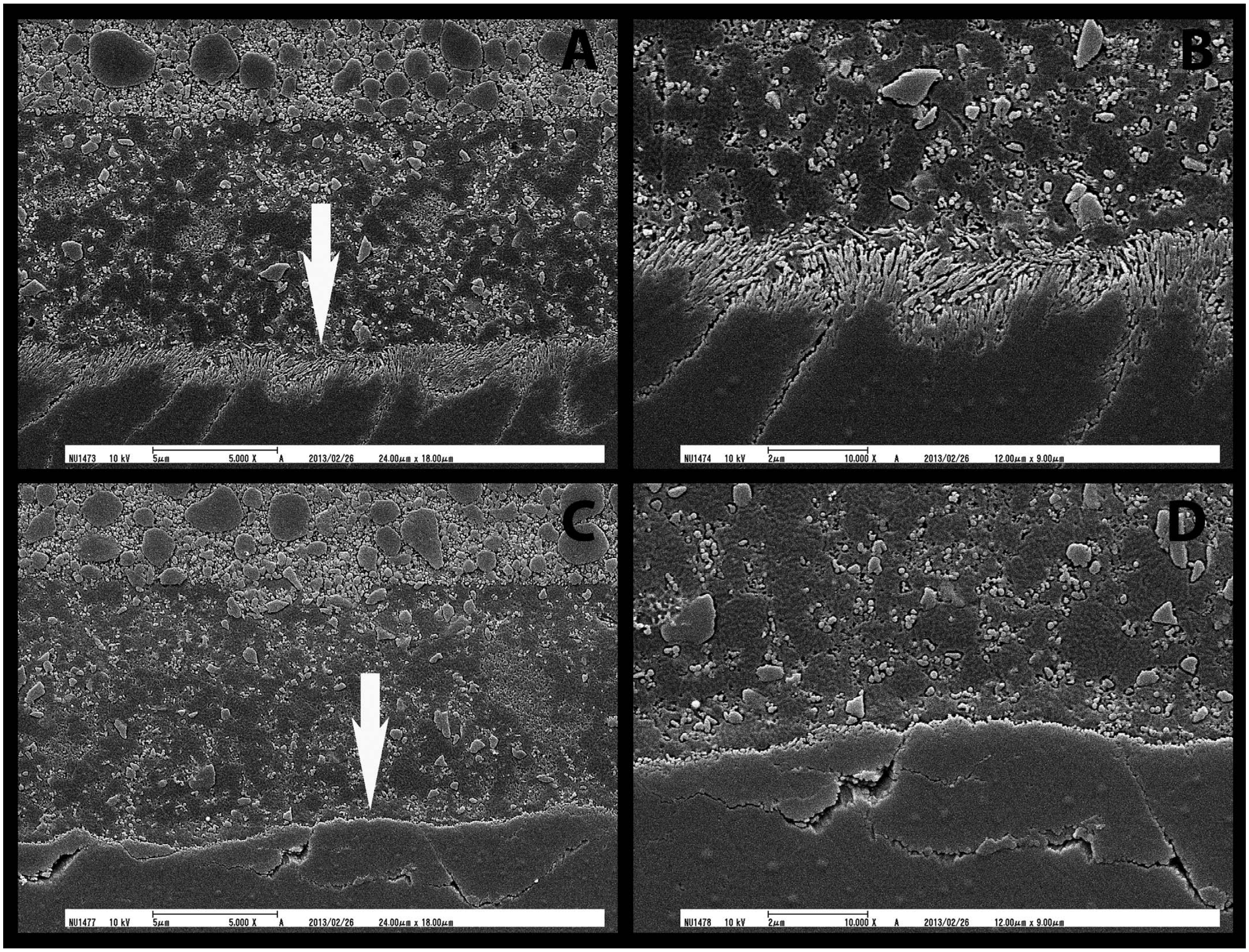

Figure 4. *(a) Optibond XTR—restorative/enamel interface with phosphoric acid pre-etching (5000×). (b) Optibond XTR—restorative/enamel interface with phosphoric acid pre-etching (10,000×). (c) Optibond XTR—restorative/enamel interface without phosphoric acid pre-etching (5000×). (d) Optibond XTR—restorative/enamel interface without phosphoric acid pre-etching (10,000×).*

of enamel is not routinely recommended by manufacturers. The evidence from several studies,[7,12,19] including the present study, comparing phosphoric acid pre-etching of enamel vs no pre-etching clearly shows increased enamel bond strengths following pre-etching.

Bonding resin-based materials to dentin continues to be a challenge. 2-hydroxyethyl methacrylate (HEMA) is a water-soluble methacrylate monomer frequently employed in dental adhesives. HEMA purportedly enhances the wetting properties of the adhesive solution and the penetration efficacy of the adhesive into demineralized dentin as a result of its polar properties and small dimensions.[37,38] HEMA has been reported[39] to have the capability of increasing the bond strength to dentin. Because of its hydrophilic character, HEMA is frequently used as an ingredient to improve miscibility of both the hydrophobic and hydrophilic components of adhesive solutions to prevent phase separation.[31]

While HEMA has known advantages for adhesive bonding to mineralized tooth structures, concerns have been expressed about the use of HEMA in adhesive dental products. One of the reported drawbacks of HEMA is the potential for allergenic issues, especially to the skin.[40,41] Other problems reported[29,42] include deterioration of mechanical properties of the polymerized adhesive caused by its characteristics, which enhance water uptake, swelling, and staining.

In an effort to reduce possible allergenic problems and to achieve long-term durability, some single-step

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

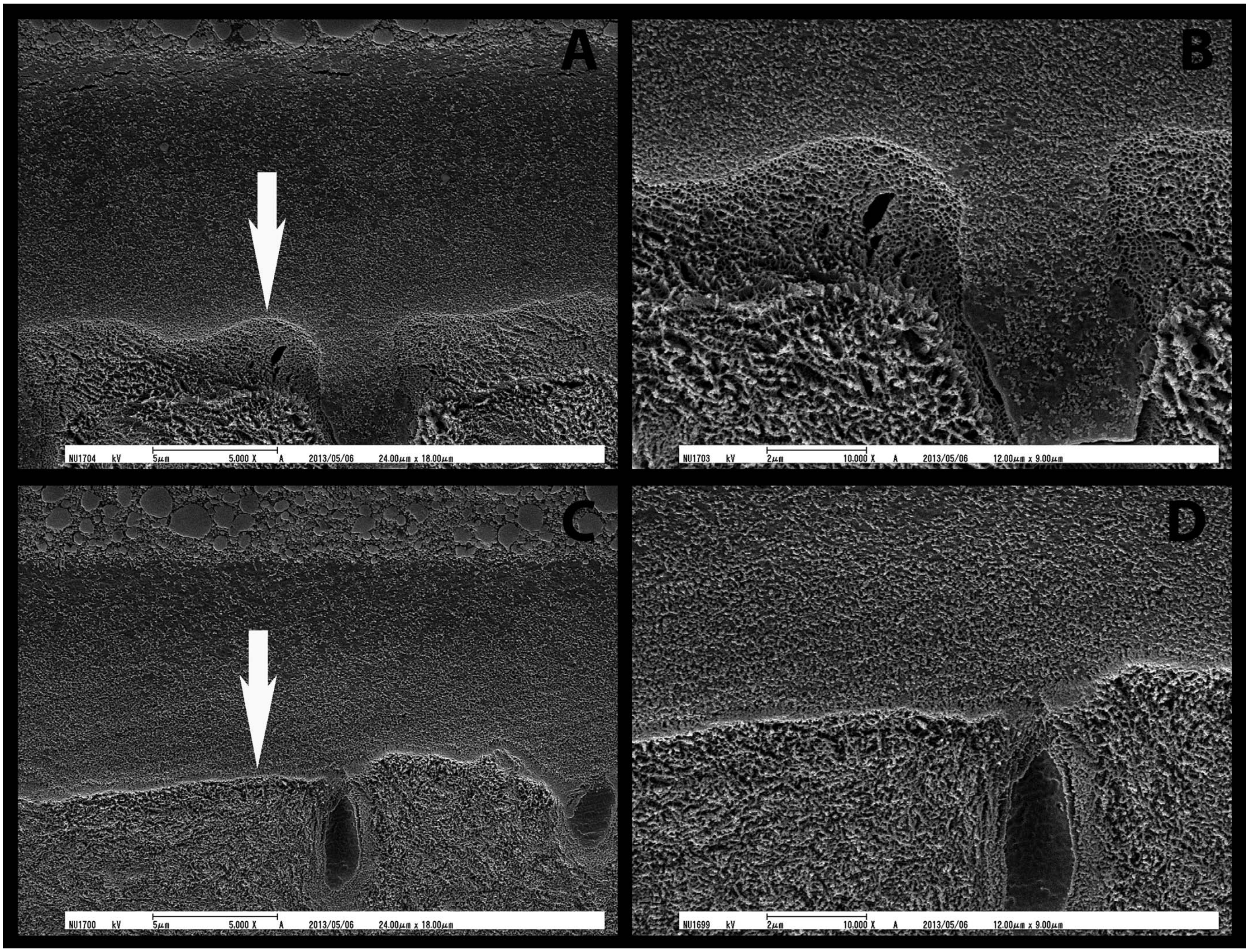

Figure 5. *(a) Scotchbond Universal—restorative/dentin interface with phosphoric acid pre-etching (5000×). (b) Scotchbond Universal—restorative/dentin interface with phosphoric acid pre-etching (10,000×). (c) Scotchbond Universal—restorative/dentin interface without phosphoric acid pre-etching (5000×). (d) Scotchbond Universal—restorative/dentin interface without phosphoric acid pre-etching (10,000×).*

self-etching adhesives do not include HEMA in the composition. In this study, SU and OX contain HEMA; however, GB does not contain HEMA as an ingredient and is classified as a HEMA-free, single-step self-etching adhesive. The results of this study show that the SBS and SFL to dentin for SU and OX tended to decrease with phosphoric acid pre-etching of the dentin surface prior to the application of the adhesives but that this decrease was not significant ($p>0.05$). For the HEMA-free GB adhesive, phosphoric acid pre-etching of the dentin surface significantly decreased ($p<0.05$) SBS and SFL, and the values were significantly less ($p<0.05$) than for OX and SU. Therefore, the null hypothesis that phosphoric acid pre-etching does not affect the SBS and SFL of dentin was not rejected for SU and OX, but it was rejected for GB.

The SEM examinations of the adhesive interface with the mineralized tooth structures revealed differences among the self-etching systems and with phosphoric acid pre-etching vs no pre-etching. With phosphoric acid pre-etching of dentin, a hybrid layer of approximately 2-5 μm was observed with the GB adhesive (Figure 6a,b), compared to a hybrid layer in the range of 3-5 μm for both the SU and OX adhesives (Figures 5a,b and 7a,b). A typical hybrid layer was not found with SU and GB when phosphoric acid pre-etching was not used on dentin (Figures 5c,d and 6c,d). For the OX adhesive, a hybrid layer was found with or without the use of phosphoric acid pre-etching of dentin; however, the width of the hybrid layer with phosphoric acid pre-etching (Figure 7a,b) was approximately double (3-5

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

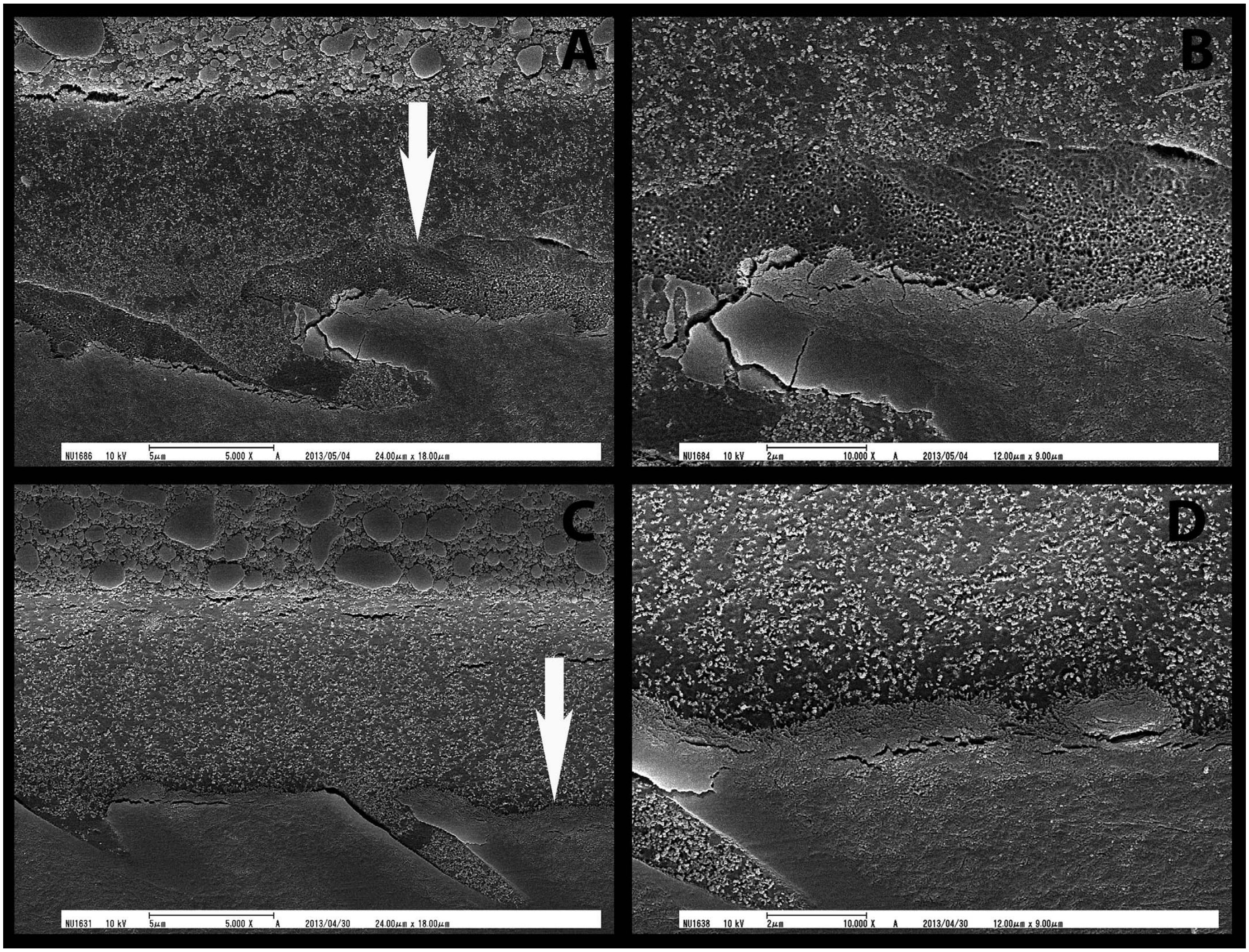

Figure 6. *(a) G-ænial Bond—restorative/dentin interface with phosphoric acid pre-etching (5000×). (b) G-ænial Bond—restorative/dentin interface with phosphoric acid pre-etching (10,000×). (c) G-ænial Bond—restorative/dentin interface without phosphoric acid pre-etching (5000×). (d) G- ænial Bond—restorative/dentin interface without phosphoric acid pre-etching (10,000×).*

μm) that found without phosphoric acid pre-etching (Figure 7c,d).

Phosphoric acid conditioning of dentin, followed by air-drying of the treated surface, has been shown[43] to result in collapsed collagen fibrils that inhibit resin monomer penetration into the entire depth of the decalcified dentin. Adhesives that contain hydrophilic HEMA and water, such as the SU single-step self-etching adhesive and the OX two-step self-etching adhesive, may help to re-expand collapsed collagen fibrils and enhance the penetration of adhesive monomers into demineralized dentin. In an effort to further facilitate bonding to mineralized tooth structures, SU also contains 10-methacryloxydecyl dihydrogen phosphate (MDP) and Vitrebond copolymer. The MDP purportedly has the potential to develop chemical bonds to hydroxyapatite, and the Vitrebond copolymer is included to develop ionic bonds to hydroxyapatite and/or collagen.[44,45] However, even if hydrophilic components of an adhesive have penetrated into demineralized surfaces, it is possible that the resin components themselves may have been hampered in penetrating the exposed collagen network, leading to a decrease in bond strength.

The GB adhesive demonstrated statistically significant ($p<0.05$) lower SBS and SFL values when using phosphoric acid pre-etching of the dentin. While a HEMA-free single-step adhesive may have benefits for long-term bonding durability,[46-48] it might induce droplets and blisters in the adhesive layer or on the interface due to phase

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

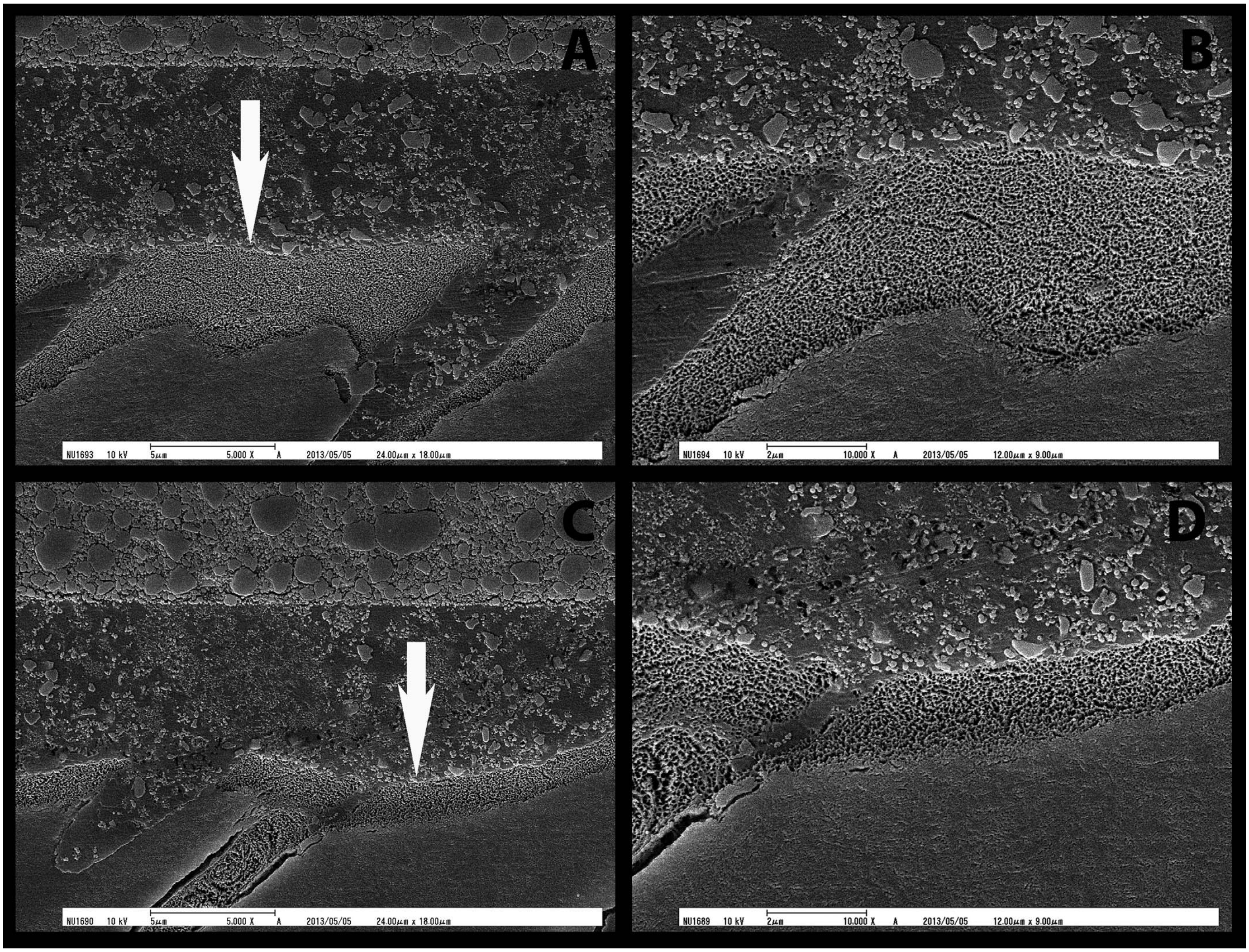

Figure 7. *(a) Optibond XTR—restorative/dentin interface with phosphoric acid pre-etching (5000×). (b) Optibond XTR—restorative/dentin interface with phosphoric acid pre-etching (10,000×). (c) Optibond XTR—restorative/dentin interface without phosphoric acid pre-etching (5000×). (d) Optibond XTR—restorative/dentin interface without phosphoric acid pre-etching (10,000×).*

separation or the more hydrophobic nature of the components.[31] It may be possible that these defects provide vulnerable regions for crack initiation and propagation from load stress resulting in lower bond strength. In addition, a previous study[49] of the GB adhesive demonstrated that resin tag formation, produced under vacuum treatment of dentin, did not contribute to the μ-TBS. Therefore, the principal method of adhesion to the dentin for GB was not dependent on resin tag formation but on chemical bonding to the hydroxyapatite. From this perspective, using phosphoric acid pre-etching on dentin may have extensively removed hydroxyapatite from the surface, which is necessary to achieve chemical bonding, resulting in an adverse effect on the dentin bonding of GB. The results of the present study clearly demonstrated a decrease in SBS and SFL with the GB system when the dentin surface was pre-etched with phosphoric acid and support the theory that the loss of mineralized dentin from the surface resulted in lower adhesion because of reduced chemical bonding.

Fatigue failure is a result of nucleation of microcracks, propagation and eventual coalescence of cracks leading to catastrophic failure.[24] Nucleation is considered to occur at flaws in the materials or at interfaces, such as scratches, voids, and inclusions, which might be weak points where high stress intensities can develop under load applications. In addition, it is important to consider the influence of different adherent substrates, as well as mechanical properties of adhesives, and crack propagation from repeated subcritical loading.

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

Manufacturers' directions for self-etching adhesives now often give practitioners a choice of whether to use phosphoric acid pre-etching on enamel. The SBS and SFL data in the present study clearly show that phosphoric acid conditioning of enamel prior to the application of the three adhesive systems tested improved the adhesion of a resin composite material (Table 3). The opposite was true for dentin. The SBS and SFL to dentin for all three systems were decreased with phosphoric acid pre-etching (Table 4).

It is interesting to note that the system (OX) that produced the highest SBS and SFL values also yielded the highest ratio of SFL/SBS for both enamel and dentin. While the SBS values provide a relative ranking of the adhesive characteristics of a system, the SFL value is a better measure of endurance. The data in Table 3 for enamel and in Table 4 for dentin demonstrate clear differences in the resistance of bonds to failure with cyclic loading.

It might be speculated that the reason for differences in SFL between enamel and dentin were caused by not only physical properties of adherent substrates themselves but also by adhesive layer conversion after evaporation of water and solvent. Enamel is homogeneous in nature and is primarily composed of hydroxyapatite. In comparison, dentin is heterogeneous, consisting of hydroxyapatite and collagen. Overall, the water content of dentin is significantly higher than that of enamel, and this may influence the effectiveness of evaporation of solvents, which may result in a reduction of the degree of conversion, leading to lower mechanical properties. From the results of the failure modes observed in dentin bonding, adhesive mode failures tended to increase in SBS and SFL specimens with phosphoric acid pre-etching, except in the case of the GB adhesive (GB demonstrated 100% adhesive failure for all conditions). On the other hand, failure modes of enamel for all three adhesives demonstrated a different trend between SBS and SFL; adhesive mode failures tended to decrease in SBS, when the use of phosphoric acid pre-etching was compared to the same self-etch system without the use of pre-etching, but in SFL adhesive mode failures tended to increase.

The clinical relevance of fatigue testing gains strength from an earlier study[50] showing a larger percentage of gap formation at resin composite/enamel margins for self-etching systems when compared to etch-and-rinse adhesives. Frankenberger and Tay[50] conducted a study comparing marginal gap formation of Class II resin composite restorations bonded with both etch-and-rinse and self-etching adhesives using simultaneous mechanical loading and thermocycling (thermomechanical fatigue loading, TML). In reporting the results for marginal quality in enamel, these authors reported that while all adhesive systems showed a significant loss ($p<0.05$) of gap-free margins after TML compared to results prior to TML, etch-and-rinse systems performed significantly better than did self-etching systems. Dentin margins, like enamel, showed a high percentage of gap-free margins before TML. All the adhesive systems exhibited a significant decline in the percentage of gap-free dentin margins after TML. The results of their study clearly show the effect of TML fatigue loading on both enamel and dentin margins of adhesively bonded Class II resin composite restorations. In addition, clinical studies[13,47,51-54] have found increased marginal breakdown for restorations bonded with self-etching adhesives compared to those with etch-and-rinse adhesives. Since some of the self-etch adhesives may have laboratory bond strengths that are similar to those of the etch-and-rinse adhesives, the reason for more and earlier failures may be attributed to lower fatigue resistance.

Generally, failure in fatigue testing is the result of cumulative damage over time. How different adherent substrates, especially enamel and dentin, are related to crack propagation and bond failures requires further investigation. Additional fatigue testing is needed to investigate the long-term durability of adhesively bonded materials to mineralized tissues.

CONCLUSIONS

Phosphoric acid pre-etching of enamel produced significantly higher ($p<0.05$) SBS and SFL of a resin composite bonded to enamel using three self-etching adhesive systems when compared to similar values associated with no pre-etching. The use of phosphoric acid pre-etching on dentin prior to the application of the three adhesive systems resulted in a decrease in SBS and SFL when compared to values obtained using the adhesives without pre-etching with phosphoric acid.

SBS and SFL testing of bonds using phosphoric acid etching prior to application of the self-etch adhesives clearly demonstrated different tendencies between enamel and dentin. The effect of phosphoric acid pre-etching (prior to application of self-etch adhesives) on bond performance was adhesive

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

system and tooth substrate dependent. The results of this study have significant implications for the selection and technical use of self-etching adhesive systems.

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.

(Accepted 3 January 2014)

REFERENCES

1. De Munk J, Van Meerbeek B, Inoue S, Vargas M, Yoshida Y, Armstrong S, Lambrechts P, & Venherle G (2003) Microtensile bond strengths of one and two-step self-etch adhesives to bur cut enamel and dentin *American Journal of Dentistry* **16(4)** 414-420.
2. Goracci C, Sadek FT, Monticelli F, Cardoso PE, & Ferrari M (2004) Microtensile bond strength of self-etching adhesives to enamel and dentin *Journal of Adhesive Dentistry* **6(4)** 313-318.
3. De Munk J, Vargas M, Iracki J, Van Landuyt K, Poiterin A, Lambrechts P, & Van Meerbeek B (2005) One-day bonding effectiveness of new self-etch adhesives to bur-cut enamel and dentin *Operative Dentistry* **30(1)** 39-49.
4. Brackett W, Ito S, Nishitani Y, Haisch L, & Pashley D (2006) The microtensile bond strength of self-etching adhesives to ground enamel *Operative Dentistry* **31(4)** 332-337.
5. Longuercio AD, Moura SK, Pellizzaro A, Dal-Bianco K, Patzlaff RT, Grande RHM, & Reis A (2008) Durability of enamel bonding using two-step self-etch systems on ground and unground enamel *Operative Dentistry* **33(1)** 79-88.
6. Barkmeier WW, Erickson RL, Kimmes NS, Latta MA, & Wilwerding TM (2009) Effect of enamel etching time on roughness and bond strength *Operative Dentistry* **34(2)** 217-222.
7. Erickson RL, Barkmeier WW, & Latta MA (2009) The role of etching in bonding to enamel: A comparison of self-etching and etch-and-rinse adhesive systems *Dental Materials* **25(11)** 1459-1467.
8. Miguez P, Castro P, Nunes M, Walter R, & Pereira PN (2003) Effect of acid-etching on the enamel bond of two self-etching systems *Journal of Adhesive Dentistry* **5(2)** 107-112.
9. Van Landuyt KL, Kanumilli P, De Munk J, Peumans M, Lambrechts P, & Van Meerbeek B (2006) Bond strength of a mild self-etch adhesive with and without prior acid-etching *Journal of Dentistry* **34(1)** 77-85.
10. Frankenberger R, Lohbauer U, Roggendorf MJ, Naumann M, & Taschner M (2008) Selective enamel etching reconsidered: Better than etch-and-rinse and self-etch? *Journal of Adhesive Dentistry* **10(5)** 339-344.
11. Watanabe T, Tsubota K, Takamizawa T, Kurokawa H, Rikuta A, Ando S, & Miyazaki M (2008) Effect of prior acid etching on bonding durability of single-step adhesives *Operative Dentistry* **33(4)** 426-433.
12. Erickson RL, Barkmeier WW, & Kimmes NS (2009) Bond strength of self-etch adhesives to pre-etched enamel *Dental Materials* **25(10)** 1187-1194.
13. Peumans M, De Munke J, Van Landuyt KL, Poitevin A, Lambrechts P, & van Meerbeek B (2010) Eight-year clinical evaluation of a 2-step self-etch adhesive with and without selective etching *Dental Materials* **26(12)** 1176-1184.
14. Sano H, Yoshikawa T, Pereira PNR, Kanemura N, Morigami M, Tagami J, & Pashely DH (1999) Long-term durability of dentin bonds made with a self-etching primer, in vivo *Journal of Dental Research* **78(4)** 906-911.
15. Spencer P, & Swafford JR (1999) Unprotected protein at the dentin-adhesive interface *Quintessence International* **30(7)** 501-507.
16. Sato M, & Miyazaki M (2005) Comparison of depth of dentin etching and resin infiltration with single-step adhesive systems *Journal of Dentistry* **33(6)** 475-484.
17. Frankenberger R, Strobel WO, Krämer N, Lohbauer U, Winterscheidt J, Winterscheidt B, & Petschelt A (2003) Evaluation of the fatigue behavior of the resin-dentin bond with the use of different methods *Journal of Biomedical Materials Research Part B: Applied Biomaterials* **67B(2)** 712-721.
18. De Munk J, Braem M, Wevers M, Yoshida Y, Inoue S, Suzuki K, Lambrechts P, & Van Meerbeek B (2005) Micro-rotary fatigue of tooth-biomaterial interfaces *Biomaterials* **26(10)** 1145-1153.
19. Erickson RL, De Gee AJ, & Feilzer AJ (2006) Fatigue testing of enamel bonds with self-etch and total-etch adhesives systems *Dental Materials* **22(11)** 981-987.
20. Erickson RL, Barkmeier WW, & Kimmes NS (2009) Fatigue of enamel bonds with self-etch adhesives *Dental Materials* **25(6)** 716-720.
21. Barkmeier WW, Erickson RL, & Latta MA (2009) Fatigue limits of enamel bonds with moist and dry techniques *Dental Materials* **25(12)** 1527-1531.
22. Draughn R (1979) Compressive fatigue limits of composite restorative materials *Journal of Dental Research* **58(3)** 1093-1096.
23. De Munk J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M, & Van Meerbeek B (2005) A

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

critical review of the durability of adhesion to tooth tissue: Methods and results *Journal of Dental Research* **84(2)** 118-132.

24. Baran G, Boberick K, & McCool J (2001) Fatigue of restorative materials *Critical Reviews in Oral Biology & Medicine* **12(4)** 350-360.
25. Abo T, Uno S, & Sano H (2004) Comparison of bonding efficacy of an all-in-one adhesive with a self-etching primer system *European Journal of Oral Sciences* **112(3)** 286-292.
26. Adebayo OA, Burrow MF, & Tyas MJ (2008) Bonding of one-step and two-step self-etching primer adhesives to dentin with different tubules orientations *Acta Odontologica Scandinavica* **66(3)** 159-168.
27. Kimmes NS, Barkmeier WW, Erickson RL, & Latta MA (2010) Adhesive bond strengths to enamel and dentin using recommended and extended treatment times *Operative Dentistry* **35(1)** 112-119.
28. Pashley EL, Agee KA, Pashley DH, & Tay FR (2002) Effects of one versus applications of an unfilled, all-in-one adhesive on dentin bonding *Journal of Dentistry* **30(2)** 83-90.
29. Tay FR, King NM, Chan KM, & Pashley DH (2002) How can nanoleakage occur in self-etching adhesive systems that demineralize and infiltrate simultaneously? *Journal of Adhesive Dentistry* **4(4)** 255-269.
30. Van Landuyt KL, Snauwaert J, De Munke J, Peumans M, Yoshida Y, Poitevin A, Coutinho E, Suzuki K, Lambrechts P, & Van Meerbeek B (2007) Systematic review of the chemical composition of contemporary dental adhesives *Biomaterials* **28(26)** 3757-3785.
31. Van Landuyt KL, De Munke J, Snauwaert J, Coutinho E, Poitevin A, Yoshida Y, Inoue S, Peumans M, Suzuki K, Lambrechts P, & Van Meerbeek B (2005) Monomer-solvent phase separation in one-step self-etch adhesives *Journal of Dental Research* **84(2)** 183-188.
32. Van Landuyt KL, Snauwaert J, De Munke J, Coutinho E, Poitevin A, Yoshida Y, Suzuki K, Lambrechts P, & Van Meerbeek B (2007) Origin of interfacial droplets with one-step adhesives *Journal of Dental Research* **86(8)** 739-744.
33. Van Landuyt KL, Peumans M, De Munke J, Lambrechts P, & Van Meerbeek B (2005) Extension of a one-step self-etch adhesive into a multi-step adhesive *Dental Materials* **22(6)** 533-544.
34. Van Landuyt KL, Kanumilli P, De Munke J, Peumans M, Lambrechts P, & Van Meerbeek B (2006) Bond strength of a mild self-etch adhesive with and without prior acid-etching *Journal of Dentistry* **34(1)** 77-85.
35. Perdigão J, & Geraldeli S (2003) Bonding characteristics of self-etching adhesives to intact versus prepared enamel *Journal of Esthetic and Restorative Dentistry* **15(1)** 32-41, Discussion 42.
36. Tsujimoto A, Iwasa M, Shiimamura Y, Murayama R, Takamizawa T, & Miyazaki M (2010) Enamel bonding of single-step self-etch adhesives: Influence of surface energy characteristics *Journal of Dentistry* **38(2)** 123-130.
37. Toledano M, Osorio R, Moreira MA, Cabrerizo-Vilchez MA, Gea P, Tay FR, & Pashley DH (2004) Effect of the hydration status of the smear layer on the wettability and bond strength of a self-etching primer to dentin *American Journal of Dentistry* **17(5)** 310-314.
38. Van Landuyt KL, Snauwaert J, Peumans M, De Munke J, Lambrechts P, & Van Meerbeek B (2008) The role of HEMA in one-step self-etch adhesives *Dental Materials* **24(10)** 1412-1419.
39. Nakaoki Y, Nikaido T, Pereira PN, Inokoshi S, & Tagami J (2000) Dimensional changes of demineralized dentin treated with HEMA primers *Dental Materials* **16(6)** 441-446.
40. Sandberg E, Bergenholtz G, Eklund C, & Dahlgren UI (2002) HEMA bound to self-protein promotes auto-antibody production in mice *Journal of Dental Research* **81(9)** 633-636.
41. Lonnroth EC, Wellendorf H, & Ruyter E (2003) Permeability of different types of medical protective gloves to acrylic monomers *European Journal of Oral Sciences* **111(5)** 440-446.
42. Moszner N, Salz U, & Zimmermann J (2005) Chemical aspects of self-etching enamel-dentin adhesives: A systematic review *Dental Materials* **21(10)** 895-910.
43. Ikeda M, Tsubota K, Takamizawa T, Yoshida T, Miyazaki M, & Platt JA (2008) Bonding durability of single-step adhesives to previously acid-etched dentin *Operative Dentistry* **33(6)** 702-709.
44. Yoshioka M, Yoshida Y, Inoue S, Lambrechts P, Vanherle G, Nomura Y, Okazaki M, Shintani H, & Van Meerbeek B (2002) Adhesion/decalcification mechanisms of acid interactions with human hard tissues *Journal of Biomedical Materials Research* **59(1)** 56-62.
45. Nezu T, & Winnik FM (2000) Interaction of water-soluble collagen with poly (acrylic acid) *Biomaterials* **21(4)** 415-419.
46. Torkabadi S, Nakajima M, Ikeda M, Foxton RM, & Tagami J (2008) Bonding durability of HEMA-free and HEMA-containing one-step adhesives to dentine surrounded by bonded enamel *Journal of Dentistry* **36(1)** 80-86.
47. Van Landuyt KL, Peumans M, De Munck J, Cardoso MV, Ermis B, & Van Meerbeek B (2011) Three-year clinical performance of a HEMA-free one-step self-etch adhesive in non-carious cervical lesions *European Journal of Oral Sciences* **119(6)** 511-516.

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access

48. Takahashi M, Nakajima M, Hosaka K, Ikeda M, Foxton RM, & Tagami J (2011) Long-term evaluation of water sorption and ultimate tensile strength of HEMA-containing/-free one-step self-etch adhesives *Journal of Dentistry* **39(7)** 506-512.

49. Lohbauer U, Nikolaenko SA, Petshelt A, & Frankenberger R (2008) Resin tags do not contribute to dentin adhesion in self-etching adhesives *Journal of Adhesive Dentistry* **10(2)** 97-103.

50. Frankenberger R, & Tay FR (2005) Self-etch vs etch-and-rinse adhesives: Effect of thermo-mechanical fatigue loading on marginal quality of bonded resin composite restorations *Dental Materials* **21(5)** 397-412.

51. Bittencourt D, Ezecelevski IG, Reis A, Van Dijken JW, & Loquercio AD (2005) An 18 months' evaluation of self-etch and etch-and-rinse adhesive in non-carious cervical lesions *Acta Odontologica Scandinavica* **63(3)** 173-178.

52. Loquercio AD, Bittencourt D, Baratieri LN, Reis A, & Van Dijken JW (2007) A 36- month evaluation of self-etch and etch-and-rinse adhesives in non-carious cervical lesions *Journal of the American Dental Association* **138(4)** 507-514.

53. Ritter AV, Heyman HO, Swift EL Jr, Sturdevant JR, Wilder AD Jr (2008) Clinical evaluation of an all-in-one adhesive in non-carious cervical lesions with different degrees of dentin sclerosis *Operative Dentistry* **33(4)** 370-378.

54. Perdigão J, Dutra-Corrêa M, Castilhos N, Carmo AR, Anauate-Netto C, Cordeiro HJ, Amore R, & Lewgoy HR (2007) One-year clinical performance of self-etch adhesives in posterior restorations *American Journal of Dentistry* **20(2)** 125-133.

Downloaded from https://prime-pdf-watermark.prime-prod.pubfactory.com/ at 2025-09-01 via free access