

# A Comprehensive Laboratory Screening of Three-Step Etch-and-Rinse Adhesives

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## Clinical Relevance

The evaluation of several bonding and mechanical properties in short-term laboratory screening tests allowed better screening of the adhesives available on the market without requiring long-term studies.

## SUMMARY

**Objectives:** This study evaluated several bonding (microtensile bond strengths [ $\mu$ TBS], nano-

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leakage [NL], and *in situ* degree of conversion [ISDC] on dentin) and mechanical properties (ultimate tensile strength [UTS], degree of conversion [DC], water sorption [WS], and solubility [SL] in water) of four three-step etch-and-rinse adhesives in the short term.

**Methods:** A total of 28 molars were used in this study. The dentin surfaces were bonded with the following adhesives: All-Bond 3 (ALB3); Fusion Duralink (FSDL); Optibond FL (OBFL), and Scotchbond Multi-Purpose (SBMP). After each adhesive-system application, composite resin build-ups were added. For bonding tests, specimens were sectioned in order to obtain bonded sticks. The sticks were divided to be tested for  $\mu$ TBS (0.5 mm/min), for NL (n=2), and ISDC (n=2). For NL, they were immersed in 50% silver nitrate and analyzed by scanning electron microscopy. For ISDC, the hybrid layer was evaluated by micro-Raman spectroscopy. An hourglass-shaped matrix (UTS) or disk-shaped matrix (WS and SL) was filled with primer and adhesive (1:1 ratio) and light-polymerized. For UTS evaluation, the specimens were tested under tension. For WS and SL, specimens were desiccated and stored

in distilled water to evaluate water diffusion kinetics over a 28-day period. The DC of the adhesives was evaluated by Fourier transformed infrared spectroscopy. The data from each test were analyzed by appropriate statistical methods.

**Results:** OBFL resulted in the highest  $\mu$ TBS, lower NL, higher ISDC and DC, and higher UTS than other adhesives ( $p < 0.05$ ), as well as lower WS (similar to ALB3 and FSDL) and SL (similar to ALB3 and SBMP) ( $p > 0.05$ ). ALB3 showed a higher NL and the lowest DC value. FSDL showed the highest NL and SL and the lowest ISDC. SBMP showed the lowest pattern of WS ( $p < 0.05$ ).

**Conclusion:** OBFL showed the best results in all the properties evaluated, and it can be considered the gold standard of the three-step etch-and-rinse adhesive systems.

## INTRODUCTION

The use of 85% phosphoric acid to improve the infiltration of an acrylic resin into enamel was the genesis of all dental adhesive systems used in dentistry.<sup>1</sup> The interaction of dental adhesives with enamel and dentin results from resin monomers permeating the microporosities created by acidic agents and polymerized monomers subsequently becoming wrapped around the exposed hydroxyapatite crystals and/or collagen fibers.<sup>2</sup>

In spite of the different classifications that have appeared within the last two decades, dental adhesives are currently classified according to how they interact with the dental substrate and thus are divided into etch-and-rinse (ER) and self-etch (SE) adhesives.<sup>2</sup> The number of application steps categorizes adhesive systems within each of the two strategies. For example, ER adhesive systems can be available in a three-step and a two-step protocol, depending on whether the primer and bonding resin are separate or combined in one bottle.

Although three-step ER adhesives have been considered the clinical gold standard in dental bonding,<sup>3-6</sup> this issue seems to be controversial, according to recent systematic reviews of the literature.<sup>3,5,7-9</sup> The retention rates of three-step ER systems are quite variable, with an annual failure rate varying from 0% to 16%.<sup>3</sup> Furthermore, Peumans and others<sup>3</sup> in their systematic review reported that at least three out of 10 three-step ER adhesives did not meet the requirements of the American Dental Association guidelines for provi-

sional and full acceptance of the restorations, and in some of the clinical studies reviewed, they did not gain full acceptance.

It is claimed that the use of a hydrophobic resin coating in the three-step ER is responsible for better *in vitro* and *in vivo* performance than that of their 2-step counterparts<sup>10</sup>; however, one cannot rule out the role of the chemistry of three-step ER systems, which varies considerably depending on the brand.

For instance, the type of solvent presented in the formulation of the primer has been mentioned as a factor affecting the performance of the materials, with the ethanol-based systems performing better than the acetone-based types.<sup>4</sup> Moreover, the bonding resin usually claimed to be a hydrophobic resin coating can contain hydrophilic monomers, such as hydroxyl-ethyl-methacrylate (HEMA), which may ultimately influence the bond performance.<sup>11</sup> Other differences such as filler loading may also impact the material's performance.

Based on the foregoing, the aim of this study was to compare several bonding and mechanical properties of three-step ER adhesives available on the market. The microtensile bond strengths ( $\mu$ TBS), nanoleakage (NL), *in situ* degree of conversion (ISDC) on dentin and ultimate tensile strength (UTS), degree of conversion (DC), water sorption (WS), and solubility in water (SL) for all the adhesives were also evaluated.

## METHODS AND MATERIALS

### Tooth Selection and Preparation

A total of 28 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 after wet grinding the occlusal enamel with 180-grit silicone-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 testing resin-dentin  $\mu$ TBS, NL, and measurement of ISDC.

### Adhesive and Restorative Procedure

Teeth were randomly assigned for bonding with four different materials ( $n=7$ ): All-Bond 3 (ALB3; Bisco Inc, Schaumburg, IL, USA); Fusion Duralink (FSDL;

Table 1: Adhesive Materials (Manufacturer), Composition (Batch No.), and Application Mode of the Adhesive Systems Used

Adhesives (Manufacturer)	Composition (Batch No.)	Mode of Application
All-Bond 3 (Bisco)	Etchant: UNI-ETCH-37: 37% phosphoric acid, polymer thickener (1100005635). Adhesive: Part A ethanol, sodium benzene sulfinate dehydrate, NTG-GMA (1100005448); Part B: Bis(glyceryl 1,3 dimethacrylate) phosphate, HEMA, biphenyl dimethacrylate (1100005448). Resin: Bis-GMA, urethane dimethacrylate, Sr glass (1100001528).	1. Application of 37% phosphoric acid (15 s) 2. Rinse (15 s). 3. Air-dry, leaving the preparation visibly moist. 4. Mix equal amounts of part A and B in mixing well with a microbrush for 5 s. 5. Apply one coat under finger pressure for 15-20 s. 6. Air-dry under maximum pressure for 15 s. 7. Light-polymerize for 10 s at 1200 mW/cm <sup>2</sup> . 8. Apply a thin layer of All-Bond Resin. 9. Light-polymerize for 10 s at 1200 mW/cm <sup>2</sup> .
Fusion Duralink (Angelus)	Etchant: 37% orthophosphoric acid, water, thickener, pigments (22458). Primer: methacrylate esters, ethanol, water (14545). Adhesive: methacrylate esters, photoinitiators, polymerization accelerators (14549).	1. Apply the phosphoric acid gel on dentin for 15 s. 2. Rinse the acid gel with a water spray for 15 s. 3. Remove the excess water with absorbent paper or a clean brush, leaving the surfaces slightly wet (shiny). 4. With a disposable brush, apply a layer of primer on dentin and rub it slightly for 30 s. 5. Apply a light air jet from a distance of 10 cm for 10 s; the dentin should be shiny and without excess primer. 6. With another disposable brush, apply a thin and uniform layer of adhesive on dentin. 7. Light-polymerize for 10 s at 1200 mW/cm <sup>2</sup> .
Optibond FL (Kerr)	Etchant: 37.5% phosphoric acid, water, silica thickener (3676600). FL Prime: HEMA, GPDM, MMEP, water, ethanol, CQ, BHT (3539622). FL Adhesive: Bis-GMA, HEMA, GDMA, CQ, ODMAB, filler (fumed SiO <sub>2</sub> , barium aluminoborosilicate, Na <sub>2</sub> SiF <sub>6</sub> ), coupling factor A174 (approximately 48 wt% filled) (3538016).	1. Apply etchant on dentin for 15 s. 2. Rinse thoroughly for 15 s. 3. Air-dry for 3 s (do not desiccate). 4. Apply primer with brushing motion for 15 s. 5. Air-dry for 5 s. 6. Using same applicator, apply adhesive with light brushing motion for 15 s. 7. Air-thin for 3 s. 8. Light-polymerize for 20 s at 1200 mW/cm <sup>2</sup> .
Scotchbond Multi-Purpose (3M ESPE)	Etchant: 35% phosphoric acid, silica thickener (N261433). Primer: HEMA, polyalkenoic acid polymer, water (N322814). Adhesive: Bis-GMA, HEMA, tertiary amines, and photo-initiator (N342538).	1. Apply etchant for 15 s on dentin. 2. Rinse thoroughly for 15 s. 3. Dry for 5 s. 4. Apply primer on dentin for 10 s. 5. Dry gently for 5 s. 6. Apply adhesive. 7. Light-polymerize for 10 s at 1200 mW/cm <sup>2</sup> .

Abbreviations: BHT, butylated hydroxytoluene; Bis-GMA, bisphenol A diglycidyl methacrylate; CQ, camphorquinone; GPDM, glycerol phosphate dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; MMEP: mono-2-methacryloyloxyethyl phthalate; NTG-GMA: N-tolyglycine glycidyl methacrylate; ODMAB: 2-(Ethylhexyl)-4-(dimethylamino)benzoate.

Angelus, Londrina, Brazil); Optibond FL (OBFL; Kerr, Orange, CA, USA), and Scotchbond Multi-Purpose (SBMP; 3M ESPE, St Paul, MN, USA). Each adhesive system was applied on the flat dentin surfaces, according to the manufacturers' instructions (Table 1).

On each prepared surface a composite restoration (Filtek Z350, 3M ESPE) was built up in two increments of 2 mm and was light-polymerized for 40 seconds using a LED light-curing unit set at 1200 mW/cm<sup>2</sup> (Radii-cal, SDI Limited, Bayswater, Australia). The same light-curing unit was used throughout this study.

### Microtensile Bond Strength

After the restored teeth had been stored in distilled water at 37°C for 24 hours, they were longitudinally sectioned in the mesio-to-distal and buccal-to-lingual directions across the bonded interface, using 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<sup>2</sup>, measured with a digital caliper (Digimatic caliper, Mitutoyo, Tokyo, Japan). Four resin-dentin bonded sticks from each tooth were not tested in the tensile mode, because they were used for the ISDC and NL evaluations.

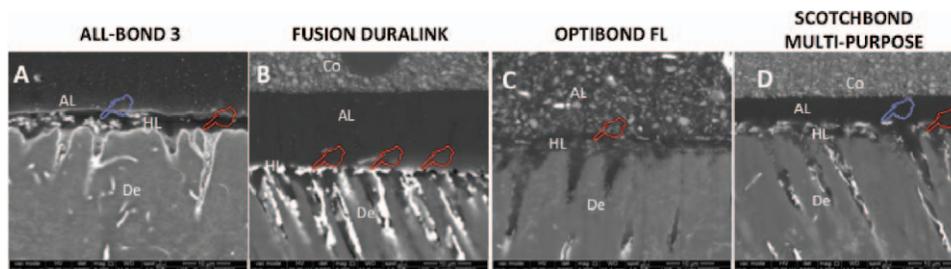


Figure 1. Representative backscatter scanning electron microscope images of the resin-dentin interfaces bonded to each one of the three-step etch-and-rinse adhesive systems tested. The amount of nanoleakage was lower and practically occurred within the hybrid layer for Optibond FL (red hand). For Fusion Duralink, the amount of nanoleakage was higher than other materials; with most silver nitrate uptake occurring throughout the entire thickness of the HL (red hands). Nevertheless, All-Bond 3 and Scotchbond Multi-Purpose showed an intermediate amount of silver nitrate uptake, which occurred in the same points of the HL (red hands) and the AL, forming so-called water trees (blue hands) (Co, composite; De, dentin; HL, hybrid layer; AL, adhesive layer).

All the remaining bonded sticks were attached to a Geraldeli jig<sup>12</sup> (Odeme Biotechnology, Joaçaba, Brazil) with cyanoacrylate adhesive and tested under tensile forces (Model 5565, Instron, Canton, OH, USA) at 0.5 mm/min until failure. The  $\mu$ TBS values were calculated by dividing the load at failure by the cross-sectional bonding area. The failure mode was classified as cohesive (failure exclusively within dentin or resin composite), adhesive (failure at the resin/dentin interface), or mixed (failure at the resin/dentin interface that included cohesive failure of the neighboring substrates). The failure mode was analyzed under a stereomicroscope at 100 $\times$  magnification (Olympus SZ40, Tokyo, Japan). Because few specimens presented premature failures, they were included in the bond-strength mean.

### Nanoleakage Evaluation

Two resin-dentin bonded sticks were placed in ammoniacal silver nitrate<sup>13</sup> in darkness (24 hours), rinsed thoroughly in distilled water, and immersed in photo-developing solution (8 hours) under a fluorescent light to reduce silver ions to metallic silver grains. Specimens were polished down with 600-, 1000-, 1200-, 1500-, 2000-, and 2500-grit SiC paper and 1 and 0.25  $\mu$ m diamond paste (Buehler Ltd) using a polishing cloth. They were ultrasonically cleaned, air-dried, mounted on stubs, and sputter-coated with carbon-gold (MED 010, Balzers Union, Balzers, Liechtenstein). Resin-dentin interfaces were analyzed in a scanning electron microscope operated in the backscattered mode (LEO 435 VP, LEO Electron Microscopy Ltd, Cambridge, UK) (Figure 1).

Three pictures from each bonded stick were taken.<sup>14</sup> The relative percentage of NL in each image was measured by a blinded researcher, using the UTHSCSA ImageTool 3.0 software program (Depart-

ment of Dental Diagnostic Science at The University of Texas Health Science Center, San Antonio, TX, USA).

### In Situ Degree of Conversion

The adhesive interfaces of the two other resin-dentin bonded sticks were wet polished with 1500-, 2000-, and 2500-grit SiC paper for 15 seconds each. They were ultrasonically cleaned for 20 minutes in distilled water and stored in water at 37°C for 24 hours prior to performing the DC readings. The micro-Raman spectrophotometer (Bruker Optik GmbH, Ettlingen, Baden-Württemberg, Germany) 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  $\approx 3 \mu$ m, spectral resolution  $\approx 5 \text{ cm}^{-1}$ , accumulation time of 30 seconds with six coadditions, and magnification of 100 $\times$  (Olympus UK, London, UK) to a  $\approx 1 \mu$ m beam diameter. Spectra were taken at the dentin-adhesive interface, at three different sites for each specimen.

Spectra of unpolymerized adhesives were taken as reference. Postprocessing of spectra was performed using the Opus Spectroscopy Software Program version 6.5 (Bruker Optik GmbH, Ettlingen, Baden-Württemberg, Germany). The ratio of the double-bond content of the monomer to the polymer in the adhesive was calculated according to the following formula:

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

where  $R$  is the ratio of aliphatic and aromatic peak areas at 1639  $\text{cm}^{-1}$  and 1609  $\text{cm}^{-1}$  in polymerized and unpolymerized adhesives.

### Ultimate Tensile Strength

An hourglass-shaped metal matrix (10 mm long, 2 mm wide, and 1 mm deep with a cross-sectional area of  $0.8 \text{ mm}^2$ ) was isolated with petroleum jelly. To simulate a clinical application, the primer was first inserted into a metal matrix and gently air-dried in accordance with the manufacturer's directions (Table 1). Then, the bonding resin was put into the metal matrix and slightly mixed with the primer using a microbrush. The mixture was again air-dried in accordance with the manufacturer's recommendations (Table 1), and all visible air bubbles trapped in the bonding resin were carefully removed. The bonding resin and the primer were added in a ratio of 1:1. A thin strip of polyester sheeting was placed over the bonding resin, and the surface was light-polymerized for 40 seconds. Eight specimens were prepared for each group, and were tested under tensile forces as described for the  $\mu\text{TBS}$  test.

### Degree of Conversion of the Adhesive Pellicle

The bonding resin was mixed with the primer in a ratio of 1:1 and placed on a thin strip of polyester sheeting in the same way as reported for the UTS. Then, the adhesive was covered with another thin strip of polyester sheeting and light-polymerized for 40 seconds. Each thin adhesive layer was carefully removed with a blade and stored in a dark and dry environment for 24 hours, after which the DC was determined by Fourier transformed infrared analysis (Spectrum 100, Perkin Elmer, Waltham, MA, USA).

The spectra of the polymerized and unpolymerized bonding resins were obtained with 32 scans at a resolution of  $4 \text{ cm}^{-1}$  in transmission mode. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak height at  $1640 \text{ cm}^{-1}$ ) against an internal standard before and after specimen polymerization. The aromatic C=C bond (peak height at  $1610 \text{ cm}^{-1}$ ) absorbance was used as an internal standard. The DC was determined by subtracting the % C=C from 100%. Five specimens were tested for each group.

### Water Sorption and Solubility

The bonding resin was mixed with the primer in a ratio of 1:1 and placed on a thin strip of polyester sheeting in the same way as reported for the UTS. Ten resin disks of each adhesive were produced in a

circular metal mold (5.8 mm diameter, 0.8 mm thick) after isolation with petroleum jelly. The primer and bonding resin were applied in a ratio of 1:1 as previously reported for the UTS test. All visible air bubbles trapped in the adhesives were carefully removed. Next, the solvent evaporation was performed with an air syringe at a distance of 10 cm for 40 seconds. A thin strip of polyester sheeting was placed on top of the adhesive, which was light-polymerized for 40 seconds to allow the specimen to be removed without permanent deformation.

WS and SL were determined according to the International Organization for Standardization (ISO) specification 4049.<sup>15</sup> Immediately after polymerization, the specimens were placed in a desiccator, transferred to a preconditioning oven at  $37^\circ\text{C}$ , and left undisturbed for 10 days. After this period, specimens were repeatedly weighed at 24-hour intervals until a constant mass ( $m_1$ ) was obtained (ie, variation was less than 0.2 mg in any 24-hour period). Thickness and diameter of the specimens were measured using a digital caliper, rounded to the nearest 0.01 mm, and these measurements were used to calculate the volume of each specimen (in  $\text{mm}^3$ ).

After this, specimens were then individually placed in sealed vials containing 10 mL of distilled water (pH 7.2) at  $37^\circ\text{C}$ . After fixed time intervals of 1, 2, 3, 4, 5, 6, 7, 14, and 28 days of storage, the vials (15 mL; Eppendorf of Brazil, São Paulo, Brazil) were removed from the oven and left at room temperature for 30 minutes. The specimens were washed in running water, gently wiped with a soft absorbent paper, weighed on an analytical balance ( $m_2$ ), and returned to the vials containing 10 mL of fresh distilled water. After 28 days of storage, the specimens were dried in a desiccator containing fresh silica gel in an oven at  $37^\circ\text{C}$  and left undisturbed for 10 days. They were weighed daily until a constant mass ( $m_3$ ) was obtained (as previously described). The initial mass determined after the first desiccation process ( $m_1$ ) was used to calculate the change in mass after each fixed time interval during the 28 days of storage in water. Changes in mass were plotted against the storage time in order to obtain the kinetics of WS during the entire period of water storage.

WS and SL over the 28 days of water storage were calculated using the following formulas:  $\text{WS} = (m_2 - m_3) / V$  and  $\text{SL} = (m_1 - m_3) / V$ .

Table 2: Number and Percentage of Specimens (%) According to Fracture Mode on Microtensile Bond-Strength Test; Means and Standard Deviations of Microtensile Bond Strength ( $\mu$ TBS), Nanoleakage (NL), and In Situ Degree of Conversion (ISDC)<sup>a</sup>

Adhesive Systems	Fracture Pattern				$\mu$ TBS (MPa)	NL (%)	In Situ DC (%)
	A	C	A/M	PF			
ALB3	39 (78)	7 (14)	1 (2)	3 (6)	41.5 ± 3.2 B	8.2 ± 2.1 b,c	73.6 ± 4.5 <sup>c</sup>
FSDL	33 (77)	4 (9)	2 (5)	4 (9)	43.5 ± 6.6 B	10.1 ± 2.0 c	66.4 ± 4.5 <sup>d</sup>
OBFL	25 (57)	4 (9)	9 (20)	6 (14)	59.6 ± 5.6 A	2.81 ± 0.8 a	92.7 ± 4.6 <sup>a</sup>
SBMP	37 (76)	8 (16)	1 (2)	3 (6)	43.9 ± 2.5 B	6.9 ± 1.8 b	83.6 ± 4.5 <sup>b</sup>

Abbreviations: A, adhesive fracture mode; A/M, adhesive/mixed fracture mode; C, cohesive fracture mode; PF, premature failures.  
<sup>a</sup> Similar capital ( $\mu$ TBS), lowercase (NL), and superscript letters (DC) are not statistically significant (Tukey test;  $p < 0.05$ ).

**Statistical Analysis**

The values originating from the same specimen for  $\mu$ TBS, NL, and ISDC were averaged for statistical purposes. The  $\mu$ TBS, NL and ISDC means for every group were expressed as the average of the seven teeth used per group. Data from  $\mu$ TBS, NL, ISDC, UTS, and DC of the adhesive pellicle were individually analyzed using one-way analysis of variance (ANOVA) and the Tukey *post hoc* test ( $\alpha=0.05$ ). Data from WS and SL were calculated for each experimental condition, and the data after 28 days were analyzed by one-way ANOVA (adhesive) and the Tukey *post hoc* test at  $\alpha = 0.05$ .

**RESULTS**

**Microtensile Bond Strengths**

The failure modes of all experimental groups are shown in Table 2. The majority of the specimens (84.4%) presented adhesive/mixed failures. Dentin and resin cohesive failures were observed in 7.0% of the specimens. A number of premature failures (8.6%) were observed.

One-way ANOVA detected significant differences between the  $\mu$ TBS values (Table 2;  $p < 0.001$ ). OBFL resulted in the highest mean  $\mu$ TBS (Table 2). All other adhesives had statistically similar mean  $\mu$ TBS ( $p > 0.05$ ).

**Nanoleakage**

Significant differences were detected in the NL values (Table 2;  $p < 0.0001$ ). OBFL showed the lowest mean NL (Table 2). SBMP showed intermediate values, but only statistically different from FSDL ( $p < 0.01$ ). The mean NL associated with ALB3 was similar to those of SBMP and FSDL ( $p > 0.05$ ). Examples of the NL pattern can be seen in Figure 1.

**In Situ Degree of Conversion**

One-way ANOVA detected significant differences in the ISDC means (Table 2;  $p < 0.00001$ ). OBFL showed the highest mean ISDC and FSDL showed the lowest (Table 2). FSDL and SBMP showed intermediate values, with the former showing the lower mean ISDC (Table 2).

**Ultimate Tensile Strength**

Statistically significant differences were detected in the UTS means (Table 3;  $p < 0.001$ ). OBFL showed the highest mean UTS (Table 3). All other materials had statistically similar mean UTS ( $p > 0.05$ ).

**Degree of Conversion**

One-way ANOVA detected statistically significant differences (Table 3;  $p < 0.00001$ ): OBFL showed the highest mean DC, whereas ALB3 resulted in the lowest (Table 3). FSDL and SBMP showed interme-

Table 3: Means and Standard Deviation of Ultimate Tensile Strength (UTS), Degree of Conversion of Adhesive Pellicle (DC), Water Sorption (WS), and Solubility (SL) of Each Adhesive System Tested<sup>a</sup>

Adhesive Systems	UTS (MPa)	DC (%)	WS ( $\mu$ g/mm <sup>3</sup> )	SL ( $\mu$ g/mm <sup>3</sup> )
ALB3	34.0 ± 5.1 B	65.4 ± 1.9 d	0.14 ± 0.04 <sup>B</sup>	0.05 ± 0.08 <sup>a</sup>
FSDL	34.8 ± 5.3 B	70.7 ± 6.8 c	0.07 ± 0.02 <sup>A</sup>	0.5 ± 0.07 <sup>b</sup>
OBFL	48.8 ± 5.2 A	93.9 ± 3.9 a	0.12 ± 0.02 <sup>A,B</sup>	0.05 ± 0.02 <sup>a</sup>
SBMP	33.3 ± 6.1 B	83.8 ± 4.6 b	0.80 ± 0.22 <sup>C</sup>	0.02 ± 0.03 <sup>a</sup>

<sup>a</sup> Similar capital (UTS), lowercase (DC), capital superscript (WS), and lowercase superscript letters (SL) are statistically similar (Tukey test;  $p < 0.05$ ).

diate values, with the latter showing the lowest mean DC (Table 3).

### Water Sorption and Solubility

Significant differences were also detected in terms of WS and SL values (Table 3;  $p < 0.001$  and  $p < 0.01$ , respectively). FSDL and OBFL showed the lowest mean WS; SBMP resulted in the highest mean WS (Table 3;  $p < 0.001$ ). FSDL showed an intermediate mean WS, which was similar to that of OBFL (Table 3;  $p > 0.05$ ). FSDL resulted in the highest mean SL in comparison with all the other materials (Table 3;  $p < 0.001$ ). All other adhesives had statistically similar mean SL ( $p > 0.05$ ).

### DISCUSSION

The results of this study confirmed that there were several differences between the three-step ER adhesive systems tested. Among the adhesive evaluated, only OBFL and SBMP have been extensively evaluated. When the immediate bond strengths of OBFL and SBMP were compared with each other, controversial results were obtained.<sup>16-23</sup> This lack of consensus among studies can be attributed to methodological differences. A systematic review of bond-strength tests<sup>24</sup> reported that SBMP and OBFL are usually reported as being similar when assessed by shear or microshear bond-strength tests. However, OBFL usually presents significantly higher bond strength values when tested in tensile and microtensile bond-strength tests such as the type observed in the present study.

An earlier study<sup>25</sup> reported that OBFL exhibited a very uniform hybrid layer, whereas the hybrid layer formed with SBMP showed a varying electron density with a less sharply demarcated transition to the unaffected dentin. This observation suggested a less-than-optimal resin infiltration, as has been reported by other authors,<sup>26-29</sup> and this is corroborated by our NL results.

SBMP contains a specific polyalkenoic acid copolymer (PAC) that was primarily added to the composition of the resin-modified glass ionomer Vitrebond (3M ESPE). PAC bonds chemically and spontaneously to hydroxyapatite in glass ionomer materials,<sup>30</sup> which may explain why an ER with PAC showed more enhanced bond strength than a PAC-free adhesive with the same composition.<sup>31</sup> On the other hand, it has been demonstrated that because PAC is a compound with a high molecular weight, it does not dissolve in the adhesive solution, which may lead to phase separation and formation of resin

globules within the polymer.<sup>28</sup> In addition, the collagen network can filter it out and the PAC can be deposited as a distinct gel on the exposed collagen network surface.<sup>28,32</sup>

In a more extreme case, the gel can hinder adequate monomer infiltration, and the hybrid layer produced would be constituted of collagen and linear polymer chains, with entrapped residual water and insufficiently removed solvent. The presence of water may reduce the degree of conversion of the material, which is shown by the presence of silver nitrate grains, thus explaining why a higher NL and a lower DC (*in situ* and from the adhesive pellicle) was observed for SBMP when compared with OBFL.

The primer of SBMP contains approximately 50 volume percent (vol%) of water, whereas the OBFL primer contains 23 vol% of water and 29 vol% of ethanol.<sup>25</sup> The high boiling temperature and low vapor pressure of water, when compared with that of ethanol, makes this solvent more difficult to remove in comparison with water-ethanol solutions.<sup>11</sup> The excess water in the adhesive film reduces the degree of conversion of SBMP and diminishes the UTS of the material by preventing molecule approximation during polymerization. A poorly polymerized adhesive is more prone to WS, as could be detected in this study.<sup>33,34</sup>

The adhesives ALB3 and FSDL also had a lower DC than SBMP did, and they did not present such a high WS. Thus, other factors apart from lower DC may be responsible for this finding. SBMP is the only material that contains the hydrophilic monomer HEMA in the bonding resin. HEMA can reduce the vapor pressure of water,<sup>35</sup> leading to solvent retention. Additionally, poly (HEMA) formed after polymerization behaves as a hydrogel, which swells and rapidly takes up water. Water droplets were found to be located adjacent to the adhesive resin-composite interface formed by HEMA-rich adhesives<sup>36,37</sup> The literature has confirmed that SBMP usually showed poor long-term *in vitro* and *in vivo* results when compared with OBFL<sup>22,38</sup> and the clinical results of this material are usually controversial.<sup>3,38</sup>

The bond strength of ALB3 and FSDL was similar to that of SBMP; however, these materials showed the lowest DC (*in situ* or from the adhesive pellicle) and the highest NL values when compared with OBFL and SBMP. This was expected, given that it was recently demonstrated that the DC is negatively correlated with the NL.<sup>39</sup> Conversion of monomer into polymer (percentage of C=C incorporated into polymer chains as C=C) plays an important role in

successful dentin bonding.<sup>40</sup> To some extent it is true that increased permeability of the adhesive layer is observed when there are unreacted monomers within the hybrid layer.<sup>41,42</sup> This results in the formation of a porous hybridoid structure with reduced sealing ability, which is prone to silver nitrate uptake,<sup>43,44</sup> as could be seen in the results of the present study. Unfortunately, the reason why ALB3 and FSDL showed higher amount of NL and lower DC is not clear, and future studies need to be conducted to test these hypothesis.

Earlier studies reported negative solubility values for three-step ER,<sup>45-47</sup> which does not agree with the present findings. Contrary to this study, in which a mixture of primer and bonding resin was used for specimen fabrication, the previous studies only evaluated the bonding resin. The mixture of the primer with the bonding resin affects the mechanical properties of the adhesive interface when compared only with the bonding resin.<sup>48,49</sup>

Materials with a high SL usually present a high level of WS. WS causes polymer swelling, thereby facilitating the elution of unreacted monomers and/or solvents trapped in the polymer network.<sup>40</sup> However, the adhesive system FSDL showed the highest SL in this study without presenting a high WS. This fact along with the low DC of this material suggests that many unbound oligomers and residual monomers were readily leached out without the need for polymer plasticization by water. The high amount of silver nitrate uptake in the adhesive layers produced by FSDL reinforces this hypothesis. Because the manufacturer does not specify the material composition, it is quite difficult to interpret the study findings based on its chemistry. Moreover, as far as we know, no published article with FSDL was found, and future studies need to be conducted to confirm the present results.

The good performance of OBFL in this study is in agreement with the literature findings. OBFL usually showed the best performance in all tests, confirming that it is the gold standard in terms of ER adhesives<sup>2-7</sup> in both laboratory<sup>18,22</sup> and clinical studies.<sup>38,50,51</sup> At least two hypotheses can be used to explain these good results. Sezinando and others<sup>52</sup> speculated that the higher bond-strength durability of this material is due to the presence of glycerol phosphate dimethacrylate, which can interact chemically with hydroxyapatite.<sup>53,54</sup> Additionally, OBFL has a bonding layer with very high filler loading (48 vol%). This filled adhesive, along with the hybrid layer, may also create an artificially elastic cavity wall<sup>55</sup> and act as a potential elastic shock absorber.<sup>56</sup>

during polymerization of the composite resin. ALB3 also has filler in its composition (>40%), but the benefit of its presence was not confirmed in terms of immediate bond strength and NL into the dentin. Of course, further long-term *in vitro* and clinical studies need to be conducted to prove this hypothesis, mainly because the only clinical study<sup>57</sup> that was found with ALB3 showed very promising results, as was pointed out in the recent systematic review of clinical studies published by Chee and others.<sup>7</sup>

## CONCLUSIONS

The evaluation of several bonding ( $\mu$ TBS, NL, and ISDC on dentin) and mechanical (UTS, DC, WS, and SL in water) properties in the short term allowed the adhesives available on the market to be more effectively screened, without requiring long-term studies. OBFL showed the best results in the all properties evaluated, and it can be considered the gold standard in the three-step ER adhesive systems.

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## 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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