Bioactive Two-step Approach: Promising Bonding Strategy for a One-step Self-etch Universal Adhesive

Linhong Wang[a] / Fei Chen[b] / Fan Yang[c] / Shuhei Hoshika[d] / Monica Yamauti[e] / Yunqing Liu[f] / Hidehiko Sano[g]

Purpose: To evaluate the potential of an additional application of two novel hydrophobic experimental adhesive resins with or without bioactive zinc fluoride glass to promote the bond strength of a one-step self-etch universal adhesive.

Materials and Methods: Three self-etch universal adhesives, G-Premio Bond (GPB), Scotchbond Universal (SBU) and Clearfil SE Bond 2 (SE2), and two experimental adhesive resins, BZF210 and BZF21, were used in this study; thus, five groups were formed: GPB, GPB+BZF210, GPB+BZF21, SBU, and SE2. The adhesives were applied to flat dentin surfaces according to each manufacturer's instructions. The microtensile bond strengths (μTBS) were evaluated after 24-h water storage. The fracture modes and interfacial structures were analyzed using SEM, while elemental analysis was performed using SEM-EDS. The data were analyzed using one-way ANOVA and the Games-Howell test ($p < 0.05$).

Results: Significantly higher μTBS was achieved by additional application of BZF210 (48.68 ± 6.59 MPa) and BZF21 (58.58 ± 2.84 MPa) compared with GPB (33.57 ± 4.22 MPa) alone. Most failures occurred above the smear layer in GBP, while more cohesive and mixed failures were observed in GBP+BZF210, GPB+BZF21, SBU, and SE2. The interfacial structures revealed that GBP+BZF210 and GPB+BZF21 had more and longer resin tags than did GPB. SEM-EDS showed a particularly high peak of zinc in GPB+BZF21.

Conclusions: The bond strength of GPB was significantly improved by the additional application of BZF210 and BZF21. Using an additional bioactive hydrophobic layer on a one-step, self-etch universal adhesive can significantly improve its bonding efficacy and extend its clinical options.

Keywords: adhesive, dental bonding, microtensile bond strength, scanning electron microscopy.

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Self-etch adhesives are becoming increasingly popular in clinical use thanks to advantages such as ease of use, acceptable bond strength, user friendliness, and less technique sensitivity. They are classified into two types according to the application procedures: two-step self-etch adhesives and one-step, self-etch adhesives.[41] Compared with the two-step self-etch adhesives, the one-step self-etch adhesives are associated with lower bond strength and poorer durabil-

[a] *Attending Doctor, Department of Stomatology, Zhejiang Provincial People's Hospital, People's Hospital of Hangzhou Medical College, Hangzhou, Zhejiang, China; Visiting Scholar, Department of Restorative Dentistry, Division of Oral Health Science, Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan. Performed μTBS test, SEM, EDS, statistical evaluations, wrote the manuscript.*

[b] *PhD Student, Department of Restorative Dentistry, Division of Oral Health Science, Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan. Performed experiments μTBS test and SEM.*

[c] *Professor, Department of Stomatology, Zhejiang Provincial People's Hospital, People's Hospital of Hangzhou Medical College, Hangzhou, Zhejiang, China. Designed the experiment, proofread the manuscript, commented on the manuscript at all stages.*

[d] *Assistant Professor, Department of Restorative Dentistry, Division of Oral Health Science, Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan. Discussed the results, commented on the manuscript.*

[e] *Associate Professor, Department of Restorative Dentistry, Division of Oral Health Science, Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan. Discussed the results, proofread the manuscript, contributed to discussion at all stages.*

[g] *PhD Student, Department of Restorative Dentistry, Division of Oral Health Science, Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan. Revised the manuscript, helped perfom the experiment.*

[h] *Professor, Department of Restorative Dentistry, Division of Oral Health Science. Graduate School of Dental Medicine, Hokkaido University, Sapporo, Japan. Proofread the manuscript, contributed to discussion.*

Correspondence: *Prof. Dr. Fan Yang, Department of Stomatology, Zhejiang Provincial People's Hospital, People's Hospital of Hangzhou Medical College, Shangtang Road 158#, Hangzhou 310014, Zhejiang, China. Tel: +86-571-8589-3206; e-mail: yangfan@hmc.edu.cn*

Table 1 Chemical composition of each group and manufacturer's instructions for application

Groups and Lot No.	Chemical formulation and pH	Manufacturer's instructions
G-Premio Bond Lot No. 1703031 (GC; Tokyo, Japan)	10-MDP, 4-META, methacrylate acid ester, distilled water, acetone, photo initiators, silica. pH=1.5	1. Apply G-Premio Bond using a microbrush. 2. Leave undisturbed for 10 s after application. 3. Dry thoroughly for 5 s with oil-free air under maximum air pressure. 4. Light cure for 10 s.
G-Premio Bond + BZF-210 Lot No. 1703031 Lot No. 170809 (GC, Tokyo, Japan)	G-Premio Bond: (as previously). BZF-210: Dimethacrylate monomer, bis-GMA, UDMA, photoinitiator, silica filler. pH=1.5	1. Apply G-Premio Bond using a microbrush. 2. Leave undisturbed for 10 s after application. 3. Dry thoroughly for 5 s with oil-free air under maximum air pressure. 4. Apply using BZF-210 with a microbrush. 5. Dry with oil-free air under soft air pressure. 6. Light cure for 10 s.
G-Premio Bond + BZF-21 Lot No. 1703031 Lot No. 170519 (GC)	G-Premio Bond: (as previously). BZF-21: Dimethacrylate monomer, bis-GMA, UDMA, photoinitiator, zinc fluoride glass, silica filler. pH=1.5	1. Apply G-Premio Bond using a microbrush. 2. Leave undisturbed for 10 s after application. 3. Dry thoroughly for 5 s with oil-free air under maximum air pressure. 4. Apply using BZF-21 with a microbrush. 5. Dry with oil-free air under soft air pressure. 6. Light cure for 10 s.
Scotchbond Universal Lot No. 669820 (3M Oral Care; St Paul, MN, USA)	10-MDP, HEMA, ethanol, water, dimethacrylate resins, methacrylate-modified polyalkenoic acid copolymer, polyacrylic acid copolymer, silane, fillers, initiators. pH=2.7	1. Apply SBU adhesive on the surface and rub it for 20 s. 2. Gently air dry the adhesive for approximately 5 s for the solvent to evaporate. 3. Light cure for 10 s.
Clearfil SE Bond 2 Lot No. C60080 Lot No. CK0123 (Kuraray; Tokyo, Japan)	Primer: 10-MDP, HEMA, hydrophilic aliphatic dimethacrylate, CQ, DEPT, water. Bond: 10-MDP, Bis-GMA, HEMA, hydrophobic aliphatic dimethacrylate, CQ, DEPT, colloidal silica. Primer: pH=1.9	1. Apply the primer and leave for 20 s. 2. Gentle air blowing. 3. Apply the adhesive for 10 s. 4. Gentle air blowing. 5. Light cure for 10 s.
Clearfil AP-X Lot No. 8A0064 (Kuraray)	Bis-GMA, TEG-DMA, silane barium glass filler, silane silica filler, silanated colloidal silica, CQ, pigments, others.	Used as the composite for the bonding procedures.

Abbreviations: 10-MDP: 10-methacryloxydecyl dihydrogen phosphate; 4-META: 4-methacryloyloxyethyl trimellitic anhydride; bis-GMA: 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane; UDMA: urethane dimethacrylate or 1,6-di(methacryloyloxyethylcarbamoyl)-3,30,5-trimethylhexaan; HEMA: 2-hydroxyethyl methacrylate; CQ: dl-camphorquinone; DEPT: N,N-diethanol-p-toluldine; TEG-DMA: triethyleneglycol dimethacrylate.

ity due to their high concentration of hydrophilic monomers and a high amount of residual water in the adhesive layer that may reduce the degree of conversion, resulting in poorer mechanical properties of the adhesive layer.[3,17,37]

Recent studies have shown that the bond strength of several one-step self-etch adhesives can be improved by double application of the adhesive or by additional application of a hydrophobic adhesive resin layer.[1,9,14,18,19,23,39] However, the effect of this alternative technique seems to vary with different brands. G-Premio Bond (GPB, GC; Tokyo, Japan) is a 2-hydroxyethyl methacrylate (HEMA)-free universal adhesive that is compatible with etch-and-rinse, self-etch, and selective-etch techniques and provides multiple choices. Some previous studies have demonstrated that the bond strength of GPB is not as high as that of some other adhesives.[11,25] The lower bond strength is attributed to the phase separation that usually occurs in HEMA-free, one-step self-etch adhesives, and strong or prolonged air blowing is recommended.[8,11,12,38]

Two novel, experimental hydrophobic adhesive resins, BZF210 (GC) and BZF21 (GC) have been fabricated; BZF21 contains bioactive zinc fluoride glass while BZF210 does not. The zinc fluoride glass added to BZF21 is bioactive and can gradually release zinc (Zn) and fluoride (F) ions. F provides an anti-bacterial effect for dental tissues and prevents secondary caries, enhances remineralization, and prevents demineralization in dentin.[4,24] Meanwhile, adhesives containing Zn have been reported to inhibit the activity of matrix metalloproteinases (MMPs), reduce the collagen degradation within the hybrid layer,[2,35] improve the integrity of this layer,[34] inhibit demineralization, and promote remineralization.[36] However, it should be noted that Zn can chemically combine with 10-methacryloxydecyl dihydrogen phosphate (10-MDP) and form Zn-MDP complexes

Table 2 μTBS (MPa) and fracture modes of each group (n = 5/group)

Group	μTBS (mean ± SD)	Fracture mode (%)			
		CD	CC	A	M
GPB	33.57 ± 4.22^{A}	0	0	90	10
GPB+BZF210	48.68 ± 6.59^{B}	25	0	55	20
GPB+BZF21	58.58 ± 2.84^{C}	35	0	60	5
SBU	61.27 ± 10.72^{C}	35	5	30	30
SE2	66.32 ± 9.53^{C}	40	5	30	25

Different superscript letters indicate significantly different means ($p<0.05$). (Abbreviations: μTBS: microtensile bond strength; A: adhesive failure; CD: cohesive failure within dentin; CC: cohesive failure within composite resin; M: mixed failure.

that reduce Ca-MDP salt formation in self-etching adhesives, and it could compromise bonding to dentin.[7]

Therefore, the aim of this study was to evaluate the potential of two novel hydrophobic adhesive resins, BZF210 and bioactive BZF21, to promote bond strength when used after the application of GPB as a primer, thus converting a one-step self-etch universal adhesive to a two-step adhesive. The null hypothesis was that the bonding performance of GPB would not be affected by using an additional hydrophobic resin layer of BZF210 and BZF21.

MATERIALS AND METHODS

Tooth Selection and Preparation

Extracted noncarious human third molars (n = 35) were used in this study. The teeth were collected under a protocol reviewed and approved by the University of Hokkaido's Ethics Committee (#2003-17). They were stored in an aqueous solution of 0.5% chloramine-T at 4°C and used within three months after extraction. The teeth were randomly assigned into 5 experiments groups. Twenty-five teeth were used for the microtensile bond strength (μTBS) test and were further randomly divided into 5 groups with 5 teeth in each group. Four sticks from the central area were tested, resulting in a total of 20 sticks per group. Additionally, five teeth (one tooth per group) were used for SEM resin-dentin interface observation, and the other five teeth (one tooth per group) were used for analysis via scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM-EDS).

Adhesives and Bonding Procedure

Flat, mid-dentin surfaces were obtained by removing the coronal enamel of each tooth with a gypsum model trimmer under water cooling. Stereoscopy was used to confirm that no enamel remained on the dentin surface. The exposed dentin surfaces were polished with 600-grit SiC paper (Sankyo-Rikagaku; Saitama, Japan) for 60 s under continuous water cooling to produce a standardized smear layer prior to bonding.[22]

Table 1 shows the chemical formulations and manufacturer's instructions of the materials used in the study. Three commercial self-etch adhesives were used in this study: GPB, Scotchbond Universal (SBU, 3M Oral Care; St Paul, MN, USA) and Clearfil SE Bond 2 (SE2, Kuraray Noritake; Tokyo, Japan). Two novel experimental adhesive resins BZF210 and BZF21 were additionally applied after GPB. SBU and SE2 were chosen as control groups. SBU is a one-step self-etch universal adhesive, and SE2 is a classic two-step self-etch adhesive. The experimental groups were as follows: (1) GPB; (2) GPB+BZF210; (3) GPB+BZF21; (4) SBU; (5) SE2. After each adhesive application, resin composite blocks (Clearfil AP-X, Kuraray Noritake) were constructed in increments to a height of 4 mm; each incremental layer was light cured for 40 s per side using a light source at 500 mW/cm^2 (Pencure, J Morita; Tokyo, Japan). The prepared teeth were stored in distilled water at 37°C for 24 h.

Microtensile Bond Strength Test (μTBS)

Bonded dentin sticks (cross-sectional area: approximately 1 mm^2) were obtained from the prepared teeth by sectioning them with a low-speed diamond saw (Isomet Low Speed Saw, Buehler; Lake Bluff, IL, USA) under copious water cooling. Four sticks from the central area of each tooth were collected and fixed onto a Ciucchi's jig with cyanoacrylate glue (Model Repair 2 Blue, Dentsply Sankin; Otahara, Japan). The μTBS test was carried out at a crosshead speed of 1 mm/min in a desktop testing apparatus (EZ Test, Shimadzu; Kyoto, Japan) until failure occurred. The μTBS was expressed in MPa, obtained by dividing the applied force (N) at the time of fracture by the bonded area (mm^2), and the μTBS values of four beams from the same tooth were averaged for statistical purposes. The results were analyzed using one-way ANOVA and the Games-Howell test ($n = 5$, $p < 0.05$).

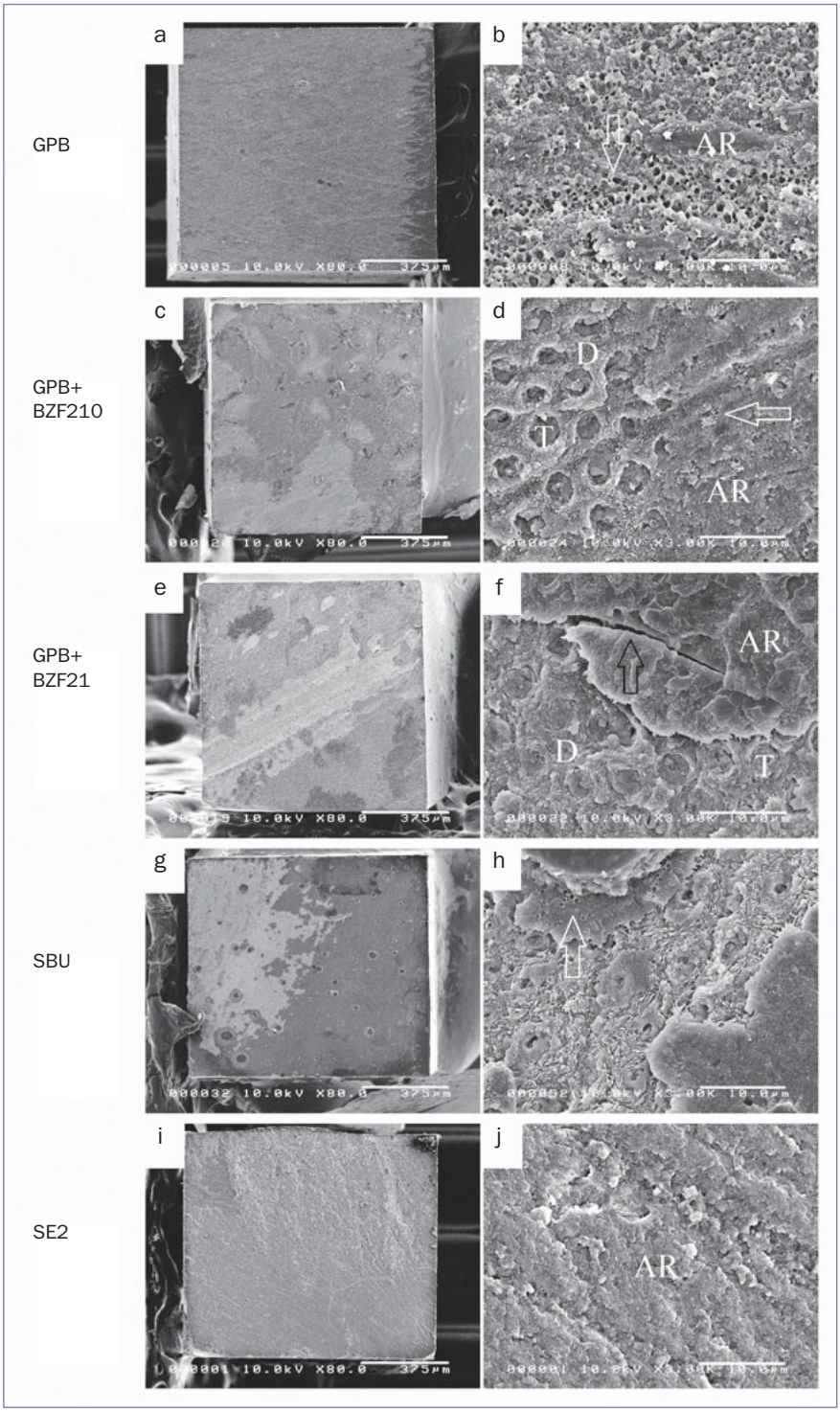

Fig 1 Representative SEM images of the dentin part of adhesive failure in each group at 80X and 3000X magnification. (a, b): GPB group: numerous, variously sized bubbles (white arrow) on top of the scratches were observed, and no dentinal tubules were exposed; (c, d): GPB+BZF210 group: small bubbles (white arrow) within the adhesive resin (AR); (e, f): GPB+BZF21 group: failure occurred on top of the smear layer and between the AR, most of the dentin tubules were plugged by resin tags (T), and cracks (black arrow) in the AR were observed; (g, h): SBU group: failure occurred on the top of the smear layer and between AR, all the dentin tubules were blocked by resin tags (T), and small bubbles (white arrow) within AR were found ; (i, j): SE2 group: failure occurred within the AR, and no dentin tubules or smear layer were observed (AR: adhesive resin; D: dentin; T: plugged resin tags).

Fracture Mode Analysis

After the μTBS test, the fractured dentin surfaces were examined at lower magnification (80X) to determine the mode of fracture, and specific features were further examined at 3000X magnification. Four fracture mode categories were distinguished: A, adhesive failure; CD, cohesive failure within dentin; CC, cohesive failure within composite resin; or M, mixed failure. Representative fractured specimens were mounted on aluminum stubs and coated with Pt-Pd using an ion sputter coater (E-1030, Hitachi; Tokyo, Japan) for 150 s. The fractured dentin surfaces were observed using a scanning electron microscopy (SEM; S-4000, Hitachi) at an accelerating voltage of 10 kV.

Interfacial Structure Observation

One tooth per group was prepared and sectioned into slabs parallel to the long axis of the tooth using a low-speed diamond saw. Two slabs from the central part of the tooth were randomly selected and prepared for SEM observation by the following protocol. Slab surfaces were sequentially polished with SiC papers (600-, 800-, and 1000-grit) under running water. Subsequently, the slabs were polished on a special soft cloth using diamond pastes (Buehler) with a grit size of 6, 3, or 1 μm, and the specimens were cleaned using an ultrasonic device for 3 min after each paste polishing. The specimens were immersed in 1 M hydrochloric acid (HCl) for 30 s and 5% sodium hypochlorite (NaOCl) for 5 min, followed by rinsing with distilled water. The slabs were left to air dry for 24 h. Finally, they were sputter coated with Pt-Pd for 150 s and examined using FE-SEM (S400, Hitachi) at 3000X magnification.

SEM-EDS Analysis

Both the pure adhesive resins and resin-adhesive-dentin interfaces were observed using electron dispersive X-ray spectroscopy (SEM-EDS; S-2380 N, Hitachi). One droplet of each adhesive resin was light cured for 10 s, two slabs of each group was prepared as previously for SEM analysis except for the immersion in 1 M hydrochloric acid (HCl) for 30 s and 5% sodium hypochlorite (NaOCl) for 5 min. All the slabs were left to air dry for 24 h, mounted on aluminum stubs and sputter coated with carbon (CC-40F; Meiwafosis; Osaka, Japan). The element composition on the surfaces of the light-cured pure adhesive resins and dentin-bonded interfaces underwent SEM-EDS area and linear scan analysis at an accelerating voltage of 15 kV.

RESULTS

μTBS Test

The mean μTBS are summarized in Table 2. Significantly higher values were achieved with the additional application of BZF210 (48.68 ± 6.59 MPa) or BZF21 (58.58 ± 2.84 MPa) on top of GPB than with GPB alone (33.57 ± 4.22 MPa) ($p < 0.05$). The bond strength of the GPB+BZF210 group was significantly lower than that of the GPB+BZF21 group ($p < 0.05$). There was no significant difference in the mean μTBS among GPB+BZF21, SBU (61.27 ± 10.73 MPa) and SE2 (66.32 ± 9.53 MPa) ($p > 0.05$), which were significantly higher than those of the GPB and GPB+BZF210 groups ($p < 0.05$).

Fracture Mode Analysis

The fracture mode distribution is summarized in Table 2. The GPB group showed 90% adhesive failure and 10% mixed failure. The smear layer was clearly present in the dentin part of adhesive failure in GPB, and a large number of different-sized bubbles on top of the scratches were observed with no dentinal tubule exposure (Fig 1b). However, in the GPB+BZF210 group, there was 25% cohesive failure within the dentin, 55% adhesive failure and 20% mixed fail-

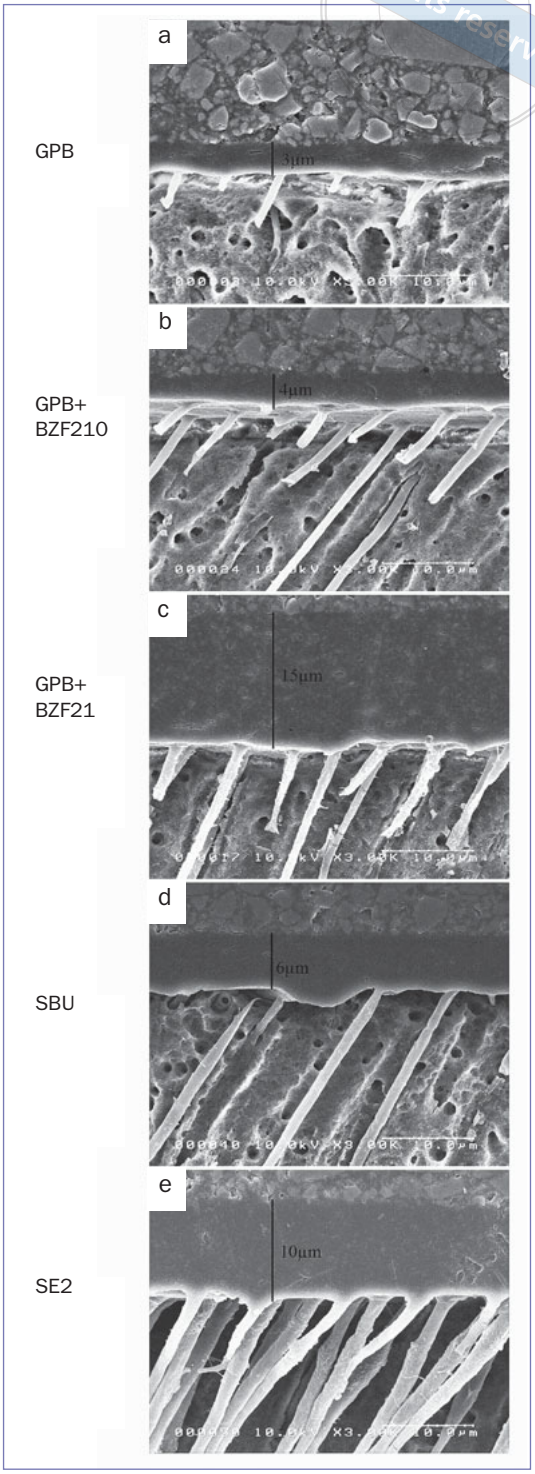

Fig 2 Representative SEM images of the interfacial structure of each group. (a): GPB group: nonuniform adhesive layer with short, sparsely distributed resin tags; (b): GPB+BZF210 group: longer, more numerous resin tags were observed; (c): GPB+BZF21 group: uniform adhesive layer with a thickness of approximately 15 μm; (d): SBU group: long resin tags were apparent; (e): SE2 group: large number of long resin tags with a nearly 10-μm-thick adhesive layer.

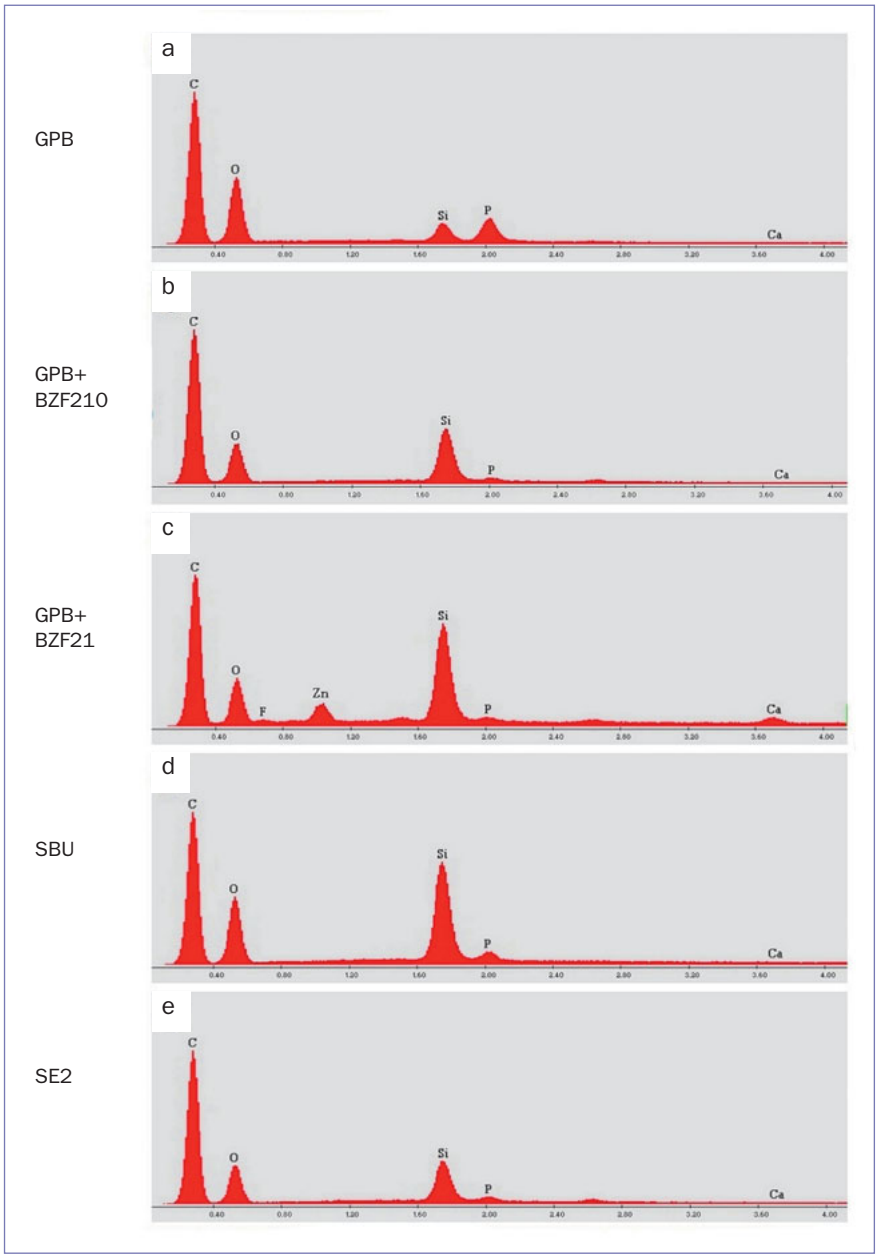

Fig 3 SEM-EDS area scan images on the surfaces of each adhesive resins. A particularly high peak of Zn was found in the GPB+BZF21 group compared with the other groups (C: carbon; O: oxygen; Zn: zinc; F: fluorine; P: phosphorus; Si: silicon; Ca: calcium).

ure. Small bubbles were occasionally observed above the scratches or within the adhesive resin (Fig 1d). In the GPB+BZF21 group, 35% cohesive failure in dentin, 60% adhesive failure and 5% mixed failure were observed. For the dentin part of adhesive failure in GPB+BZF21, failure occurred mostly on the top of the smear layer and between the smear layer and the adhesive resin, several dentin tubules were plugged by resin tags, cracks in the adhesive layer were occasionally observed, and bubbles were scarcely detected (Fig 1f). In the SBU and SE2 groups, less adhesive failure occurred; more cohesive and mixed failure modes were observed. For the dentin part of adhesive failure in SBU, failure mainly occurred on the top of the smear layer and between the smear layer and the adhesive resin; all the dentin tubules were blocked by resin tags, and bubbles were sporadically found within the adhesive resin (Fig 1h). For the dentin part of adhesive failure in SE2, most of the failure occurred within the adhesive layer or between the adhesive layer and composite resin; no dentin tubules, smear layer, and or bubbles were observed (Fig 1j).

Interfacial Structure Observation

SEM images of the interfacial structure of each adhesive are presented in Fig 2. In the GPB group, the thickness of

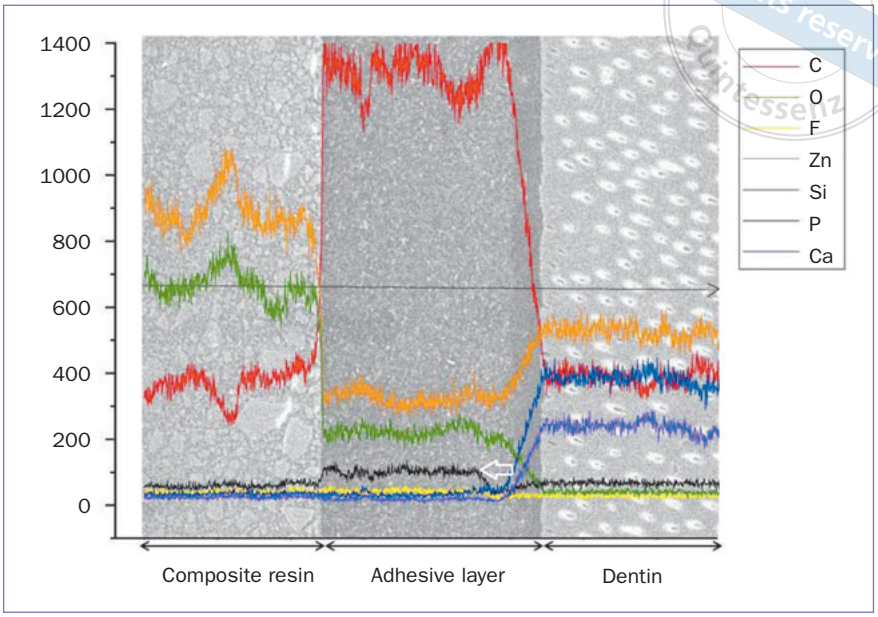

Fig 4 SEM-EDS linear scan images of the resin-adhesive-dentin interface in the GPB+BZF21 group. High content of Si (green curve) and O (orange curve) in the composite resin, high content of C (red curve) in the adhesive layer and a high content of P (blue curve) and Ca (purple curve) in dentin were observed. The content of Zn (black curve) in the adhesive layer was higher than that in the composite resin and dentin part, and the curve gradually dropped before the hybrid layer (white arrow), while the content of F (yellow curve) in the adhesive layer seemed similar to the composite resin and dentin part (C: carbon; O: oxygen; Zn: zinc; F: fluorine; P: phosphorus; Si: silicon; Ca: calcium).

the adhesive layer was nonuniform and less than 4 μm; few resin tags were observed, and most of them were very short (Fig 2a). When BZF210 and BZF21 were applied on GPB, uniform bonding layers with a more and longer resin tags were formed. Particularly in the BZF21 group, the thickness of the adhesive layer was approximately 15 μm (Fig 2c), which was thicker than that formed by GPB and GPB+BZF210 (Fig 2b). In the SBU group, an approximately 6-μm-thick adhesive layer at the resin-dentin interface and long resin tags could be observed (Fig 2d). In the SE2 group, long resin tags were very numerous, and the thickness of the adhesive layer was nearly 10 μm (Fig 2e).

SEM-EDS Analysis

The SEM-EDS area scan analysis of the adhesive resin surfaces revealed a high peak of Zn in the GPB+BZF21 group (Fig 3c), which was distinct from the peaks in the other groups (Figs 3a, 3b, 3d, 3e). For the elemental distribution analysis across the resin-adhesive-dentin interface, a high content of silicon (Si) and oxygen (O) was found in composite resin, a high carbon (C) content in the adhesive resin layer and a high calcium (Ca) and phosphate (P) content in dentin. In the GPB+BZF21 group, the content of Zn (black curve) in the adhesive layer was significantly higher than that of the composite resin and dentin part, but it was interesting to observe that the curve gradually dropped before the site of the hybrid layer, approximately at the area mixed with the adhesive resin, primer, and smear layer (Fig 4). In contrast, the content of F (yellow curve) was not completely clear. However, the adhesive layer seemed to be similar to the composite resin and dentin. SEM-EDS was not the best tool for F detection (Fig 4).

DISCUSSION

Dental adhesives are intricate mixtures of various ingredients, and the bonding performance is material and bonding-strategy dependent.[16,40] The chemical formulation, especially that of some specific functional monomers, plays an important role in the bonding efficacy, durability, and biocompatibility.[16] In this study, the application of both BZF210 and BZF21 significantly improved the bond strength when they were used as an additional hydrophobic resin layer on GPB. Therefore, the null hypothesis that the bond strength of GPB was not affected by the adjunctive use of BZF210 and BZF21 was rejected. Phase separation in GPB could have impaired the bonding efficacy to dentin.[38] Indeed, a large amount of blister-like areas was observed in the SEM failure mode observations of GPB in this study (Fig 1b). This finding agrees with some previous studies, where variously sized voids were shown in this acetone-based, HEMA-free, self-etching system or under very insufficient solvent evaporation conditions, implying that the weak point of GPB in bonding is between the adhesives and resin.[11,26] The failure mode analysis of GPB further confirmed this characteristic feature, in that most failure occurred above the smear layer with numerous voids of different sizes and no dentinal tubule exposure (Fig 1b).

After additional application of BZF210 or BZF21 on GPB, the bond strength was significantly enhanced in this study. Several mechanisms have been proposed for this better performance of adhesives after the additional hydrophobic adhesive resin application. The additional application of hydrophobic adhesive resin significantly increased the mechanical properties of the adhesive layer, a feature closely

related to the high bond strength.[16] The application of additional adhesive resin probably increased the conversion of monomers to polymers and the amount of cross linking, an increase which is significantly related to the bond strength.[28] 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane (bis-GMA) and urethane dimethacrylate or 1,6-di(methacryloyloxyethylcarbamoyl)-3,30,5-trimethylhexane (UDMA), the main hydrophobic monomers in BZF210 and BZF21, are most frequently used as cross linkers in adhesives,[40] and provide superior mechanical strength to the adhesive by forming a close connection with the composite resin, as well as providing lower polymerization shrinkage.[29] On the other hand, it is noticeable that bubbles at GPB interface dramatically decreased after the application of both BZF210 (Fig 1d) and BZF21 (Fig 1f). It was suggested that the use of adhesive resins BZF210 or BZF21 could facilitate the infiltration of resin components into dentin, mixing them with the blister-like zone, dramatically decreasing the number of voids, and forming a dense bonding layer. All these factors could have enhanced the bond strength.[6]

Applying the BZF210 and BZF21 also markedly increased the thickness of the adhesive layer, especially in the GPB+BZF21 group (Fig 2c). This uniform, dense, thick bonding layer could significantly reduce the contraction stress generated during the placement of the composite restoration, and this stress was significantly absorbed and relieved.[5] The thickness of the adhesive layer in the GPB+BZF21 group was nearly 15 μm (Fig 2c), and it was approximately three times thicker than that of the GPB group (Fig 2a). It is possible that this thick, uniform hydrophobic adhesive layer could dilute the hydrophilic and acidic resin components from GPB and reduce the water absorption.[10] Furthermore, this thick hydrophobic coat seems to limit the diffusion of water induced by pulpal pressure through the hybrid layer to the interface, which could inhibit polymerization and weaken the resin-adhesive-dentin interface.[27,32]

In this study, zinc fluoride glass was specifically present in BZF21, showing slight improvement in the 24-h bond strength to dentin. The mechanism related to the ability of zinc fluoride glass to improve bond strength still needs further investigation. Incorporation of silica fillers into the hydrophobic adhesive resin might be related to the optimized mechanical properties of the adhesive interface and could have promoted good initial bond strength of the adhesive.[30] It is speculated that the addition of zinc fluoride glass potentially increased the viscosity of BZF21 compared with BZF210 and enhanced the thickness of the bonding layer remarkably. Furthermore, both fillers (silica and zinc fluoride glass) in BZF210 and BZF21 were silanated. This silanated filler could improve the physical and mechanical properties of the adhesive resin.[15] Moreover, silanization of bioactive glass may protect the glass from leaching at early stages of water storage.[20]

Additionally, the innovative zinc fluoride glass in BZF21 is bioactive and can constantly release Zn and F ions. In the SEM-EDX analysis, it was found that this thick adhesive layer in the GPB+BZF21 group contains a high amount of Zn (Figs 3 and 4). The silanization of the fillers does not prevent Zn and F ion release from the glass fillers.[13] Adhesives containing zinc have been confirmed to increase the quality and longevity of the resin-dentin interface by reducing MMP-mediated collagen degradation,[2,21] inhibiting dentin demineralization,[31] and inducing remineralization. However, Zn can interact with 10-MDP, forming Zn-10-MDP complexes, reducing Ca-10-MDP salt formation and impacting 10-MDP dentin infiltration.[7,33] Our study also further confirmed that it is advantageous to add zinc to the adhesive resin of self-etching adhesives. Compared with the adhesive failure between the GPB+BZF210 and GPB+BZF21 groups, the residual 10-MDP from the GPB might have combined with Zn in the adhesive resin and enhanced the strength of the bonding layer; thus, more mixed adhesive failures occurred in the GPB+BZF21 group than in GPB+BZF210 group, and fractured surfaces of GPB+BZF21 samples showed cracks in the hydrophobic resin layer (Fig 1f). In the SEM-EDS linear scan, the curve of Zn gradually dropped toward dentin (Fig 4, white arrow). This drop may suggest that Zn undergoes some chemical reactions with the residual 10-MDP from GPB and then could not be detected in the hybrid layer or dentin.

Further research on the effect of the innovative bioactive zinc fluoride ion-releasing adhesive resin BZF21 is still needed, such as the long-term effect on the bond strength to dentin and caries prevention ability in vivo.

CONCLUSION

The bond strength of GPB can be significantly improved when it is used with an additional hydrophobic resin layer as a two-step self-etch universal adhesive. Moreover, the zinc fluoride glass present in BZF21 could be responsible for higher bond strengths.

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Clinical relevance: Converting G-Premio Bond into a two-step, self-etch universal adhesive by the application of a bioactive BZF21 layer may improve its bond strength. The bioactive, two-step self-etch adhesive approach could provide dentists with more clinical options for different patient profiles.