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Immediate Adhesive Properties to Dentin and Enamel of a Universal Adhesive Associated With a Hydrophobic Resin Coat

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Clinical Relevance

Multi-mode adhesives may be optimized when they are used as self-etch adhesives on dentin with a separate enamel etching step.

SUMMARY

Objectives: To evaluate the effect of acid etching and application of a hydrophobic resin coat on the enamel/dentin bond strengths and degree of conversion (DC) within the hybrid layer of a universal adhesive system (G-Bond Plus [GB]).

Methods: A total of 60 extracted third molars were divided into four groups for bond-strength testing, according to the adhesive strategy: GB applied as a one-step self-etch adhesive (1-stepSE); GB applied as in 1-stepSE followed by one coat of the hydrophobic resin Heliobond (2-stepSE); GB applied as a two-step etch-and-rinse adhesive (2-stepER); GB applied as in 2-stepER followed by one coat of the hydrophobic resin Heliobond (3-stepER). There were 40 teeth used for enamel micro-shear bond strength (µSBS) and DC; and 20 teeth used for dentin microtensile bond strength (µTBS) and DC. After restorations were constructed, specimens were stored in water (37°C/24 h) and then tested at 0.5 mm/min (µTBS) or 1.0 mm/min (µSBS). Enamel-resin

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and dentin-resin interfaces from each group were evaluated for DC using micro-Raman spectroscopy. Data were analyzed with two-way analysis of variance for each substrate and the Tukey test (α=0.05).

Results: For enamel, the use of a hydrophobic resin coat resulted in statistically significant higher mean enamel μSBS only for the ER strategy (3-stepER vs 2-stepER, *p*<0.0002). DC was significantly improved for the SE strategy (*p*<0.00002).

For dentin, the use of a hydrophobic resin coat resulted in significantly higher dentin mean μTBS only for the SE strategy (2-stepSE vs 1-stepSE, *p*<0.0007). DC was significantly improved in groups 2-stepSE and 3-stepER when compared with 1-stepSE and 2-stepER, respectively (*p*<0.0009).

Conclusions: The use of a hydrophobic resin coat may be beneficial for the selective enamel etching technique, because it improves bond strengths to enamel when applied with the ER strategy and to dentin when used with the SE adhesion strategy. The application of a hydrophobic resin coat may improve DC in resin-dentin interfaces formed with either the SE or the ER strategy. On enamel, DC may benefit from the application of a hydrophobic resin coat over 1-stepSE adhesives.

INTRODUCTION

A new family of dental adhesives, known as "universal" or "multi-mode" adhesive systems, has been recently introduced. These novel adhesives give the dentist the opportunity to decide which adhesive strategy to use: etch-and-rinse (ER) or self-etch (SE).[1-3] This versatile new adhesion philosophy advocates the use of the simplest option for each strategy (ie, one-step self-etch [1-stepSE] or two-step etch-and-rinse [2-stepER] adhesive).

It has been reported that 1-stepSE adhesives result in water permeability in dentin,[4-6] as well as osmotic blistering in enamel, which may affect clinical durability.[7] Due to equivalent water contents between 1-stepSE adhesives and the new multi-mode adhesive solutions, degradation of the bonding interface might also occur with the latter. In fact, a recent *in vitro* study[3] showed that a multi-mode adhesive applied as a 2-stepSE resulted in higher bond strengths and increased degree of conversion, compared with other simplified universal adhesives. On the other hand, prior application of phosphoric acid with multi-mode adhesives improved the bond strength to enamel but negatively affected the dentin hybridization quality.[8] It is still controversial whether acid etching prior to the application of 1-stepSE adhesives affects the respective dentin bond strengths.[9-12]

One-step SE adhesives result in thin adhesive layers that are prone to polymerization inhibition by oxygen.[13] The monomer solutions are composed of high concentrations of hydrophilic and/or ionic resin monomers.[14] The presence of up to 40% water in the composition of SE adhesives[15] triggers the dissociation of the weak acidic methacrylate monomers into ionized forms for permeation into the smear layer and underlying mineralized dentin.[14,16]

However, excess water may reduce the performance of adhesives by inhibiting the optimal copolymerization of the adhesive monomers,[17,18] leading to phase separation.[19,20] These mechanisms compromise the final structure of the polymer and its mechanical properties,[21] accelerating degradation and resulting in lower resin-dentin bond strength.[22-24] Therefore, the placement of an additional hydrophobic resin coat has been advocated to increase the performance of 1-stepSE adhesives both *in vitro*[25-28] and clinically.[29,30] Due to the recent introduction of multi-mode adhesives, there is no evidence of the effect of a hydrophobic bonding resin on their behavior.

Dissolved hydroxyapatite crystals and residual smear layer are incorporated in the hybridized complex of SE adhesives.[31,32] Except for very acidic SE systems,[33,34] the whole extension of the demineralized dentin depth is impregnated with resin monomers, preventing the technique sensitivity characteristic of bonding to moist etched dentin.[35-37] A disadvantage of the SE approach, specifically one-step adhesives, is the reduction in enamel bonding effectiveness.[38,39] The increase in surface area in intact and ground enamel obtained with SE adhesives is lower than that achieved with phosphoric acid.[39] The performance of 1-stepSE adhesives improves when enamel is etched with phosphoric acid.[10]

This study compared the enamel microshear (μSBS) and dentin microtensile bond strengths (μTBS) of the multi-mode adhesive G-Bond Plus (GB; GC Corporation, Tokyo, Japan) (also available as G-ænial Bond), applied as an ER or as a SE adhesive, in combination with one coat of the hydrophobic resin Heliobond (Ivoclar Vivadent, Schaan, Liechtenstein). The *in situ* degree of conversion (DC), in enamel and dentin, of the adhesive interface was also evaluated. The hypotheses tested were that the application of a hydrophobic resin coat after GB would not influence 1) the enamel and dentin bond strengths; 2) the DC of the adhesive at the enamel- and dentin-resin interfaces.

METHODS AND MATERIALS

Tooth Selection and Preparation

A total of 60 extracted, caries-free, human third molars were used. The teeth were collected after obtaining the patients' informed consent under a protocol approved by the local Ethics Committee Review Board. The teeth were disinfected in 0.5% chloramine, stored in distilled water, and used within six months after extraction.

A flat occlusal dentin surface was exposed in 20 teeth after wet grinding the occlusal enamel with #180-grit silicon-carbide (SiC) paper for 60 seconds. The exposed dentin surfaces were further polished with wet #600-grit SiC paper for 60 seconds to standardize the smear layer. These teeth were used for dentin microtensile bond strength (μTBS) and measurement of *in situ* degree of conversion in dentin-resin interfaces.

Four flat enamel surfaces (buccal, lingual, and proximals) were exposed in 40 teeth after wet grinding the enamel with #180-grit SiC paper for 60 seconds. The enamel surfaces were further polished with wet #600-grit SiC paper for 60 seconds. Twenty teeth were used for enamel microshear bond strength (μSBS), whereas the remaining 20 teeth were used for measurement of *in situ* DC in enamel-resin interfaces.

Experimental Design

The enamel (n=40) and dentin (n=20) specimens were randomly assigned into four groups according to the combination of the independent variables: adhesive strategy (ER or SE) and the hydrophobic resin coating (with or without). All teeth for each test (μSBS, μTBS, and DC) were randomized in block (http://www.sealedenvelope.com). A person not involved in the research protocol performed this procedure using computer-generated tables.

In all groups, the universal adhesive system GB (GC Corporation, Tokyo, Japan) was used: 1) GB applied as a 1-stepSE adhesive; 2) GB applied as in 1-stepSE followed by one coat of a hydrophobic resin coat (Heliobond, Ivoclar Vivadent, Schaan, Liechtenstein) (2-stepSE); 3) GB applied as a 2-stepER adhesive; and 4) GB applied as in 2-stepER followed by one coat of Ivoclar Vivadent Heliobond (3-stepER). All details regarding the adhesive composition are displayed in Table 1.

Restorative Procedure

The adhesive system was applied according to the manufacturer's instructions, except that the manufacturer does not recommend dentin etching with phosphoric acid. Please refer to Table 1 for more details.

After the bonding procedures, all teeth received a nanofilled composite restoration (Filtek Z350, 3M ESPE, St Paul, MN, USA) in two increments of 2 mm each. Each increment was light-polymerized for 40 seconds using an LED light-curing unit set at 1200 mW/cm^2 (Radii-cal, SDI Limited, Bayswater, Victoria, Australia). A radiometer (Demetron LED Radiometer, Kerr Sybron Dental Specialties, Middleton, WI, USA) was used to check the light intensity after finishing five specimens.

Specimen Preparation for Dentin μTBS

After storage of the restored teeth in distilled water at 37°C for 24 hours, the dentin specimens were longitudinally sectioned in mesiodistal and buccal-lingual directions across the bonded interface with a low-speed diamond saw (Isomet, Buehler Ltd, Lake Bluff, IL, USA) to obtain resin-dentin sticks with a cross-sectional area of approximately 0.8 mm^2 measured with a digital caliper (Digimatic Caliper, Mitutoyo, Tokyo, Japan). All specimens, from each tooth, were used for the μTBS evaluation, except that two sticks were randomly selected for measurement of the *in situ* DC.

Resin-dentin bonded sticks were attached to a grooved Geraldeli jig[40] (Odeme Biotechnology, Joaçaba, Santa Catarina, Brazil) with cyanoacrylate adhesive and tested in tension (Model 5565, Instron, Canton, OH, USA) at 0.5 mm/min until failure. The most peripheral sticks were discarded. The μTBS were calculated by dividing the load at failure by the cross-sectional bonding area.

The failure mode was classified as cohesive (C; failure exclusively within dentin or resin composite), adhesive (A; failure at the resin-dentin interface), or mixed (M; failure at the resin-dentin interface that included cohesive failure of the neighboring substrates). The failure mode analysis was performed under a stereomicroscope at 100× magnification (Model SZ40, Olympus, Tokyo, Japan).

Specimen Preparation for Enamel μSBS

Prior to applying the adhesive, each tooth was mounted in a polyvinyl chloride ring filled with acrylic resin (AutoClear, DentBras, Pirassununga, São Paulo, Brazil), displaying the buccal enamel

Table 1: *Adhesive Materials (Batch Number), Composition, and Application Mode of the Adhesive Systems Used*

Materials (Batch number)	Composition	SE Strategy		
Heliobond (N37749)	Bis-phenol glycidyl methacrylate (bis-GMA), triethylenedimethacrylate (TEGDMA)		**Without Hydrophobic Bonding Resin**	**With Hydrophobic Bonding Resin**
G-Bond Plus (1102221)	Acetone, dimethacrylate, triethylenedimethacrylate (TEGDMA), 4-methacryloyloxyethyl trimellitic acid (4-MET), phosphoric acid ester monomer, silicon dioxide, photo initiator	Dentin	1. Apply adhesive using a microbrush. 2. Leave undisturbed for 10 s after the application. 3. Dry thoroughly for 5 s with oil-free air under maximum air pressure. Use vacuum suction to prevent splatter of the adhesive. 4. Light-cure for 10 s.	5. After applying the adhesive in the SE mode, apply a very thin layer of Heliobond with a microbrush. 6. Air blow to achieve an optimally thin layer. 7. Light-cure for 10 s.
		Enamel	1. Apply adhesive using a microbrush 2. Leave undisturbed for 10 s after the application. 3. Dry thoroughly for 5 s with oil free air under maximum air pressure. Use vacuum suction to prevent splatter of the adhesive. 4. Light-cure for 10 s.	5. After applying adhesive in the SE mode, apply a very thin layer of Heliobond with a microbrush. 6. Air blow to achieve an optimally thin layer. 7. Light-cure for 10 s.
Filtek Z350 (7WN)	Bis-GMA, UDMA (urethane dimethacrylate), TEGDMA, Bis-EMA (ethoxylated bisphenol-A dimethacrylate), silanated silica, silanated zirconia, photoinitiators	N/A	N/A	

surface on the top of the cylinder. The delimitation of the bonding area was performed according to Shimaoka and others (2011).[41] An acid-resistant, double-faced adhesive tape (Adelbras Ind e Com Adesivos Ltda, São Paulo, Brazil) was perforated with a Hygenic Ainsworth-style rubber-dam punch (Coltene, Alstätten, Switzerland).[41]

After the application of the adhesive system, polyethylene Tygon tubes (Tygon Medical Tubing Formulations 54-HL, Saint Gobain Performance Plastics, Akron, OH, USA) with an internal diameter of 0.8 mm were sectioned to obtain 0.5 mm-high matrices. A second lateral section was made to reduce the external diameter of the matrix. Each matrix was positioned over the double-faced tape with the lumen coincident with a perforation. An operator trained in the μSBS technique positioned seven to nine matrices per tooth. Resin composite was carefully packed inside each tube, and a clear Mylar matrix tape was placed over the filled tube and pressed gently into place. Resins were light-cured for 20 seconds. All restorative procedures were made under magnifying loupes.

After storage of the restored teeth in distilled water for 24 hours at 37°C, the Tygon tubes and the double-faced adhesive tape were carefully removed, exposing the composite cylinders. Each specimen was examined under a stereomicroscope at 10× magnification to identify those with evidence of air bubbles or gaps at the interface, which were discarded.

The specimens were attached to a shear-testing fixture (Odeme Biotechnology) and tested in a universal testing machine (Kratos IKCL 3-USB, Kratos Equipamentos Industriais Ltda, Cotia, São Paulo, Brazil). A thin wire (0.2 mm diameter) was looped around the base of each composite cylinder, making contact with half of its circumference, always keeping the setup aligned (resin-enamel interface, the wire loop, and the center of the load cell) to ensure the correct orientation of the shear forces.[42] A shear load was applied at a crosshead of 1 mm/min until failure. The μSBS values were calculated by dividing the load at failure by the surface area (mm^2) to determine the shear bond strength in megapascals.

Table 1: *Adhesive Materials (Batch Number), Composition, and Application Mode of the Adhesive Systems Used (ext.)*

Materials (Batch number)	**ER Strategy**	
Heliobond (N37749)	**Without Hydrophobic Bonding Resin**	**With Hydrophobic Bonding Resin**
G-Bond Plus (1102221)	1. Apply 34% phosphoric acid gel (Scotchbond Universal Etchant, 3M ESPE, St Paul, MN, USA) for 10 s. 2. Rinse for 5 seconds and gently dry. 3. Apply adhesive using a microbrush. Leave undisturbed for 10 s after the application 4. Dry thoroughly for 5 s with oil free air under maximum air pressure. 5. Light-cure for 10 s. Note: The manufacturer does not recommend dentin etching with phosphoric acid.	6. After applying the adhesive in the ER mode, apply a very thin layer of Heliobond with a microbrush . 7. Air blow to achieve an optimally thin layer. 8. Light-cure for 10 s.
	1. Apply 34% phosphoric acid gel for 10 s. 2. Rinse for 5 seconds and gently dry. 3. Apply adhesive using a microbrush. Leave undisturbed for 10 s after the application. 4. Dry thoroughly for 5 s with oil free air under maximum air pressure. 5. Light-cure for 10 s.	6. After applying the adhesive in the ER mode, apply a very thin layer of Heliobond with a microbrush 7. Air blow to achieve an optimally thin layer 8. Light-cure for 10 s
Filtek Z350 (7WN)		

Degree of Conversion *in situ*

Two resin-dentin bonded sticks from each tooth prepared for μTBS and the remaining 20 teeth prepared for μSBS were used for measurement of *in situ* DC in enamel. The adhesive interface of each bonded stick was wet polished with #1500-, #2000-, and #2500-grit SiC paper for 15 seconds each. Then they were ultrasonically cleaned for 20 minutes in distilled water and stored in water for 24 hours at 37°C prior to performing the DC readings. The micro-Raman spectroscopy analysis was carried out using Senterra equipment (Bruker Optik GmbH, Ettlingen, Baden-Württemberg, Germany). The micro-Raman spectrometer was first calibrated for zero and then for coefficient values using a silicon specimen. Specimens were analyzed using the following micro-Raman parameters: 20-mW neon laser with 532-nm wavelength, spatial resolution of ≈3 μm, spectral resolution ≈5 cm^{-1}, accumulation time of 30 seconds with 6 coadditions, and magnification of 100× (Olympus UK, London, UK) to a beam diameter of ≈1 μm. Spectra were taken at the dentin-adhesive and enamel-adhesive interface at three different sites for each specimen. The average value of the measurements taken from the same tooth was used for statistical purposes. Spectra of uncured adhesives were taken as reference. Post-processing of spectra was performed using the dedicated Opus Spectroscopy Software, version 6.5 (Bruker Optik GmbH). The ratio of double-bond content of monomer to polymer in the adhesive was calculated according to the following formula:

$$DC(\%) = \left(1 - \frac{R_{(cured)}}{R_{(uncured)}}\right) \times 100,$$

where R is the ratio of aliphatic and aromatic peak areas at 1639 cm^{-1} and 1609 cm^{-1} in cured and uncured adhesives, respectively. The *in situ* DC values of all resin-dentin and enamel-bonded specimens from the same tooth were averaged for statistical purposes.

Statistical Analysis

A power analysis was calculated separately for enamel μSBS and for dentin μTBS using $\alpha = 0.05$ and a power of 80%, using mean bond strengths reported in the literature for G-Bond, the predecessor of GB.

The resin-dentin μTBS and resin-enamel μSBS of all specimens (with adhesive/mixed failure) from the same tooth were averaged for statistical purposes. Similarly, the same procedure was performed for the DC measurements so that the experimental unit in this study was the tooth. Specimens with cohesive and premature failures were not included in data analysis. Data from μTBS and μSBS were analyzed separately using two-way analysis of variance

(ANOVA) (adhesive strategy vs hydrophobic resin coat) and a Tukey *post hoc* test at $\alpha = 0.05$. For *in situ* DC, the data were analyzed with three-way ANOVA (adhesive strategy vs hydrophobic resin coat vs. substrate) and a Tukey *post hoc* test at $\alpha = 0.05$.

RESULTS

Bond Strengths

The use of a hydrophobic resin coat resulted in statistically significant higher mean enamel μSBS for the ER strategy (3-stepER vs 2-stepER, $p<0.0002$; Table 2). All other groups had a statistically similar mean μSBS ($p>0.05$; Table 2).

For dentin, the use of a hydrophobic resin coat resulted in a significantly higher mean μTBS for the SE strategy (2-stepSE vs 1-stepSE, $p<0.0007$; Table 2) but not for the ER strategy. All other mean μTBS were statistically similar ($p>0.05$; Table 2).

For dentin μTBS, the majority of the specimens (86.6% to 95.1%) showed adhesive/mixed failures (Table 3). For enamel μSBS, the majority of the specimens (86.0% to 96.6%) showed adhesive/mixed failures (Table 3).

Degree of Conversion

The use of a hydrophobic resin coat significantly improved the DC in dentin irrespective of the bonding strategy ($p<0.0009$; Table 4). In enamel, an increase in the DC was observed only in the SE strategy ($p<0.00002$; Table 4). The highest DC was found in dentin for both strategies when the hydrophobic bonding resin was used.

DISCUSSION

SE dental adhesives are a sophisticated blend of hydrophilic and hydrophobic reactive monomers and mono-functional comonomers, polymerization initiators, at least two solvents including water, cross-linking monomers, stabilizers, and filler particles.[14] Contemporary SE adhesives contain specific monomer molecules that combine unsaturated polymerizable functions with carboxylate or phosphate acidic groups.[14,43]

The composition of GB or G-ænial Bond, a multimode adhesive, is similar to that of 1-stepSE adhesives. GB is a new version of the 1-stepSE adhesive G-Bond (GC Corporation). The UDMA monomer was replaced in the newer version with a different dimethacrylate monomer; whereas, the concentration of the phosphate monomer was increased[8] to make the monomer solution more acidic (pH=1.5 vs pH=2.0, respectively,[8] for GB and G-Bond). The newest version is, therefore, a mild one-bottle SE adhesive indicated as a "total" SE adhesive or as a "partial" SE adhesive[8] with selective enamel etching. The respective manufacturer does not recommend using GB on phosphoric acid-etched dentin. Nevertheless, we used this adhesive experimentally as an ER adhesive due to the fact that some clinicians may etch dentin inadvertently.

Concerns about incomplete adhesive infiltration of ER adhesives into the collagen network of the demineralized zone prompted research on the hermetic seal of the hybrid layer against silver particles. Reports on water permeation and sorption within the hybrid layer and adhesive resin films are related to polymer hydrophilicity.[44,45] The acidic monomer solution in SE adhesives must be able to simultaneously demineralize and infiltrate dentin to form a hybrid layer that has been shown to have fewer defects than that of ER adhesives.[8] In fact, Hanabusa and others[8] described more defects within the dentin hybrid layer formed by GB when used as an ER adhesive than when used as a SE adhesive.

Our results showed that the use of a hydrophobic resin coat in dentin increased the mean bond strengths for the SE approach, which has been reported before in several studies with other SE adhesives.[25-28] The monomer solutions from 1-stepSE adhesives lack a nonsolvated resin coating,[46] which makes them permeable membranes.[4-7] This permeable structure would allow rapid dentinal fluid transudation across the polymerized adhesive,[15] specifically in 2-hydroxyethyl-methacrylate (HEMA)-containing adhesives.[47]

The mono-functional comonomer HEMA acts as a solvent and helps prevent hydrophilic and hydrophobic phase separation.[20,43,48] However, HEMA may retain water, compromising the DC and resulting in hydrolytic degradation. Together these factors reduce the durability of the adhesive interface over time.[4,48]

Theoretically, the absence of HEMA in GB, as well as in its predecessor G-Bond, may result in longer stability of the resin-dentin interface compared with adhesives that contain HEMA[49] because water sorption is more pronounced when HEMA is present.[47] On the other hand, the lack of HEMA may result in phase separation at the interface, previously observed with G-Bond,[48] which may be a limiting factor for improved performance of the material.

Table 2: *Mean and Standard Deviation (MPa) of Microshear (μSBS) and Microtensile Bond Strength (μTBS) of the Experimental Groups, as Well as the Statistical Significance*[a]

Adhesive System	Groups	μSBS Enamel	μTBS Dentin
G-Bond Plus	Self-etch without bond	14.7 ± 1.1 B	13.4 ± 1.3 b
	Self-etch with bond	15.0 ± 2.7 B	20.4 ± 1.5 a
	Etch-and-rinse without bond	15.9 ± 2.8 B	19.1 ± 0.7 a
	Etch-and-rinse with bond	20.6 ± 3.4 A	17.6 ± 1.2 a

[a] Identical uppercase (enamel) and lowercase (dentin) letters indicate the means are not statistically different (Tukey test; $p<0.05$).

The mean dentin μTBS obtained in our study with GB was somewhat lower than those obtained by other research groups.[8,50] It has been demonstrated that the mechanical properties of GB are lower than those of other 1-stepSE adhesives.[47] In 2002 and 2005, Takahashi and others[23] and Reis and others,[24] respectively, reported that there is a positive correlation between dentin microtensile bond strengths and the ultimate tensile strength of the adhesive, which would explain the low dentin bond strengths obtained with GB in the present study.

Additionally, factors related to the methodology may have accounted for this difference in the mean μTBS. In the Hanabusa and others study,[8] authors only used nine central sticks from each tooth to reduce substrate variability, whereas in our study we used sticks from the entire interface. One study reported lower μTBS for peripheral specimens than for centrally located specimens.[51] Furthermore, the cross-head speed in our study was 0.5 mm/min, whereas in the Hanabusa and others study[8] it was 1.0 mm/min. A comparative study reported higher μTBS for Clearfil SE Bond when greater cross-head speed was used. A more uniform stress-time pattern was observed for 1 mm/min.[52] In the case of the 2011 Goracci and others study,[50] although the authors used the same cross-head speed as in our study, they applied GB on dentin under agitation, not following the manufacturer's instructions (Table 1). It has been shown that dynamic application of SE adhesives results in greater bond strengths.[53,54]

The DC measured in the dentin-resin interfaces was significantly higher when a hydrophobic resin coat was used. This difference was expected, according to the previous literature finding[55,56] where 1-stepSE was compared with 2-stepSE adhesives. However, an increase in DC has not been previously reported after adding an extra hydrophobic resin coat to a specific 1-step adhesive.

One-step SE and 2-stepER adhesives may exhibit droplets from water attraction and osmosis through the cured adhesive layer.[57-60] Osmosis droplets are observed at the transition between the adhesive layer of 1-stepSE and 2-stepER adhesives and the composite resin material.[57-60] This transition contains uncured monomers from the oxygen-inhibition layer,[48,57,58] which would have resulted in decreased DC in our study. The hydrophobic resin coat would have copolymerized with the uncured surface of the adhesive layer from the 1-step adhesive, resulting in higher DC due to the consumption of residual double bonds.

For enamel, we would have expected an increase in bond strengths compared with the original G-

Table 3: *Number and Percentage of Specimens (%) According to Fracture Pattern Mode From the Experimental Groups in the Microshear (μSBS) and Microtensile Bond Strength (μTBS) Tests*

Adhesive System	Adhesive Strategy	Hydrophobic Resin Coat	Fracture Pattern (μSBS)			
			A	C	A/M	PF
G-Bond Plus	Self-etch	Without	33 (57.9)	6 (10.5)	16 (28.1)	2 (3.5)
		With	39 (61.9)	5 (7.9)	17 (27.0)	2 (3.2)
	Etch-and-rinse	Without	26 (49.1)	3 (5.7)	23 (43.3)	1 (1.9)
		With	39 (66.1)	1 (1.7)	18 (30.5)	1 (1.7)
G-Bond Plus	Self-etch	Without	42 (80.8)	2 (3.8)	3 (5.8)	5 (9.6)
		With	56 (90.3)	0 (0.0)	2 (3.2)	4 (6.5)
	Etch-and-rinse	Without	44 (72.2)	1 (1.6)	14 (22.9)	2 (3.3)
		With	42 (82.4)	0 (0.0)	6 (11.8)	3 (5.8)

Abbreviations:A, adhesive fracture mode; A/M, adhesive/mixed fracture mode; C, cohesive fracture mode; PF, premature failures.

Table 4: *Mean and Standard Deviation (%) of* In Situ *Degree of Conversion (DC) Values of the Experimental Groups, as Well as the Statistical Significance*[a]

Adhesive System	Groups	DC% Enamel	DC% Dentin
G-Bond Plus	Self-etch without bond	72.7 ± 4.9 D	58.3 ± 4.8 F
	Self-etch with bond	83.1 ± 4.2 B	92.3 ± 5.2 A
	Etch-and-rinse without bond	81.8 ± 3.7 B,C	69.3 ± 5.5 E
	Etch-and-rinse with bond	79.4 ± 2.9 C	94.8 ± 4.5 A

[a] Identical uppercase letters indicate the means are not statistically different (Tukey test; $p<0.05$)

Bond applied as a SE adhesive, because pH has decreased to 1.5 in the multi-mode version. For the original G-Bond (pH=2.0), in a 2006 study Perdigão and others[61] obtained 18.3 MPa to ground enamel, whereas in 2007 De Munck and others[62] obtained a mean enamel μTBS of 19.8 MPa. In 2013, Reis and others[63] obtained a mean of 17.2 MPa for G-Bond to ground enamel. For GB (pH=1.5) Hanabusa and others[8] obtained a mean enamel μTBS of 23.1 MPa. In our study, we obtained slightly lower enamel bond strengths with GB, 14.7-15.0 MPa. This may have been the result of the wider bonding areas required in the μSBS as compared with the μTBS. The μSBS test has resulted in lower enamel bond strengths for the SE adhesives Clearfil SE Bond and Adper Prompt L-Pop when compared with their μTBS values.[64] It has been reported that μTBS values tend to be higher because the defect concentration in the small cross-sectional interfacial areas is lower.[65]

Although Pashley and Tay[39] reported that the cohesive strength of the adhesive layer might be more relevant than the etching potential of an enamel adhesive for acidic SE adhesives,[10,66] the hydrophobic resin coat application, which increases the cohesive strength of the adhesive layer, was not able to improve the enamel-dentin bonds in our study. This similarity in enamel bond strengths with and without the hydrophobic resin coat may be a result of the poor enamel-etching pattern obtained with the application of the SE adhesive, because the ability of the acidic agent to chemically etch enamel is directly related to the respective enamel bond strengths. The additional hydrophobic resin coat is unable improve bond strengths[27,63] because it has no influence in the etching pattern.

In spite of the similarity in mean enamel μSBS, DC was significantly higher when GB was used in SE mode with the extra hydrophobic resin coat (2-stepSE). In fact, a good correlation was previously observed between bond strengths and DC when SE adhesives were applied on enamel[67] but not when ER adhesives were applied.[68] Two factors may have played a role in this increase in DC for the 2stepSE compared with the 1-stepSE on enamel. First, the presence of residual uncured monomers on the top of the cured GB adhesive would have caused lower DC. This was probably reduced with the extra hydrophobic coat. Second, the evaporation of all water from the interface, which prevents the approximation of the polymer chains, would have been more difficult to accomplish in the 1-stepSE group due to the presence of microscopic osmotic blisters.[7] The hydrophobic resin coat application may have aided in the evaporation of solvents and residual water.

One of the limitations of our study has to do with the lack of thermal fatigue or long-term water storage. Thermal fatigue may not be relevant because the susceptibility of adhesives to thermal fatigue depends on the specific composition of each adhesive.[69] However, water storage may correlate better with clinical behavior. In fact, Heintze and others[70] reported that dentin μTBS of adhesive systems after water storage for six months showed a good correlation with marginal discoloration in clinical Class V restorations. With this in mind, future studies in our laboratory will analyze the effect of long-term water storage on the *in vitro* performance of the multi-mode adhesive GB.

We failed to reject the first null hypothesis, given that the application of a hydrophobic resin coat after GB increased the enamel μSBS for the ER adhesion strategy and the dentin μTBS for the SE adhesion strategy. We also failed to reject the second null hypothesis because the application of a hydrophobic resin coat after GB increased *in situ* DC for enamel-resin interfaces when GB was used in SE mode and for dentin-resin interfaces for both the SE and the ER adhesion strategies.

CONCLUSIONS

Within the limitations of this *in vitro* study, the use of a hydrophobic resin coat may be beneficial for the selective enamel etching technique, because it improves bond strengths to enamel when applied with the ER strategy, and to dentin when used with the SE adhesion strategy. The application of a hydrophobic resin coat may improve DC in resin-dentin interfaces formed with either the SE or the ER strategy. On enamel, DC may benefit from the application of a hydrophobic resin coat over 1-stepSE adhesives.

Conflict of Interest

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

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