Dentin bonding performance and interface observation of an MMA-based restorative material

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The purpose of this study was to evaluate bonding performance and dentin interface acid resistance using a 4-META/MMA-TBB based restorative material (BF) compared to a conventional 4-META/MMA-TBB resin cement (SB), and the effect of sodium fluoride (NaF) addition to the materials. Dentin surfaces were treated with 10% citric acid-3% ferric chloride (10-3) or 4-META containing self-etching primer (TP), followed by application of BF or SB polymer powders with or without NaF, to evaluate microtensile bond strength (µTBS) in six experimental groups; 10-3/SB, 10-3/BF, TP/SB, TP/BF, TP/SB/NaF and TP/BF/NaF. SEM observation of the resin-dentin interface was performed after acid-base challenge to evaluate interfacial dentin resistance to acid attack. TP/BF showed highest µTBS, while NaF polymers decreased µTBS. TP/BF showed funnel-shaped erosion at the interface, however, NaF polymers improved acid resistance of interface. In conclusion, BF demonstrated high µTBSs and low acid-resistance at the interface. NaF addition enhanced acid resistance but decreased µTBS.

Keywords: 4-META/MMA-TBB, Fluoride release, Bond strength

INTRODUCTION

Recently, various types of dentin bonding systems are available for direct/indirect restoration in dentistry. A 4-META/MMA-TBB resin is a unique adhesive luting cement, which has been accepted over the past few decades.¹⁻³ The 4-META/MMA-TBB resin is composed of three main components; the liquid, the powder and the initiator. The liquid is based on methyl methacrylate (MMA) with a functional monomer of 4-methacryloxyethyl trimellitate anhydride (4-META), while the powder is composed of polymethyl methacrylate (PMMA). The chemical initiator contains partially oxidized tri-n-butyl borane (TBB), which promotes interfacial polymerization in the presence of intrinsic water of tooth substrates. The three components are mixed together just before application, and are auto-polymerized. Previous in vitro studies reported that 4-META/MMA-TBB resin provided high initial bond strength to dentin⁴⁻⁶, and a good dentin bonding durability⁷,⁸. However, the mechanical properties of this material are lower than those of filler loaded dimethacrylate-based composite materials, such as the commonly available resin composites⁹,¹⁰.

Recently, a new restorative material based on the 4-META/MMA-TBB resin has been developed. The manufacturer states that due to its improved mechanical properties compared to the conventional 4-META/MMA-TBB resin cement by addition of multi-functional methacrylates and filler particles as the components, the new material is more suitable as a restorative material that can be applied in thin layers to restore incisal and occlusal surfaces such as in the cases that have undergone erosive wear¹¹,¹². Therefore, the current study evaluated the microtensile bond strength (µTBS) of the newly developed restorative material with the conventional pretreatment approach or using a newly developed self-etching primer.

Tsuchiya et al.¹³ and Waidyasekera et al.¹⁴ reported that an acid-base resistant zone (ABRZ) was created beneath the hybrid layer in self-etching systems, but not in phosphoric acid-etching systems. A similar phenomenon was confirmed in the 4-META/MMA-TBB resin¹⁵,¹⁶. This study assessed the morphology of adhesive-dentin interface after acid-base challenge by scanning electron microscope (SEM) and transmission electron microscope (TEM) observation¹⁷,¹⁸,¹⁹. Meanwhile, fluoride-release from the self-etch adhesive systems played an important role to enhance the ABRZ formation²⁰,²¹,²². Therefore, another purpose of this study was to evaluate the effects of NaF addition to the MMA-based filling material on dentin bonding performance and acid resistance at the interface.

MATERIALS AND METHODS

Caries free extracted human third molars were collected with ethical approval following the guidance of the Ethical Committee at Tokyo Medical and Dental University under protocol number 725. The teeth were cleaned of debris and then stored frozen until experiment.
Materials used in this study
Table 1 listed the compositions of the materials employed in this study. The conventional 4-META/MMA-TBB cement, Super Bond C&B (SB; Sun Medical, Moriyama, Japan) was used as a control. A new 4-META/MMA-TBB restorative material, Bondfill SB (BF; Sun Medical) was used. Effec of sodium fluoride (NaF) addition to PMMA polymer was evaluated using a commercially available product, Polymer F3 (SB/NaF; Sun Medical). Additionally, an experimental powder was prepared (BF/NaF) which contained BF and the same concentration of NaF (7 wt%) in Polymer F3.

For dentin pretreatment, one acid etching solution and one self-etching primer, Teeth Primer (TP; Sun Medical) were used (Table 2). Green Activator (10-3; Sun Medical) is composed of 10% citric acid and 3% ferric chloride, while TP contains 4-META.

Experimental groups
In order to compare the effect of pretreatment, 10-3 or TP were used for pretreatment followed by the original liquid and powder of SB or BF. In this manner, four groups were formed with the following material combinations; 10-3 and SB (10-3/SB), 10-3 and BF (10-3/BF), TP and SB (TP/SB) and TP and BF (TP/BF).

Two additional groups were investigated to understand the effect of NaF in polymer composition; TP/SB/NaF and TP/BF/NaF.

Microtensile bond strength test
The coronal portion of human third molar was removed to expose a flat, mid-coronal dentin surface using model trimmer (Y-230, Yoshida, Tokyo, Japan). The exposed dentin surface was ground using 600-grit silicon carbide paper under a water stream to produce a standardized smear layer. The teeth were randomly assigned into six groups prior to material application.

The ground dentin surfaces were conditioned with 10-3 or TP according to the manufacturer’s instructions. After dentin conditioning, each powder-liquid mixture of 4-META/MMA-TBB resin was applied on the dentin surfaces with a brush-on technique according to the manufacturer’s instructions for 1 mm in height by a hole of paraffin wax and bonded a PMMA rod (10 mm in diameter, 10 mm in height) as a buildup for µTBS test. The bonded specimens were left at room temperature for 30 min to secure the initial polymerization, and then stored in distilled water at 37°C for 24 h. The specimens were then perpendicularly sectioned at the dentin-adhesive interface into approximately 1×1 mm beams with a low-speed diamond saw (Isomet 1000, Buehler, Lake Bluff, IL, USA). These specimens were then fixed to a handy-type universal testing machine (EZ-Test, Shimadzu, Kyoto, Japan) with a cyanocrylate adhesive (Zapit, Dental Ventures of American, Anaheim Hills, CA, USA) and subjected to µTBS testing at a crosshead speed of 1 mm/min.

After debonding, failure modes were inspected by a SEM (JSM-5310LV, JEOL, Tokyo, Japan) and classified into three categories: (1) adhesive failure; (2) cohesive failure in resin; or (3) cohesive failure in dentin.

Statistics
Each test group comprised 20 specimens (n=20). The mean bond strengths obtained were analyzed in two stages using two-way ANOVA (p=0.05), first with pretreatment (10-3 and TP) and powder (SB and BF) as factors and then in TP-treated specimens with powder

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Table 1 Adhesive materials used in this study

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Liquid</th>
<th>Powder</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super Bond C&amp;B SB</td>
<td>MMA</td>
<td>4-META</td>
<td>PMMA</td>
<td>TBB</td>
</tr>
<tr>
<td>Bondfill SB BF</td>
<td>MMA</td>
<td>4-META, Dimethacrylate</td>
<td>PMMA, TMPT filler</td>
<td>TBB</td>
</tr>
</tbody>
</table>

All materials are manufactured by Sun Medical, Moriyama, Japan.
4-META: 4-methacryloxyethyl trimellitate anhydride; MMA: methyl methacrylate; NaF: sodium fluoride; PMMA: polymethyl methacrylate; TBB: tri-n-butyl borane; TMPT: trimethylolpropanetriacrylate.

Table 2 Dentin pretreatments used in this study

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Code</th>
<th>Component</th>
<th>pH</th>
<th>Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green activator</td>
<td>10-3</td>
<td>10% citric acid, 3% ferric chloride, water</td>
<td>0.74</td>
<td>Apply 10 s, rinse and dry</td>
</tr>
<tr>
<td>Teeth primer</td>
<td>TP</td>
<td>4-META, reductant, water, acetone</td>
<td>3.1</td>
<td>Apply 20 s, gentle air dry</td>
</tr>
</tbody>
</table>

Both materials are manufactured by Sun Medical, Moriyama, Japan.
4-META: 4-methacryloxyethyl trimellitate anhydride.
Table 3 Effect of pretreatment on microtensile bond strength (MPa±SD) (Exp. 1)

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>SB</th>
<th>BF</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-3</td>
<td>29.4±8.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>38.0±8.7&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>TP</td>
<td>32.8±6.4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>46.3±8.3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Number of specimens: 20

Values with same superscript letters were not statistically significant differences (p>0.05).

RESULTS

Microtensile bond strength test

Table 3 showed the mean µTBSs of SB and BF to dentin treated with 10-3 and TP. Two-way ANOVA revealed that BF provided higher bond strengths than SB with either TP or 10-3 dentin pretreatments. The highest values were obtained with TP/BF, that were significantly higher than 10-3/BF (p<0.05). The failure modes of the debonded specimens after µTBS test were summarized in Fig. 1. Cohesive failures in resin were observed in more than 80% of specimens in all the groups. No cohesive failure in dentin was observed.

Table 4 showed the additional effect of NaF in the powder on µTBSs of SB and BF to TP-treated dentin.
Table 4  Effect of NaF in adhesive resin on microtensile bond strengths to self-etched dentin (MPa±SD) (Exp. 2)

<table>
<thead>
<tr>
<th>Powder</th>
<th>SB</th>
<th>BF</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF-free</td>
<td>32.8±6.4</td>
<td>46.3±8.3</td>
</tr>
<tr>
<td>NaF-contained</td>
<td>24.9±9.4</td>
<td>29.4±6.4</td>
</tr>
</tbody>
</table>

Number of specimens: 20
Values with same superscript letters were no statistically significant differences (p>0.05).

Two-way ANOVA revealed that both TP/SB/NaF and TP/BF/NaF had significantly lower bond strength to dentin compared to NaF-free TP/SB and TP/BF groups (p<0.05). The failure modes of the debonded specimens after the test were summarized in Fig. 2. Similar to other specimens, cohesive failures in resin were observed in more than 80% of the cases and no cohesive failure in dentin was found.

**SEM observations of the adhesive-dentin interface**

The SEM images of the adhesive-dentin interfaces after acid-base challenge were revealed in Fig. 3. The depth of demineralized dentin with an artificial demineralization solution, so called the outer lesion (OL), was 10–15 µm in all the groups. In the 10-3 solution groups (Fig. 3a and b), thickness of the hybrid layer was approximately 2 µm in 10-3/SB (Fig. 3a) and 1 µm in 10-3/BF (Fig. 3b), respectively. The bonding interface made a right angle at the flat surface of the OL. In all the TP self-etching groups (Fig. 3c, d, e and f), 1 µm-thick hybrid layer was observed. However, morphological changes at the interface after the acid-base challenge were different among the four following groups; TP/SB, TP/BF, TP/SB/NaF and TP/BF/NaF. In TP/SB (Fig. 3c), the bonding interface made a right angle with the OL, while a funnel-shaped area of demineralization at the junction of the bonding interface was observed in TP/BF (Fig. 3d).

TP/SB/NaF (Fig. 3e), the zone along the interface at the dentin side increased in thickness and sloped towards the border of the OL. In TP/BF/NaF (Fig. 3f), a similar slope formation was observed at the interface, and no funnel-shaped area of demineralization appeared at the junction. Nevertheless, formation of ABRZ beneath the hybrid layer was not confirmed in any of the groups under ×3,500 magnification.

**Fluoride ion measurement**

The amount of fluoride ion release from the materials for each measurement period was summarized in Fig. 4. The cumulative amount of fluoride ion release from the materials was summarized in Fig. 5. Fluoride ion release was not detected from the SB and BF, however a high amount of fluoride ion release was seen at the first day in both SB/NaF and BF/NaF (burst effect). The amount of fluoride ion release from BF/NaF was twice the amount of that from SB/NaF (p<0.05). There were significant differences at the 6th and 14th day (p<0.05). The amount of fluoride ion release decreased with increase of storage time and achieved plateau over 28 days.

**DISCUSSION**

BF is a new filling material which is based on 4-META/MMA-TBB resin, especially developed for restoration to the erosive lesions due to tooth wear. BF is composed of liquid, powder, and catalyst, which are similar to SB; however, the liquid contains dimethacrylates and the powder contains trimethylolpropanetrimethacrylate (TMPT) filler as additions to increase the mechanical property. Therefore, BF can play a role not only as an adhesive cement, but also as a restorative composite material. The results indicated that BF provided higher µTBSs to dentin than SB, which could be explained by the improved mechanical properties due to addition of TMPT fillers to BF.

In order to evaluate dentin bonding performances of the two MMA-based adhesive resins, the different types of pretreatment solutions, 10-3 and TP were used in the current study. Dentin pretreatment with TP provided significantly higher bond strengths than that with 10-3. The 10-3 solution is an acid etchant, which contains 10% citric acid and 3% ferric chloride, FeCl₃. The 10-3 solution is milder than the common phosphoric
Fig. 3 Ultrastructure of resin-dentin interface under 3,500 observation:
(a) Resin-dentin interface of 10-3/SB group. Outer lesion of approximately 15 µm depth was observed. Hybrid layer of approximately 2 µm thickness was clearly detected. (b) Resin-dentin interface of 10-3/BF group. Outer lesion of approximately 10 µm depth was observed. Hybrid layer of approximately 1 µm thickness was detected. (c) Resin-dentin interface of TP/SB group. Outer lesion of approximately 15 µm depth was observed. Hybrid layer of approximately 1 µm thickness was clearly detected. (d) Resin-dentin interface of TP/BF group. Outer lesion of approximately 20 µm depth was observed. Hybrid layer of approximately 1 µm thickness was detected. There was wall lesion at bottom of resin-dentin interface. (e) Resin-dentin interface of SB/NaF group. Outer lesion of approximately 10 µm depth was observed. Hybrid layer of approximately 1 µm thickness was detected. There was sloped area around bottom of resin-dentin interface. (f) Resin-dentin interface of BF/NaF group. Outer lesion of approximately 20 µm depth was observed. Hybrid layer of approximately 1 µm thickness was detected. There was sloped area at bottom of resin-dentin interface. D: dentin; HL: hybrid layer; OL: outer lesion; R: resin.

Fig. 4 The amount of F-ion release for each period. BF/NaF and SB/NaF released large amount of fluoride ion at primary stage afterward the amount of fluoride ion release decreased. There were significant differences at day 1, 6 and 14 ($p < 0.05$). BF and SB released no fluoride ion.

Fig. 5 The cumulative amount of fluoride ion release. BF/NaF and SB/NaF reached plateau at day 21, 28. BF and SB released no fluoride ion.

The self-etching primer, TP, contains 4-META in the solution. Imai et al. postulated that polymerization of 4-META/MMA-TBB resin was initiated by radicals from the TBB catalyst and accelerated by ferric ions absorbed onto dentin collagen, when dentin was treated with 10-326), improving reliability of 4-META/MMA-TBB resin bonding to dentin substrate8,27). The self-etching primer, TP, contains 4-META in the solution. 4-META is expected to play important roles in dentin bonding, such as demineralizing of the smear layer, promotion of monomer penetration into dentin and possibly chemical bonding to dentin minerals29. Yoshida et al.29 reported chemical bonding
strength of several acidic monomers to hydroxyapatite (HAp). They reported that a phosphoric acid monomer, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) showed the highest chemical bonding to HAp. Chemical bonding performance of 4-MET (hydrated 4-META) was lower than MDP. The current results suggested that TP had a greater ability to accelerate the polymerization of 4-META/MMA-TBB resin at the interface and improved bond strength when compared to 10-3 solution10).

In the SEM observation of the adhesive/dentin interface, formation of the hybrid layer was observed in all the groups. Dentin treated with 10-3 created thicker hybrid layer than that with TP. The pH values of 10-3 and TP were 0.74 and 3.1, respectively. Different pH values of the two pretreatment solutions caused the different depth of demineralization of dentin. However, thickness of the hybrid layer depended not only on the depth of etching with pretreatment solutions, but also the penetration of the adhesive ingredients. Application of 10-3 created approximately 2 μm thick hybrid layer in SB, while approximately 1 μm thick hybrid layer was observed in BF. The presence of dimethacrylates and TMPT fillers in BF may hamper monomer penetration into dentin, and explain thinner the hybrid layer with funnel-shaped acid dissolution at the interface.

In the clinics, secondary caries around restorations is still one of the main problems nowadays10,33). In the SEM study on assessment of artificial secondary caries formation at the adhesive/dentin interface of the composite restorations, Tsuchiya et al.13) firstly reported a new zone, named ABRZ, beneath the visible hybrid layer in the self-etching adhesive, which was different from the conventional hybrid layer and caries-inhibition zone in a fluoride-releasing material, such as glass-ionomer cement20). However, it was reported that the ABRZ was found in the self-etching adhesives but not in the acid etching adhesives11,14). The ABRZ was supposed to play an important role in prevention of secondary caries, sealing of restoration margins and promotion of restoration durability. Waidyasekera et al.10) reported that the ABRZ is not purely dentin, but a combination of dentin and the adjacent hybrid layer. In the current study, the ABRZ formation was not observed at the resin-dentin interface either with acid etching using 10-3 or with self-etching using TP. It should be noted that similar to the previous studies, the SEM observations of the adhesive interface were performed under ×3,500 magnification. A higher magnification might be able detect ABRZ in specimens treated with TP. Previously, Takagaki et al. reported that no ABRZ was observed at the interface of 4-META/MMA-TBB resin with acidic etching with phosphoric acid and 10-310), while Nurrohman et al. reported that the ABRZ formation was observed with a self-etching primer in an MMA-based adhesive system10).

The funnel-shaped demineralization was observed in the TP/BF group after the acid-base challenge. Inoue et al. reported that a 4-MET contained self-etch adhesive system, Unifil Bond, formed funnel-shaped erosion beneath the ABRZ after the acid-base challenge18). The formation of the funnel-shaped erosion may be due to dimethacrylate and TMPT filler included in the adhesive and low chemical reactivity of 4-META with HAp. As mentioned earlier, large-size particles such as TMPT filler and multi-functional methacrylate in BF might inhibit penetration of monomer into dentin substrate. Such erosive lesion was not observed in TP/SB. Furthermore, 4-META is present in both the primer and the adhesive liquid of the TP/BF group. The interface created with TP/BF may be weak against acid attacks, because of low chemical affinity of 4-META to HAp29).

The funnel-shaped erosion was not created in the experimental material, TP/BF/NaF, and formation of a slope was furthermore observed along the adhesive interface. Addition of NaF in TP/BF may have the capacity to break through the high susceptibility of the adhesive interface against acid attack. Iijima et al. reported that 4-META/MMA-TBB resin with NaF containing powder showed caries-preventive effect33). However, the NaF contained in the adhesives showed an adverse effect on bond strength, possibly due to lower mechanical strength of the polymer. Kawabata et al.41) reported shear bond strengths of orthodontic brackets to enamel using modified 4-META/MMA-TBB resins, which were prepared by adding additives, such as poly(DL-lactide-co-glycolide), calcium fluoride and α-tricalcium phosphate to the polymer powder of 4-META/MMA-TBB resin. They reported that the incorporation of each additive decreased its bond strength due to the decrease of polymer content.

Clinically, the erosive tooth wear is most frequently found on incisal and occlusal surfaces that are in occlusion with opposing teeth15,56). Protection of these surfaces against further wear without excessive removal of tooth tissue requires a material that provides excellent adhesion, is mechanically strong against fracture and wear when applied in thin layers and is sufficiently resistant against acid challenge at the interface. The result of this study confirm that TP/BF has improved bond strength and possibly better mechanical properties; further study should be carried out to evaluate other properties, such as wear resistance against tooth brushing and masticatory force of the newly developed restorative material to confirm its utility for such an application.

CONCLUSION

The 4-META/MMA-TBB resin-based filling material, Bondfill SB, demonstrated higher dentin bond strengths than a conventional 4-META/MMA-TBB resin, Super Bond C&B in both the acid etching and self-etching modes. The SEM observations of the adhesive-dentin interface indicated that erosive weak zone was detected along the adhesive-dentin interface after the acid-base challenge in Bondfill SB, however, the interface was enhanced by addition of NaF in the PMMA powder.
REFERENCES