Tensile Bond Strength of 4-META/MMA-TBB Resin to Ground Bovine Enamel Using a Self-etching Primer

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The purpose of this study was to examine the effectiveness of self-etching primer in adhering 4-META/MMA-TBB resin to bovine enamel. In this study, we designed an original self-etching primer which contained an aqueous mixture of 4-MET, 35 wt% HEMA, and ferric chloride. The polished bovine enamel surface was treated with self-etching primer for 30 seconds. Tensile bond strength of 4-META/MMA-TBB resin to enamel was measured after 1-day immersion in water at 37℃. The self-etching primer containing 30 wt% 4-MET and 35 wt% HEMA (4MET30) gave a significantly higher bond strength of 11.2±2.8 MPa than other self-etching primers. The addition of ferric chloride into 4MET30 primer significantly decreased tensile bond strength. SEM observation revealed that 4MET30 treatment produced no distinct dissolution on enamel. When compared with phosphoric acid etching, the self-etching primer containing 30 wt% 4-MET and 35 wt% HEMA was more superior in adhering 4-META/MMA-TBB resin to enamel.

Key words: Tensile bond strength, 4-META/MMA-TBB resin, Self-etching primer

INTRODUCTION

Currently, adhesive resin cements are widely used in dental clinics, such as in the cementation of inlays, crowns and posts, and the bonding of orthodontic brackets. One available adhesive resin cement is the 4-META/MMA-TBB resin. It is prepared as follows: Step 1. Dissolve 4-methacryloxyethyl trimellitate anhydride (4-META), an adhesive monomer4-3, in methyl methacrylate (MMA). Step 2. Polymerize monomer mixture of 4-META and MMA by partially oxidized tri-n-butyl borane (TBB) initiator in the presence of poly(methyl methacrylate) (PMMA).

4-META/MMA-TBB resin is commercially available in Japan under the brand name Superbond C&B (Sunmedico Co. Ltd., Shiga, Japan) and in North America as C&B-Metabond (Parkell, Farmingdale, USA). 4-META/MMA-TBB resin has been on the market for about two decades and has earned an exceptional reputation for its strong bonding to tooth substrate, metals, and porcelains4-10. For tight adhesion of 4-META/MMA-TBB resin to enamel, manufacturers recommend applying 65 wt% phosphoric acid etchant to enamel.

Recently, instead of phosphoric acid etching, self-etching primers have become widely used in composite resin restoration11-13. Self-etching primers function as an etching reagent and a primer, and are mainly aqueous mixtures of acidic monomers such as phosphate monomer, carboxylic acid monomer, and water-soluble monomers (such as 2-hydroxyethyl methacrylate (HEMA)). Self-etching primers hold a few advantages over phosphoric acid etching. These advantages are mainly: No rinsing is required after applying self-etching primer. Self-etching primer helps to reduce both the number of clinical steps and length of operation time because it does not require separate acid-etching and water-rinsing steps — it simply dries in air. According to Bishara et al.14, self-etching primer treatment resulted in less residual adhesive remaining on the tooth after debonding the orthodontic bracket. This result was obtained after orthodontic brackets were bonded with photocurable composite adhesive. The authors claimed this would benefit clinicians because it helps to reduce the time needed for teeth cleaning after debonding.

We have reported on the effectiveness of self-etching primer in adhering 4-META/MMA-TBB resin to ground bovine enamel15,16. In the previous study, self-etching primers composed of phosphate methacrylate or amino acid methacrylate, HEMA, and ferric chloride — were prepared and their effectiveness evaluated. It was found that a self-etching primer which comprised 30 wt% methacryloxyethyl phosphate, 35 wt% HEMA, and 5 wt% ferric chloride, and a primer which comprised 20 wt% methacryloxy tyrosine, 35 wt% HEMA, and 3 wt% ferric chloride produced tensile bond strengths compatible with or higher than phosphoric acid etching.

To learn more about the effectiveness of self-etching primers in adhering 4-META/MMA-TBB
resin to enamel, we prepared a new self-etching primer which comprised carboxylic acid monomer, HEMA, and ferric chloride. The efficacy of this original self-etching primer was evaluated by measuring the tensile bond strength between 4-META/MMA-TBB resin and enamel. New insights were gained into the role of ferric chloride in self-etching primer.

MATERIALS AND METHODS

Adhesion test
A 4-META/MMA-TBB resin cement kit (Sunmedical Co. Ltd., Shiga, Japan) was used. Its components are listed in Table 1. Phosphoric acid (65 wt%) was included in the kit as the etching agent. The monomer mixture of 4-META and MMA was polymerized by a partially oxidized TBB initiator.

For the carboxylic acid monomer, 4-methacryloxyethyl trimellitic acid (4-MET) was used in this study. Fig.1 shows the structures of 4-MET and HEMA. Table 2 lists the components and compositions of nine experimental self-etching primers tested in this study.

Five types of self-etching primer were prepared by adding 0, 5, 10, 20, 30 wt% 4-MET to an aqueous solution of 35 wt% HEMA (Merck, Darmstadt, Germany). These primers do not contain ferric chloride. Four types of self-etching primer were prepared by adding 0.5, 1, 3, 5 wt% ferric chloride (Wako Pure Chemical Industries Ltd., Osaka, Japan) to an aqueous solution of 30 wt% 4-MET and 35 wt% HEMA. Table 2 also lists the pH of each self-etching primer, determined by a pH meter (M-220, Corning, NY, USA). The pH value of 65 wt% phosphoric acid was less than 0.01.

![Structure of 4-META and HEMA](image)

Fig. 1 Schematic illustration of the specimen for tensile bond strength measurement.

![Schematic illustration of the specimen for tensile bond strength measurement](image)

Table 1 Components of 4-META/MMA-TBB resin

<table>
<thead>
<tr>
<th>Material</th>
<th>Component</th>
<th>Batch No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching agent</td>
<td>65 wt% phosphoric acid</td>
<td>VM2</td>
</tr>
<tr>
<td>Polymer powder</td>
<td>Polymethyl methacrylate</td>
<td>VE1</td>
</tr>
<tr>
<td>Monomer liquid</td>
<td>4-META, MMA</td>
<td>VV3</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Partially oxidized TBB</td>
<td>VG11</td>
</tr>
</tbody>
</table>

Table 2 Composition and pH of the original self-etching primers

<table>
<thead>
<tr>
<th>Self-etching primer</th>
<th>4-MET</th>
<th>HEMA</th>
<th>FeCl₃</th>
<th>H₂O</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4MET0</td>
<td>0</td>
<td>35</td>
<td>0</td>
<td>65</td>
<td>4.5</td>
</tr>
<tr>
<td>4MET5</td>
<td>5</td>
<td>35</td>
<td>0</td>
<td>60</td>
<td>2.1</td>
</tr>
<tr>
<td>4MET10</td>
<td>10</td>
<td>35</td>
<td>0</td>
<td>55</td>
<td>2.0</td>
</tr>
<tr>
<td>4MET20</td>
<td>20</td>
<td>35</td>
<td>0</td>
<td>45</td>
<td>1.8</td>
</tr>
<tr>
<td>4MET30</td>
<td>30</td>
<td>35</td>
<td>0</td>
<td>35</td>
<td>1.6</td>
</tr>
<tr>
<td>4MET30-0.5Fe</td>
<td>30</td>
<td>35</td>
<td>0.5</td>
<td>34.5</td>
<td>0.92</td>
</tr>
<tr>
<td>4MET30-1Fe</td>
<td>30</td>
<td>35</td>
<td>1</td>
<td>34</td>
<td>0.74</td>
</tr>
<tr>
<td>4MET30-3Fe</td>
<td>30</td>
<td>35</td>
<td>3</td>
<td>32</td>
<td>0.16</td>
</tr>
<tr>
<td>4MET30-5Fe</td>
<td>30</td>
<td>35</td>
<td>5</td>
<td>30</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
then treated with one of the self-etching primers. After 30 seconds, any excess self-etching primer was blown away using compressed air. The area of adhesion was standardized using a piece of 300 μm-thick masking tape with a hole measuring 4.0 mm in diameter. The catalyst, partially oxidized TBB, was added to the monomer liquid to prepare an active monomer liquid. The polymer powder and active monomer liquid were mixed and applied to bond a sandblasted stainless steel rod to the enamel using brush dip technique. After curing the resin, the specimens were stored in water at 37°C for 24 hours. The tensile bond strength was measured using a universal testing machine (TCM-500CR, Shinkoh, Tokyo, Japan) at a cross-head speed of 2 mm/min.

As a control, phosphoric acid etching was used to adhere the 4-META/MMA-TBB resin to an enamel surface, according to manufacturer’s instructions. The flat, polished bovine enamel surface was etched with 65 wt.% phosphoric acid. After 30 seconds, the etched enamel surface was rinsed with running water and then dried with compressed air. Bonded specimens were prepared according to the method described above. The bond strength, after 24-hour immersion in water at 37°C, was measured using a universal testing machine.

Ten specimens were tested in each test condition. Bartlett’s test for equality of variances was first performed. If equality of variance was present, significant differences in the measurement would be determined by analysis of variance (ANOVA) and Scheffe’s test for multiple comparisons of the means. If equality of variance was not present, significant differences in the measurement would be determined by analysis of variance (ANOVA) and Games-Howell’s test for multiple comparison of the means.

This test – where bovine were used – serves only as a screening test. The final evaluation of the efficacy of self-etching primer for clinical use will be conducted using human teeth.

**FE-SEM observation**

Field-emission scanning electron microscopy (FE-SEM) was performed using a JSM-6340F (JEOL, Tokyo, Japan) after platinum sputtering.

Polished, flat enamel surfaces were prepared as described above. The enamel surfaces were treated with 4MET0, 4MET30, 4MET30-0.5Fe, or 4MET30-5Fe primer for 30 seconds respectively. The samples were then dehydrated through a graded series of ethanol, dried using a critical drying apparatus, and ion-coated with platinum. Finally, the enamel surfaces treated were observed by FE-SEM. As a control, the enamel surface after phosphoric acid etching was also observed.

### Table 3  Influence of the concentration of 4-MET (in self-etching primer) on the tensile bond strength of 4-META/MMA-TBB resin to enamel (mean±SD, MPa)

<table>
<thead>
<tr>
<th>Pretreatment reagent</th>
<th>Tensile bond strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid etchant</td>
<td></td>
</tr>
<tr>
<td>4MET0</td>
<td>12.±3.4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET5</td>
<td>6.±2.2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET10</td>
<td>7.7±3.8&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET20</td>
<td>7.9±1.4&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET30</td>
<td>11.2±2.8&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

n=10 for each treatment
Mean values with different superscripts are significantly different from each other (p<0.05)

### Table 4  Influence of the concentration of ferric chloride (in self-etching primer) on the tensile bond strength of 4-META/MMA-TBB resin to enamel (mean±SD, MPa)

<table>
<thead>
<tr>
<th>Pretreatment reagent</th>
<th>Tensile bond strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4MET30</td>
<td>11.2±2.8&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET30-0.5Fe</td>
<td>8.5±3.6&lt;sup&gt;b,c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET30-1Fe</td>
<td>8.1±2.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET30-3Fe</td>
<td>5.7±2.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4MET30-5Fe</td>
<td>1.9±0.8&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

n=10 for each treatment
Mean values with different superscripts are significantly different from each other (p<0.05)

**RESULTS**

Table 3 lists the tensile bond strengths to enamel using 4MET0, 4MET5, 4MET10, 4MET20, and 4MET30 primers, including the bond strength to enamel etched with phosphoric acid. The data were analyzed by Scheffe’s test and given as follows: Phosphoric acid etching gave a tensile bond strength of approximately 12 MPa. 4MET0, 4MET5, 4MET10, and 4MET20 self-etching primers gave significantly lower bond strengths than phosphoric acid etching (p<0.05). Bond strength of 4MET30 primer was approximately 11MPa, significantly higher than 4MET0 and 4MET5 primers (p<0.05). No significant differences in bond strength between phosphoric acid etching and 4MET30 primer (p>0.05) were noted.

Table 4 lists the tensile bond strengths to enamel using 4MET primer containing ferric chloride. The data were analyzed by Games-Howell’s test and given as follows: 4MET30, which contained no ferric chloride, showed significantly higher bond strength than 4MET30-1Fe, 4MET30-3Fe, and 4MET30-5Fe (p<0.05); in other words, addition of ferric chloride into 4MET30 primer tended to reduce tensile bond strength. Bond strength of 4MET30-5Fe was approximately 2 MPa – the significantly lowest (p<0.05) in bond strength.
Fig. 3 FE-SEM views of enamel surfaces after polished (a) and after phosphoric acid etching (b).

Fig. 4 FE-SEM images of enamel surfaces after 4MET0 (a) and 4MET30 (b) self-etching primer treatment.

Fig. 5 FE-SEM images of enamel surfaces after 4MET30-0.5Fe (a) and 4MET30-5Fe (b) self-etching primer treatment.

Figs. 3(a) and 3(b) show respectively the FE-SEM views of enamel surfaces after polishing and after phosphoric acid etching. Scratches due to polishing were observed on polished surfaces. However, after phosphoric acid etching, a roughened enamel surface was observed. The periphery of enamel prisms was preferentially removed, while the prism core was also roughened by partial dissolution.

Figs. 4(a) and 4(b) show respectively the FE-SEM images of enamel surfaces after 4MET0 and 4MET30 self-etching primer treatments. The surface appearances were totally different from that of phosphoric acid etching. The enamel surfaces were slightly dissolved. There was no distinct dissolution of enamel, and no enamel prism cores could be identified. There were also no distinct differences between 4MET0 primer and 4MET30 primer treatments on the enamel surfaces.
Figs. 5(a) and 5(b) show respectively the FE-SEM images of enamel surfaces after 4MET30-0.5Fe and 4MET30-5Fe primer treatments. After 4MET30-0.5Fe primer treatment, the enamel surface was slightly dissolved with some precipitate formation on the enamel surface. 4MET30-5Fe primer treatment produced a more roughened enamel surface than other self-etching primers. The dissolution of prism peripheries was more clearly recognized in the 4MET30-5Fe specimens.

**DISCUSSION**

This study revealed that 4MET30 self-etching primer, composed of 30 wt% 4MET and 35 wt% HEMA, yielded tight adhesion of 4-META/MMA-TBB resin to enamel. The tensile bond strength after 4MET30 primer treatment was compatible with that after phosphoric acid etching, although there was less dissolution of the enamel surface after 4MET30 primer application.

Increasing the 4-MET concentration decreased the pH of the self-etching primer, i.e., the latter's acidity was increased. In other words, increased acidity of the self-etching primer increased the bond strength of 4-META/MMA-TBB resin to enamel when the self-etching primer did not contain ferric chloride, although there was no distinct dissolution of the enamel surface.

It is generally recognized that after etching, mechanical retention by cured resin tags on a roughened enamel contributes significantly to the adhesion of dental resin to enamel. However, the appearance of 4MET30-treated enamel surface was completely different from that etched by phosphoric acid; there was no dissolution and no roughening of the 4MET30-primed enamel surface. These findings suggest that the main adhesion contributor comes not from the mechanical retention obtained by macromineral tags, but from the formation of micro-resin tags. Moreover, Fujisawa et al. reported the presence of ionic interaction between 4-MET and calcium by high-resolution proton-nuclear magnetic resonance measurement. Likewise in the present study, it is presumed that the same kind of interaction, such as ionic interaction between 4-MET and other components in the self-etching primer, contributed appreciably to the high bond strength obtained.

Addition of ferric chloride into 4MET30 self-etching primer decreased the bond strength, although its addition increased both the acidity of the self-etching primer and the demineralization degree of the enamel surface. 4MET30-5Fe produced a rougher enamel surface than 4MET30 and 4MET30-0.5Fe. The results of this study were in total contrast to the results of our previous study where addition of ferric chloride into phosphate methacrylate self-etching primer increased the bond strength, but this did not happen when ferric chloride was added to carboxylic acid self-etching primer.

The 4-META/MMA-TBB resin system recommends that dentin should be pretreated with a citric acid-ferric chloride mixture. But the effect of ferric chloride in adhering 4-META/MMA-TBB resin to dentin is still debatable. It has been suggested that ferric chloride suppressed dentin collagen’s denaturation during the demineralization process with acidic reagents. However, Kameyama et al. reported that citric acid conditioner which contained ferric chloride was less effective for heated dentin to recover the bond strength than HEMA application. Imai et al. suggested that ferric ions adsorbed onto dentin collagen may promote MMA polymerization initiated by TBB, thus influencing the bond strength of 4-META/MMA-TBB resin to dentin. Taira et al. also reported that ferric ions accelerated the initial polymerization of MMA, leading to strong bonding of 4-META/MMA-TBB resin to dentin. The difference in polymerization behavior of PMMA/MMA resin when initiated by TBB, as compared with other initiators such as camphor quinine/amine system, is further elucidated by Hirabayashi et al. and Hirabayashi.

For enamel adhesion, the influence of collagen denaturation on bond strength is negligible. In the present study, the addition of ferric chloride into self-etching primer was expected to improve the initial interfacial polymerization of MMA and produce rougher enamel. However, the bond strength unexpectedly decreased when ferric chloride was added into 4MET primer, although the enamel surface was rougher. The difference between our previous primer and this primer was the acid monomer type: phosphate methacrylate versus carboxylic acid methacrylate. It is presumed that difference in ionic interaction behavior between ferric ions and acidic monomer will influence tensile bond strength, although the detailed ionic interaction behaviors of these monomers are not clear.

In the present study, we also examined the bond strength to enamel polished with #1,000-grit stones. It is presumed that different polishing or grinding techniques such as diamond bur will influence the thickness of smear layer. The influence of smear layer’s thickness should be further investigated in another study. The effectiveness of the present self-etching primer in its bonding to unground human enamel should also be examined. Pasley et al. investigated the aggressiveness of commercially available self-etching primers on unground enamel by SEM or TEM (transmission scanning microscopy). They observed the dissolution patterns and formation of hybrid layer on unground enamel. Sirirungrojying et al. demonstrated the effectiveness of a commercially available self-etching primer in binding orthodontic bracket to intact human
enamel using 4-META/MMA-TBB resin. The effectiveness of self-etching primer treatment in adhering 4-META/MMA-TBB resin to dentin will also be further investigated.

In conclusion, this study revealed that a 4MET30 self-etching primer — which was composed of 30 wt% 4MET and 35 wt% HEMA — may be an alternative to phosphoric acid etching in adhering TBB-initiated 4-META/MMA resin cement to enamel, though there was less dissolution of the enamel surface. As for bonding between 4-META/MMA-TBB resin and enamel, the addition of ferric chloride into 4MET30 self-etching primer was not effective in improving bond strength.

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