Bonding of self-adhesive resin cements to enamel using different surface treatments: bond strength and etching pattern evaluations

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This study evaluated the shear bond strengths and etching patterns of seven self-adhesive resin cements to human enamel specimens which were subjected to one of the following surface treatments: (1) Polishing with #600 polishing paper; (2) Phosphoric acid; (3) G-Bond one-step adhesive; or (4) Phosphoric acid and G-Bond. After surface treatment, the human incisor specimens were bonded to a resin composite using a self-adhesive resin cement [Maxcem (MA), RelyX Unicem (UN), Breeze (BR), BisCem (BI), seT (SE), Clearfil SA Luting (CL)] or a conventional resin cement [ResiCem (RE)]. Representative morphology formed with self-adhesive resin cements showed areas of etched enamel intermingled with areas of featureless enamel. In conclusion, etching efficacy influenced the bonding effectiveness of self-adhesive resin cements to unground enamel, and that a combined use of phosphoric acid and G-Bond for pretreatment of human enamel surfaces improved the bond strength of self-adhesive resin cements.

Keywords: Self-adhesive resin cement, Bond strength, Enamel

INTRODUCTION

In current dental practice, minimal intervention is a widely advocated concept which promotes minimally invasive procedures —treatment approaches that preserve as much sound tooth structure as possible1). In accordance with the minimal intervention principle, the use of enamel adhesive techniques has greatly increased in dentistry in recent years, with many innovative applications being found in prosthodontics such as veneers and resin-bonded fixed partial dentures2,3). An apparent advantage of applying enamel adhesive techniques to these prosthodontic restorations is the preservation of dental hard tissues.

Inspired by the industrial use of 85% phosphoric acid to facilitate the adhesion of paints and resins to metallic surfaces, Buonocore envisioned the use of acids to etch enamel for sealing pits and fissures in 19554). Adhesion to enamel is achieved through acid etching of this highly mineralized substrate, which substantially enlarges its surface area for bonding. Further research into the underlying mechanism of the bond suggested that tag-like resin extensions were formed and micromechanically interlocked with the enamel microporosities created by etching5,6). Conventional resin cements are based upon the use of an etch-and-rinse or self-etch adhesive followed by a low-viscosity resin composite. However, this multi-step application technique is complex and rather technique-sensitive7).

Now that conventional resin cements have established a reputation for acceptable bonding effectiveness8), recent efforts focused on how to simplify the multi-step bonding process and reduce its sensitivity to errors during clinical handling. Recently, so-called universal, all-purpose or multipurpose, self-adhesive resin cements are commercially available now, and they purportedly bond to a multitude of substrates such as enamel, dentin, amalgam, metal, and porcelain9-12). In addition, self-adhesive cements that require only single-step application have been proposed for luting zirconium-based restorations13,14). For these systems, their resin matrix consists of multifunctional acid methacrylates that purportedly react with the substrate and contribute to the adhesion mechanism9). However, with regard to adhesion between self-adhesive resin cements and enamel, no conclusive results have been obtained for the bond strength, failure mode, and etching pattern.

For successful long-term retention of restorations15) and for good marginal adaptation16), it is imperative that a luting material be reliably bonded to both the restorative material and tooth structures. RelyX Unicem, which features a simplified application procedure, has been proposed as an alternative to the currently used systems for luting conventional ceramics as well as metal-based and high-strength ceramic restorations17,18). In light of the importance of reliable bonding, the following null hypotheses were examined in this study: (1) The use of phosphoric acid and G-Bond for luting does not improve bonding effectiveness; (2) There are no differences in shear bond strength between self-adhesive resin cements and conventional resin cements.

MATERIALS AND METHODS

Specimen preparation

Non-carious human incisors were stored in 0.5%
chloramine in water at 4°C for a maximum of 6 months until use. The teeth were embedded in chemically cured acrylic resin (d=25 mm, h=30 mm). They were ground flat with 600-grit polishing paper used on a polisher (EcoMet 3, Buehler, IL, USA) to obtain a flat enamel surface of about 6 mm diameter.

Specimens were randomly assigned to four groups according to the type of surface treatment applied:

Type I (#600): Enamel surfaces were polished with 600-grit polishing paper used on a polisher.

Type II (Phosphoric acid): 35% phosphoric acid (Panavia Etching Agent V, Kuraray Medical, Tokyo, Japan) was applied for 60 seconds, then rinsed with an air-water spray from a dental three-way syringe and air-dried.

Type III (G-Bond): One-step adhesive (G-Bond, GC, Tokyo, Japan) was applied for 10 seconds and gently air-blown. Excess agent was removed with strong air, and light curing was applied for 10 seconds.

Type IV (PG): Both phosphoric acid and G-Bond were applied.

<table>
<thead>
<tr>
<th>Table 1 List of materials used in this study</th>
</tr>
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<tbody>
<tr>
<td>Product/Code/Lot No./Manufacturer</td>
</tr>
<tr>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>Resin cements</td>
</tr>
<tr>
<td>Maxcem/MA/2772209/</td>
</tr>
<tr>
<td>Kerr (CA, USA)</td>
</tr>
<tr>
<td>RelyX Unicem/UN/304133/</td>
</tr>
<tr>
<td>3M ESPE (MN, USA)</td>
</tr>
<tr>
<td>Breeze/BR/162835/</td>
</tr>
<tr>
<td>Pentron Clinical Technologies (CT, USA)</td>
</tr>
<tr>
<td>BisCem/BI/700009638/</td>
</tr>
<tr>
<td>Bisco (IL, USA)</td>
</tr>
<tr>
<td>seT/SE/S0711272/</td>
</tr>
<tr>
<td>SDI (Victoria, Australia)</td>
</tr>
<tr>
<td>Clearfil SA Luting/CL/0005AA/</td>
</tr>
<tr>
<td>Kuraray Medical (Tokyo, Japan)</td>
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<tr>
<td>ResiCem/RE/0107/</td>
</tr>
<tr>
<td>Shofu (Kyoto, Japan)</td>
</tr>
<tr>
<td>One-step self-etch adhesive</td>
</tr>
<tr>
<td>G-Bond/0610051/</td>
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<tr>
<td>GC (Tokyo, Japan)</td>
</tr>
<tr>
<td>Resin composite</td>
</tr>
<tr>
<td>Gradia/0306241/</td>
</tr>
<tr>
<td>GC (Tokyo, Japan)</td>
</tr>
</tbody>
</table>

Bis-GMA: bisphenol-A-diglycidyl methacrylate; GPDM: glycerol dimethacrylate dihydrogen phosphate; HEMA: 2-hydroxyethyl methacrylate; MDP: 10-methacryloxyloxyceyl dihydrogen phosphate; MMA: methyl methacrylate; TEGDMA: triethylene glycol dimethacrylate; UDMA: urethane dimethacrylate; 4-AET: 4-acryloxyethyltrimellitic acid; 4-MET: 4-methacryloyloxyethyl trimellitic acid.
Specimens from each group were further divided into seven subgroups according to the number of resin cements investigated in this study (total: 168, \( n = 6 \) per subgroup). Table 1 lists the materials used in this study, including their chemical compositions and application procedures, while Fig. 1 shows the bonding procedure. The resin cements used in this study were six self-adhesive resin cements [Maxcem (MA; Kerr, CA, USA), RelyX Unicem (UN; 3M ESPE, MN, USA), Breeze (BR; Pentron Clinical Technologies, CT, USA), BisCem (BI; Bisco, IL, USA), seT (SE, SDI, Victoria, Australia), Clearfil SA Luting (CL; Kuraray Medical, Tokyo, Japan)] and one conventional resin cement [ResiCem (RE; Shofu, Kyoto, Japan)].

After surface treatment, each bonding area was delineated by a masking tape with a 5-mm-diameter hole. All self-adhesive resin cements were applied using the bonding procedures according to the manufacturers’ instructions. The conventional resin cement, ResiCem, was not used in conjunction with the primer according to the manufacturer’s instruction; instead, it was applied like a self-adhesive resin cement. After applying the resin cement, a tube with an internal diameter of 8 mm and a height of approximately 2 mm was placed on the uncured-resin bonding surface. The tube was filled with a resin composite (Gradia, GC, Tokyo, Japan) and cured with a light curing unit (G-Light, GC, Tokyo, Japan; 1200 mW/cm² light intensity). The specimens were then immersed in distilled water at a temperature of 37°C for 24 hours.

**Shear bond strength test**
Shear bond strength was determined according to ISO/TS 11405:2003\(^{19}\) using a universal testing machine (Servo Pulser EHF-FDI, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/min. Shear bond strength was expressed in MPa and was derived from dividing the imposed force (N) at the time of fracture by the bonding area (approx. 20 mm\(^2\)).

Fracture surfaces of the samples were examined using an optical light microscope (MZ7.5, Leica Microsystems, Germany) at 32× magnification. Failure modes which were thus observed were classified as follows: (A) Adhesive failure at resin-enamel interface; (B) Mixed failure, where adhesive failure occurred with a thin layer of luting material remaining on the enamel surface; (C) Cohesive failure in luting material; (D) Partial cohesive failure in enamel or resin composite.

**Statistical analysis**
Statistical analysis was performed using two-way and one-way analysis of variance (ANOVA) models and Tukey’s HSD test for post hoc pairwise comparisons (\( p < 0.05 \)). Mean shear bond strengths of seven different resin cement groups with four different surface treatments were compared using a two-factor ANOVA model. One-way ANOVA model was used to evaluate the differences among the resin cements within each of the four surface treatment groups. Then, for each resin cement, a similar series of one-way ANOVA models was used to evaluate the differences among the four surface treatment methods.

**Scanning electron microscopy (SEM)**
Twelve additional teeth were selected for SEM examination to assess the effect of surface treatments on enamel surface morphology and the etching patterns of resin cements and G-Bond.

1. Effect of surface treatments on enamel surface morphology
After sputter-coating with a gold-palladium alloy conductive layer (Ion Sputter E-1030, Hitachi, Tokyo, Japan), enamel surfaces which had been subjected to four different surface treatments were examined using a scanning electron microscope (SEM; S-4000, Hitachi, Tokyo, Japan) with an acceleration voltage of 5 kV.

2. Etching patterns of resin cements and G-Bond
Enamel specimens polished with 600-grit polishing paper were applied with one of the seven resin cements or G-Bond for 60 seconds. The surfaces were then removed of all agents, soluble organic and inorganic products using alternating washes of distilled water and acetone, air-dried, and examined by SEM.

**RESULTS**

**Shear bond strength**
ANOVA revealed that the factors of resin cement and surface treatment (\( p < 0.01 \)), and their interaction (\( p > 0.01 \)), had a significant effect on shear bond strength.
Figure 2 shows the mean shear bond strength values for all the seven resin cement groups and the four surface treatments. The mean values were 6.4±2.8 MPa for #600, 13.9±1.9 MPa for phosphoric acid, 11.3±1.7 MPa for G-Bond, and 15.9±2.2 MPa for PG.

For shear bond strength of enamel to MA, UN, BR, BI, SE, CL, and RE, the results were in ascending order of #600 polishing<one-step self-etch adhesive G-Bond<phosphoric acid etching<PG.

The bond strength of RE with #600 polishing was relatively low and the mean value was 1.4±1.0 MPa. Conversely, the bond strength of the MDP-containing self-adhesive cement CL with #600 polishing was relatively high with a mean value of 9.8±1.9 MPa. Similarly, the use of CL with PG treatment resulted in the highest bond strength value (17.6±1.4 MPa).

The failure modes are shown in Table 2. For #600 polishing, phosphoric acid etching, and G-Bond, most of the failures were observed to be adhesive failure at the resin-enamel interface for all the resin cements. In contrast, more occurrences of mixed failure and cohesive failure were found for PG treatment.

**SEM**

Figure 3 shows the SEM photographs of the four surface treatments. With #600 polishing, a smear layer covering the underlying substrate was observed on the enamel surface. With phosphoric acid etching, typical keyhole-shaped enamel prisms or rods were observed. With G-Bond application, a thick adhesive layer was observed on the enamel surface. On the other hand, the thick adhesive layer was not observed with PG treatment but seemed to have infiltrated into the enamel surface.

As for the etching patterns of the resin cements and G-Bond, their representative SEM photographs are shown in Fig. 4.

**DISCUSSION**

Smear layer is defined as “any debris, calcific in nature, produced by reduction or instrumentation of dentin, enamel or cementum”\(^{20,21}\). However, this iatrogenically produced layer of debris has an adverse influence on any adhesive bond formed between a cut tooth and the restorative material\(^{21-23}\). Two strategies are used to overcome the low attachment strengths of the smear layer: removal of the smear layer prior to bonding (etch-and-rinse approach, such as phosphoric acid etching), or use of bonding agents that can penetrate beyond the smear layer and incorporate the latter into the bonding layer (self-etch approach, such as self-adhesive resin cements and G-Bond)\(^{24}\). With self-adhesive resin cements, the rationale is to superficially demineralize the enamel and simultaneously infiltrate the etched, exposed enamel with resin to create a resin-reinforced hybrid layer\(^{8}\).

Pashley et al. have classified self-etching systems into three categories according to their etching efficacy:

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>#600 Polishing</th>
<th>Phosphoric Acid</th>
<th>G-Bond</th>
<th>PG</th>
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<tr>
<td>MA</td>
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<td>6/0/0/0</td>
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<td>BR</td>
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<td>2/0/4/0</td>
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<tr>
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<td>SE</td>
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<td>6/0/0/0</td>
<td>1/2/1/2</td>
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<tr>
<td>CL</td>
<td>6/0/0/0</td>
<td>5/0/0/1</td>
<td>6/0/0/0</td>
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<tr>
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</table>

Failure modes: A/B/C/D
A: Adhesive failure at resin-enamel interface; B: Mixed failure, where adhesive failure occurred with a thin layer of luting material remaining on the enamel surface; C: Cohesive failure in luting material; D: Partial cohesive failure in enamel or resin composite.
Clearfil Mega Bond (Kuraray Medical, Osaka, Japan), the least aggressive system (mild), had a pH value of 2.0, while the Non-Rinse Conditioner (Dentsply DeTrey, Konstanz, Germany) that produced moderate etching had a pH value of 1.2. Prompt L-Pop (3M ESPE, Seefeld, Germany), the most aggressive system at etching unground enamel, had a pH value of 1.0 and that approached the effect achieved using 32% phosphoric acid etching. Further, SEM examination results of demineralization correlated well with the pH values. Regarding their effects on bond strength, mild self-etching systems tend to provide excellent dentin bond strengths but poorer enamel bonds, whereas more aggressive self-etch systems provide the reverse25).

In the present study, a similar difference in aggressiveness was also observed. SEM examination of enamel surface morphology showed that self-adhesive resin cements produced a very mild etching effect on unground enamel, with the bulk of the surface remaining unetched. G-Bond produced a moderate ‘coral-like’ etching pattern. On the other hand, 37% phosphoric acid etching, being the most acidic of the three self-etching adhesives, produced a highly porous surface on aprismatic enamel.

Fig. 3 Sample SEM photographs of different surface treatments: (a) #600; (b) phosphoric acid; (c) G-Bond; (d) PG. In (a), the smear layer completely covered the underlying substrate. In (b), typical keyhole-shaped enamel prisms or rods were seen. In (c), a thick adhesive layer was observed. In (d), the thick adhesive layer was not observed but seemed to have infiltrated into the enamel surface.

SEM photographs of the etching patterns of self-adhesive resin cements showed that the smear layer was partially dissolved (Figs. 4(a)–(f)). Although the etching patterns of the resin cements presented some micromorphological differences, these differences were not strong enough to affect their failure modes—which was predominantly adhesive failure at the resin-enamel interface. Further, shear bond strength test revealed that with #600 polishing, self-adhesive resin cements failed to exhibit acceptable bond strengths. Minute amounts of water left in the smear layer and intrinsic water in enamel most probably led to limited ionization of the demineralizing monomers, which was one more indication that resin cements or adhesives are able to absorb water from their bonding surfaces through diffusion26).

As for self-etching adhesive systems, their
Fig. 4 SEM photographs of the etching patterns of resin cements and G-Bond, where: (a) MA; (b) UN; (c) BR; (d) BI; (e) SE; (f) CL; (g) RE; (h) G-Bond. Arrowheads indicate etched enamel (10,000× magnification).

In (a, b, d, e, f), areas of etched enamel intermingled with areas of featureless enamel. However, (f) was better defined than (a, b, d, e).

In (c, h), similar morphology was seen as BR and G-Bond contained the same adhesive monomer 4-MET. However, (c) was mostly featureless and less defined than (h).

RE contained a small amount of adhesive monomer (4-AET), but (g) showed no evidence of acid attack. With G-Bond, a moderate ‘coral-like’ etching pattern was produced in (h).
composition comprises water because it is needed to enable ionization of acidic monomers and demineralization of hard dental tissues. On the other hand, the presence of water can be a bane because residual water and hydrophilic solvent within the interfacial structure weakens bond integrity, providing channels for nanoleakage and may even affect the polymerization of infiltrated monomers\(^{37,38}\). Against this background, the tooth surface must be dried by air after applying G-Bond. However, due to excessive simplification of the clinical application procedure in the present study, residual water and adhesive solvent was not removed and the resultant interfacial structure became more hydrophilic\(^{29,30}\), thereby rendering it to be more prone to hydrolytic degradation\(^{31}\).

RE contained a small amount of adhesive monomer (4-AET). However, when it was applied with a simplified application procedure on enamel surface pretreated with #600 polishing, poor bond strength (1.4±1.0 MPa) was obtained. SEM photograph of the etching pattern of RE showed that the smear layer was not dissolved (Fig. 4g). Nonetheless, when RE was applied on enamel surfaces pretreated with phosphoric acid and G-Bond, shear bond strength test revealed that bond strengths comparable to those of self-adhesive resin cements were achieved.

The main objectives of acid conditioning are removing the smear layer and rendering the enamel surface more receptive for bonding\(^{27,28}\). Similarly in this study, enamel was treated with phosphoric acid with a view to achieving the objectives of smear layer removal and enamel demineralization. Consequently, the acid-treated enamel surface had a high surface energy\(^{34,35}\) and enamel demineralization. Consequently, the acid-treated enamel surface had a high surface energy\(^{34,35}\), thereby rendering it to be more prone to hydrolytic degradation\(^{31}\).

Further, shear bond strength test revealed that the differing compositions and solvents of self-adhesive resin cements were achieved. When phosphoric acid was used in combination with G-Bond, SEM photograph showed that after phosphoric acid removed mineral deposits from the enamel surface, the one-step adhesive, G-Bond, infiltrated the exposed enamel surface (Fig. 3d). Furthermore, shear bond strength test revealed that a combined use of phosphoric acid and G-Bond resulted in significantly greater bond strength to enamel than use of G-Bond alone. In contrast, use of G-Bond alone resulted in only a moderate etching pattern (Fig. 3c); the adhesive did not infiltrate into the smear layer, and hence a thick adhesive layer was created. In light of these findings, the first null hypothesis was rejected.

On pretreatment with G-Bond, no significant differences in shear bond strength were observed among the seven resin cements. This finding showed that the differing compositions and solvents of self-adhesive and conventional resin cements did not affect bond strength. Therefore, the second null hypothesis was partially proved.

**CONCLUSION**

A combined use of phosphoric acid and G-Bond for pretreatment of human enamel surfaces improved the bonding effectiveness of self-adhesive resin cements. This was chiefly because etching efficacy was an important contributing factor to the bonding effectiveness of self-adhesive resin cements to unground enamel. Representative morphology formed with self-adhesive resin cements showed areas of etched enamel intermingled with areas of featureless enamel, and shear bond strength test further revealed that self-adhesive resin cements failed to achieve acceptable bonding effectiveness. Therefore, pre-treatment with phosphoric acid is recommended when using self-adhesive resin cements to bond to enamel.

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