Bonding durability against water of a fluorine-containing resin for precious metal alloys

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In order to clarify the effect of fluorination of an adhesive resin on the durability of the resin bond to precious metal alloys, 2,2,2-trifluoroethyl methacrylate (TFEMA)-poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA)/TBBO adhesive resin was prepared. The tensile bond strength of this resin to precious metal alloys treated with 9,10-epithiodecyl methacrylate (EPSMA) generally increased in the order Ag alloy<Pd alloy<Au alloy after thermal cycling; bond strength was decreased by thermal cycling. The water sorption of TFEMA-PTFEMA/TBBO resin was much higher than that of MMA-PMMA/TBBO resin because of phase separation. For Au alloy, the bonding durability of TFEMA-PTFEMA/TBBO resin against penetration of water was comparable to that of MMA-PMMA/TBBO resin; however, for Pd and Ag alloys the performance of the fluorinated resin was markedly inferior to that of MMA-PMMA/TBBO resin. These reduced tensile bond strengths were considered to be caused by insufficient copolymerization with EPSMA molecules adsorbed on the precious metal alloys.

Keywords: Fluorine-containing resin, Thiirane monomer, Tensile bond strength

INTRODUCTION

Recently, chemical surface treatments using application of adhesion-promoting monomers to precious metals have attracted interest as a method to improve the bonding between metals and resins, since the application method is simpler and less expensive than other methods and does not require any proprietary equipment. The principle of this method is based on the fact that thiol compounds, i.e. mercaptans (-SH), possess specific chemical affinity for gold. Sulfur-containing adhesive monomers such as triazinedithione¹, thiophosphoric acid², thiouracil³ and dithiolane⁴ have been used as the principal components of commercial precious metal primers, demonstrating that these monomers adsorbed on precious metals significantly improve the bond strength of resins by their copolymerization with the matrix monomers of the resin. More recently, thiirane monomers have been shown to have potential as adhesion-promoting treatments for precious metals, with satisfactory storage stability and excellent solubility⁵,⁶. Laboratory evaluations have demonstrated that the combination of thiirane adhesive monomers and MMA-PMMA resin is one of the most promising adhesive bonding systems for precious metals. However, there is still room for further improvement in the long-term water durability of resin bonds to precious metals, since MMA-PMMA resins possess some degree of hydrophilicity⁷.

It is well known that organic fluorine compounds are superior with respect to their water repellency and chemical stability as well as stain and discoloration resistance. Many fluorine-substituted methacrylate monomers have been introduced into dental materials such as denture base resins and their related materials⁸-¹², composite resins¹³, dental acrylic resins¹⁴ and dental coating materials¹⁵ with the aim of improving the properties of non-fluorinated materials. In the field of dental adhesives, fluorooalkyl methacrylate has been added to experimental primers to enhance the durability of the adhesive layer; measurements of shear bond strengths revealed that addition of the fluorinated monomer resulted in stable adhesion to dentin¹⁶,¹⁷. Thus, fluorination of the cured adhesive resin layer is considered to be quite effective in improving the long-term durability against water of the resin bond to precious metals. Nevertheless, no studies of fluorination of MMA-PMMA/TBBO adhesive resin have yet been published. Therefore, the purpose of this study was to prepare a fluorinated powder-liquid adhesive resin and to ascertain the effect of fluorination of the adhesive resin on the long-term water durability of the resin bond to precious metal alloys. First, a polymer powder, poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA), was synthesized by suspension polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA), and an experimental TFEMA-PTFEMA/TBBO resin was prepared using TFEMA liquid, PTFEMA powder and tri-n-butylborane oxide (TBBO) as polymerization initiator. Then, two precious metal alloy specimens treated with a thiirane adhesion-promoting monomer were butt-jointed with the adhesive resin and tensile bond strengths were measured after 0, 1,000, 2,000, 3,000 and 4,000 thermal cyclings. The dependence of the long-term water durability of the resin bond on the number of thermal cyclings was assessed by comparison of the experimental TFEMA-PTFEMA/TBBO resin with
conventional MMA-PMMA/TBBO resin.

MATERIALS AND METHODS

Materials

An adhesion-promoting monomer for precious metals, 9,10-epithiodecyl methacrylate (EP8MA), was synthesized according to previously described methods. Monomer liquid, 2,2,2-trifluoroethyl methacrylate (TFEMA), was purchased commercially from Daikin Industries, Ltd. (Osaka, Japan) and was passed through a basic alumina column to remove polymerization inhibitors. Polymer powder, poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA), was synthesized by the suspension polymerization method. TFEMA (20 g) was poured into 60 ml of demineralized water in a flask. Then, 4 mg of sodium n-dodecyl sulfate (Kanto Chemical Co., Inc., Tokyo, Japan) as a surfactant, 4 g of a dispersant, and 0.4 g of benzoyl peroxide (BPO) (Kanto Chemical Co., Inc., Tokyo, Japan) as polymerization initiator were added. The flask was then placed in a water bath under a gentle nitrogen stream, stirred at 800 rpm and kept at 70°C for 6 hours and then at 90°C for another 30 min for polymerization. After cooling the flask to room temperature, 1 g of nitric acid was added and the dispersant was dissolved. The resulting polymer beads were separated with suction filtration; then they were washed with demineralized water and dried under vacuum for 14 hours, yielding minute white particles of polymer. The yield of PTFEMA was 84.1%. The structures of these compounds are shown in Fig. 1.

Polymerization initiator for an experimental adhesive resin, tri-n-butylborane oxide (TBBO), was obtained from Sun Medical Co., Ltd. (Kyoto, Japan) as a dental adhesive resin, Super-Bond C & B. Three kinds of dental precious metal alloys, Casting Gold M.C. Type IV (Au alloy; GC Dental Products Corp., Tokyo, Japan), Castwell M.C. (Pd alloy; GC Dental Products Corp., Tokyo, Japan) and Sunsilver CB (Ag alloy; Sankin Kogyo Co. Ltd., Tokyo, Japan), were selected as adherends, and their compositions are given in Table 1.

Surface treatment agent and experimental adhesive resin

Surface treatment agent for the precious metals was prepared by dissolving EP8MA in ethanol at a concentration of 1.0 mol%. An experimental TFEMA-PTFEMA/TBBO resin was cured with TBBO initiator. One drop of TBBO was added to TFEMA liquid in a dappen dish immediately before use; the concentration of TBBO was about 8.0 wt%. PTFEMA powder was placed in another dish and the resin was applied by the brush-on technique.

Measurement of temperature change during curing of adhesive resin

PTFEMA powder (0.2 g) and TFEMA liquid containing 8 wt% of TBBO (0.145 ml) were mixed and placed in a polyethylene mold (8 mm in diameter and 12 mm in depth). A thermocouple (Thermo Recorder RT-11; Espec MIC Corp., Aichi, Japan) was embedded directly into

![Chemical structures of liquid and powder components and the adhesion-promoting monomer for precious metals.](image)

Table 1 Compositions of dental precious metal alloys

<table>
<thead>
<tr>
<th>Precious metal alloy</th>
<th>Code</th>
<th>Manufacturer</th>
<th>Composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting Gold M.C. Type IV</td>
<td>Au alloy</td>
<td>GC</td>
<td>Au 70 Cu 14 Ag 10 Pt 3 Pd 3</td>
</tr>
<tr>
<td>Castwell M.C.</td>
<td>Pd alloy</td>
<td>GC</td>
<td>Ag 45 Pd 20 Cu 18 Au 12 Others 5</td>
</tr>
<tr>
<td>Sunsilver CB</td>
<td>Ag alloy</td>
<td>Sankin</td>
<td>Ag 79 Zn 7 In 7 Cu 5 Others 2</td>
</tr>
</tbody>
</table>

GC (GC Dental Products Corp., Tokyo, Japan), Sankin (Sankin Kogyo Co. Ltd., Tokyo, Japan).

Metal specimens were cylindrically shaped (5 mmφ×4 mm) and had an exterior screw on one side which was connected with jigs for the tensile test.
the center of the curing material, and the temperature change during polymerization was recorded for 30 min at 25°C.

**Surface finishing of metal adherends**
The metal adherends were cylindrical (5 mm diameter × 4 mm high). Each metal specimen had an exterior screw on one side connected to a jig for the tensile test. In addition, the surface of each metal specimen was lapped to a smooth mirror finish with lapping film (Sumitomo 3M Ltd., Tokyo, Japan) using a sequence of #1,000, #2,000, and #4,000 grit to eliminate mechanical retention due to surface irregularities. The specimen was washed with acetone and allowed to dry naturally in air.

**Measurement of tensile bond strength to precious metal alloys**
Five microliters of the surface treatment agent was placed on the adherend surface and allowed to remain for 1 day. The surface was washed with acetone to remove excessive monomer and allowed to dry prior to bonding. Two specimens of each metal were butt-jointed together with TFEMA-PTFEMA/TBBO resin using the brush-on technique. Excess resin outside the circumference of the cylinder was removed with a double-edged razor blade (FEATHER Safety Razor Co. Ltd., Osaka, Japan) and the assembly was left to stand undisturbed for 90 min at room temperature to allow adequate cure of the resin. At 90 min after cementation the bonded specimens were stored in water at room temperature until all of the specimens were ready to be thermocycled. The specimens were then thermocycled 0, 1000, 2000, 3000, and 4000 times in water at temperatures of 4 and 60°C, with a one-minute dwell time at each temperature. Tensile bond strength measurements were made on 5 specimens for each metal with a universal testing machine (Autograph AGS-1000A; Shimadzu Co., Kyoto, Japan) at a crosshead speed of 2 mm/min. The mean and standard deviation of 5 replications were calculated for each condition and the results were analyzed at the 95% confidence level by the t-test.

**RESULTS**
PTFEMA powder, TFEMA liquid and TBBO initiator were mixed in a polyethylene mold, and the temperature change of the resin mixture during the curing process was continuously recorded with a thermocouple. The thermograms obtained for TFEMA-PTFEMA/TBBO resin as well as MMA-PMMA/TBBO resin are shown in Fig. 2. The peak temperatures of the exothermic polymerization reactions of TFEMA-PTFEMA/TBBO resin and MMA-PMMA/TBBO resin were 30.5°C at 16.2 min and 51.7°C at 4.5 min, respectively. The fluorinated resin demonstrated a temperature rise of 8.0°C and the non-fluorinated resin a rise of 29.1°C.

Five microliters of an adhesion-promoting EP8MA treatment agent at relatively high concentration (1.0 mol%) in ethanol was applied to the precious metal alloy surface for one day, and excess monomer on the treated surface was washed off prior to bonding to obtain maximum performance. After rinsing with acetone, the surface became visually indistinguishable from that before the application of the treatment agent, and therefore EP8MA was considered to be retained in extremely small quantities. None of the bonded specimens showed any spontaneous interface failures upon exposure to severe thermal cycling for up to 4000 cycles. Thus, the water durability of the fluorinated resin bond to precious metal alloys was significantly enhanced by the surface treatment with EP8MA. The appearance of debonded surface after the tensile test changed with thermal cycling. The failure modes before thermal cycling of Au alloy, Pd alloy and Ag alloy were nearly cohesive and then a partial interface failure at the peripheral region of the adhesion interface.

**Water sorption and solubility measurement**
TFEMA-PTFEMA/TBBO resin was cured for 90 min in a Teflon mold (5 mm diameter × 1 mm high) by holding it between two glass plates. After removal from the molds, three cured specimens were weighed (W0) and immersed in demineralized water at 37°C. The specimens were then weighed once a day until the weight reached a constant value (W1). The samples were removed from the water and dried under vacuum. After removing the absorbed water from the resin samples, they were weighed in an analytical balance (W2). Water sorption and solubility were calculated from following formulas:

Water sorption (%) = 100(W1 - W2) / W2
Solubility (%) = 100(W0 - W2) / W0

The water sorption and solubility of MMA-PMMA/TBBO resin were also measured for comparison by the same procedure as above.

Fig. 2 Temperature changes during the curing process of TFEMA-PTFEMA/TBBO and MMA-PMMA/TBBO resins.
increased with thermal cycling. Au alloy and Pd alloy demonstrated a combination of a cohesive failure and an interface failure after 4,000 thermal cyclings, while Ag alloy revealed almost complete interface failure.

The means and standard deviations of the tensile bond strengths of TFEMA-PTFEMA/TBBO resin to Au alloy, Pd alloy and Ag alloy treated with EP8MA primer are summarized in Table 2. The mean bond strength of the resin to precious metal alloys generally increased in the order Ag alloy < Pd alloy < Au alloy after thermal cycling, although the values gradually decreased with thermal cycling. The mean bond strengths ranged from 26.7 to 15.8 MPa for Au alloy, from 26.7 to 12.2 MPa for Pd alloy and from 19.9 to 3.1 MPa for Ag alloy. The decrease in mean bond strength with thermal cycling was statistically significant in many cases ($p<0.05$, Table 2).

Cured TFEMA-PTFEMA/TBBO resins stored in water were weighed once a day for up to 32 days. The change of weight is illustrated in Fig. 3. The weight of the fluorinated resins increased with time of immersion, and a constant weight was achieved at 30 days. Weight increase after immersion in water continued much longer for TFEMA-PTFEMA/TBBO resin than for MMA-PMMA/TBBO resin, which attained a constant weight after about 2 days, as shown in Fig. 3. The results of a water immersion test are summarized in Table 3. TFEMA-PTFEMA/TBBO resin demonstrated higher water sorption than did MMA-PMMA/TBBO resin, and the difference was statistically significant ($p<0.05$). The solubility of the former resin tended to be smaller than that of the latter ($p>0.05$).

**DISCUSSION**

MMA-PMMA/TBBO resins are considered to be especially suited as dental adhesive resins. A typical commercial product is Super-Bond C&B, manufactured by Sun Medical Co. Ltd. (Kyoto, Japan). Cured MMA-PMMA/TBBO resin is mainly composed of poly(methyl methacrylate), and it has been reported that the water sorption of the cured resin after 6 weeks of immersion in water was 2.61%\(^20\). The water content of an adhesive resin is particularly important in determining the long-term durability against water of a resin bond to precious metals, since water molecules that diffuse toward the adhesion interface promote the deterioration of the resin bond\(^21,22\). In order to reduce the water content of polymers, their fluorinated homologues are often utilized as alternatives. To give a typical example, the water content of the bulk polymer of 2,2,2-trifluoroethyl methacrylate has been reported to be 0.30% in contrast to that of methyl methacrylate at 0.89%\(^23\). A heat-curing resin consisting of TFEMA

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**Table 2** Tensile bond strength (MPa) of TFEMA-PTFEMA/TBBO adhesive resin to precious metal alloys treated with EP8MA

<table>
<thead>
<tr>
<th>Adherend</th>
<th>0</th>
<th>1,000</th>
<th>2,000</th>
<th>3,000</th>
<th>4,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au alloy</td>
<td>24.9 (0.9)(^a)</td>
<td>26.7 (1.8)(^a)</td>
<td>15.8 (2.1)(^b)</td>
<td>16.9 (0.8)(^b)</td>
<td>16.9 (2.0)(^b)</td>
</tr>
<tr>
<td>Pd alloy</td>
<td>26.7 (1.2)(^a)</td>
<td>18.9 (1.4)(^b)</td>
<td>14.9 (0.4)(^c)</td>
<td>13.8 (2.3)(^c)</td>
<td>12.2 (1.8)(^d)</td>
</tr>
<tr>
<td>Ag alloy</td>
<td>19.9 (1.4)(^a)</td>
<td>11.0 (2.2)(^b)</td>
<td>3.1 (0.5)(^d)</td>
<td>4.6 (1.0)(^e)</td>
<td>4.9 (0.7)(^e)</td>
</tr>
</tbody>
</table>

*Difference between the resins is significant at $p<0.05$. ( ): SD

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**Table 3** Water sorption and solubility of TFEMA-PTFEMA/TBBO and MMA-PMMA/TBBO resins

<table>
<thead>
<tr>
<th>Adhesive resin</th>
<th>Water sorption (%)</th>
<th>Solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFEMA-PTFEMA/TBBO</td>
<td>9.9 (0.5)(^*)</td>
<td>0.82 (0.08)</td>
</tr>
<tr>
<td>MMA-PMMA/TBBO</td>
<td>3.6 (0.1)(^*)</td>
<td>2.05 (0.97)</td>
</tr>
</tbody>
</table>

*Difference between the resins is significant at $p<0.05$. ( ): SD

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![Fig. 3](image-url)

**Fig. 3** Weight changes of TFEMA-PTFEMA/TBBO and MMA-PMMA/TBBO resins as a function of immersion time in water.
liquid, PTFEMA powder and BPO was polymerized by the dough molding method and the water sorption of the cured resin was found to be 0.1 mg/cm², which was about one-fifteenth of the value for the control MMA-PMMA powder-liquid resin. Thus, investigations of fluorinated acrylic resins to improve various properties of dental resins have been promising. Nothing is, however, known about fluorination of cold-curing resins used as adhesives, and this is the reason why we studied TFEMA-PTFEMA/TBBO resin as an adhesive for precious metal alloys.

Experimental TFEMA-PTFEMA/TBBO resin did not require special handling when the resin was applied by the brush-on technique, but PTFEMA powder was less soluble in TFEMA liquid compared with the analogous components of MMA-PMMA/TBBO resin, resulting in a longer working time. The curing characteristics of adhesive resins can be evaluated by their setting time and peak temperature, although these characteristics are highly dependent on the volume of the resin mixture, meaning that a resin will cure in a shorter time with a higher peak temperature as the amount of resin increases. The differences in curing behavior between TFEMA-PTFEMA/TBBO and MMA-PMMA/TBBO resins are evident from Fig. 2. The overall rate of polymerization of TFEMA-PTFEMA/TBBO resin was significantly slower than that of MMA-PMMA/TBBO resin, since the former showed a peak temperature at 16.2 min and the latter at 4.5 min. This phenomenon suggests that TFEMA monomer is considerably inferior to MMA monomer in polymerization reactivity. The overall rate of polymerization can be increased by increasing the amount of initiator. However, the concentration of TBBO initiator is already high, about 8 wt% in monomer liquid, even in standard conditions for the polymerization of acrylic resin monomers. Therefore, we were unable to increase the concentration of TBBO in the monomer liquid without impairing the excellent water repellency of the cured TFEMA matrix phase. The initial temperature peak of the TFEMA-PTFEMA/TBBO resin and the temperature shoulder of the MMA-PMMA/TBBO resin shown in Fig. 2 were considered to be caused by heat evolution when the resin components were mixed, since the powder-liquid resins without TBBO exhibited temperature peaks at almost similar positions.

The thiirane monomer EP8MA is a colorless liquid at room temperature and exists as a stable sulfide in a primer solution. Once the primer solution is applied to a precious metal surface, the episulfide ring is cleaved on the surface of the metal, resulting in the formation of structures analogous to the mercapto group adsorbed on a precious metal. Thus, adsorbed EP8MA molecules are considered to form tight self-assembled structures on adherend substrates, and the adsorbed EP8MA monomers copolymerize with the matrix monomers, such as TFEMA, of an adhesive resin, resulting in the formation of a rather stable resin bond to the precious metal. The long-term bonding durability against water of TFEMA-PTFEMA/TBBO resin for precious metal alloys was evaluated on the basis of this putative adhesion mechanism. As shown in Table 2, the changes in the tensile bond strengths of the resins with thermal cycling were strongly dependent on the type of precious metal alloy. The mean tensile bond strength to Au alloy after 1,000 thermal cyclings exceeded the value before thermal cycling, although the difference was statistically insignificant ($p>0.05$). This may be partly due to an increase in the mechanical strength of the adhesive layer caused by post-polymerization with residual TBBO initiator in the early stages of thermal cycling.

It is rather difficult to obtain long-term water durability for Ag alloy because of its susceptibility to oxidation compared with Au alloy or Pd alloy, and therefore the results obtained for Ag alloy were significantly inferior to those for the other two metals ($p<0.05$). The tensile bond strengths of MMA-PMMA/TBBO resin to precious metal alloys treated with EP8MA were previously investigated under the same conditions, where mean bond strengths after 4,000 thermal cyclings were 36.1 MPa for Au alloy, 34.7 MPa for Pd alloy and 30.2 MPa for Ag alloy. The values for MMA-PMMA/TBBO resin were much higher than those for TFEMA-PTFEMA/TBBO resin, although it is

| Table 4 Retention rate (%) of tensile bond strength after thermal cycling in water relative to the strength before thermal cycling |
|-----------------|-----------------|-------------|-------------|-------------|
| Adhesive resin  | Adherend        | 0           | 1,000       | 2,000       | 4,000       |
| TFEMA-PTFEMA/TBBO | Au alloy       | 100.0       | 107.2       | 63.5        | 67.9        |
| TFEMA-PTFEMA/TBBO | Pd alloy       | 100.0       | 70.8        | 55.8        | 45.7        |
| TFEMA-PTFEMA/TBBO | Ag alloy       | 100.0       | 55.3        | 15.6        | 24.6        |
| MMA-PMMA/TBBO*  | Au alloy       | 100.0       | 95.0        | 85.6        | 85.3        |
| MMA-PMMA/TBBO*  | Pd alloy       | 100.0       | 94.4        | 84.0        | 81.5        |
| MMA-PMMA/TBBO*  | Ag alloy       | 100.0       | 90.0        | 81.3        | 77.2        |

* The values were calculated from the experimental data published in literature.
difficult to compare the bonding durability against water of different types of resins on the basis of values of tensile bond strength, since tensile bond strength depends on both interfacial durability against water and the cohesive strength of the resin itself\textsuperscript{20}. Therefore, the retention rate of tensile bond strength after thermal cycling in water relative to the strength before thermal cycling was used to evaluate the water durability of TFEMA-PTFEMA/TBBO resin in comparison with MMA-PMMA/TBBO resin, as summarized in Table 4. The dependency of the tensile bond strength of TFEMA-PTFEMA/TBBO resin on both the nature of the adherend and the extent of thermal cycling was quite significant when compared with MMA-PMMA/TBBO resin. The results with the former resin consequently emphasize the difference in the adsorbed structure of EP8MA on the adherend surface, since the relatively low copolymerization reactivity of TFEMA resulted in the selection of an adhesive monomer with ordered self-assembled structures\textsuperscript{22}. The reduction in tensile bond strength to Au alloy of TFEMA-PTFEMA/TBBO resin was statistically significant after 1,000 thermal cyclings; thereafter, the bond strength remained almost constant between 2,000 and 4,000 thermal cyclings, as was the case for MMA-PMMA/TBBO resin. This phenomenon suggests that the fluorinated resin is particularly suitable for treated adherend surfaces with ordered self-assembled structures of a thiirane monomer.

The water sorption of TFEMA-PTFEMA/TBBO resin was much higher than that of MMA-PMMA/TBBO resin, which was unexpected. The water sorption of TFEMA-PTFEMA heat-curing resin with BPO was less than one-tenth of the value obtained for MMA-PMMA heat-curing resin with BPO\textsuperscript{14}. Therefore, the abnormally high water sorption of the fluorinated resin was probably due to the initiator, TBBO. It has been reported that the block copolymer of TFEMA with a hydrophilic monomer exhibits a phase-separated structure because of the extreme difference in their polarity\textsuperscript{27}. In TFEMA-PTFEMA/TBBO resin, the concentration of TBBO in the TFEMA monomer liquid was relatively high, 8 wt\%, and TBBO is known to exhibit a hydrophilic nature in polymerization reactions\textsuperscript{28}. TFEMA-PTFEMA/TBBO resin became opaque after 1 day of immersion in water, suggesting that the cured resin could be phase separated, resulting in increased water sorption.

It is well known that sorbed water molecules act as a plasticizer for acrylic adhesive resins and that the tensile strength falls gradually with increasing content of water\textsuperscript{29}. As a specific example, the ultimate tensile strength of poly(methyl methacrylate) decreases by 20% of its dry value after 2 wt\% of water sorption\textsuperscript{30}. Thus, the distinct decrease in mean tensile bond strength to Au alloy between 1,000 and 2,000 thermal cyclings observed for TFEMA-PTFEMA/TBBO resin was considered to be mainly attributable to the reduction in tensile strength of the resin caused by sorbed water. Taking into consideration the reduction in mechanical strength caused by sorbed water, the bonding durability of TFEMA-PTFEMA/TBBO resin against penetration of water molecules along the adhesion interface for Au alloy appears to be comparable to that of MMA-PMMA/TBBO resin, suggesting that the fluorinated resin is a promising adhesive resin for Au alloy since it additionally possesses oil repellency. The water durability of the TFEMA-PTFEMA/TBBO resin bond to precious metal alloys decreased in the order Au alloy > Pd alloy > Ag alloy. The performance of the fluorinated resin for Pd alloy and Ag alloy was markedly inferior to that of MMA-PMMA/TBBO resin. This appeared to be caused by insufficient copolymerization with EP8MA molecules adsorbed on these precious metal alloys due to the lower polymerization reactivity of TFEMA-PTFEMA/TBBO resin compared with MMA-PMMA/TBBO resin. TFEMA-PTFEMA heat-curing resin was reported to be easily polymerized with 1 wt\% of BPO and the cured resin revealed reduced water sorption\textsuperscript{14}. Therefore, BPO-amine redox initiator system would be one of the suitable polymerization initiators for TFEMA-PTFEMA adhesive resin. Thus, an alternative polymerization initiator should be investigated to make the most of the water-repellent properties of TFEMA-PTFEMA powder-liquid resin, leading to further progress in the development of a new type of fluorinated adhesive resin.

**CONCLUSION**

In order to clarify the effect of fluorination of the adhesive resin on the water durability of a resin bond to precious metal alloys, TFEMA-PTFEMA/TBBO resin was prepared and tensile bond strengths to precious metal alloys treated with EP8MA were measured after thermal cycling. The mean bond strength of the resin to precious metal alloys generally increased in the order Ag alloy < Pd alloy < Au alloy after thermal cycling; however, the values gradually decreased with thermal cycling. The bonding durability of TFEMA-PTFEMA/TBBO resin for Au alloy was comparable to that of MMA-PMMA/TBBO resin; however, the performance of the fluorinated resin for Pd alloy and Ag alloy was markedly inferior to that of MMA-PMMA/TBBO resin. The reduced tensile bond strengths and high water sorption of the fluorinated resin were considered to be caused by TBBO initiator. A polymerization initiator that can substitute for TBBO should be developed to make the most of the water-repellent characteristics of TFEMA-PTFEMA powder-liquid resin.

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