https://doi.org/10.4047/jap.2024.16.2.105

# Effect of universal adhesive pretreatments on the bond strength durability of conventional and adhesive resin cements to zirconia ceramic

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**Received** November 24, 2023 /
**Last Revision** March 28, 2024 /
**Accepted** April 9, 2024

**PURPOSE.** This study aimed to evaluate the effect of pretreatment of three different universal adhesives (Single Bond Universal [SBU], All-Bond Universal [ABU], and Prime&Bond universal [PBU]) on the bonding durability of an adhesive (Panavia F 2.0, PF) and a conventional (Duo-Link, DL) resin cements to air-abraded zirconia. **MATERIALS AND METHODS.** Rectangular-shaped zirconia specimens were prepared. The chemical composition and surface energy parameters of the materials were studied by Fourier transform infrared spectroscopy and contact angle measurement, respectively. To evaluate resin bonding to the zirconia, all the bonding specimens were immersed in water for 24 h and the specimens to be aged were additionally thermocycled 10000 times before the shear bond strength (SBS) test. **RESULTS.** The materials showed different surface energy parameters, including the degree of hydrophilicity/hydrophobicity. While the DL/CON (no pretreatment) showed the lowest SBS and a significant decrease in the value after thermocycling ($P < .001$), the PF/CON obtained a higher SBS value than the DL/CON ($P < .001$) and no decrease even after thermocycling ($P = .839$). When the universal adhesives were used with DL, their SBS values were higher than the CON ($P < .05$), but the trend was adhesive-specific. In conjunction with PF, the PF/SBU produced the highest SBS followed by the PF/ABU ($P = .002$), showing no significant decrease after thermocycling ($P > .05$). The initial SBS of the PF/PBU was similar to the PF/CON ($P = .999$), but the value decreased after thermocycling ($P < .001$). **CONCLUSION.** The universal adhesive pretreatment did not necessarily show a synergistic effect on the bonding performance of an adhesive resin cement, whereas the pretreatment was beneficial to bond strength and durability of a conventional resin cement. [J Adv Prosthodont 2024;16:105-14]

**KEYWORDS**
Universal adhesive; Resin cement; Zirconia ceramic; Bonding durability; Surface energy parameters

https://doi.org/10.4047/jap.2024.16.2.105

## INTRODUCTION

Among metal-free restoration options, the use of zirconia ceramics based on yttria stabilized polycrystalline tetragonal zirconia (Y-TZP) has increased rapidly due to their esthetic properties, high mechanical properties, and excellent biocompatibility.[1] Zirconia ceramic restorations that do not require high retention may be luted with conventional cements because of their superior mechanical properties.[1-3] In clinical practice, however, a long term durable bond to zirconia is essential when the retention of the restorations is not sufficient. In such cases, clinically appropriate adhesive protocols are required.

Zirconia ceramics show difficulties in forming a reliable and durable mechanical or chemical bond to resin cements when compared to silica-based ceramics. Conventional bonding protocols including hydrofluoric acid etching and silane coupling agent treatment are not effective for zirconia ceramics due to their surface characteristics.[4] In order to achieve durable resin bonding to zirconia, alternative mechanical and chemical surface treatments have been investigated. It has been reported that the use of resin cements or primers/adhesives containing an acidic adhesive monomer such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP) to airborne-particle abraded zirconia surfaces is effective for micromechanical and chemical bonding to zirconia.[4,5]

Conventional bisphenol A-glycidyl methacrylate (bis-GMA)-based resin cements do not effectively adhere to zirconia ceramics because they do not contain any acidic adhesive monomers. Meanwhile, few "adhesive" cements, such as MDP-based luting agents, have shown satisfactory bond strength to zirconia.[6] In addition, single step self-adhesive resin cements, which contain a resin matrix packed with multifunctional acid methacrylates, have been introduced to simplify the cementation procedures.[6] When conventional resin cements are used, the pretreatment of primers or adhesives containing adhesive monomers to zirconia are required for chemical adhesion. In general, the adhesive and self-adhesive resin cements do not need such a pretreatment for chemical adhesion, as phosphate groups of MDP monomers in the materials directly react with the hydroxyl groups of the zirconia surfaces.[4]

Recently, new MDP-containing single-bottle adhesives have introduced to the dental market. These materials are called ''universal'' adhesives because they can be used in multi modes (etch-and-rinse or self-etch modes) on the tooth substrates.[7] These adhesives can also be used for the bonding of resin-based materials to various indirect restorative substrates including zirconia, without the additional use of a primer. Kim *et al*. reported that new universal adhesives showed better performance in terms of the resin bonding to zirconia ceramic compared with a conventional MDP-containing primer.[3]

In the present study, it was assumed that the additional pretreatment of universal adhesives to zirconia before the application of an MDP-containing resin cement could enhance the resin bond strength and its durability to zirconia. In contrast, it was also supposed that the increased amount of acidic and hydrophilic adhesive monomers at the resin-zirconia bonding interface could facilitate water sorption, thereby adversely affecting the bonding durability.[8,9] Thus, the purpose of this study was to determine whether the additional pretreatment of three different universal adhesives before the application of an MDP-containing adhesive resin cement would synergistically affect the resin bonding to airborne-particle abraded zirconia. A conventional resin cement was also tested for comparison. The first null hypothesis tested was that there would be neither positive nor negative effect of universal adhesive use on the bond strength and durability of the adhesive resin cement to zirconia ceramic. The second null hypothesis was that there would be no significant differences in bonding to zirconia among the three universal adhesives when the conventional resin cement was used.

## MATERIALS AND METHODS

For this study, three commercially available universal adhesives and two (Duo-Link as conventional and Panavia F 2.0 as adhesive) resin cements were selected. Their codes, main compositions, batch numbers, manufacturers, and application procedures are summarized in Table 1. The manipulation of the materials was performed according to the instructions of

the manufacturers. Rectangular-shaped (10 mm × 10 mm × 1 mm) zirconia specimens (Everest ZS-Ronde, Kaltenbach & Voigt GmbH, Biberach, Germany) were prepared by sintering according to the manufacturer's instructions.

To investigate their chemical composition of the universal adhesives and resin cements, their Fourier transform infrared (FTIR) spectra were acquired using a FTIR spectrophotometer (IRPrestige-21, Shimadzu Corp.; Kyoto, Japan) equipped with an attenuated total reflectance (ATR) unit (MIRacle, Pike Technologies Inc.; Madison, WI, USA).[2,10] For the measurement of the universal adhesives, a liquid plate insert, with Teflon liquid holder in its center, was placed on the ATR surface. A small amount of each universal adhesive was contacted on the ATR surface and air-dried. In the case of the resin cements, a small amount of each freshly mixed material was applied on the ATR surface. The absorbance spectrum was obtained by scanning the specimens 32 times over a 4000 - 700 $cm^{-1}$ range at a resolution of 4 $cm^{-1}$. The spectra were analyzed and their peaks were assigned based on references.

The contact angles (CAs,Θ) of the universal adhesives and resin cements were measured to calculate the surface energy parameters of materials.[11,12] For the CA measurements of the universal adhesives, the zirconia plates were polished with 600-grit abrasive paper and cleaned ultrasonically in 96% ethanol.[13] One of the universal adhesives was applied on each zirconia specimen surface and air-dried. Each adhesive-treated zirconia surface was covered by a polyester film and a glass slide and then light-cured by placing the light guide tip of a dental light-curing unit (LCU, Bluephase® 20i, IvoclarVivadent; Schaan, Liechtenstein) against the glass slide. To measure the CAs of the resin cements, the mixed resin paste was syringed into a stainless steel split mold with a dimension of 10 mm × 10 mm × 1 mm and was covered by a polyester film and a glass slide and then light-cured as described above.

For each of three test liquids with known surface energy parameters (water, glycerol, and 1-bromonaphthalene), the CAs (5-μL droplet) were determined on the adhesive-treated zirconia or resin cement surfaces using a goniometer (OCA 15 plus, DataPhysics; Filderstadt, Germany) (n = 5).

The surface energy parameters of the materials were calculated based on the Young-Dupré equation combined with the Lifshitz-van der Waals (LW)/Lewis acid-base (LAB) theory[11,12]: $\gamma_l(1 + \cos\Theta) = 2[(\gamma_s^{LW}\gamma_l^{LW})^{1/2} + (\gamma_s^{+}\gamma_l^{-})^{1/2} + (\gamma_s^{-}\gamma_l^{+})^{1/2}]$, where $\gamma_l$ and $\gamma_s$ are the surface tensions of the liquid (l) and solid (s), respectively; the superscripts + and – indicate the acid and base components, respectively. The total surface energy $\gamma_s$ was determined by: $\gamma_s = \gamma_s^{LW} + 2(\gamma_s^{+}\gamma_l^{-})^{1/2}$. In addition, the

**Table 1.** Universal adhesives and resin cements used in this study and their application procedures

| Product (code) | Main composition (batch No.) | Manufacturer | Application procedure |
|---|---|---|---|
| Single Bond Universal (SBU) | MDP, DMA, HEMA, Vitrebond copolymer, silane, ethanol, water, filler, initiators (90521C) | 3M Deutschland GmbH, Neuss, Germany | Apply the adhesive and allow it to react for 20 s. Gently air dry for 5 s. |
| All-Bond Universal (ABU) | MDP, bis-GMA, HEMA, ethanol, water, initiators (1900006405) | Bisco Inc., Schaumburg, IL, USA | Apply the adhesive and air dry. Light cure for 10 s. |
| Prime&Bond universal (PBU) | MDP, PENTA, bi- and multifunctional acrylate, isopropanol, water, initiator, stabilizer (1908001132) | Dentsply DeTrey GmbH, Konstanz, Germany | Apply the adhesive and slightly agitate for 20 s. Light cure for 10 s. |
| Duo-Link (DL) | Base: bis-GMA, TEGDMA, UDMA, glass filler; Catalyst: bis-GMA, TEGDMA, glass filler (1500003655) | Bisco Inc., Schaumburg, IL, USA | Mix Base and Catalyst. Light cure for 40 s. |
| Panavia F 2.0 (PF) | A: MDP, DMA, silica, CQ (830233); B: DMA, barium glass, sodium fluoride (830059) | Kuraray Noritake Dental Inc., Okayama, Japan | Mix pastes A and B. Light cure for 20 s. |

Abbreviations: bis-GMA, bisphenol A-glycidyl methacrylate; CQ, camphorquinone; DMA, dimethacrylate; HEMA, hydroxyethly methacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; PENTA, dipentaerythritolpentaacrylate monophosphate; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

https://doi.org/10.4047/jap.2024.16.2.105

$\gamma_{sw}^{LW}$ and the $\gamma_{sw}^{AB}$ were calculated using the following equations, respectively: $\gamma_{sw}^{LW} = [(\gamma_s^{LW})^{1/2} - (\gamma_w^{LW})^{1/2}]^2$ and $\gamma_{sw}^{AB} = 2[(\gamma_s^+\gamma_s^-)^{1/2} + (\gamma_w^+\gamma_w^-)^{1/2} - (\gamma_s^+\gamma_w^-)^{1/2} - (\gamma_w^+\gamma_s^-)^{1/2}]$, where w refers to water. The degree of hydrophobicity was expressed as the magnitude of $\Delta G_{sws}$ (= $-2\gamma_{sw}$), in which G is the free energy and $\gamma_{sw} = \gamma_{sw}^{LW} + \gamma_{sw}^{AB}$.[12,14]

The prepared zirconia specimens were embedded using an acrylic resin. Each zirconia surface was air-abraded with 50 μm $Al_2O_3$ (pressure: 0.25 MPa; angle: perpendicular to the surface; distance: 10 mm; time: 15 s),[12,15] cleaned ultrasonically in 96% ethanol, and finally air-dried.

The resin bonding to the zirconia specimens and debonding were performed according to the protocol of the notched-edge shear bond strength test (Ultradent Products Inc., South Jordan, UT, USA).[16] One of the three universal adhesives was applied over the air-abraded zirconia surface and light-cured according to each manufacturer's instructions (Table 1). Non-adhesive treated zirconia specimens were also prepared as the control (CON) group. Using the bonding clamp, each mixed resin cement (either DL or PF) was packed into the button mold insert (internal diameter: 2.38 mm) and light-cured. In this way, one bonded resin cement cylinder was made on one zirconia specimen.[17]

Prior to debonding, all the resin-zirconia specimens were immersed in distilled water at 37°C for 24 h.[16] For each resin cement, the zirconia specimens with each universal adhesive (a total of four groups including the CON group) were divided into two groups depending on the subsequent aging method (n = 10). The specimens to be aged were additionally thermocycled 10,000 times between 5°C and 55°C water baths with a dwelling time of 30 s and an exchange time of 5 s between each bath.[2]

For debonding, the specimens were engaged at their resin cylinder bases with a notched-edge shear blade in a universal testing machine until bonding failure occurred (crosshead speed: 1.0 mm/min). Shear bond strength (SBS) values in MPa were calculated from the maximum load divided by the bonding area. The fractured zirconia surfaces were observed under an optical microscope (SZ61, Olympus; Tokyo, Japan) to determine the bonding failure mode, which was classified into one of the following three types: A, adhesive failure at the resin-zirconia interface; C, cohesive failure within the resin cement; and M, combination of these failure modes.

The CAs for the universal adhesives and SBS values were examined for the normality of distribution with the Shapiro-Wilk test and the equality of variances with the Levene test. As meeting the required criteria for parametric analysis, the results were analyzed with one-way (universal adhesive CAs) and three-way analysis of variance (ANOVA) (SBS; three variables: universal adhesive, resin cement, and aging), respectively. Thereafter, Tukey's test was used as post hoc analysis. The CAs of the two resin cements were analyzed using Student's t-test. Statistical analyses were carried out using SPSS 17.0 for Windows (SPSS Inc., Chicago, IL, USA) at a level of significance of $\alpha = .05$.

## RESULTS

Figure 1 shows the representative FTIR spectra of the air-dried universal adhesives and freshly mixed resin cements. For the three universal adhesives, broad absorption bands indicating hydrogen-bonded hydroxyl (O-H) stretching vibrations were detected in the 3500 - 3250$cm^{-1}$ region. The universal adhesives showed the phosphorus-oxygen double bond (P=O) and phosphorus-oxygen-alkyl (P-O-C) stretching vibrations around 1250 and 1050 $cm^{-1}$, respectively. The resin cement PF also showed the P=O and P-O-C peaks in the wavenumber regions while the resin cement DL did not present the clear P=O and P-O-C peaks.

The surface energy parameters of the universal adhesives and resin cements derived from the CA measurements with three liquids of different surface tensions are summarized in Table 2. The $\gamma_s$ values of the universal adhesives ranged from 51.0 to 54.4 $mJ/m^2$. There were no significant differences in the $\gamma_s^{LW}$ value among the three adhesives ($P > .05$). The $\gamma_s^-$values were greater than $\gamma_s^+$values for all three materials. Among the three adhesives, PBU exhibited the smaller $\gamma_s^-$ and the highest $\Delta G_{sws}$ followed by ABU ($P < .05$) and lastly by SBU ($P < .05$). PF showed a significantly higher $\gamma_s$ value than DL between the two resin cements ($P < .001$). The $\gamma_s^{LW}$ was significantly larger in DL than in PF ($P = .042$), but the $\gamma_s^+$, $\gamma_s^-$, and $\gamma_s^{AB}$ val-

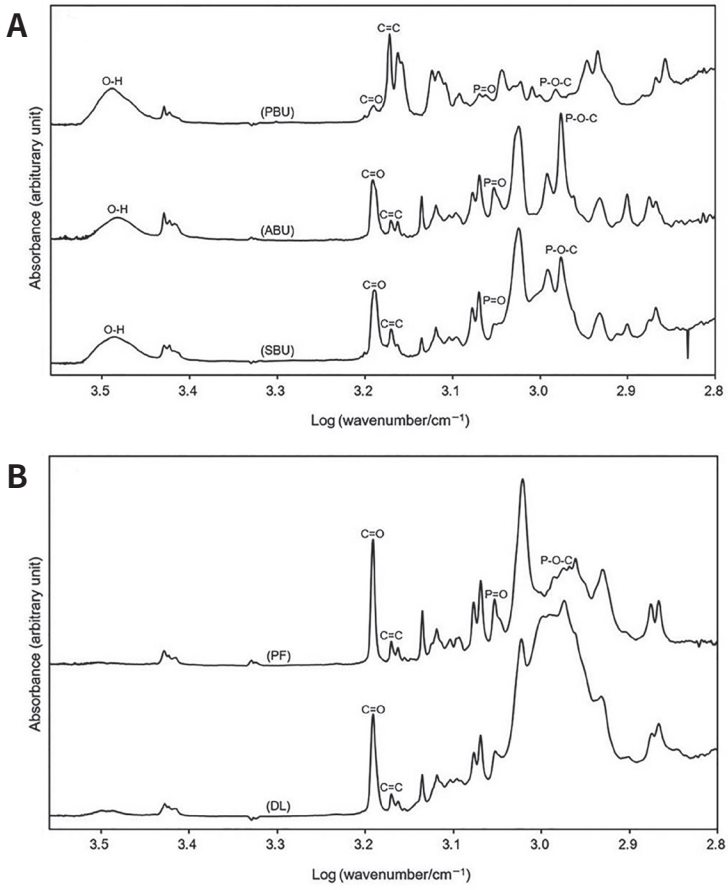


**Fig. 1.** FTIR spectra of universal adhesives (A) and resin cements (B) used in this study: SBU, Single Bond Universal; ABU, All-Bond Universal; PBU, Prime&Bond universal; DL, Duo-Link; PF, Panavia F 2.0.

**Table 2.** Surface energy parameters (mJ/m$^2$) of the universal adhesives and resin cements used (n = 5)

| Material | | $\gamma_s$[1] | $\gamma_s^{LW}$ | $\gamma_s^+$ | $\gamma_s^-$ | $\gamma_s^{AB}$ | $\Delta G_{sws}$ |
|---|---|---|---|---|---|---|---|
| Universal adhesive | SBU | 54.4 (1.0)$^{a2}$ | 47.7 (1.2)$^a$ | 0.5 (0.1)$^a$ | 21.8 (1.1)$^a$ | 6.7 (0.6)$^a$ | -16.6 (1.4)$^a$ |
| | ABU | 52.3 (1.3)$^{ab}$ | 46.4 (1.4)$^a$ | 0.5 (0.1)$^a$ | 19.2 (1.8)$^b$ | 5.9 (0.4)$^a$ | -21.0 (2.6)$^b$ |
| | PBU | 51.0 (1.8)$^b$ | 46.8 (1.7)$^a$ | 0.3 (0.1)$^b$ | 16.8 (1.0)$^c$ | 4.2 (0.5)$^b$ | -26.7 (1.7)$^c$ |
| Resin cement | DL | 49.0 (1.9)$^{a3}$ | 46.8 (1.5)$^a$ | 0.1 (0.03)$^a$ | 20.7 (2.9)$^a$ | 2.2 (0.5)$^a$ | -19.1 (5.3)$^a$ |
| | PF | 55.6 (1.5)$^b$ | 44.8 (0.9)$^b$ | 1.0 (0.4)$^b$ | 29.0 (0.4)$^b$ | 10.8 (2.2)$^b$ | -2.8 (0.9)$^b$ |

[1] $\gamma_s$, total surface energy; $\gamma_s^{LW}$, Lifshitz-van der Waals component; $\gamma_s^+$, acid component; $\gamma_s^-$, base component; $\gamma_s^{AB}$, acid/base component; and $\Delta G_{sws}$, degree of hydrophobicity/hydrophilicity.
[2] Within the same column, the same lowercase superscript letters show no significant differences among the three universal adhesives ($P > .05$).
[3] Within the same column, the same lowercase superscript letters show no significant difference between the two resin cements ($P > .05$).

ues of PF were greater than those of DL ($P < .05$). The $\Delta G_{sws}$ values of the resin cements indicated that PF exhibited significantly higher hydrophilicity than DL ($P = .002$).

Table 3 lists the results of the three-way ANOVA of the SBS data. The results indicated that the type of universal adhesive (including CON), type of resin cement, and aging significantly affected the SBS values ($P < .05$). Moreover, significant interactions were found between adhesive and aging as well as ad-

https://doi.org/10.4047/jap.2024.16.2.105

**Table 3.** Three-way ANOVA results of the shear bond strength data

| Source of variation | df | Sum of squares | Mean squares | F | *P* |
|---|---|---|---|---|---|
| UA | 3 | 8343.871 | 2781.290 | 171.319 | < .001 |
| RC | 1 | 152.490 | 152.490 | 9.393 | .003 |
| Aging | 1 | 435.600 | 435.600 | 26.832 | < .001 |
| UA × RC | 3 | 2586.481 | 862.160 | 53.106 | < .001 |
| UA × Aging | 3 | 420.341 | 140.114 | 8.631 | < .001 |
| RC × Aging | 1 | 0.025 | 0.025 | 0.002 | .969 |
| UA × RC × Aging | 3 | 96.074 | 32.025 | 1.973 | .121 |

UA, universal adhesive; RC, resin cement.

hesive and cement ($P < .001$). There was no significant interaction between resin cement and aging ($P = .969$). The results of the SBS values and respective failure modes for each group are summarized in Table 4. The DL/CON group showed a mean initial (24 h water immersion at 37°C) SBS value of 9.2 MPa, but there was a significant decrease in the value (to 3.3 MPa) after aging by thermocycling ($P < .001$). The PF/CON group showed a significantly higher SBS than the DL/CON ($P < .001$), and no significant decrease in the value was detected even after thermocycling ($P = .839$). When the universal adhesives were used together with DL, their SBS values were significantly higher than the CON group even after thermocycling ($P < .05$), but the trend was adhesive-specific. There were no significant differences in the initial value between the DL/SBU and DL/ABU groups ($P > .05$) without a significant decrease in the value even after thermocycling ($P > .05$). In contrast, the DL/PBU group showed significantly lower initial SBS value than the other two DL/adhesive groups ($P < .05$), and there was a significant decrease in the value after thermocycling ($P = .002$). Unlike the case of DL, the universal adhesives pretreatment before the use of PF did not necessarily improve the resin bonding to zirconia. The PF/SBU group showed the highest SBS value followed by the PF/ABU group ($P = .002$), and the values did not significantly decrease even after thermocycling ($P > .05$). On the other hand, the SBS of the PF/PBU group exhibited a statistically similar initial value to the PF/CON ($P = .999$). After thermocycling, moreover, the value significantly decreased ($P < .001$), being significantly lower than that of the PF/CON group ($P < .001$). For all the groups, the failure modes were predominantly adhesive, especially after thermocycling. In the case of the SBU and ABU groups before thermocycling, the occurrence of mixed failures slightly increased.

## DISCUSSION

This study aimed to investigate the effect of pretreatment of three different universal adhesives before the application of either a conventional or an MDP-containing resin cement to zirconia ceramic. The SBS results for the adhesive resin cement PF showed that the values before and after thermocycling were definitely adhesive dependent (Table 4). Therefore, the first null hypothesis that there is no effect of universal adhesive use on the bond strength and durability of the adhesive resin cement to zirconia was rejected. The second null hypothesis was also rejected because there were significant differences in bonding to zirconia among the three universal adhesives when the conventional resin cement DL was used (Table 4).

Together with the bond strength testing, the universal adhesive and resin cements used in this study were characterized in terms of FTIR spectroscopy (Fig. 1) and surface energy parameter calculation (Table 2). In the case of the universal adhesives, their FTIR spectra were obtained after air-drying on the ATR surface to remove the solvent components.[10] The FTIR analysis revealed that the three universal adhesives contained a phosphoric ester monomer with phosphate group (MDP according to the manufacturers, Table 1). In addition, the three universal adhesives showed

**Table 4.** Mean shear bond strengths (SBSs) and their respective standard deviations (SDs) and failure modes (n = 10)

| Resin cement | Universal adhesive | Before thermocycling | | After thermocycling | |
|---|---|---|---|---|---|
| | | SBS (SD) | Failure mode | SBS (SD) | Failure mode |
| DL | CON | 9.2 (3.0)$^{Aa1}$ | A (10)[3] | 3.3 (1.8)$^{Aa2}$ | A (10) |
| | SBU | 32.5 (4.8)$^{Ba}$ | A (8), M (2) | 31.0 (3.2)$^{Ba}$ | A (10) |
| | ABU | 29.8 (5.1)$^{Ba}$ | A (8), M (2) | 30.6 (3.0)$^{Ba}$ | A (10) |
| | PBU | 23.0 (4.3)$^{Ca}$ | A (10) | 16.5 (3.8)$^{Ca}$ | A (10) |
| PF | CON | 22.3 (4.2)$^{Ab}$ | A (9), M (1) | 20.8 (3.7)$^{Ab}$ | A (10) |
| | SBU | 32.8 (4.6)$^{Ba}$ | A (7), M (3) | 32.4 (4.9)$^{Ba}$ | A (10) |
| | ABU | 25.2 (4.1)$^{Ab}$ | A (8), M (2) | 24.2 (5.4)$^{Ab}$ | A (10) |
| | PBU | 22.1 (4.2)$^{Aa}$ | A (10) | 11.7 (2.5)$^{Cb}$ | A (10) |

[1] For each resin cement, the same uppercase superscript letters within the same column show no significant differences among the four adhesive conditions ($P > .05$). The same lowercase superscript letters within the same column show no significant differences between the two resin cement conditions within each adhesive ($P > .05$).
[2] When the SBS values were compared within the same row, only the DL/CON, DL/PBU and PF/PBU groups showed a significant difference in SBS value ($P < .05$).
[3] A, adhesive failure; M, mixed failure. The number in the parentheses indicates the number of the specimens in each group.

the absorption band indicating O-H stretching vibrations around the 3500 - 3250 $cm^{-1}$ region. The FTIR spectrum of the adhesive resin cement PF exhibited the peaks indicating the presence of MDP monomer. However, PF did not show such absorption band of O-H stretching vibrations, indicating that the material is basically hydrophobic notwithstanding the inclusion of MDP monomer.

To calculate the surface energy parameters of the adhesive and cement materials, the acid-base theory of adhesion was applied among several surface energy calculation models.[18] The LW/LAB approach decomposes the surface energy into LW and LAB interactions.[2,19] Thus, the surface energy of a solid can be separated into three components (dispersive [$\gamma_s^{LW}$], acid [$\gamma_s^+$], and base [$\gamma_s^-$]components). In this study, water ($\gamma_s^+ = \gamma_s^-$) and glycerol ($\gamma_s^- > \gamma_s^+$) were used as polar fluids. In contrast, 1-bromonaphthalene ($\gamma_s^+ = 0$ and $\gamma_s^- = 0$) was used as an apolar liquid. It can be assumed that surface energy parameters of monomer and polymer are similar because all groups and segments of the monomers are also present in the polymeric material.[11,20] In this study, therefore, CA measurements were performed on the light-cured materials and the surface energy parameters were calculated from the CA data. In the case of the universal adhesives, in addition, the materials were applied on zirconia surfaces, air-dried, and light-cured prior to CA measurements. Also based on the acid-base theory, the magnitude of $\Delta G_{sws}$ can be used as the quantitative measure of the surface hydrophobicity or hydrophilicity.[14] When $\Delta G_{sws}$ is positive, the interaction of the material with water dominates (hydrophilic material); when the value is negative, the polar cohesive attraction between the water molecules dominates (hydrophobic material).[14]

In the context of a hydrogen bond, the $\gamma_s^+$ and $\gamma_s^-$ are considered as the hydrogen bond donating (HBD) and the hydrogen bond accepting (HBA) components, respectively.[2,19] Although water is considered to be neutral ($\gamma_s^+ = \gamma_s^-$), most materials are predominantly basic and, therefore, have a primarily HBA nature.[2] This study also showed large $\gamma_s^-$ and very small $\gamma_s^+$ values for all the materials tested (Table 2). In addition, significant differences were found in the $\gamma_s^-$ values across the two resin cements as well as the three universal adhesives. It can be suggested that the HBA ($\gamma_s^-$) component of the materials interacted with the HBD ($\gamma_s^+$) component of the zirconia surface.[2] Therefore, the magnitude of $\gamma_s^-$ value may reflect the bonding capabilities of the materials (SBU > ABU > PBU; PF > DL in this study). The $\Delta G_{sws}$ values indicating the degree of hydrophobicity/hydrophilicity revealed that the all the three adhesives after the removal of the most of the solvents by air-drying were basically hydrophobic. According to the $\Delta G_{sws}$ value, the univer-

https://doi.org/10.4047/jap.2024.16.2.105

sal adhesive PBU was the most hydrophobic, and it showed the inferior bonding to the zirconia surface (Table 4). In the case of the resin cements, significant differences were found in all the parameters, implying the adhesive resin cement PF had superior bonding capabilities (higher $\gamma_s^-$) and greater hydrophilic nature (lower $\Delta G_{sws}$ value), although both materials had hydrophobic nature. This can be attributed to the difference in the presence or amount of acidic monomers or the type of their polar functional group in their composition (Table 1).[9] Polymers containing more polar groups that can form ionic attractions or hydrogen bonds are more hydrophilic, while those with less polar groups are hydrophobic.[9,21] In the case of PF, it seems that the hydrophobicity of the mixed paste developed following the radical polymerization reactions.[9]

To evaluate the resin bond strength to zirconia, the protocol of the notched-edge shear bond strength test was used.[16] In addition, 10000 thermal cycles were used to evaluate bonding durability of the adhesives and resin cements to zirconia ceramic. It might be provisionally assumed that the cycles are equivalent to one year of clinical service.[22] Although, in this study, deterioration of the interfacial bonding was obtained by aging with 10,000 thermal cycles, long-term water aging is required to properly predict the clinical performance of the adhesive interface when considering the service life of zirconia restorations and the harsh oral environment.[23]

The surface energy (Table 2) and SBS (Table 4) results imply that even the non-self-adhesive material DL has some adhesive capability to zirconia. However, when DL was bonded directly to the sandblasted zirconia surfaces, the SBS values significantly decreased after thermocycling (Table 4).[24] In the oral environment, greater moisture sensitivity of a restoration may increase the risk of bond degradation at the marginal gap.[9] Sorption and solubility properties of a resin material are greatly affected by the chemical composition and hydrophilic constituents of resin matrix.[9,25] The DL contains urethane dimethacrylate (UDMA) as one of the monomers (Table 1), which tends to be more hydrophilic than the other matrix resin monomers such as bis-GMA because its urethane group contains the hydrophilic amide linkage.[26] This may be detrimental to the long-lasting resin bonding with zirconia. The SBS results confirm that the pretreatment of a primer or an adhesive to zirconia surface is essential for durable resin bonding when a conventional resin cement is used.[13,27] When the universal adhesives were applied to zirconia prior to the use of the conventional resin cement DL, the SBS values significantly increased. However, the trend was dependent on the adhesives used. SBU and ABU, which showed significantly higher $\gamma_s^-$ values and greater HBA nature than PBU (Table 2), also produced significantly higher SBS values than PBU. The SBS values for SBU and ABU did not significantly decrease even after thermocycling. In DL/PBU, in contrast, there was a significant decrease in SBS after thermocycling. Therefore, the SBS results of DL largely reflect the combined effects of micromechanical interlocking by zirconia sandblasting and chemical bonding by the adhesive pretreatment.

Unlike DL, the adhesive resin cement PF has a strong self-adhesion property to zirconia due to the inclusion of the phosphate monomer MDP in its composition (Table 1).[4] When PF was applied to sandblasted zirconia, high mean pre- and post-thermocycling SBS values of 22.3 and 20.8 MPa, respectively, were achieved even without the use of any universal adhesives. This finding confirms the efficacy of MDP monomer within the material in durable bonding with zirconia.[2,4,28] When the adhesive monomers are used together with the MDP-containing material PF, the bonding interface may be more hydrophilic than in the cases of the non-MDP-containing material DL, potentially resulting in higher water sorption because the phosphate group can form a hydrogen bond with water during the thermocycling procedures.[21] After thermocycling, however, the trend in SBS was also dependent on the adhesives used, like in the case of DL. SBU showed a synergistic effect in terms of SBS when used together with PF even after thermocycling. Thus, the degree of hydrophilicity/hydrphobicity, expressed by $\Delta G_{sws}$ (Table 2), of SBU may be optimal in bonding with zirconia when the material is used together with PF. On the other hand, such synergistic effect in resin bonding was not clearly seen in ABU and PBU. Moreover, the post thermocycling SBS values were significantly lower in the PF/PBU than in

the DL/PBU.

The present study investigated how the pretreatment of three different universal adhesives before the application of a conventional and an adhesive resin cements would affect bonding with zirconia. It was found that the SBS values were greatly adhesive-specific for both cement types and the additional use of the adhesives did not necessarily show a synergistic effect in terms of SBS. However, generalizing the results directly to the clinical situation should be done with caution. Only limited numbers of materials (three adhesives and two resin cements) were tested in this study. In addition, the surface energy parameters of the materials tested are not sole determinant of the resin bond strength with zirconia. Further research is still needed to develop a more comprehensive *in vitro* and *in vivo* study that aims to determine the best clinical option for resin bonding to zirconia ceramic.

## CONCLUSION

The purpose of this study was to evaluate the effect of three different universal adhesive (SBU, ABU, and PBU) pretreatment on the bonding durability of an adhesive (PF) and a conventional (DL) resin cements to zirconia ceramic. The materials showed different surface energy parameters, including the degree of hydrophilicity/hydrophobicity. It was found that the SBS values were greatly adhesive-specific for both cement types and the additional pretreatment of the adhesives did not necessarily show a synergistic effect in terms of SBS. Within the limitations of this study, SBU showed the best bonding performance, followed by ABU and then PBU. In particular, the combined use of PBU and PF produced inferior performance in terms of bonding durability.

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