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In vitro evaluation of adhesive characteristics of 4-META/MMA-TBB resin with organic filler

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ABSTRACT

Objectives. A commercial restorative material, BondfillSB (BF), is a modification of 4-META/MMA-TBB resin cement. BF uses a self-etching primer and added pre-polymerized organic fillers. We compared BF with another self-etching system, EasyBond (EB), in shear bond strength, bonded interface characteristics to human dentin and contraction gap when used in bulk-filling.

Methods. Shear bond strength of BF and EB + Z100 (Z), bonded by different experience-level operators, was evaluated. Bonded interfaces were characterized by SEM, AFM, and AFM based nano-indentation. Contraction gaps (CG) at 0 h and 24 h after polymerization were evaluated for BF or EB bulk filled class I cavities. To meet the clinical recommendation, BF's powder was replaced by experimental radioopaque powder (BFO) for the CG study. EB was used with Z (EBZ) or with a resin marketed for bulk-fill base (SureFil-SDR-flow (EBSF)).

Results. Shear bond strengths (Mean $\pm$ Standard Deviation (S.D.)) of BF (37.4 ± 2.6 MPa; $n = 36$) were higher and less variable than EBZ (18.2 ± 7.6 MPa; $n = 36$) ($p < 0.0001$, One-way ANOVA). Weibull characteristic strength (η) differed significantly between materials ($p < 0.0001$) but not between operators ($p = 0.90$). EBZ often had non-uniform interfaces and a wider band of reduced elastic modulus (E) of greater than $20 \mu\text{m}$ across the interface. BF had uniform interfaces and a smaller width of affected dentin under the interface ($\sim 1 \mu\text{m}$). There was a difference in dentin- E between EBZ and BF up to $9 \mu\text{m}$ from the interface (mixed-effects model; $P = 0.03$). A stratified linear regression model used for CG. EBSF and BFO showed significantly smaller CG than EBZ at time 0. None of three combinations showed any significant change between 0h-CG and 24h-CG.

Significance. BF possessed bonding characteristics required to serve as a restorative.

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Abbreviations: 4-META, 4-methacryloxyethyl trimellitate anhydride; BIS-GMA, bisphenol A diglycidyl ether dimethacrylate; BHT, butylated hydroxytoluene; EBPADMA, ethoxylated bisphenol A dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; MMA, methyl methacrylate; PMMA, poly methyl methacrylate; TBB, tri-n-butylborane; TEGDMA, triethylene glycol dimethacrylate; TMTP, trimethylol-propane-trimethacrylate.

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1. Introduction

There is increasing need to restore worn dentition since people live longer and retain more teeth than ever [1], and non-carious lesions have become more prominent in the adult population [2]. Historically non-carious cervical lesions (NCCL) and occlusal dentin defects due to attrition have been harder to restore than class 1 and 2 stress-bearing lesions [3,4], because flex and compression can occur simultaneously on a tooth with eccentric occlusal loading [5]. Although, with the improvements in adhesive technology, NCCL restored with 2 step self-etching adhesive were recently reported to have a 96% retention rate after 13 years [6]. Restoring those lesions with materials with lower moduli of elasticity could be effective [7] since when the failure rate was higher with older bonding systems, lower modulus materials showed better clinical results [8].

Recently a new restorative material was introduced, 4-META/MMA-TBB (4-methacryloxyethyl trimellitate anhydride/methyl methacrylate/tri-*n*-butylborane) resin restorative material, Bondfill SB (BF) (Sun Medical Co., Ltd, Moriyama, Japan) that is a modification of 4-META/MMA-TBB resin cement, C&B Metabond (Super-Bond) (Sun Medical) (CBM). It has been modified by adding trimethylol-propane-trimethacrylate (TMPT) organic filler [9] and uses a self-etching primer instead of 10% citric acid with ferric chloride (10-3) etch and rinse system.

The original resin cement CBM is unfilled monomethacrylate base resin. It was suggested monomethacrylate polymerizes with less cross linking due to molecular structure than dimethacrylate based resins [10], which results in lower flexural modulus [11]. CBM is reported to have lower elastic modulus and lower or similar flexural strengths than other dimethacrylate based resin cements or composite resins (CR) [12–15]. CBM has flexural modulus of 1.7 GPa [12], flexural strength reports varied from 88 [12] to 130 MPa [13]. The flexural modulus is lower than dimethacrylate base resin cements, such as Panavia F (Kuraray, Okayama, Japan), Unicem (3M ESPE) ~7 GPa [14] or various CRs (3.45–11.3 GPa) [15]. Flexural strengths of other resin based cements range from 94 to 176 MPa [12], CRs ranged from 66 to 147 MPa [15]. All such values reported above were obtained from 3 point bending tests.

Most resin cements contain about 50% inorganic fillers by weight [16]. Theoretically, filler content of a resin composite material is related to various properties of the material. Thus modifying resin composition by adding fillers could affect properties such as compressive strength, wettability [17], wear resistance [18] and polymerization shrinkage [19]. Adding 2% of untreated poly methyl methacrylate (PMMA) fillers to MMA improved physical properties, but more (23.1%) caused debonding between matrix and fillers [17].

Adding prepolymerized TMPT to the original CBM did not contribute significantly to improved wear resistance of BF whereas TMPT used in CR had higher wear resistance than CBM [20], but the flexural strength and tensile bond strength to enamel was unchanged between BF and CBM [21].

In the first part of this study we investigated if BF has comparable bond strength and interface characteristics so

the material can be suitable to restore NCCL and attrition lesions based on the standard approach to restore them with lower moduli materials. It has been used clinically based on that assumption [22,23] but no long term reports have been made.

We chose a one bottle adhesive system and light-cure conventional resin restorative as controls. BF system consists of 2 steps from etching to placement of the restoration. The number of steps is equivalent to using a one bottle adhesive combined with traditional light-cure CR.

Special attention and techniques are required for large and deep CR restorations. If the contraction force is greater than the bond strength between dentin and resin, it will accumulate stress to cause micro cracks or debonding [24,25]. Bulk-filling using contemporary resin materials results in larger contraction gaps compared to the incremental filling method and will leave uncured resin if the depth is greater than the depth of cure limit. Newly introduced resin restoratives designed for bulk-fill have new polymer formulations with improved polymerization with less stress and deeper depth of cure than conventional resin materials [26] but the gap formation result is unknown. An alternate approach is initiating polymerization at the dentin-resin interface to alter the direction of polymerization shrinkage and location of the accumulated stress [27,28].

In the second part of this paper, we sought to determine if BF can be used as a bulk-fill material without the introduction of significant contraction gaps. It is based on the result of the first part and a previous report of 4-META/MMA-TBB indicating it provides interfacial polymerization [27,28]. BF is a chemical cure resin so that there is no depth of cure limit of curing as with light curing CR. It has been reported that the reductant metal ions in the primer are the promoters of interfacial polymerization in MMA-TBB system, resulting in contraction towards the dentin wall instead of the center of the mass [27,29]. BF is not radio-opaque and to be useful as a bulk-fill material in the clinical setting, this is an important characteristic. Thus we used an experimental radio-opaque powder provided by the manufacturer to replace the powder in BF commercial kit. Bulk-fill flowable CR was used with all-in-one adhesive used in part one of this study to determine if it has effects on gap formation.

The hypotheses tested were: (1) self-etching primer with 4-META/MMA-TBB restorative system has no significant difference in shear bond strength (SBS) and interface characteristics, as compared to a traditional restorative material used with a self-etching adhesive system; and (2) use of this system results in significantly lower contraction gaps when used as a bulk-fill material.

2. Materials and methods

The tooth specimens used for this study were prepared from sound human molars, collected from subjects requiring extractions following a protocol approved by the UCSF Committee on Human Research. Teeth were sterilized by gamma radiation [30] and stored in Hank's balanced salt solution (HBSS) without glucose until used.

Table 1 – Adhesive and restorative materials.

1.1—Materials, composition and lot							
Material	Code	Composition	Lot #	Function			
Bondfill SB (Sun Medical)	BF		KT1				
Teeth Primer	BF-T	Water, acetone, 4-MET, reductant	ES1	Self-etching primer			
Bondfill liquid	BF-L	MMA, 4META, hydrophobic dimethacrylate	ER2	Restorative material with adhesive function			
Catalyst V		TBB, solvent	ER2				
Bondfill Powder	BF-P	PMMA, TMPT reactive organic filler	ER11				
Experimental Radio-opaque Powder RO3	BF-PO	PMMA, TMPT reactive organic filler, inorganic additives	N/A	Modified powder with radio-opacity			
3M ESPE, Adper EasyBond (3M ESPE)	EB	HEMA, Bis-GMA, methacrylated phosphoric esters, 1,6 hexanediol dimethacrylate, methacrylate functionalized polyalkenoic acid, dispersed bonded silica filler, ethanol, water. Initiators based on camphorquinone	480148	Self-etching primer and adhesive system			
3M ESPE, Z100 (3M ESPE)	Z	Bis-GMA, TEGDMA, silanated zirconium silica, synthetic mineral	394568	Restorative material			
SureFil®SDR®flow (Dentsply Caulk, Milford, DE)	SF	Strontium alumino-fluoro-silicate glass, barium-alumino-fluoro-borosilicate glass, modified urethane dimethacrylate resin, EBPADMA, TEGDMA, camphorquinone photoinitiator, photoaccelerator, BHT, UV stabilizer, titanium dioxide, iron oxide pigments, fluorescing agent	1204162	Restorative material. Posterior bulk fill flowable base			
1.2—Combination used and steps in resin-based restoration for shear bond strength and contraction gap test							
	Code	Etchant (1)	Primer (2)	Adhesive (3)	Restorative (4)	Shear bond strength	Contraction gap
Combination #1	BF	BF-T			BF-L + BF-P	X	
Combination #2	EBZ	EB			Z	X	X
Combination #3	EBSF	EB			SF		X
Combination #4	BFO	BF-T			BF-L + BF-PO		X
4-META: 4-methacryloxyethyl trimellitate anhydride, BIS-GMA: Bisphenol A diglycidyl ether dimethacrylate, BHT: Butylated hydroxytoluene, EBPADMA: Ethoxylated Bisphenol A dimethacrylate, HEMA: 2-hydroxyethyl methacrylate, MMA: methyl methacrylate, PMMA: poly methyl methacrylate, TBB: tri-n-butylborane, TEGDMA: triethylene glycol dimethacrylate, TMTP: trimethylol-propane-trimethacrylate.							

2.1. Adhesive and restorative materials

The adhesives and restorative systems used in this study are listed in Table 1.1. Roles of the components and rendered tests for the 2 hypotheses are listed in Table 1.2.

For hypothesis (1), two combinations of self-etching restorative systems were compared. Combination #1 (BF), the modified 4-META/MMA-TBB (BF) consisted of a self-etching primer and MMA based restorative with adhesive characteristics. Restorative material is self-curing and comes with a PMMA powder and liquid. The recommended method for placing is the dip-brush method as for CBM, which is not very commonplace for most western clinicians. Combination #2 (EBZ), consisted of Adper EasyBond (3M ESPE, St. Paul, MN) (EB) self-etching single bottle adhesive used with Z100 (Z) (3M ESPE) restorative.

For hypothesis (2), EB was used for Combination #2 (EBZ) and Combination #3 (EBSF) in which, Z was replaced with bulk-fill material, SureFil SDR flow (SF) (Dentsply Caulk Milford, DE). BF is not radio-opaque, which would be clinically necessary for the bulk-fill use. Thus in Combination #4 (BFO): BF's powder

(BF-P) was replaced with experimental radio-opaque powder (BF-PO) provided by the manufacturer. In preliminary study in our lab, we confirmed BF and BFO had similar characteristics in shear bond strength and elastic modulus as determined by nanoindentation (results not shown).

2.2. Shear bond strength test

Extracted teeth ($n=72$) were sectioned with a slow speed water cooled saw with a diamond blade (Buehler, Lake Bluff, IL) to yield proximal surfaces, then finished to #320 grit roughness with silicon carbide paper (Buehler) to create a smear layer with similar roughness to the carbide bur [31]. In part one, two operators of different levels of bonding experience prepared specimens to evaluate the difficulty of learning the dip-brush technique: veteran (V) who was a clinical dentist, with experience in the lab for more than 10 years, and novice (N), student volunteer who had no previous bonding experience. Combinations BF and EBZ were used to make bonded specimens after studying manufacturers' instructions (written and video). The novice received hands-on

demonstration by the veteran once for each combination. Demetron Optilux VC-401 (Kerr, Orange, CA) with a light output intensity 400–500 mW/cm², was used to light cure the materials. EB was cured for 40 s (double of recommended cure time). Z was placed in small increments, cured 80 s at each increment (double of recommended cure time). Each specimen was mounted for single plane shear test ($n = 36$ /combination) as described previously [32]. Briefly, mylar tape with a 3 mm diameter hole was applied to the dentin surface to obtain standardized bonded areas. Bonded specimens were stored 24 h in 100% humidity before bond strength testing. The test specimens were loaded parallel to the bonded interface, using a universal testing machine (Instron Model 1122, Instron Corp., Canton, MA, USA), with cross head speed 5 mm/min. Failure patterns (interfacial or cohesive within dentin or composite) were examined with a stereomicroscope at 30× magnification.

2.3. Bonded interface characteristics

2.3.1. Preparation of the specimens

AFM: An occlusal dentin disk was prepared from each of 6 extracted molars by cutting with a slow speed water cooled saw with a diamond blade. The distance from the dentin enamel junction (DEJ) and orientation of the dentin tubules of the dentin disk used for this part of the studies were equivalent to the shear bond test specimen. The surface was finished to #320 grit roughness with silicon carbide paper then bonded by V, using combination BF and EBZ as shear bond test specimens except thickness of the Z and BF were about 1 mm. After storing in HBSS for 24 h in 100% humidity, bonded specimens were cross sectioned and polished to 0.25 μm with diamond paste suspension (Buehler) for AFM (Contact mode) imaging and AFM-based nanomechanical testing to determine reduced elastic modulus (E).

SEM: Bonded specimens for scanning electron microscopy (SEM) were prepared in the same way as for AFM ($n = 6$ for each combination). One half of each bonded specimen was cross sectioned and polished, then the hybrid layer was revealed with 0.1M HCl and 10% NaOCl [33]. The other half was fractured. All specimens were fixed as described elsewhere [31], then the bonded specimens were sputter-coated with a 10–20 nm thick Au thin film using a sputter coater (Denton Vacuum Inc., Model # Desk II, Moorestown, NJ).

2.3.2. AFM (Contact mode—wet) and SEM images of bonded interfaces

Conventional atomic force microscopy (AFM) (Nanoscope III, Bruker, Santa Barbara, CA) was used to obtain topographic images of the cross sectioned bonded specimens in wet condition, using contact mode with silicon nitride tip (NP-10, Bruker, Camarillo, CA), which yields sharper, better quality images than the nano-indentation tip.

SEM images were obtained using a Hitachi S-4300 field emission gun scanning electron microscope (Hitachi High Technologies America, Pleasanton, CA) at an accelerating voltage of 20 kV. SEM images at 60–1000× were taken to evaluate bonded interfaces of cross-sectioned segments.

2.3.3. Nano mechanical properties of bonded interfaces

Nanoindentation was used in this study to assess the quality of the bonded interface. Nanoindentations on bonded and cross sectioned specimens were made in a liquid cell containing distilled and filtered water (“wet” condition) with the standard head replaced by a Triboscope indenter system (Hysitron Inc., Minneapolis, MN), nPoint closed loop scanner (4715120-MM, nPoint, Madison, WI) and AFM, as described elsewhere [34]. A cube corner diamond indenter with a tip radius of about 20 nm was used for indentations and imaging. Fused silica was used for calibration of the machine compliance, the elastic modulus, and to define the tip area function for indentation depths over a range of 50–600 nm with the cube corner tip. Indentation loads of 400 μN on sound dentin resulted in indentation depths between 180 and 260 nm.

A linear series of indentations, spaced at approximately 1–2 μm intervals across the bonded interfaces at 2 randomly selected areas per specimen were evaluated ($n = 3$ specimens/combination, 2 lines/specimen). Preliminary studies revealed the width of the region of interest was about 5 μm under the interface, requiring a narrower distance between indentations to capture the differences. Preliminary study using indentation intervals of 1, 2 and 5 μm with 150 μN load on demineralized dentin showed no significant difference in indentation depth at the maximum load (h_{max}) between any of the indentation intervals used, thus no edge effects were evident with 1 μm intervals (data not shown). Target indentation depth was 200 nm on the affected dentin. Means of E for Z and BF were computed from the 2 μm separated indentations. AFM imaging ensured positioning of the indenter on the intertubular dentin. Indents on tubules and any peritubular dentin were excluded from further analysis. The indentation load–displacement data were analyzed to determine the reduced elastic modulus according to the method of Oliver and Pharr [35].

$$E = \frac{\sqrt{\pi}}{2\sqrt{a}} S$$

The reduced elastic modulus E is calculated from the contact stiffness, S , defined as the slope of the linear portion of the force/displacement curve during unloading near the maximum load and “ a ” is the contact area of the indentation.

2.4. Contraction gap evaluation for bulk-fill specimens

Extracted and sterilized human third molars ($n = 12$ /combination) were used to evaluate combinations #2, 3 and 4 (Table 1). 3 × 3 × 3 mm class I preparations were made with a high speed hand piece with a water cooled cylindrical diamond bur. The cusp tips were ground to obtain flat occlusal surfaces perpendicular to the long axis of the teeth using a belt grinder (Buehler), then polished with #320 grit silicon carbide paper before the class I cavity preparation. After preparing class I preparations with primer or adhesive, restorative materials were bulk-filled and cured. Six of the bonded specimens of each combination were immediately cross sectioned with a slow speed saw and polished as described previously for AFM and light microscopy evaluation. The other six were stored for 24 h in DI water before sectioning. The average of 3 gap width measurements at

Table 2 – Variation in shear bond strength (MPa) by material and operator.

Material/ Operator	N (PTF) ^a	Mean (SD)	Weibull modulus (m) (95% CI)	Characteristic strength, Weibull scale (η)	Interface failure + PTF	Cohesive failure ^b
BF/Nov	18 (0)	37.5 (3.01)	14.1 (9.85, 20.1)	39.0 (37.6, 40.3)	0%	38.9%
BF/Vet	18 (0)	37.3 (2.17)	21.5 (14.9, 31.0)	38.3 (37.4, 39.2)	0%	22.2%
EBZ/Nov	18 (2)	17.8 (8.33)	2.02 (1.34, 3.06)	19.6 (15.5, 24.8)	11.1%	5.6%
EBZ/Vet	18 (0)	18.6 (6.91)	3.08 (2.13, 4.44)	20.8 (17.8, 42.4)	5.6%	0%

Abbreviations: PTF: Pre test failure, SD: Standard deviation, CI: Confidence intervals, Nov: Novice, Vet: Veteran. SBS: Shear bond strength.

According to a linear regression Weibull model of SBS as a function of material and operator, and their interaction, the characteristic strength (η) differs significantly between materials ($p < 0.0001$) but not between operators ($p = 0.90$).

^a For two PTFs, SBS levels were imputed as 1 MPa with interface failure when estimating table quantities.

^b Percentage of the specimens that solely failed cohesively.

randomly selected positions along 50 μ m interface width at the center of the pulpal floor and 0.5 mm from the pulpal-axial line-angle on the axial wall were recorded as the gap measurement. Low magnification light microscopy was used in addition to AFM to confirm the selected 50 μ m width of region of interest was representative of the overall trend of the specimen. The location of separation along 50 μ m was also classified and recorded as (1): interfacial, if the separation occurred at more than 50% of the observed interface between EB/Z, EB/dentin, EB/SF or BFO/dentin. Due to the composition design of BFO (Table 1.2), there is no interfacial failure of BFO on the composite resin side. (2): cohesive, if it was in EB, Z, SF, BFO or dentin, and (3): “mixed” if the fracture was both interfacial and cohesive; none of these failure modes occupied more than 50% length of the observed fracture surface. Contact mode AFM in dry condition or light microscopy was used if the gap was very wide.

2.5. Statistics

Shear bond strength: Pre-test failures were imputed as SBS = 1 in order to include these outcomes in all analyses. Analysis of variance was used to estimate mean and standard deviation (S.D.) per group. Weibull failure analysis was used to estimate maximum likelihood means (95% confidence intervals (C.I.)) of modulus and characteristic strength, by restorative material and clinical experience, and to test for differences between materials and operators.

Elastic modulus across the interface: Line profiles were obtained for $\pm 30 \mu$ m from the adhesive/dentin interface. To focus on the most relevant aspect of affected dentin depth under the adhesive, the plots were constrained to distances of 0–14 μ m. Values below 0.1 (tubules) and above 24 GPa (peritubular dentin) were excluded from the analysis, assuming these did not represent intertubular dentin. Mixed-effects linear regression was used to estimate mean (95% C.I.) elastic modulus as a function of categorical distance from the adhesive/dentin interface (location identified visually using AFM images) into the restorative material (negative distances) and into the dentin, by material (BF or EBZ). The model accounted for correlations among measurements within indentation lines and specimens.

Contraction gap width comparisons: We used a stratified linear regression model to estimate mean (95% C.I.) gap width (μ m) as a function of material (EBZ = control; BFO = test 1; EBSF = test 2), time (0 vs 24 h), and their interaction, stratified by location

(axial, pulpal). Within location, p -values with 2 degrees of freedom were used to assess statistical significance of differences between materials at baseline, changes over time within material, and differential changes over time among materials.

3. Results

3.1. Shear bond strength

The mean ($\pm$ S.D.) shear bond strength (SBS) of BF (37.4 ± 2.6 MPa; $n = 36$) was higher and less variable than that of EBZ (18.2 ± 7.6 MPa; $n = 36$) ($p < 0.001$), whereas there was no significant difference between operators for either system (BF: $p = 0.82$, EB: $p = 0.78$) (Table 2, Fig. 1). EBZ had larger S.D., with lowest SBS value less than 10 MPa. There were 2 EBZ specimens by operator N that failed before shear force was applied. Those pre test failure (PTF) values were recorded as “1”, included in analyses reported in Table 2 and Fig. 1. Both combinations exhibited mixed failure patterns (Table 2). BF showed 11 cohesive failures (7 prepared by N, and 4 by V) 25 mixed failures. EBZ showed 1 cohesive failure by N, 2 adhesive failures including PTF, 1 adhesive failure prepared by V and 32 mixed failures.

The Weibull “modulus” is the estimated slope (or “shape” parameter) of a Weibull model relating the cumulative probability of fracture (P_f) with SBS, where both P_f and SBS are expressed on the natural logarithm scale. A material’s “characteristic strength” (or Weibull “scale” parameter) is its SBS value when $P_f = 0.632$, or 63.2%. Fig. 1 shows that the Weibull modulus and characteristic strength of BF are higher than those of EB, regardless of operators. Quinn & Quinn note that, “For materials with low Weibull moduli (i.e., the flaw sizes are quite variable) fracture can occur from a large portion of the test specimen. On the other hand, the origin sites are concentrated to only the highest stressed regions if the Weibull modulus is large, since flaw sizes are all similar in size [36]”. Thus our findings indicate that flaw sizes are less variable with BF than with EB.

3.2. Bonded interface characteristics

Figs. 2–4 show BF and EBZ bonded interfaces of typical specimens in micrographs obtained with AFM (Fig. 2) and SEM (Figs. 3 and 4). The AFM images were from cross sectioned and polished specimens in the hydrated condition. BF had uniform interfaces (Fig. 2A1) with a slight valley, approximately 1.5 μ m

Fig. 1 – Weibull plots for the shear bond strength (SBS) of BF and EBZ bonded by two operators with different experience levels (N—Novice, V—veteran). Based on a Weibull model relating the cumulative probability of fracture (P_f), the Weibull modulus (slope) and characteristic strength (η) (estimated value of SBS where the horizontal reference line, marking 63.2% probability of failure, intersects the modulus) of BF are steeper and stronger, respectively, than these features of EBZ, regardless of the operator.

Fig. 2 – A1, B1, C1: AFM topographic images of 2 systems evaluated in wet condition. EBZ showed 2 different zones with or without a detectable adhesive layer (B1, C1). C1 was captured with the nano-indentation diamond tip after a line of indentations, showing nano-indentations across the interface in the center of the image (arrows). A2, B2, C2 are 3D AFM topographic images in wet condition. BF showed a smooth and even interface without gap between dentin and restorative material (A1, A2). EBZ showed dentin etched in scalloped pattern. There were grooves between dentin/adhesive and adhesive/restorative (C2). All specimens were polished.

Fig. 3 – SEM image of BF. Lower magnification of cross sectioned and polished specimen, treated with HCl to reveal hybrid layer (A), shows tight and even interface between BF and dentin. TMPT fillers (T) in different sizes were apparent. Non polished surface appeared rough with exposed TMPT fillers (A, arrow) but they seemed to be bonded to PMMA base and polishable without popping off (C). Fractured specimens (B and D) showed smooth tight interface. There was no detectable hybrid layer or adhesive layer with either sectioning method.

in width, just below the BF in the 3D height image at higher magnification (Fig. 2A2). Since it was not apparent in the fractured specimen of BF (Fig. 3B and D), it was attributed to the polishing procedure. There was no delamination between BF and dentin. The bond strength was high enough and survived

the dehydration and vacuum of SEM observation. There was no detectable thick hybrid layer or adhesive layer. Resin tag penetration was minimal. EBZ had two different appearances. One appearance had a very thin barely detectable layer, shown in Fig. 2B1, B2 and the left half of Fig. 4B. The other appearance

Fig. 4 – SEM images of EBZ. Bonded specimens were treated with HCl to reveal hybrid layer after being polished (A). Fractured specimen (B) had uneven interface with the area with lack of adhesive (left half) and with adhesive (right half with arrow showing the EB layer). Polished specimen (C) shows adhesive layer and resin tags. There was a gap under adhesive layer (C and D).

Fig. 5 – (A) Elastic modulus of cross sectioned and polished bonded specimens measured in wet cell. BF showed narrow affected dentin region under the adhesive–restorative. EBZ showed higher variability among specimens, especially at and proximal to the adhesive/resin interface. (B) To summarize model findings, we estimated the mean (95% CI) BF–EBZ difference in *E* values as of each distance from the interface at affected dentin zone. *E* was significantly higher in the BF than the EBZ group at distances of 1–3 μm but differences between groups diminished thereafter.

showed an adhesive layer about 12 μm in width (Fig. 2C1). An AFM 3D image in wet cell and SEM of polished specimen (Fig. 2C2, Fig. 4C) showed intermittent areas of grooves between dentin and the bonding agent. The dentin surface was etched in a scalloped pattern. The 2 different appearances were repeatedly observed in specimens as shown in Fig. 4B. EBZ had some, but not all, tubules filled with resin tags. BF's untreated surface appeared rougher than Z (Fig. 3A and Fig. 4A) with TMPT spheres raised above the MMA substrate. There was a wide range in the filler sphere size. Specimens polished with diamond paste showed no ditch or pit from the filler loss. TMPT beads are polishable and were not pulled from the substrate (Fig. 3A).

3.3. Nano mechanical properties across bonded interface

Fig. 5A shows elastic modulus (*E*) of BF and EBZ bonded to dentin. EBZ showed larger variation in mechanical property profiles proximal to the bonded interface due to the inconsistent detectable adhesive layer shown in SEM and AFM evaluation in the previous section. BF itself had a much lower *E* value (3.7 ± 0.68 GPa (Mean $\pm$ S.D.)) compared to the conventional restorative Z (19.6 ± 3.73 GPa), and it consistently showed well bonded uniform interfaces with a ~ 1 μm depth of affected dentin under the bonded interface. EBZ had a wider band of reduced *E* (Fig. 5A). After the rapid drop to almost 3 GPa, it recovered gradually to the normal *E* value of sound dentin (17–20 GPa) ~ 10 μm from the interface. The total width of reduced mechanical property was greater than 20 μm across the interface. BF had a smaller width of affected dentin under the interface (~ 1 μm). There was a difference between EBZ and BF from 1 to 3 μm ($p < 0.001$) and at 9 μm from the interface ($P = 0.03$) (Fig. 5B).

3.4. Contraction gap

For each material and time, 6 specimens were used with no missing values. Contraction gap measurements of the 3 combinations immediately after placement of restorative and changes 24 h later are shown in Table 3. Combination $\times$ time interaction was not significant at either location evaluated ($p = 0.67$ at axial, $p = 0.92$ at pulpal). There were significant differences among 3 combinations tested in the width of contraction gap formed. Z was not designed for bulk-fill so when used with EB there was large contraction gap formation. For both locations, the model identified significantly smaller gaps at time 0 in EBSF and BFO than EBZ ($P = 0.04$ at axial, < 0.0001 at pulpal). If the same adhesive EB was used with the low-shrinkage material SF, the contraction gap was significantly reduced. BFO had significantly lower contraction gap than EBZ and was equivalent to EBSF. EBSF and BFO did not have any significant difference in contraction gap on different locations of the cavity. There was no significant change in contraction gap between 0 h and 24 h after the restoration was completed in any of the three combinations. Fig. 6 shows light microscopy and AFM micrographs of cross sectioned and polished specimens of each combination. EBSF and BFO showed some resin tags and well preserved bonding (Fig. 6B1, B2, C1, C2). EBZ showed large contraction gaps and broken bonding with no resin tags left in the lumen (Fig. 6A1, A2) and had larger gaps at pulpal floor than at axial sites ($P < 0.005$).

80% of EBZ had cohesive separation; separated in adhesive itself and left fragments on both sides of the interface. 4% ($n = 1$) was mixed, 4% was interfacial (between dentin and EB) out of 24 recorded measurements (axial, pulpal for 0 h and 24 h, $n = 6 \times 4$ conditions). 12% of EBZ had no gap. For EBSF, 17% separated in adhesive, and 8% separated at interface (between dentin and EB). 75% did not show any gap. 4% of BFO fractured

Table 3 – Contraction gap width (μm) and its change after storage of bulk filled materials as a function of location.

Location	Combination	Estimated mean (95% CI)		p-value		
		0 h	Δ at 24 h	Within combination Δ at 24 h	Difference to EBZ	
					0 h	Δ at 24 h
Axial	EBZ	3.00 (1.28, 4.72)	1.58 (–0.85, 4.02)	0.19	–	–
	EBSF	0.08 (–1.64, 1.81)	0.08 (–2.35, 2.52)	0.94	0.02	0.38
	BFO	0.40 (–1.32, 2.12)	0.65 (–1.79, 3.09)	0.59	0.04	0.58
Pulpal	EBZ	30.8 (25.6, 36.0)	–2.00 (–9.37, 5.37)	0.58	–	–
	EBSF	1.58 (–3.63, 6.80)	–0.58 (–7.96, 6.79)	0.88	<0.0001	0.78
	BFO	0.08 (–5.13, 5.30)	0.10 (–7.27, 7.47)	0.98	<0.0001	0.68

CI: Confidence intervals.

Fig. 6 – Light microscopy and AFM topographic images of bonded interface at the pulpal floor: A1, A2: EBZ, B1, B2: EBSF, C1, C2: BFO, respectively. All but EBZ had smooth even interface without gap. C1 shows polymer particles of various sizes in BFO. *Note the scale bars are different in A2 (height).

in adhesive, 21% separated at the interface between BFO and dentin. 75% did not show any gap.

4. Discussion

Placing a resin-based restoration actually involves 4 steps. The 3 steps (1) etching, (2) priming and (3) adhesive proposed by Van Meerbeek's classification [37] and the 4th step is placing a restorative material. Resin bonding systems have been simplified by reducing and consolidating steps to reduce the chance for clinical errors [38]. EB uses the latest all-in-one system combining steps (1), (2) and (3) in one bottle, requiring only 1 step before placing a restorative material. BF combines (1) and (2) in a self-etching primer. The 2nd step is a restorative material with (3) and (4) combined. So the total number of steps required until finishing the restoration is two, which is the same as the all-in-one systems (shown in Table 1.2).

In the present study, we used a single plane lap shear method consisting of 2 shear plates, so we could apply the shear force parallel to the tested interface without a blade [32].

Both bonding systems provided similar shear bond strength to dentin as reported by others for self-etching primer and all-in-one systems [39–41]. EBZ had large standard deviations in bond strength and a smaller Weibull Modulus than BF. SEM imaging and AFM based mechanical testing results showed inconsistent bonding interfaces created by EBZ.

EBZ seemed to be more technique sensitive than BF. However, Weibull analysis shown in Fig. 1 and Table 2 suggested that operator experience did not matter for either of the systems tested. Even though the required number of steps seemed to be the same in Table 2, using BF involves more components and mixing them in addition to using the brush and dip technique. The Novice, who had no previous experience with bonding, produced specimens with consistently good bonding with BF compared to the one bottle system. Our findings agreed with Soderholm et al.'s study of shear bond strength prepared by operators with different levels of experience. They reported that all products evaluated had large S.D., but could not conclude that the all-in-one system performed better for less experienced operators. However, they could not deny the claim that it was less technique sensitive than etch

and rinse system [39]. Bond strengths of 20 MPa or more have been reported to be required to withstand the debonding force caused by contraction stress [42]. Our results showed BF had consistent results satisfying the suggested requirement. EBZ yielded lower values with higher S.D. and thus may require very careful clinical application and consideration to reduce contraction force, such as incremental placement, to avoid undesired clinical outcomes.

The failure mode was predominantly mixed failures for both EBZ and BF. BF does not have an adhesive/CR interface, thus for BF “mixed” is a combination of failure in BF itself and dentin/BF interface. BF showed more cohesive failure than EB. This may be related to the lower elastic modulus of BF (3.7 GPa) as compared with Z (19.6 GPa).

The retention mechanism of self-etching adhesives involves micro-mechanical bonding and nanotag resin encapsulation of collagen fibers and mineral remnants by chemical interaction of functional monomers with the hydroxyapatite [43,44]. Thickness of the hybrid layer and demineralized zones depends on the pH/acidity of the solution [45,46]. The problems of all-in-one systems lie in diffusion of the acidic primer, which has to penetrate into the dentin with the adhesive. Hydrophobic components such as dimethacrylates tend to cluster together before polymerization to create hydrophobic domains. Obtaining an even distribution of hydrophilic and hydrophobic components in 1 bottle without phase separation seemed to be challenging [43]. Phase separation can create water-trees and uneven, weaker interfaces, which will affect the durability of bonded interfaces [47].

EBZ (pH 2.4) [48] is considered as an “ultra-mild” self-etching primer, and formed a hybrid layer width of a few hundred nanometers as has been observed with TEM [45,48]. The self-etching primer in BF (pH 3, reported by the manufacturer and confirmed in our lab) uses 4-MET as a functional monomer. There is no data in the literature on the hybrid layer with this particular primer on dentin. However neither EBZ nor BF showed thick hybrid layers; neither could be detected in AFM or SEM specimens treated with HCl in the current study.

Further, nanomechanical properties across the bonded interface were used to determine the width of the functional interface and influence of the acid under the hybrid layer. BF showed very narrow interfaces and smaller zones of partially demineralized dentin compared to EBZ. Nurrohmah et al. reported dentin bonded with EB produced a zone that was less resistant to an acid–base challenge under an acid–base resistant apatite-rich zone (=hybrid layer), observed as a funnel-shaped lesion [45]. This zone is consistent with the wider band of reduced mechanical properties of the dentin side of EBZ shown in Fig. 5.

On the CR side of the EB adhesive layer, Z adjacent to the adhesive shows small particles in AFM polished specimens shown in Fig. 2B1 and C1. This might be caused by removal of the substrate during polishing because the residual acid in the adhesive or oxygen inhibited layer of EB interfered with polymerization of Z, leaving the CR softer than the area further from the interface. EBZ resulted in 2 different kinds of interfaces as shown in SEM and AFM (Figs. 2 and 4). The authors tried to create one of the interfaces intentionally by adjusting the moisture of dentin, rubbing, evaporating or the amount of EBZ, but the outcome evaluated by cross sectioning

was inconsistent. These observations of the bonded interface may be related to the lower bond strength of EB in this study. In contrast, the BF system has the adhesive function in the restorative material, not in the self-etching primer. So, BF can avoid the acidic primer problem of acid penetration into the dentin with the adhesive, which may explain the smaller width of affected dentin under the bonded interface in addition to higher pH of BF.

Contraction stress and gap formation are influenced by many factors, such as class of resins, the initiator and kinetics of polymerization, filler content and resin matrix composition, that will dictate the amount of volumetric shrinkage [49,50]. The restorative we used in this study, Z100 (Z), showed characteristics of high shrinkage and high stress resin [19], whereas SF showed lower contraction stress and higher shrinkage [51]. This can explain why EBSF produced smaller contraction gaps than EBZ in our study when the same adhesive (EB) was used. Even with the lower contraction stress material SF, some (17%) of the EBSF produced a gap within EB, which supports the idea that the adhesive layer itself of all-in-one systems is weak [47] and that, as shown by our shear bond tests, some of EBZ specimens were below the 20 MPa bond strength required to withstand the contraction stress [42]. There is no published report on contraction stress or shrinkage for BF. However, both EBSF and BFO showed notable shrinkage at the top of the restoration after polymerization when we were preparing specimens.

There are two possible reasons for smaller gap formation with BF. One is that BF is chemically cured and the polymerization takes longer than the light curing system EBZ. Slow chemical curing can reduce gap formation, especially when used in high C-factor preparations [52]. Comparison of polymerization shrinkage stress in chemically cured and light cured resin restoratives suggested slower polymerization yields smaller contraction stress and stress rate [52]. Secondly, TBB initiator used with a primer with reductant metal ion starts polymerization adjacent to the dentin [27,29] so that contraction occurs toward dentin walls. Polymerization shrinkage is highest at the time of curing but internal stresses gradually decrease with time, although some materials continue polymerization for longer periods [19,52,53].

Further studies of the wear rates of BF and BFO are warranted since they have lower mechanical properties than composite resin based restoratives. In addition evaluation of polishability is needed to determine its suitability to use without veneering composite in low stress bearing areas. For use as a base material, adhesive characteristics of BFO should be evaluated in more detail in the future.

5. Conclusions

BF had higher shear bond strength and smaller S.D. than EBZ. There was no significant difference between operators for either system. BF had more uniform interfaces with smaller zones of demineralized dentin underneath, whereas EBZ showed variation in interface topography and mechanical properties. BFO showed significantly smaller contraction gap than EBZ and was similar to EBSF.

Disclosure

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