Technical note

Effect of Adding Ethylene Glycol Dimethacrylate to Resin Cements: Durability against Thermal Stress of Adhesion to Titanium

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The present study was conducted to examine the effect of the addition of a dimethacrylate to resin cements on bond strength between titanium and resin after thermocycling. Titanium disks, polished and treated with a phosphate monomer, were bonded to acrylic rods using two types of experimental resin cements. The cements were composed of methyl methacrylate (MMA) containing a tributylborane initiator and 0-10 wt% of ethylene glycol dimethacrylate (EGDMA) and two types of polymer component of hard poly (MMA) or soft fluoropolymer (2-6F). The bonded specimens were subjected to a thermocycling test in water and then to tensile strength testing. The addition of 5% or more dimethacrylate monomer to the two MMA-based resin cements caused a drastic decrease in bond strength to the metal after the thermocycling test. The resin prepared with soft 2-6F as a polymer component was significantly more durable than the rigid type resin based on PMMA. However, even a 1% addition of EGDMA to the 2-6F resin resulted in a significant decrease in durability.

Key words: Adhesion to metal, Crosslinking, Durability

INTRODUCTION

For resin-bonded prostheses, two commercial resin cements composed of dimethacrylates (PA) (Panavia EX, Kuraray Co., Okayama, Japan) and monomethacrylate (SB) (Super-Bond C & B, Sun Medical Co., Shiga, Japan) have been among the most popular luting agents. However, previous publications have suggested that there were considerable differences in durability to thermal stress between these two resin cements1-3). Tensile bond strengths decreased by 38% and 30% after 80,000 cycles of thermocycling when a tin-plated alloy was luted together with PA and SB, respectively1). Shear bond strengths decreased by 50% for PA and 12% for SB after 20,000 thermocycles when a porcelain was luted together with these two resins2). Tensile bond strengths decreased by 74% and 31% after 500 thermocycles when a titanium and an acrylic resin were luted with PA and SB, respectively3). Thus the decrease in bond strengths after thermocycling for PA was higher than that for SB.

This difference in durability may partly be interpreted by the differences in the type of structure of base luting resin: PA and SB produce a crosslinked and linear structure, respectively after curing. This may be because a resin luting agent producing a heavily crosslinked structure is less durable to thermal stress. Ikeda has reported that PA with high elastic modulus was least durable against thermocycling...
and that an experimental resin composed of fluoropolymer/MMA with relatively low elastic modulus was most durable among four resins studied. He suggested that the elastic modulus of resin is correlated with its durability. The addition of polymethacrylate monomers to resin usually produces crosslinking, increases elastic modulus, and may, therefore, decrease durability.

The purpose of this study was to examine in detail the effect on the durability of the addition of a dimethacrylate monomer to a fluoropolymer/MMA resin with low elastic modulus.

MATERIALS AND METHODS

Titanium (JIS class 2, Toho Titanium Co., Tokyo, Japan) was used as a metal in this study.

The bonding systems consisted of a primer and two types of resin cement. The metal primer was an acetone solution of 5% 10-methacryloyloxydecyl dihydrogen phosphate (MDP) which is used in PA as an effective phosphate monomer for bonding dental metals. The PMMA/MMA resins comprised PMMA (powder of the SB) and MMA containing 0, 5, 10 wt% ethylene glycol dimethacrylate (EGDMA) and 10 wt% tributylborane (TBB) initiator (Super-Bond C & B, Sun Medical Co., Shiga, Japan). A new type of experimental resin (2-6F/MMA) was composed of 70 wt% vinylidene fluoride/hexafluoropropylene copolymer (2-6F) (Daiei G101, Daikin Chemical Co., Osaka, Japan) and 30 wt% MMA containing 0 or 0.1-10 wt% EGDMA and 10 wt% TBB.

The titanium disk specimens (15 mm in diameter and 8 mm in thickness) were cut from a rod, finished with 600-grit silicon carbide paper, cleaned ultrasonically in acetone, and air-dried. After application of the metal primer to the metal surface and air-drying for 3 min, the specimens were cleaned ultrasonically in acetone for 5 min to remove excessive primer component and air-dried again. The surface was covered with an adhesive masking tape of 50 μm thickness with a 5-mm-diameter hole to control the bonding area. The luting resin was applied to the surface by brush-on technique and an acrylic rod (8 mm in diameter, 30 mm in length, with a hole in one end through which a metal pin could be passed to attach it to the testing machine) was affixed. After bonding, the test specimens were left undisturbed for 1 hr in air at room temperature, and then thermocycled in a thermocycling testing machine (Rika Kogyo Co., Hachioji, Tokyo, Japan) for 2,000 or 3,000 times between water baths held at 4 and 60°C with a dwelling time of 1 min and an exchange time of 3 s between baths. Each specimen was then tested for tensile failure on a universal testing machine (Autograph AGS 1000A, Shimadzu Co., Kyoto, Japan) with a crosshead speed of 2 mm/min.

Five specimens were tested in each group and means and standard deviations were calculated. The effect of the addition of EGDMA to the two MMA-based resins was compared by one-way ANOVA for each number of thermocyclings within the two types of resin groups. Mean values were multiply compared with post hoc Fisher's
protected least significant difference test using a software system (StatView, Abacus Concepts Inc., Berkeley, CA, USA).

After the bond tests, the fracture surfaces were examined through a magnifying glass (×10) to identify the mode of failure. The failure mode of each specimen was assigned to adhesive and cohesive failure or their combination (mixed failure). No failure occurred at the resin/acrylic rod interface.

RESULTS

The effect of the addition of EGDMA to the two MMA-based resins on durability of bond strength is summarized in Table 1. Before thermocycling, no significant effect (p>0.45) of EGDMA on bond strength was found within each PMMA/MMA or 2-6F/MMA resin group and all specimens failed cohesively. After 2,000 cycles, bond strengths for PMMA/MMA resins decreased significantly (p<0.0001). Bond strengths for 2-6F/MMA resin containing less than 0.5% EGDMA were statistically the same (p>0.05) after thermocycling up to 3,000 cycles. Bond strengths for the 2-6F resins containing 1-10% EGDMA decreased significantly (p<0.02) after 3,000 cycles, with the mean values being decreased with an increase in the amount of crosslinking agent.

While specimens of all the PMMA-based resins and 2-6F resins containing more than 5% EGDMA failed predominantly in a mixed mode after thermocycling, those of the other 2-6F resins demonstrated cohesive failure.

Table 1 Effect of addition of ethylene glycol dimethacrylate (EGDMA) to MMA-based resins on durability for thermocycling of tensile bond strength between titanium and acrylic rod

<table>
<thead>
<tr>
<th>Resin</th>
<th>EGDMA in MMA (wt%)</th>
<th>Tensile bond strength, Mean* SD (MPa)</th>
<th>Frequency of thermocycling (cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>2,000</td>
</tr>
<tr>
<td>2-6F/MMA</td>
<td></td>
<td>0</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>10.7</td>
<td>Aa</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>9.0</td>
<td>Aa</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>9.4</td>
<td>Aa</td>
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<tr>
<td></td>
<td>0.5</td>
<td>9.7</td>
<td>Aa</td>
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<tr>
<td></td>
<td>1.0</td>
<td>10.5</td>
<td>Aa</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>11.6</td>
<td>Aa</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>11.4</td>
<td>Aa</td>
</tr>
<tr>
<td>PMMA/MMA</td>
<td></td>
<td>10.0</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>21.2</td>
<td>Xa</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>22.6</td>
<td>Xa</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>20.8</td>
<td>Xa</td>
</tr>
</tbody>
</table>

* Means in upper-case (A,B,C for 2-6F/MMA and X,Y for PMMA/MMA) on the same columns or lower-case (a,b,c) on the same line showed no significant differences at the level of 0.05
As part of a study to understand the poor durability of PA resin to thermal stress, the effect of crosslinking was studied using ethylene glycol dimethacrylate (EGDMA) as a crosslinking agent in MMA-based resins. A detailed study of the effect was performed using a 2-6F resin. Previously, the durability of one type of 2-6F/MMA resin with elastic modulus of 2.00 GPa was studied and found to be better than that of PMMA/MMA resin with the modulus of 2.33 GPa\(^3\). In our study another type of 2-6F/MMA resin with lower elastic modulus of 0.75 GPa was used as a main base resin. We selected it to determine how durability is affected by crosslinking even with a resin having lower elastic modulus. While the soft 2-6F resin was used mainly, a PMMA/MMA resin with elastic modulus of 2.33 GPa was also used as a base resin for comparison purposes.

The decrease in bond strengths was significant for the resins containing more than 5% EGDMA. The addition of 5 and 10% EGDMA to 2-6F/MMA resin decreased bond strength to 29 and 23% of the initial values, respectively, after 2,000 cycles. These values were considerably lower than 93% obtained without EGDMA. This trend of decrease in bond strength was similar but more remarkable for the PMMA/MMA resins: Bond strengths of the PMMA resin containing 5 and 10% EGDMA dropped to 20 and 11% of the initial values, respectively, after 2,000 cycles, while the value obtained without EGDMA was 67%.

No significant difference in bond strength was observed among the 2-6F resins containing less than 0.5% EGDMA up to 3,000 cycles. However, a 1% addition of the crosslinking agent to the low modulus 2-6F resin resulted in a significant decrease in durability.

The effect of crosslinking in a resin cement on durability has rarely been published. However, our study demonstrated clearly that the addition of more than 5% dimethacrylate monomer to resins resulted in a drastic decrease in durability. From this aspect, the poor durability of PA resin could be well understood because it is composed of dimethacrylate monomers and has a heavily crosslinked structure.

REFERENCES

リングに石英管を挿入埋没して2時間放置後、埋没材の硬化膨張によって生じた石英管周辺のスペースに低融合金を充填した。また、700 ℃まで昇温加熱し、総膨張によって生じたスペースに銀合金を充填した。得られた鋳造体を樹脂包埋後、石英管の直径方向に分割し、各断面における合金の厚さを測定した。総膨張によって検討する場合には、アスベストリボンの合わせ目に対する石英管の方向を2種類設け、その結果、低融合金の厚さは測定箇所によらずほぼ一定の値を示したが、銀合金の厚さは面外性がみられ、特にリングの開放端方向およびアスベストリボンの合わせ目方向の値が大きかった。結論として、鋳型内において硬化膨張は均一に発現したが、加熱膨張において異方性が認められ、その程度は、埋没材周囲の環境により大きく影響を受けることが確認された。

光重合レジンの重合に及ぼす波長の影響
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干渉フィルターを用いて光照射器から狭い波長域の一定強度の光を取り出し、照射時間変化させ、試作光重合コンポジットレジンをフィルム状に重合した。重合した試験片の赤外線吸収スペクトルを残留モノマーの溶出前後で測定し、反応率(DC)および重合率(PC)を求めた。410〜550 nmの各波長でレジンを重合することができ、照射量が少ないときは、DC、PCともに波長の影響が認められた。CQの光吸収範囲(410〜490 nm)では、照射量が増加するにしたがい、重合に及ぼす波長の影響は小さくなった。最も効果的な波長は470 nmであったが、全体的にみて効果的な波長範囲は450〜490 nmであると示唆された。また、光重合は照射量の少ない重合の開始段階では、CQの吸光度につよく影響されるが、DCあるいはPCの照射エネルギー量との関係から波長だけでなく照射エネルギー量によっても影響されることが示唆された。

チタンの接着におけるレジンセメントへのエチレングリコールジメタクリレートの添加が熱的ストレス耐久性に及ぼす影響
今井庸二、池田 泰
東京医科歯科大学医用器材研究所生体機能材料部門

レジンセメントへのジメタクリレートの添加が熱サイクル後のチタンとレジンの接着強さにおよぼす影響を検討した。チタン円板を研磨、リン酸エステル系モノマーで処理後、2つのタイプの試作レジンセメントを用いてアクリル法を接着した。セメントは、トリプチルボランと6%のエチレングリコールジメタクリレート(EGDMA)を含むメチルメタクリレート(MMA)およびかたれポリMMAあるいはわるいフルオロポリマー(2-6F)というポリマー成分から成っていた。