Effect of a self-etching primer and phosphoric acid etching on the bond strength of 4-META/MMA-TBB resin to human enamel

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The purpose of this study was to evaluate the shear bond strength and durability of 4-META/MMA-TBB resin to human enamel. A self-etching primer that contained 4-META (Teeth Primer, TP) and 35–45% or 60–65% concentrations of phosphoric acid (K-Etchant Gel, KE, and Super Bond C&B Red Activator, RA) were used as the surface treatment agents. A methyl methacrylate (MMA)-based self-polymerizing resin (Super-Bond C&B) was used as a luting agent. The shear bond strength was determined both pre and post thermocycling. The results were statistically analyzed with a non-parametric procedure. The post-thermocycling shear bond strength of the TP group was significantly higher than that of other groups, and that of the KE group was significantly higher compared with the RA group. These results demonstrated that 4-META was effective. Furthermore, when the degree of tooth demineralization was compared, surface treatment with less demineralization using TP was the most effective treatment.

Keywords: Bond strength, Phosphoric acid, 4-META, 4-META/MMA-TBB resin, Enamel

INTRODUCTION

Phosphoric acid etching treatment has been reported to be effective for the adhesion of resin to enamel1,2). In dental treatment, adhesion that targets the enamel is necessary to adhere fixed dental prostheses, such as resin-bonded fixed partial dentures3-7) and porcelain laminate veneers8,9). Furthermore, variations in the phosphoric acid concentration caused by enamel demineralization have been reported10-15) and the phosphoric acid concentration has been reported to affect the depth of enamel demineralization in the phosphoric acid etching process11). Regarding the bond strength of resin to enamel via the phosphoric acid concentration, the adhesion of resin to enamel by this process is the main factor in the micro-mechanical interlocking that occurs as a result of the enamel’s demineralization by phosphoric acid16,17).

Recently, a self-etching primer was developed for the surface treatment of both enamel and dentin. This self-etching primer includes an acidic functional monomer for the primer itself; thus, the enamel adhesion is increased when the acid treatment is performed. There have also been reports that a combination of self-etching primer and phosphoric acid etching could result in a high bond strength that could compensate for the weakness caused by demineralization from the acidic monomer18-20).

4-methacryloyloxyethyl trimellitate anhydride (4-META) and 10-methacryloyloxydecyl dihydrogen phosphate (MDP) are well known as acidic functional monomers. There have been many reports of the bond strength to teeth using a self-etching primer containing MDP18,20-24). A methyl methacrylate (MMA)-based self-polymerizing resin (Super-Bond C&B) has been used as a luting material for resin-bonded fixed partial dentures4-7) and for orthodontic brackets21-23). This luting material contains 4-META. Phosphoric acid etching with a 60–65% concentration is recommended by the manufacturer’s instruction if 4-META/MMA-TBB resin is used to bond the enamel to a prosthesis or to orthodontic brackets. It is unclear whether a 60–65% concentration of phosphoric acid would be more suitable for bonding durability of enamel and prostheses.

There have been many reports regarding the effects of 4-META/MMA-TBB on enamel21-23,25-30), whereas there have been only a few reports of the effects of surface treatment with a primer that contains 4-META for adhesion of resin to enamel24,31). Furthermore, reports remain limited regarding the durability of resin to enamel adhesion when the tooth surface treatment agent contains 4-META.

The purpose of this study was to evaluate the shear bond strength and durability of 4-META/MMA-TBB resin to human enamel. A new minimally invasive self-etching primer that contained 4-META and two different concentrations of phosphoric acid were used as the surface treatment agent.

The null hypotheses were as follows: (1) Each of the surface treatments would provide the same shear bond strength and durability of 4-META/MMA-TBB resin to human enamel.
resin to enamel; and (2) Each different concentration of phosphoric acid etching would provide the same shear bond strength and durability to the enamel.

**MATERIALS AND METHODS**

**Materials**
The materials assessed in this study are presented in Table 1. One self-etching primer (TP, Teeth Primer, Sun Medical Co., Ltd.) and two etchants (KE, K-Etchant Gel, Kuraray Noritake Dental Inc., Tokyo, Japan; and RA, Super Bond C&B Red Activator, Sun Medical Co., Ltd.) were evaluated. TP is a single liquid containing a functional monomer and sodium sulfite as a reducing agent. The functional monomer is 4-META. The two etchants are single liquids, each containing a different concentration of phosphoric acid: 35–45% or 60–65%. A methyl methacrylate (MMA)-based self-polymerizing resin (Super-Bond C&B, Sun Medical Co., Ltd.) was used as a luting agent.

**Specimen preparation and shear bond strength testing**
Forty-four non-caries human molars were used as enamel specimens. The teeth were used within six months following extraction. This study was approved by the ethical committee of Nihon University School of Dentistry (2007-6 and 2014-4). Specimen preparation procedure is illustrated in Fig. 1. The molar roots were removed, and their crowns were bisected longitudinally in the mesiodistal direction to create 44 buccal and 44 lingual surfaces using a low-speed diamond disk (IsoMET, Buehler, Lake Bluff, IL, USA). The tooth pieces were embedded in an aluminum cylinder (13.0 mm in diameter, 7.5 mm in height) using self-polymerizing acrylic resin. The enamel surface was flattened using a silicon carbide abrasive paper (WetOrDry Sheet, 800-grit, 3M, St. Paul, MN, USA). A piece of plastic tape, 3.0 mm in diameter, was placed on

| Material/Trade name | Manufacturer | Lot. | Composition (%) |
|---------------------|--------------|------|-----------------|
| Primer              |              |      |                 |
| Teeth Primer        | Sun Medical Co., Ltd. | ER2 | 4-META 10–30%, sodium sulfite 1–5%, acetone 20–40%, water |
| Etchant             |              |      |                 |
| K-Etchant Gel       | Kuraray Noritake Dental Inc. | 0495AA | phosphoric acid 35–45%, colloidal silica |
| Super-Bond C&B Red Activator | Sun Medical Co., Ltd. | EL2 | phosphoric acid 60–65%, PVA |
| Luting material     |              |      |                 |
| Super-Bond Monomer  | Sun Medical Co., Ltd. | VT2 | MMA, 4-META |
| Super-Bond Ivory Opaque powder | Sun Medical Co., Ltd. | EF1 | PolyMMA, titanium oxide |
| Super-Bond Catalyst | Sun Medical Co., Ltd. | VV61F | TBB, TBB-O, hydrocarbon |

PVA, poly(vinyl alcohol); MMA, methyl methacrylate; 4-META, 4-methacryloyloxyethyl trimellitate anhydride; TBB, tri-n-butylborane; TBB-O, partially oxidized tri-n-butylborane

![Fig. 1 Specimen preparation procedure for shear bond strength.](image-url)
the surface of the enamel to define the bonding area.

TP was applied to 22 specimens. Following wet
washing with purified water and were dried. RA was
applied to 22 specimens for 30 s. The specimens were
washed and dried under the same conditions described
for KE. The remaining specimens, which did not undergo
treatment of the ground surfaces were washed with
purified water and dried (control).

A stainless steel ring (SUS303) was used as a mold
to make the 88 specimens, and it was filled with Super-
Bond C&B resin using a brush-dip technique. After 30
min, the bonded specimens were stored in 37°C water for
24 h. This state was defined as pre-thermocycle, and four
elements of each specimen were tested at this stage.
The four sets of eleven specimens were subsequently
thermocycled in water between 5 and 55°C for 20,000
cycles with a 60 s dwell time per bath (Thermal Shock
Tester TTS-1 LM, Thomas Kagaku, Tokyo, Japan). All
of the specimens were fixed in a steel mold and placed
in a shear bond testing jig. The shear bond strength
was determined with a mechanical testing device (Type
5567, Instron, Canton, MA, USA) at a crosshead speed
of 0.5 mm/min.

After shear bond strength testing, the debonded
surfaces were observed through an optical microscope
(57x, SZX9, Olympus, Tokyo, Japan). The resolution
power of an objective lens (DF PLAPO 1x-2, Olympus) was
approximately 4 μm. The ratio of the area of cohesive
failure to the area of specified adhesion was analyzed
and computed using image-analysis software (LMeye,
Lasertec, Yokohama, Japan).

Selected typical specimens were observed after
surface preparation, interface bonding and shear bond
testing using a scanning electron microscope (SEM,
S-4300, Hitachi High-Technologies Corp., Tokyo, Japan)
with an accelerating voltage of 15 kV.

For SEM of the bonded interface, the specimens
were prepared with the same shear bond strength test
grouping. A thin layer of 4-META/MMA-TBB resin
was applied directly to the treated surface. Following
storage in distilled water for 24 h at 37°C, the bonded
specimens were sectioned perpendicular to the resin-
enamel interface using the diamond disk (IsoMET)
under water coolant. The sectioned specimens were
wet-ground with a series of silicon carbide abrasive papers
(WetorDry Sheet, 800, 1,000, 1,200, 1,500 and 2,000-
grit) and polished using a felt (TexMet 1500, Buehler) and
monocrystalline diamond suspensions (MetaDi, 3 and 1
μm, Buehler). The specimens were then ultrasonically
cleaned for 5 min in distilled water to remove the
polishing smear layer. Surface demineralization was
performed with 6 mol/L hydrochloric acid (Wako Pure
Chemical Industries Ltd., Tokyo, Japan) for 25 s,
followed by a thorough rinse with distilled water. The
specimens were left to dry for 24 h in a desiccator. All
of the specimens were osmium sputtered in a vacuum
(Osmium coater HPC-1SW, Vacuum Device Co., Ltd.,
Mito, Japan).

Statistical analysis
The median and interquartile range of the shear bond
strength and cohesive failure ratio were determined.
The Kolmogorov-Smirnov test (GraphPad Prism 6.0,
GraphPad Software Inc., La Jolla, CA, USA) was
primarily used for the results of shear bond strength.
When the results of the Kolmogorov-Smirnov test did
not exhibit a normal distribution in at least one category,
the results were analyzed with the non-parametric
Kruskal-Wallis test (GraphPad Prism 6.0). Based on the
Kruskal-Wallis test, Steel-Dwass multiple comparisons
(Kyplot5.0, KyensLab, Tokyo, Japan) were subsequently
performed to compare the four groups’ results for each of
the pre- and post-thermocycling conditions. The
cohesive failure ratio results were also analyzed using
the Kruskal-Wallis test and Steel-Dwass multiple

The differences between the pre- and post-
thermocycling bond strength values were analyzed
with the Mann-Whitney U test (GraphPad Prism 6.0).
P-values less than 0.05 were considered statistically
significant.

RESULTS

Shear bond strength
Regarding the Kolmogorov-Smirnov test, the results of
the shear bond strength test did not exhibit a normal
distribution for the post-thermocycling KE group.
The Kruskal-Wallis test and Steel-Dwass multiple
comparisons were therefore applied to the shear bond
strength results. The Kruskal-Wallis test indicated
that the χ² value was 23.55 for the pre-thermocycling
group and 37.59 for the post-thermocycling group. The
p-value was less than 0.01 for both the pre- and post-
thermocycling bond strengths. Therefore, the pre- and
post-thermocycling results were analyzed independently
using the Steel-Dwass multiple comparison method.

The results of the shear bond strength tests and
statistical analyses are summarized in Table 2. The 24 h
median bond strengths without thermocycling ranged
from 29.1 to 31.5 MPa. The pre-thermocycling bond
strengths were categorized into two groups
(categories a and b). The median bond strengths after
20,000 thermocycles ranged from 4.6 to 26.2 MPa. The
post-thermocycling bond strengths were categorized
into four groups (categories c–f). The Mann-Whitney U
test revealed that the bond strengths of the KE and RA
groups were reduced by the application of 20,000
thermocycles, whereas the bond strengths of the TP
group did not significantly decrease (p=0.4307>0.05).
The post-/pre-
thermocycling bond strength ratios
ranged from 15.8% to 93.4%.

Failure analysis
The Kruskal-Wallis test and Steel-Dwass multiple
Table 2  Shear bond strength in MPa

|                | Pre-thermocycle | Post-thermocycle (20,000 cycles) | M-W | Post-/Pre- TC ratio (%) |
|----------------|-----------------|---------------------------------|-----|-------------------------|
|                | Median           | IQR | Median | IQR |                   |
| Control        | 29.1b            | 1.7 | 4.6f   | 0.7 | S                      | 15.8 |
| TP             | 30.4b            | 2.2 | 26.2c  | 10.0| NS                     | 93.4 |
| KE             | 31.4a            | 1.3 | 18.4d  | 4.8 | S                      | 66.4 |
| RA             | 31.5a            | 1.6 | 14.7e  | 3.4 | S                      | 47.9 |

n=11; IQR, Interquartile range; Identical lower case letters indicate values that are not significantly different (Steel-Dwass multiple comparisons; p>0.05); M-W, Abbreviation “S” indicates that the difference between the pre- and post-thermocycling shear bond strengths is significant. (Mann-Whitney U test; p<0.05); TC, thermocycling.

Table 3  Results of the cohesive failure ratio

|                | Pre-thermocycle Cohesive failure ratio | Post-thermocycles (20,000 cycles) Cohesive failure ratio |
|----------------|---------------------------------------|----------------------------------------------------------|
|                | Median | IQR | Median | IQR |                        | Median | IQR |
| Control        | 57%g   | 18  | 7%      | j   |                         | 7%      | 5   |
| TP             | 77%g   | 12  | 63%h    | 14  |                         | 63%b    | 26  |
| KE             | 66%g   | 15  | 63%h    | 26  |                         | 30%j    | 12  |
| RA             | 69%g   | 27  | 30%j    | 12  |                         | 30%j    | 12  |

n=11; IQR, interquartile range; Identical letters indicate that the values are not significantly different (Steel-Dwass multiple comparisons; p>0.05).

Comparisons were applied to the cohesive failure ratio results. The Kruskal-Wallis test indicated that the χ² value was 6.85 for the pre-thermocycling group and 32.84 for the post-thermocycling group. The p-value was less than 0.01 for the post-thermocycling cohesive failure ratio. Therefore, the post-thermocycling results were analyzed using the Steel-Dwass multiple comparison method.

The failure analysis results are summarized in Table 3. The 24 h median cohesive failure ratio without thermocycling ranged from 57% to 77%. The Kruskal-Wallis test demonstrated no significant differences among the four pre-thermocycling groups. The median cohesive failure ratio at 20,000 thermocycles ranged from 7% to 63%. The post-thermocycling cohesive failure ratio results were categorized into three groups (categories h–j). The control group exhibited the lowest cohesive failure ratio (category j).

**SEM observation**

Figure 2a shows a typical ground enamel surface; this surface exhibits overall scratching generated by abrasive paper. Figure 2b shows a typical enamel surface etched with KE; this surface exhibits the irregularities that result from preferential demineralization of the enamel and prism peripheries. Figure 2c shows a typical enamel surface etched with RA; this surface exhibits an etching pattern that differs from the enamel prism structure that results from significant demineralization of the enamel prism cores. Figure 2d shows a typical enamel surface primed with TP; this surface exhibits overall scratches similar to the ground surface of the enamel.

Figures 3a to 3d show the resin interface of representative enamel specimens of the four testing groups. The resin did not deeply infiltrate the transversely cut enamel prisms, no hybrid layer was formed, and a wide gap was observed (Fig. 3a). The resin-tag formations could be clearly identified in the specimens treated with KE (Fig. 3b) and RA (Fig. 3c). A thin hybridized smear layer with a few short resin tags could be identified in the specimen primed with TP (Fig. 3d).

Figures 4a to 4d show the debonded enamel surfaces. Figure 4a shows microscopic adhesive failure, similar to the pre-bonding state. Resin remnants could be identified on the surfaces treated with KE (Fig. 4b), RA (Fig. 4c), and TP (Fig. 4d).
Fig. 2  SEM images of the enamel surfaces treated as follows: (a) wet-ground with #800 SiC abrasive paper, (b) etched with KE, (c) etched with RA, and (d) primed with TA (original magnification ×1,000).

Fig. 3  SEM images of the resin-enamel interfaces. E: Enamel, R: 4-META/MMA-TBB, and G: Gap. Enamel surfaces were treated as follows: (a) wet-ground with #800 SiC abrasive paper, (b) etched with KE, (c) etched with RA, and (d) primed with TP (original magnification ×2,500). A thin hybridized smear layer was developed (black arrow). Short resin tags were observed (white arrows).
DISCUSSION

The purpose of this study was to evaluate the shear bond strength and durability of 4-META/MMA-TBB resin to enamel using two phosphoric acid gels with different concentrations and a self-etching primer.

According to the Kruskal-Wallis test for shear bond strength, the \( p \) value was less than 0.01 for the bond strength of the pre- and post-thermocycling specimens. Therefore, the first null hypothesis was rejected, and the findings demonstrated that each surface treatment for the enamel could affect the shear bond strength and durability of the 4-META/MMA-TBB resin. Furthermore, the results of the Steel-Dwass multiple comparison test demonstrated that the shear bond strength of pre-thermocycling was significantly higher in the RA and KE groups than in the TP and control groups. Furthermore, the post-thermocycling shear bond strength of the TP group was significantly higher than that of the other three groups, and the post-thermocycling shear bond strength was significantly higher in the KE group compared with the RA group. As a result, the second null hypothesis was rejected, and the findings indicated that the phosphoric acid concentration affected the bond durability of 4-META/MMA-TBB resin to enamel. The effectiveness of the 35–45% phosphoric acid concentration compared with the 60–65% concentration was demonstrated.

In summary, TP exhibited the highest bond durability and could be considered more effective as a surface treatment agent than phosphoric acid etching agents because of its simpler application procedure.

Many studies have reported the effects of phosphoric acid concentrations\(^{2,7,10-17}\). Silverstone reported that, when the phosphoric acid concentration exceeded 50%, the etch depth of the enamel surface was reduced\(^{11}\). Manson-Rahemtulla et al. reported that the total amount of dissolved calcium was maximized with a 40% phosphoric acid concentration, and it decreased at higher concentrations\(^{14}\). Figure 2b reveals that the enamel prism cores and peripheries were demineralized, and the etching pattern of the cobble stone appearance via preferential dissolution of the enamel prism peripheries could be observed. In comparison, in Fig. 2c, the etching pattern did not exhibit a prism structure because of under-de-mineralization of the enamel prism cores and peripheries. The likely reason for the significantly lower bond strength of the RA group, compared with the bond strength of the KE group, was under-de-mineralization caused by the 60–65% phosphoric acid concentration. The enamel prisms did not exhibit a prism structure as a result of under-de-mineralization. Additionally, the bonding area and resin-tag length were reduced (Fig. 3c); thus, the bond durability of the KE group was decreased.

TP contains 4-META as a functional monomer. 4-META is an acid anhydride compound, and the enamel was decalcified by hydrolyzed 4-META, i.e., acidic 4-methacryloyloxyethyl trimellitate (4-MET). The
SEM image of the TP-treated surface was not significant different than the SEM image of the grinding surface of the control sample (Figs. 2a and 2d). Thus, the enamel demineralization caused by TP was determined to be mild. Hotta et al. reported that the 4-MET promoted the polymerization of monomers and penetration through the enamel prism peripheries, and the 4-MET resin encapsulated the enamel prism and improved resistance to demineralization.32) Nurrohman et al. reported the reducing agent promoted the polymerization of the interface.33) Furthermore, Nagakane et al. reported the 4-MET formed a 4-METCa with the hydroxyapatite.34) In the bonded interface of the specimen treated with TP, thin hybrid layer and the short resin tags were observed (Fig. 3d, black and white arrows). It is suggested that the 4-MET infiltrate into the slightly demineralized enamel prism peripheries and the 4-META/MMA-TBB resin is formed a hybrid layer with enamel prism core. Moreover, the sodium sulfite contained in the TP would be expected to promote the polymerization from the interface of the monomers penetrated by the 4-MET. It is considered that both the 4-MET and the sodium sulfite improved the bond durability and post-polymerization properties of the 4-META/MMA-TBB resin at the interface.

The ratio of the area of cohesive failure to the fracture surface, as identified by image analysis, was not significantly different compared with the pre-thermocycling values. However, the post-thermocycling values of the KE and TP groups were significantly higher compared with the other groups, and the RA group exhibited higher values than the control group. These results demonstrated that KE and TP were effective as surface treatment agents, and 35–45% phosphoric acid demonstrated that KE and TP were effective as surface treatment agents, and 35–45% phosphoric acid and 4-META were also effective.

In summary, 4-META/MMA-TBB resin appeared to adhere effectively to enamel. The results also demonstrated Teeth Primer and 35–45% phosphoric acid obtained equivalent bond strengths; however, when the degree of tooth demineralization was compared, surface treatment with less demineralization using Teeth Primer was the most effective treatment.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (C) 24592934 (2014) from the Japan Society for the Promotion of Science (JSPS), a grant from the Dental Research Center Nihon University School of Dentistry (2014), and a grant from the Promotion and Mutual Aid Corporation for Private Schools of Japan (2012 and 2014).

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