Effect of Primers Containing Copper Salts on Bonding of TBB Resin to Enamel

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The effect of primers containing copper salts on adhesion between enamel and stainless steel was studied in a trial to improve durability of TBB type resin cements. Bovine enamel surfaces were treated with 10% phosphoric acid, then with acetone primers containing copper salts, and finally bonded with TBB resins. Tensile strengths of the bonded specimens were measured after thermocycling testing in water and compared with those obtained for commercial composite type resin cements. A combination of a primer containing copper (II) methacryloyloxyethyl succinate and 4-META/MMA-TBB resin was most effective in improving the durability, and superior to the commercial resin cements. The mean and lowest bond strength values of 21 MPa and about 12 MPa, respectively, were retained after 2,000 thermocycles.

Key words: Enamel bonding, Primer, TBB resin

INTRODUCTION

Recently, resin-bonded fixed partial dentures have become a clinically acceptable prosthesis to replace missing teeth. The introduction and development of adhesive resins have brought about major advances in resin-bonded restorations1-12. The main disadvantage of this prosthesis has been poor retention resistance to abutment teeth compared with conventional fixed partial dentures. Bonding between enamel and resin should be a matter of great concern for achieving maximal retention, minimal tooth tissue loss, and prevention of microleakage. However, only limited studies on enamel-metal bonding with two commercial resins* have been published13-15, and little work for improving the durability and reliability has been reported.

Since the reports by investigations of Buonocore16 and Bowen17, many studies of enamel bonding have been directed towards etchants and functional adhesive monomers. The polymerization initiator system is another aspect affecting bonding of resin, but little attention has been paid to the influence of the initiator system in enamel bonding. We found previously that the application of primers containing copper (II) salts before bonding with a MMA-TBB type resin is very effective in improving bond strengths to dentin pretreated with 10% phosphoric acid, and stressed that the cupric ions adsorbed onto dentin accelerate the

* Super-Bond C & B (SunMedical Co., Shiga, Japan) and Panavia EX (Kuraray Co., Osaka, Japan)
The purpose of this study was to examine the effectiveness of copper primers in bonding of enamel with MMA-TBB type resins. Tensile strengths of bonded specimens between enamel and stainless steel before and after thermocycling were evaluated and compared among five resin cements including three which are currently available commercially.

MATERIALS AND METHODS

Materials
The experimental primers used were acetone solutions containing 1 μmol/g of copper (II) salts of chloride (CC), methacrylate (CM), methacryloxyethyl succinate (CMS), or methacryloxyethyl phthalate (CMP). The five self-curing luting resins used in this study and their codes are listed in Table 1. Commercial 4-META/MMA-TBB resin consists of methyl methacrylate (MMA) containing 4-methacryloyloxyethoxy carbonyl phthalic acid anhydride (4-META), tributylborane (TBB) initiator, and polyMMA powder. The experimental phosphoric methacrylate/MMA-TBB resin (PM) was composed of MMA containing 0.5% of di(2-methacryloyloxyethyl) phosphate (DMEP), TBB initiator, and polyMMA powder. An experimental MMA-TBB resin without DMEP was also used. Two commercial composite type luting resins were used for comparison. One was a powder-liquid type resin containing 10-methacryloyloxydecyl phosphate (MDP) as an adhesive monomer in the liquid, and the other consisted of two pastes containing MDP monomer and a pair of primers, named ED primer, containing 5-(N-methacryloylamino)salicylic acid (5-NMSA) as another functional monomer.

Preparation of specimens and measurement of tensile bond strengths
The enamel surface of the labial portion of a bovine anterior tooth was flattened on a model trimmer#, lapped on a graded series of wet silicon carbide papers, and finished on 600-grit paper. The enamel surface was etched for 30 s with 10% phosphoric acid or for 60 s with 40% phosphoric acid for the composite type resins of P and P21, and blow-dried for 30 s, after which a primer was applied on the surface using a brush. The primed surface dried

Table 1  Luting resin used

<table>
<thead>
<tr>
<th>Code</th>
<th>Type of resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Methyl methacrylate-tributylborane (MMA-TBB)*</td>
</tr>
<tr>
<td>SB</td>
<td>4-META/MMA-TBB**</td>
</tr>
<tr>
<td>PM</td>
<td>Phosphoric methacrylate/MMA-TBB*</td>
</tr>
<tr>
<td>P</td>
<td>Composite#</td>
</tr>
<tr>
<td>P21</td>
<td>Composite with primer##</td>
</tr>
</tbody>
</table>

* Experimental.
** Super-Bond C&B, Sun Medical Co., Shiga, Japan.
# Panavia EX, Kuraray Co., Osaka, Japan.
## Panavia 21, Kuraray Co., Osaka, Japan.

# Custom 700, Arrow Electroncs Ind., Co., Osaka, Japan
spontaneously. The surface was covered with an adhesive masking tape with a hole of 5 mm in diameter and 50 μm thickness to define the bonding area. The surface of the stainless steel rods (8 mm in diameter and 30 mm long) was sandblasted with 50 μm alumina grit for 10 s, and then treated with a 5% solution of MDP in acetone. The mixed luting resin was applied to the pretreated enamel surface and the stainless steel rod was affixed perpendicularly on the top and kept under finger pressure. The specimens were left undisturbed for 30 min, and then stored in water at 37°C for 24 hr. This state was defined as thermocycle 0. The specimens were thermocycled in a thermocycling test machine# up to 2,000 times between water baths held at 4°C and 60°C with a dwelling time of 1 min. They were then tested for tensile bond strength in a universal testing machine* at a cross-head speed of 2 mm/min. Five specimens were tested for each group.

Data were compared concerning mean values as well as the lowest values found among five specimens in each experimental group. Mean values were analyzed by Student’s t-test or by one-way analysis of variance (ANOVA) and post hoc Duncan’s new multiple range test for which the significance level was set at p<0.01. The fractured surfaces were examined through a magnifying glass (×10) to evaluate failure modes. Failure modes were classified into: resin-enamel interface (a), within luting material (c), enamel-dentin junction (d), and within enamel substrate (e).

RESULTS

Table 2 shows the effects of copper salts contained in acetone primers on the means and lowest values measured of tensile bond strength before and after thermocycling for 500 cycles in bonding with MMA-TBB resin to enamel etched with 10% phosphoric acid. Student’s t-test indicated that the effect of thermocycling was significant only in the CMP group (p<0.01). Significant differences were found by ANOVA among six groups irrespective of thermocycling (p<0.01).

Table 2 Effects of copper primers on the strength and durability of the MMA-TBB resin bonding to enamel

<table>
<thead>
<tr>
<th>Code</th>
<th>Copper salt in acetone</th>
<th>Number of thermocycles</th>
<th>Mean±SD (MPa)**</th>
<th>Lowest value (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Acetone only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMP</td>
<td>Methacryloyloxyethyl phthalate</td>
<td>13.1±6.2 ab</td>
<td>18.1±2.7 b A 6.6±2.4 ab</td>
<td>B 13.6 4.9 A 6.8 5.1</td>
</tr>
<tr>
<td>CM</td>
<td>Methacrylate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC</td>
<td>Chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CMS</td>
<td>Methacryloyloxyethyl succinate</td>
<td>17.9±6.4 b</td>
<td>18.4±6.3 b A 10.3±3.7 abc</td>
<td>A 9.1 5.5 A 10.0 4.5</td>
</tr>
</tbody>
</table>

* Containing 1 μmol/g of each copper salt.
** Means with the same small letters in the same columns or capitals on each horizontal line in the same plane were not significantly different at the level of 0.01.

Rika Kogyo, Hachioji, Tokyo, Japan

AGS-1000A, Shimadzu Co., Kyoto, Japan
Group N was a control group using MMA-TBB resin only. Group A showed the effect of acetone without copper (II) salts; acetone was significantly effective in increasing bond strength before thermocycling when compared with group N. However, the bond strength of 18.1 MPa decreased significantly to 6.6 MPa after 500 cycles, which value was almost equivalent to that of 5.1 MPa obtained in control group N.

Groups CMP, CM, CC, and CMS were used to compare the effects of the copper salts contained in the primers. No significant differences were found among groups A, CMP, CM, CC, and CMS before or after 500 cycles except for one group: After 500 cycles, only the CMS primer (group CMS) showed a significantly higher mean bond strength and the highest lowest value of 10.2 MPa.

The modes of bond failure for each specimen are shown in Table 3, in which the failure modes are arranged in increasing order of bond strength from left to right within each group. Before thermocycling, substantial variation in failure modes was noted in most groups except groups A and CMS, in which fracture occurred mostly within the tooth substrate. After thermocycling, almost all specimens, except those of group CC, failed in mixed adhesive/cohesive modes.

Table 4 shows the results of the tensile bond strength test for three MMA/TBB-based resins with and without CMS primer and two composite type resins. ANOVA showed no significant differences in the effect of the number of thermocycles within each group for all except group SB (p>0.01). However, ANOVA revealed that significant differences existed at the same thermocycle among groups (p<0.01). The effects of CMS primer on bond strength were significantly different between groups M and CuM as well as groups SB and CuSB after 2,000 cycles.

The bond strength values of group M were significantly lower (p<0.01) than those of the other groups. While no significant effect of thermocycling was observed, the lowest values in group M decreased gradually with increases in thermocycling. The mean and lowest values of group CuM showed a trend, although this was not statistically significant to decrease after 2,000 cycles. The bond strength with 4-META/MMA-TBB resin alone (group SB) decreased significantly (p<0.01) from 22.5 MPa to 15.3 or 13.6 MPa after ther-

| Table 3 Failure mode* in each bond strength test specimen, corresponding to Table 2 |
|--------------------------|------------------|------------------|------------------|-------------------|
| Group code               | Number of thermocycles |
|                          | 0                 | 500              |
| N                        | ac                | ac               | ac               | ac                | ac                |
| A                        | ed                | ace              | e                | ace               | ac                |
| CMP                      | ace               | ac               | e                | ac                | ac                |
| CM                       | ac                | ac               | c                | de                | ac                |
| CC                       | ac                | e                | de               | ac                | c                 |
| CMS                      | ed                | ac               | ce               | ed                | ac                |

* a, adhesive failure at resin-enamel interface; c, cohesive failure within luting material; d, fracture of dentin at enamel-dentin junction; e, fracture within enamel substrate.
mocycling. However, application of CMS primer before bonding with 4-META/MMA-TBB improved durability (group CuSB). After 2,000 cycles, the mean and lowest bond strength values of 21.0 MPa and 12.3–12.8 MPa, respectively, did not change and were the highest obtained throughout the study.

Addition of DMEP to MMA-TBB resin showed a significant effect in increasing the mean and lowest values of bond strength after 2,000 cycles (group M vs PM). Combination of CMS primer with PM resin increased the lowest values of bond strength (group PM vs CuPM).

After 2,000 cycles, the mean and lowest values of bond strength with composite type resin group P were significantly lower than those obtained for all groups except group M. The other advanced composite type resin demonstrated improved durability (group P21). While the bond strength of group P decreased from 11.4 MPa to 6.6–6.9 MPa after thermocycling, the bond strength of 15 MPa for group P21 did not change. No significant differences were observed between groups P21 and SB in all mean bond strength values, but the lowest values of the latter were higher than the former.

Table 5 lists the failure modes for each specimen. The modes of failure varied widely with bonding methods and thermocycling, but in no case did failure occur at the metal-resin interface. Before thermocycling, application of CMS primer resulted in a considerable reduction in adhesive failure. The effect of thermocycling on the failure mode varied among the resins. Mixed failure of adhesive/cohesive mode increased considerably in groups M and CuM. The failure modes for groups SB and CuSB exhibited mostly an increase in tooth substrate fracture. The failure mode of group PM was practically unchanged, but that of CuPM showed a reduction in tooth substrate fracture. The mode of failure for group P was all adhesive/cohesive and this mode in group P21 increased accompanied by a decrease in cohesive failure.

<table>
<thead>
<tr>
<th>Group code</th>
<th>Copper primer</th>
<th>Type of resin</th>
<th>Mean ± SD (MPa)</th>
<th>Lowest value (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Number of thermocycles</td>
<td>0</td>
<td>500</td>
</tr>
<tr>
<td>M</td>
<td>None</td>
<td>MMA-TBB</td>
<td>7.5 ± 2.4 a</td>
<td>A 5.1 ± 2.7 a</td>
</tr>
<tr>
<td>CuM</td>
<td>CMS*</td>
<td>MMA-TBB</td>
<td>17.9 ± 6.4 bc</td>
<td>A 14.6 ± 5.4 b</td>
</tr>
<tr>
<td>SB</td>
<td>None</td>
<td>4-META/MMA-TBB</td>
<td>22.5 ± 4.9 c</td>
<td>A 15.3 ± 4.8 b</td>
</tr>
<tr>
<td>CuSB</td>
<td>CMS*</td>
<td>4-META/MMA-TBB</td>
<td>21.0 ± 4.6 c</td>
<td>A 18.1 ± 5.0 b</td>
</tr>
<tr>
<td>PM</td>
<td>None</td>
<td>PM/MMA-TBB</td>
<td>14.5 ± 5.6 abc</td>
<td>A 12.6 ± 6.8 ab</td>
</tr>
<tr>
<td>CuPM</td>
<td>CMS*</td>
<td>PM/MMA-TBB</td>
<td>22.0 ± 5.3 c</td>
<td>A 18.1 ± 5.6 b</td>
</tr>
<tr>
<td>P</td>
<td>None</td>
<td>Composite**</td>
<td>11.4 ± 6.3 ab</td>
<td>A 6.6 ± 1.8 a</td>
</tr>
<tr>
<td>P21</td>
<td>Et primer</td>
<td>Composite#</td>
<td>15.2 ± 3.1 bc</td>
<td>A 15.0 ± 6.0 b</td>
</tr>
</tbody>
</table>
DISCUSSION

We found previously that application of a primer containing copper (II) salts before bonding with MMA-TBB resin was very effective in improving the bond strength of resin to dentin treated with phosphoric acid\(^{18,19}\). The result of the present study indicated that a primer containing copper (II) salts is also effective in the bonding of resin to enamel with the MMA-TBB type resins.

An experiment, the result of which are shown in Table 2, was performed to select the copper (II) salt most suitable for the bonding of enamel. No significant differences in the mean bond strength among CM, CC, and CMS primers were observed before or after thermocycling. However, the lowest value of 10.2 MPa for CMS was almost twice those of the other primers. Therefore, we selected CMS.

In this paper, we reported the lowest bond strength values measured in each group in addition to mean and standard deviation, based on the suggestion that the lowest value is critical for clinical success in practice\(^{9,10,20}\). The lowest value should also be useful in evaluating bond strength when considering the safety factor in a clinical situation and can guarantee that even the lowest bond strength values are sufficiently strong.

Table 4 shows that clear statistically significant differences were lacking among the groups except groups M and P. However, some trends could be identified with the help of the lowest bond strength values. After thermocycling, the lowest values decreased in groups M, CuM, SB, CuPM, and P21, but remained practically unchanged in groups CuSB, PM, and P. The lowest values measured after 2,000 cycles increased in order, starting from 1.0 MPa in group M < P < CuM < P21 < PM, SB < CuPM < CuSB (12.8 MPa). This order agreed mostly with that of the mean value. These results suggested that 4-META/MMA-TBB resin in combination with CMS primer gave the strongest and most durable bond to enamel.

The CMS primer was effective for all three MMA/TBB type resins in improving bond strength, especially at its lowest value. The effect of CMS could be explained by a mechanism of interfacial initiation of polymerization, as we have proposed previously in bonding of dentin with MMA/TBB type resins\(^{19,21}\). The CMS adsorbed on the enamel surface may promote polymerization of MMA in combination with TBB. This rapid initia-
tion of polymerization from the interface may contribute to reducing undesirable effects of contraction accompanied by polymerization and thus improve bond strength. A polymerization-promoting effect of a copper salt with a structure similar to CMS has been demonstrated by a differential scanning calorimetric study on TBB-catalyzed polymerization of MMA22.

The commercial 4-META/MMA-TBB resin (SB resin) alone without CMS primer showed significant reduction in the mean as well as lowest values of bond strength and some changes in the failure mode after 500 or 2,000 cycles. The bond strength dropped after 500 cycles, however, after which it did not change significantly up to 2,000 cycles. This trend seemed to agree with the previous finding that shear bond strength between enamel and nickel–chromium alloy with SB resin dropped after 1,000 cycles, after which it remained practically unchanged up to 30,000 cycles14. In bonding of acrylic rod and bovine enamel, similar significant decreases in tensile bond strength has been reported after 200 cycles15.

Another commercial resin cement P also exhibited a pattern of changes in bond strength similar to that of SB resin after thermocycling, showing a “sudden drop followed by stabilization.” The P21 cement, a new version of P, appeared to confer improved bond strength, durability and failure mode, and the bond strength remained unchanged up to 2,000 cycles. However, it still seems to have some problems in that it showed a lower lowest value of bond strength and increasing tendency of adhesive failure after thermocycling.

The mean bond strength of group CM decreased from 17.9 MPa to 11.4 MPa after 2,000 cycles. Although this reduction was not significant, the lowest value decreased considerably from 10.3 MPa to 6.0 MPa. Moreover, the bond failure changed from that within the tooth substrate to an adhesive/cohesive mode. All these results suggested that MMA-TBB resin was not durable even in combination with CMS primer.

An MMA/TBB type resin containing a phosphate ester monomer, PM resin, was prepared and compared with commercial resins. There were no significant differences in the mean bond strength values between PM resin, 4-META/MMA-TBB resin, and the new composite type resin. However, when the lowest values of bond strength, effect of thermocycling, and failure mode were all taken into account, the total performance of the PM resin appeared slightly inferior to that of the 4-META resin and superior to the composite resin, which contains another phosphate ester monomer (MDP).

The requirements of a bonding system desirable for clinical use would be bond strength high in mean as well as lowest values, narrow in standard deviation, and high in stability against thermal and aqueous environmental stresses. Among the bonding systems evaluated in this study, only 4-META/MMA-TBB resin in combination with CMS primer appeared to meet these requirements.

In the SB resin system, treatment of enamel with phosphoric acid of dentin with a mixture of 10% citric acid and 3% ferric chloride (10–3 solution) are recommended. However, as we reported previously, use of a primer containing copper salts could eliminate the need for 10–3 solution treatment of dentin, and made it possible to treat enamel and dentin simultaneously19. Moreover, this study demonstrated that application of copper-containing primers has an additional beneficial effect in enamel bonding. Therefore, the use of a primer containing copper salts in 4-META/MMA-TBB resin has two advantages in improving bonding performance and in simplifying the bonding procedure by allowing simultaneous
treatment of enamel and dentin with phosphoric acid.

CONCLUSION

The bonding system using primers containing copper salts in combination with MMA-TBB resins showed better bonding performance than the commercial 4-META/MMA-TBB resin alone or the commercial composite type resins in bonding of enamel and stainless steel. Application of a primer containing copper (II) methacryloyloxyethyl succinate prior to bonding of 4-META/MMA-TBB resin to enamel was most effective in improving bond strength and durability against thermocycling.

REFERENCES


仮封材除去後のエナメル質および象牙質の特性
—仮封材がレジンセメントの歯質接着性に与える影響—
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岩手医科大学歯学部歯科保存学第一講座

この研究は、仮封処置がレジンセメントの歯質接着性に与える影響を検討したものである。5種の仮封材と5種のレジンセメントを実験に用いた。600本の牛歯を被験歯として使用した。仮封処置がレジンセメントの歯質接着性に与える影響は、仮封材により異なっていた。ユージノール系、非ユージノール系のいずれの仮封材も、レジンセメントの歯質接着性を減少させていた。いずれの仮封材を使用しても、エナメル質および象牙質において4-META系レジンセメントが安定した歯質接着性を示していた。

MMA-TBB系レジンによるエナメル質の接着における銅塩含有プライマーの効果
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TBB系レジンセメントの接着耐久性改善の試みとして、エナメル質とステンレス鋼の接着におよぼす銅塩含有プライマーの効果を検討した。牛歯エナメル質を10%リン酸でエッチャング後、銅塩を含むアセトンプライマーで処理し、TBB系レジンで接着した。水中での熱サイクル試験を行った後、引張り接着強さを測定した。市販のコンポジット型レジンセメントとも比較した。銅塩の塗布はMMA-TBBレジンによる接着強さの耐久性を全体的に向上させたが、2-メタクリロイルオキシエチルアルコール酸銅を含むプライマーを用いて、4-META/MMA-TBBレジンで接着した場合には最もよい耐久性が得られ、市販品よりもすぐれていた。熱サイクル2,000回後でも接着強さの平均値21MPa、最低値約12MPaが維持されていた。

陶材中元素の酸化チタンへの拡散
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徳島大学歯学部歯科理工学講座
1北海道大学歯学部歯科理工学講座

3種類の市販チタン用焼付陶材中の元素が加熱中に酸化チタンへどのように拡散するかを調べた。円板状に形成し焼成した陶材にチタンを2種類の厚さに真空蒸着し、大気中で加熱した。蒸着厚さは、表面アラサ計およびエリプソメーターによって測定した。加熱によるチタンの酸化と、薄い酸化チタンが陶材を覆った。この表面およびチタンを蒸着していない陶材の表面をX線光電子分光で解析した。その結果、チタン用焼付陶材はホウ酸の量の従来型よりも多かった。これは、チタンに合わせて熱膨張係数を小さくするためと考えられる。加熱後の酸化チタン中のチタンは2価と4価の間の價数であり、ナトリウム、カリウム、バリウムのみが加熱中に酸化チタンに拡散した。これらの元素は酸化チタン中に混合しているのではなく、チタンと複合酸化物を形成していた。これらの元素の拡散は陶材とチタンとの結合に関係していると考えられる。