Effect of silane coupling treatment and airborne-particle abrasion on shear bond strength between photo-cured bulk-fill flowable composite resin and silver-palladium-copper-gold alloy using self-adhesive resin cement

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The purpose of the present study was to examine the effects of silane coupling treatment and airborne-particle abrasion (APA) on shear bond strength (SBS) between photo-cured bulk-fill flowable composite resin and 12% silver-palladium-copper-gold (Ag-Pd-Cu-Au) alloy using self-adhesive resin cement. The six experimental groups were compared using two-way analysis of variance (ANOVA) followed by Tukey Kramer’s post-hoc test to compare SBS values among the six groups at a 95% confidence level. The SBS of APA groups was significantly higher than non-APA groups. The SBS of the specimens with silane coupling treatment increased slightly compared with specimens without silane coupling treatment. The combination of resin coating with bulk-fill resin and self-adhesive resin cement could be clinically useful when restoring a cavity with a noble metal.

Keywords: Self-adhesive resin cement, Bulk-fill resin, Shear bond strength, Silver-palladium-copper-gold alloy, Silane coupling

INTRODUCTION

Recently, a resin-coating technique has been popularly used for indirect restoration in clinic. The main aim of this technique is to protect the dentin-pulp complex from outside irritations, such as thermal stress and bacterial infection. Another aim is to enhance the bond strength between the cavity wall and the indirect restorative material. In the resin-coating technique, exposed dentin surfaces of the cavity are coated with a bonding system combined with a flowable composite resin. If the cavity is deep, the cavity will be sealed and protected by composite resin with this technique. The disadvantages of composite resin include contraction gap and micro cracking of enamel margin due to polymerization shrinkage. Shrinkage stress in composite resin restoration causes interfacial integrity failures, decreasing the bond strength between composite resin and tooth substance. In the case of deep cavity, the composite resin placement generally uses an incremental filling technique. Incremental filling can decrease the polymerization shrinkage and contraction gap. However, this technique has the disadvantage of extended treatment time.

Bulk-fill composite resin has been developed, and its use in clinic has been gradually increasing. This material possesses physical properties of deep polymerization depth and less shrinkage. Therefore, a cavity more than 2 mm deep can be restored with bulk-fill composite resin with bulk filling. The new universal and flowable type bulk-fill composite resin containing bioactive filler has been developed by Shofu (Kyoto, Japan). The bioactive filler contained in the bulk-fill composite resin is a surface pre-reacted glass-ionomer (S-PRG) filler, which forms a stable glass-ionomer on glass particles through an acid-base reaction. S-PRG fillers release aluminum (Al³⁺), boron (BO₂⁻), fluoride (F⁻), sodium (Na⁺), silicon (SiO₂²⁻), and strontium (Sr²⁺) ions. This F⁻-releasing material is expected to exert an inhibitory effect against secondary caries. The F⁻ ions released from the composite resin reduce the demineralization induced by enamel cracks or microleakage from the tooth restoration interface. Flowable resin is used for cavity base and lining. Therefore, it may be useful for resin coating when a large cavity is restored by indirect restorative treatment.

Several recently developed self-adhesive resin cements exhibit the efficacy of adhesion to tooth substrate, resin composite, ceramics, and silver-palladium-copper-gold (Ag-Pd-Cu-Au) alloy without adhesive treatment. These cements have a short setting time and less technique sensitivity compared with other resin cements needed for pretreatment adhesion. There are many reports about the bond strength between self-adhesive cement and composite resin or ceramics for indirect restoration; however, the bond strength between self-adhesive cement and an Ag-Pd-Cu-Au alloy was reported in a few studies. A metal-based indirect restoration is still applied for posterior teeth because an Ag-Pd-Cu-Au alloy is the most reliable material for stressful occlusal surfaces of posterior teeth. In the case of metal-based indirect restoration for a cavity without retained form, the adhesion between the cavity wall and the Ag-Pd-Cu-Au alloy is indispensable to prevent the restoration materials from falling. When using conventional resin cement, adhesive treatment is necessary; however, the adhesive treatment for both cavity wall and the adhesive surface of the alloy is time consuming. The use of self-adhesive cement omits the step of adhesive treatment, shortening setting time.

The purpose of the present study was to examine the effects of silane coupling treatment and airborne-
particle abrasion (APA) on shear bond strength (SBS) between cured bulk-fill flowable composite resin and Ag-Pd-Cu-Au alloy using self-adhesive cement. Our null hypothesis was that adhesive treatment for the cured bulk-fill flowable composite resin and Ag-Pd-Cu-Au alloy would not influence SBS between the cured bulk-fill flowable composite resin and the Ag-Pd-Cu-Au alloy using self-adhesive cement.

**MATERIALS AND METHODS**

Table 1 shows the materials used in this study.

**Preparation of specimens**

Forty-eight composite resin disks (4 mm diameter, 3 mm height) were prepared by photo-curing flowable composite resin (Beautifil-Bulk Flow, Shofu) in the silicone mold. The surface of the composite resin disks was polished with #600 silicon carbide paper. The composite resin disks were stored in distilled water at 37°C for one week. A cylindrical wax pattern was made by cutting wax sprue (3 mm diameter, 6 mm height). Forty-eight cylindrical metal (12% Au-Pd) rods were prepared by casting the wax patterns.

**SBS test**

A composite resin disk was embedded in the specimen holder ring using self-curing resin (Province, Shofu) so that the flat disk was parallel to and projected above the rim of the cylindrical specimen holder ring. A section of masking tape (0.12 mm thick) with a 2 mm diameter opening was attached to the central surface of the disk to define the bonding area. Table 2 shows the adhesive treatment for each experimental group (n=8). BBPR was

### Table 1  Materials used in the present study

| Materials           | Abbreviation | Composition                                      | Lot no. | Manufacturer |
|---------------------|--------------|--------------------------------------------------|---------|--------------|
| BeautiCem SA        | —            | Paste A: UDMA, FASG filler, Glass powder, Reaction initiator | 121031  | SHOFU        |
|                     |              | Paste B: UDMA, 2-HEMA, Carboxylic monomer, Phosphonic acid monomer, Zirconium silicate, Reaction initiator |         |              |
| BeautiBond Multi PR Plus | BBPR        | Ethanol, Silane coupling agent                    | 111201  | SHOFU        |
| Beautifil Bulk Flow | BBF          | Bis-GMA, UDMA, Bis-MPEPP, TEGDMA, FASG filler, S-PRG filler, Polymerization initiator | 121302  | SHOFU        |
| BeautiBond Multi    | BBM          | Acetone, Water, Bis-GMA Carboxylic monomer, TEGDMA, Phosphonic acid monomer | 111217  | SHOFU        |
| CASTWELLM.C.        |              | Au12%, Pd20%, Ag46%, Cu20%                       | 13102906 | GC           |
| 12%GOLD             |              |                                                  |         |              |
| WAX PATTERN SPRUE   | —            |                                                  | 3G6438070 | NISSIN       |

UDMA: urethane dimethacrylate, FASG filler: Fluoro Aluminosilicate Glass filler, 2-HEMA: 2-hydroxyethyl methacrylate, Bis-GMA: bisphenol-A-diglycidyl methacrylate, Bis-MPEPP: 2, 2’-bis(4-methacryloyloxy polyethoxyphenyl) propane, TEGDMA: triethyleneglycol dimethacrylate

### Table 2  Adhesive treatment for each experimental group

| Treatment for the surface of the resin composite disk | Treatment for the surface of the metal rod |
|------------------------------------------------------|-------------------------------------------|
| Group 1 BBPR (10 s)→Air blowing (3 s)                | —                                         |
| Group 2 BBM (10 s)→BBPR (5 s)→Air blowing (3 s)     | —                                         |
| Group 3 No treatment                                 | —                                         |
| Group 4 BBPR (10 s)→Air blowing (3 s)                | Airborne-particle abrasion (10 s)         |
| Group 5 BBM (10 s)→BBPR (5 s)→Air blowing (3 s)     | Airborne-particle abrasion (10 s)         |
| Group 6 No treatment                                 | Airborne-particle abrasion (10 s)         |
applied for 10 s on the surfaces of resin composite disks of Groups 1 and 4, in the absence of BBM. Additionally, in Groups 2 and 5 BBPR was applied on the resin composite disk surface for 5 s after BBM application. Finally, the surfaces of resin composite disks in Groups 3 and 4 were not treated. In Groups 4, 5, and 6, the bottom surfaces of the metal rods were sandblasted with 50 μm alumina sand (0.5 MPa, 10 s). Each adhesive material was applied to the opened surface of the composite resin disk according to the instruction of the manufacturer. After a small amount of self-adhesive cement (BeautiCem SA, Shofu) was applied on both the surface of the disk and metal rod, the metal rod was cemented to the surface of the disk. The self-adhesive cement was photopolymerized from three different directions for 20 s each, totaling 60 s (600 mW/cm²), holding the metal rod in position by finger pressure. We manually removed the excess photopolymerized cement using an explorer.

After the specimen holder rings with the adhesive specimens were stored in distilled water at 37°C for 24 h, the specimen holder rings were placed on a tabletop material tester (EZ Test 500N, Shimadzu, Kyoto, Japan), and the specimens were subjected to SBS testing at a crosshead speed of 1 mm/min using a flat end blade.

**Fracture mode analysis**
Fractured surfaces of the specimens were examined using a stereomicroscope (Leica EZ4D, Leica Camera, Wetzlar, Germany) at 35× magnification, and the fracture modes were determined according to the evaluation criteria shown in Fig. 1. We provided five evaluation criteria as follows: Af (M-C), adhesive failure occurred entirely at the interface between the metal and the resin cement; Af (R-C), adhesive failure occurred entirely at the interface between the composite resin disk and the resin cement; Cf (C), cohesive failure occurred exclusively within the resin cement; Cf (R), cohesive failure occurred exclusively within the composite resin disk; and Mf, mixed failure does not belong to the other criteria.

**Scanning electron microscope (SEM) observation**
Several representative samples were selected from each group for precise analysis of the fractured surfaces using SEM (S-800, Hitachi, Tokyo, Japan) at an accelerating voltage of 15 kV after being sputter coated with palladium and platinum.

**Statistical analysis**
The data of the SBS test were statistically analyzed using two-way analysis of variance (ANOVA), followed by Tukey Kramer’s post-hoc test to compare the SBS values among the six groups at a 95% confidence level. Statistical analysis was carried out using an add-in software package for Microsoft Excel (Bell Curve for Excel, Social Survey Research Information, Tokyo, Japan).

**RESULTS**
Table 3 shows the results of the SBS tests and failure modes. The minimum mean value of SBS was 16.12 MPa for Group 3, whereas the maximum mean value was 29.67 MPa for Group 4. First, Levene’s test was used to perform statistical analysis on data’s homoscedasticity. Results showed an absence of a statistically significant difference of variances among the experimental groups (p=0.1634). Accordingly, two-way ANOVA was used to detect the significant effects of two factors (adhesive treatment for resin composite disk and APA for metal rod) on SBS between the composite resin disk and Ag-Pd-Cu-Au alloy. Subsequently, Tukey Kramer’s post-hoc test was performed to compare SBS values among the experimental groups. The results of two-way ANOVA are shown in Table 4.

Two-way ANOVA revealed that the SBS value was significantly influenced by APA for the adhesion surface of metal rod; however, the adhesive treatment with silane coupling agent for the adhesion surface of composite resin disk did not significantly influence the SBS value.
Table 3  Shear bond strength test results

| Group     | SBS* (Mean±SD, MPa) | Failure mode** |
|-----------|---------------------|----------------|
|           | Af (M-C) | Af (R-C) | Cf (C) | Cf (R) | Mf |
| Group 1   | 18.98±8.27a       | 6          | 0      | 0      | 0   | 2  |
| Group 2   | 19.15±5.73a       | 4          | 0      | 0      | 0   | 4  |
| Group 3   | 16.12±4.26a       | 6          | 0      | 0      | 0   | 2  |
| Group 4   | 29.67±7.84b       | 0          | 1      | 0      | 0   | 7  |
| Group 5   | 27.15±5.61b       | 1          | 2      | 0      | 0   | 5  |
| Group 6   | 26.55±5.26b       | 0          | 5      | 0      | 0   | 3  |

*Value with the same superscript letters indicate no significant difference (p>0.05)

**Af (M-C): Adhesive failure between metal and cement, Af (R-C): Adhesive failure between composite resin and cement, Cf (C): Cohesive failure in cement, Cf (R): Cohesive failure in resin, Mf: Mixed failure.

Table 4  Results of two-way ANOVA

| Principal factor                        | F value      | p value     |
|-----------------------------------------|--------------|-------------|
| A: Airborne-particle abrasion for metal rod | 28.2648      | <0.000004   |
| B: Adhesive treatment for composite resin disc | 0.9092      | 0.4106      |
| Interaction between A and B             | 0.2214       | 0.8024      |

Fig. 2  Representative SEM photographs of debonded surfaces.

a: Adhesive failure between metal and cement (Group 2), b: Mixed failure (Group 2), c: Adhesive failure between metal and cement (Group 5), d: Adhesive failure between composite resin and cement (Group 5), e: Mixed failure (Group 5) Upper row, composite resin site; lower row, metal site. Left, low magnification (×70); Right, high magnification (×1,000).
The SBS value between metal rod and composite resin disk was significantly increased by the APA of the metal surface. Interaction between the two factors was not detected. In the factor of with and without APA, there were significant differences in the SBS values between Groups 1 and 4 (p=0.0212), Groups 2 and 5 (p=0.0153), and Groups 3 and 6 (p=0.0001).

The results of failure mode analysis revealed that Groups 1 and 3 exhibited adhesive failure between metal and cement (75.0%), followed by mixed failure (25.0%). Group 6 exhibited adhesive failure between resin and cement (62.5%), followed by mixed failure (37.5%). Groups 2, 4, and 5 mostly exhibited mixed failure (more than 50.0%).

Figure 2 shows representative SEM photographs of the debonded surfaces after μTBS test in Groups 2 and 5. On the SEM photographs of a and c, the debonded surface of the resin site was covered with the resin cement; thus, it was considered an adhesive failure between resin and metal. On the SEM photographs of d, the debonded surface of the metal site was covered with resin cement; thus, it was considered an adhesive failure between resin and cement. On the SEM photographs of b and e, adhesive failure was partially observed on the surface of both resin and metal; thus, it was considered mixed failure.

DISCUSSION

The results of our study show that the silane coupling treatment does not significantly increase the SBS between the ground surface of the photopolymerized BBF and the self-adhesive resin cement. The total area of the exposed fillers for the ground surface of the photopolymerized composite resin (BBF) may be 50% because BBF contains 51.0% volume of fluoro-silicate glass fillers. Although the total area of the exposed fillers was approximately one-half for the adhesive area, the silane coupling treatment for the exposed filler exhibited no significant effect on the bond strength between the ground surface of the photopolymerized BBF and the self-adhesive resin cement. No significant effect of silane coupling treatment on the bond strength between them might be attributed to the low efficacy of the silane coupling agent used in this study for adhesion between the exposed fillers on the ground surface of the photopolymerized composite resin and the self-adhesive resin cement. However, in both groups, with APA and without APA, the mean SBS of the group applied with BeautiBond Multi PR Plus (BBPR) for 10 s was slightly higher than other groups. Therefore, the silane coupling treatment by BBPR application for 10 s may be useful for increasing the bond strength between resin coating surface and self-adhesive resin cement.

Although APA the metal surface significantly increased the SBS value between metal rod and resin disk which were cemented by self-adhesive resin cement, the experimental groups without APA (Groups 1, 2, and 3) still showed relatively high SBS of 16–18 MPa. This result may be attributed to the bonding effectiveness of the carboxylic acid and phosphoric acid monomer contained in the self-adhesive cement. It is reported that use of acidic adhesive monomers and surface modification techniques improves the bond strength of resin cement to metal. The bonding ability of self-adhesive resin cement is basically dependent on the contained functional monomers that are either phosphoric or carboxylic groups. These monomers possess the capability of binding to metal ions through an acid-base reaction.

It is well known that APA a metal surface is an effective procedure for increasing the bond strength between luting cements and metal restorative materials. The results of the present study also show the significant effectiveness of APA with aluminum oxide particles for increasing the bond strength of resin cement to metal. The main effect of APA on bond strength of resin cement to metal is based on the preparation of micro-roughness on the metal surface which serves as mechanical interlock between resin cement and an ablated metal surface. Moreover, the chemical interaction between functional monomers and metal surfaces roughened by APA provides a durable adhesion of resin cement and sandblasted metal surface.

The ability of metal primer to improve the adhesion between self-adhesive resin cement and noble metal was not clarified in the present study because a metal primer application was not carried out as pretreatment. Abreu et al. reported metal primer application significantly increased bond strength to noble metal alloys, compared with oxide-only and APA pretreatments. Thus, pretreatments including APA and metal primer application could increase the bond strength of self-adhesive resin cement to noble metal.

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Resin cements have been used for indirect restoration in clinic. However, conventional resin cements need pretreatment to obtain adhesion, and pretreatment is complex and technically sensitive. Recently developed self-adhesive resin cement is simple to handle and less technically sensitive. Accordingly,
the combination of the resin coating with bulk-fill resin and self-adhesive resin cement may be clinically useful when restoring a cavity with a noble metal.

CONCLUSION

APA treatment for Ag-Pd-Cu-Au alloy showed a significant increase in the SBS between the cured bulk-fill flowable composite resin and the alloy when using self-adhesive cement. However, the SBS between them in absence of APA treatment maintained high values of 16–19 MPa. Furthermore, silane coupling treatment for the cured bulk-fill flowable composite resin showed no significant effect on the increase of the SBS between them.

CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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