Water Durability of Resin Bond to Precious Metal Alloys Using Adhesive Resins Containing Adhesion Promoting Monomers

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Received July 19, 2005/Accepted September 2, 2005

Adhesive resins for precious metals were prepared by adding an adhesion promoting monomer to MMA-PMMA/TBBO resin. Precious metal alloys bonded by the adhesive resin were thermocycled 0, 1,000, 2,000, or 4,000 times in water between 4 and 60°C, and tensile bond strengths were measured. Debonded metal surfaces after the tensile test were analyzed based on an area of cohesive failure.

Three-way ANOVA revealed that all the three parameters - adherend, adhesive monomer, and number of thermal cycles - exhibited a significant influence on bond strength. Bond strength significantly decreased with increasing number of thermal cycles except for resin with 9,10-epithiodecyl 4-vinylbenzoate (EP8VB) to Au alloy. Mean bond strength of adhesive resin with 9,10-epithiodecyl methacrylate (EP8MA), EP8VB, or 3,4-epithiobutyl 2,5-bis(methacryloyloxyethyl)propionate (EP2BMA) exceeded 22 MPa after 4,000 thermal cycles. Analysis of debonded surfaces revealed the applicability of EP8MA, EP8VB, and EP2BMA as an adhesive monomer component of adhesive resin formulations.

Key words: Adhesive resin, Bond strength, Water durability

INTRODUCTION

A number of surface modification methods - such as high-temperature oxidation, electroplating with tin, silica coating, and application of liquid Ga-Sn alloy - have been developed to obtain stable bonding of resin to precious metals. On the other hand, many sulfur-containing compounds were examined with regard to their adhesion promoting abilities for precious metals, since thiol is well-known to possess chemical affinity toward gold substrate. Some ingenious molecular designs of adhesion promoting monomer for precious metals have been developed based on the results of adhesion tests. The molecular structure consists of three parts: polymerizable double bond, connecting group, and adhesion promoting group. There are two different types of adhesion promoting group in the molecular design. One of the adhesion promoting groups utilizes tautomerism, where the stable structure with a thione type (-NH-CS-) is tautomerized to the reactive tautomer with a thiol type (-N=C(SH)-) on a precious metal surface. Sulfur-containing monomers such as thiobarbituric acid, triazinedithiones, and thiouracil belong to this tautomer type. The other adhesion promoting group makes the most use of a precursor of a mercapto compound, which is chemically stable in a solution or in a matrix monomer. A chemical reaction of the precursor occurs on a precious metal surface involving the cleavage of a single bond such as C-S or S-S, thereby resulting in the production of a thiol-like molecule bound to a precious metal. Derivative monomers of disulfide, thiirane, and dithiole are typical of the precursor type.

These adhesion promoting monomers have demonstrated excellent adhesion performance in relation to precious metal alloys, when utilized as a primer for the bond between resin and precious metal. Thus several precious metal primers containing one of the above adhesion promoting monomers have been placed on the market. Adhesion promoting monomers can also be utilized as an active ingredient added to base monomer mixtures of adhesive resins, as is the case of 4-META in Super-Bond C&B. However, there have been extremely few reports about adhesion promoting monomers contained in adhesive resins for precious metals. Thus long-term water durability of resin bond to precious metal alloys by adhesive resins containing adhesion promoting monomers for precious metals is not known in detail. In the present study, some typical adhesion promoting monomers for precious metals of the tautomer type or precursor type were added to the MMA liquid of an MMA-PMMA resin and tri-n-butylborane oxide (TBBO) was used as a polymerization initiator. Two precious metal alloy specimens were butt-jointed with the adhesive resin, and tensile bond strength was measured after 0, 1,000, 2,000, and 4,000 thermal cycles, followed by observation of the fractured surfaces after tensile testing. Dependence of long-term water durability of resin bond on the number of thermal cycles was discussed by comparing the molecular designs of adhesion.
promoting monomers for precious metals.

MATERIALS AND METHODS

Materials

Four kinds of thirane monomer, 9,10-epithiododecyl methacrylate (EP8MA)\(^2\), 9,10-epithiododecyl 4-vinylbenzoate (EP8VB)\(^3\), 2,3-epithiocyclohexyl methacrylate (EPCHMA)\(^4\) and 3,4-epithiobutyl 2,2-bis-(methacryloyloxyethyl)propionate (EP2BMA)\(^5\), and one thiobarbituric acid monomer, 5-(4-vinylbenzyl)-2-thiobarbituric acid (5VS)\(^6\), were used as adhesion promoting monomers for precious metals. They were synthesized according to previously described methods. The chemical structures of these adhesive monomers are shown in Fig.1. Methyl methacrylate (MMA) (Wako Pure Chemical Industries Ltd., Osaka, Japan) was washed successively with aqueous solutions of 5 wt% sodium hydrogen sulfite, 5 wt% sodium hydroxide, and 20 wt% sodium chloride to remove hydroquinone, and distilled under reduced pressure after drying over anhydrous sodium sulfate for one day. PMMA powder and an initiator, tri-n-butylborane oxide (TBBO), were obtained from Sun Medical Co., Ltd. (Kyoto, Japan) as a dental adhesive resin, Super-Bond C&B. Three kinds of dental precious metal alloy were selected as adherends, and their manufacturers and compositions are given in Table 1.

Experimental adhesive resins

Experimental adhesive resins consisted of MMA liquid, TBBO, and PMMA powder, i.e., MMA-PMMA/TBBO type resin. The adhesion promoting monomers – 5VS, EP8MA, EP8VB, EPCHMA, and EP2BMA – were dissolved separately in MMA monomer liquid at a concentration of 1.0 mol%. One drop of TBBO initiator was added to the MMA monomer liquid in one dappen dish immediately before use, and the concentration of TBBO in the solution was about 9.2 wt %. PMMA powder was placed in another dappen dish, and the resin was applied to the adherend surface by the brush-on technique\(^7\).

Measurement of tensile bond strengths to metal adherends

Metal adherends were cylindrically shaped (5 mm \( \times \) 4 mm). 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 a surface irregular-

![Chemical structures of adhesion promoting monomers 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>Sunsiver 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 Kyogo Co. Ltd., Tokyo, Japan).

Metal specimens were cylindrically shaped (5 mm \( \times \) 4 mm) and had an exterior screw on one side which was connected to the jig for the tensile test.
ity. After washing with acetone and drying naturally in air, two specimens of each metal were butt-jointed together with an experimental adhesive resin using the brush-on technique. Excess resin outside the circumference of the cylinder was removed using a double-edged razor blade (FEATHER Safety Razor Co. Ltd., Osaka, Japan), and the assembly was left to stand undisturbed for one hour at room temperature to allow adequate curing of the resin. One hour 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, or 4000 times in water between 4 and 60°C with a one-minute dwell time at each temperature. Tensile bond strengths of five specimens for each condition were determined 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 five replications were calculated for each condition, and the results were analyzed by three-way analysis of variance (ANOVA) and t-test at 95% level of confidence.

**Determination of the area of cohesive failure after tensile test**

Debonded metal surfaces after the tensile test were recorded photographically, and the graphics information was processed using a personal computer. Borderlines between cohesive and interface failures were visualized by means of color intensity analysis using computer graphics, and the area of cohesive failure was calculated from the area surrounded by borderlines. The percentage of the area of cohesive failure to the total cross-sectional area (5 mmΦ) was measured on five specimens for each condition. Specimens were excluded from the measurement of the area of cohesive failure if the border between cohesive and interface failures was unclear. The relative proportion of cohesive failure to the total cross-sectional area of the fractured specimen after tensile test was defined by the following equation:

$$\text{Relative proportion of cohesive failure (\%) = \frac{S}{A} \times 100}$$

where S is the area of cohesive failure measured and A is the total cross-sectional area (19.63 mm²).

**RESULTS**

Tensile bond strengths of the experimental adhesive resins to the precious metal alloys changed with thermal cycling. Three-way ANOVA revealed that tensile bond strength was significantly influenced by all three parameters: adherend (F=17.200, p=0.000), adhesive monomer (F=48.209, p=0.000), and number of thermal cycles (F=132.271, p=0.000). Two significant interactions were found between the parameters of adherend and adhesive monomer (F=4.312, p=0.000) and the parameters of adhesive monomer and number of thermal cycles (F=4.454, p=0.000). The mean and standard deviation of tensile bond strength to Au alloy, Pd alloy, and Ag alloy with five replications are summarized in Tables 2, 3, and 4 respectively. MMA-PMMMA/TBBO adhesive resins containing an adhesive monomer did not show any spontaneous interface failure with thermal cycles up to 4000 times. In other words, water durability of resin bond to precious metal alloys was significantly enhanced by the addition of an adhesive monomer to MMA-PMMMA/TBBO resin, since the control resin without any adhesive monomer revealed poor results even at 2000 thermal cycles

In the case of Au alloy, tensile bond strength decreased significantly as the number of thermal cycles increased except for the case of EP8VB as shown in Table 2 (p<0.05). The mean tensile bond strengths of EP8MA, EP8VB, and EP2BMA resins to Au alloy after 4000 thermal cycles exceeded 30 MPa, while that of 5VS was the lowest at 12.7 MPa. When compared to their initial values at 0 thermal cycle, the bond strengths of EP8MA, EP8VB, EPCHMA, and EP2BMA resins to Au alloy after 4000 thermal cycles were 76.0%, 80.5%, 52.4%, and 82.0% of their initial values respectively. The decrease in bond

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Tensile bond strength (MPa) to Au alloy of MMA-PMMMA/TBBO adhesive resin containing an adhesive promoting monomer</th>
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</thead>
<tbody>
<tr>
<td>Adhesive monomer</td>
<td>Thermal cycling</td>
</tr>
<tr>
<td>5VS</td>
<td>38.4 (2.4)a</td>
</tr>
<tr>
<td>EP8MA</td>
<td>40.9 (4.5)a</td>
</tr>
<tr>
<td>EP8VB</td>
<td>40.6 (5.2)a</td>
</tr>
<tr>
<td>EPCHMA</td>
<td>39.1 (7.8)a</td>
</tr>
<tr>
<td>EP2BMA</td>
<td>41.2 (4.3)a</td>
</tr>
</tbody>
</table>

Adhesive promoting monomer was added to MMA monomer liquid at a concentration of 1.0 mol%. Tensile bond strength after thermal cycling in water at 4 and 60°C. The same superscripts after parentheses denote insignificant differences between numbers of thermal cycling at p<0.05. ( ) : SD
strength to Au alloy became statistically significant at 1,000 thermal cycles for 5VS resin, at 2,000 thermal cycles for EPCHMA resin, and at 4,000 thermal cycles for EP8MA and EP2BMA resins, when compared with their initial values. The long-term durability of resin bond to Au alloy against water, i.e., tensile bond strength at 4,000 thermal cycles, decreased significantly in the order of EP2BMA = EP8VB = EP8MA > EPCHMA > 5VS (p < 0.05).

As seen in Table 3, tensile bond strength to Pd alloy likewise decreased significantly with increasing number of thermal cycles. The reduction in bond strength to Pd alloy with increasing number of thermal cycles was significant at 1,000 thermal cycles for 5VS and EP2BMA resins, at 2,000 thermal cycles for EP8MA and EP8VB resins, and at 4,000 thermal cycles for EPCHMA resin. The bond strengths of four adhesive resins containing a thirane derivative monomer after 4,000 thermal cycles were almost the same, which varied from 27.3 to 29.4 MPa. On the other hand, 5VS derived from thiobisbarbituric acid showed significant decrease in bond strength after 2,000 thermal cycles compared with thirane derivative monomers (p < 0.01). Thus, the long-term durability of resin bond to Pd alloy significantly decreased in the following order: EP8VB = EP2BMA = EPCHMA = EP8MA > 5VS (p < 0.01).

Results in Table 4 clearly indicated that reduction in tensile bond strength to Ag alloy was statistically significant for all adhesive resins when compared with their initial values at 0 thermal cycle (p < 0.05). The mean bond strength to Ag alloy of adhesive resin with a thirane derivative monomer at 4,000 thermal cycles was the lowest — not only amongst the different numbers of thermal cycles for Ag alloy, but also among the different precious metal alloys at 4,000 thermal cycles. Conversely, the mean bond strength of 5VS to Ag alloy was the highest among the precious metal alloys at 4,000 thermal cycles, although there were no significant differences between the bond strengths of 5VS resin (p > 0.05). The decrease in bond strength to Ag alloy with thermal cycling was significant at 1,000 thermal cycles for 5VS and EPCHMA resins, at 2,000 thermal cycles for EP8MA, EP8VB, and EP2BMA resins. The long-term durability of resin bond to Ag alloy against water significantly decreased as follows: EP8VB = EP8MA = EP2BMA > EPCHMA = 5VS (p < 0.05).

The mean bond strength of 5VS resin after 4,000 thermal cycles was lower than that of the thirane monomers in all precious metal alloys. Bond

<table>
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<tr>
<th>Table 3</th>
<th>Tensile bond strength (MPa) to Pd alloy of MMA-PMMA/TBBO adhesive resin containing an adhesion promoting monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive monomer</td>
<td>0</td>
</tr>
<tr>
<td>5VS</td>
<td>29.2 (5.0)*</td>
</tr>
<tr>
<td>EP8MA</td>
<td>41.0 (6.2)*</td>
</tr>
<tr>
<td>EP8VB</td>
<td>41.1 (5.7)*</td>
</tr>
<tr>
<td>EPCHMA</td>
<td>40.3 (6.9)*</td>
</tr>
<tr>
<td>EP2BMA</td>
<td>42.9 (4.1)*</td>
</tr>
</tbody>
</table>

Adhesion promoting monomer was added to MMA monomer liquid at a concentration of 1.0 mol%. Tensile bond strength after thermal cycling in water at 4 and 60°C. The same superscripts after parentheses denote insignificant differences between numbers of thermal cycling at p < 0.05.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Tensile bond strength (MPa) to Ag alloy of MMA-PMMA/TBBO adhesive resin containing an adhesion promoting monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesive monomer</td>
<td>0</td>
</tr>
<tr>
<td>5VS</td>
<td>38.7 (4.1)*</td>
</tr>
<tr>
<td>EP8MA</td>
<td>39.8 (3.8)*</td>
</tr>
<tr>
<td>EP8VB</td>
<td>39.6 (4.2)*</td>
</tr>
<tr>
<td>EPCHMA</td>
<td>38.5 (3.3)*</td>
</tr>
<tr>
<td>EP2BMA</td>
<td>40.1 (5.4)*</td>
</tr>
</tbody>
</table>

Adhesion promoting monomer was added to MMA monomer liquid at a concentration of 1.0 mol%. Tensile bond strength after thermal cycling in water at 4 and 60°C. The same superscripts after parentheses denote insignificant differences between numbers of thermal cycling at p < 0.05.
strength dependency of 5VS resin on precious metal alloy was not indicated in any decisive trend, although the mean bond strengths of adhesive resins with thirane monomers generally decreased in the order of Au alloy > Pd alloy > Ag alloy. The differences in tensile bond strength between 2,000 and 4,000 thermal cycles were insignificant particularly for Ag alloy, as well as for Au alloy and Pd alloy (p>0.05). Contrary to this, reduction in tensile bond strength to Ag alloy of all the adhesive resins was statistically significant after 2,000 thermal cycles when compared with their initial values at 0 thermal cycle (p<0.01).

The surfaces of debonded specimens after tensile testing showed that the area covered with a thin layer of MMA-PMMA/TBBO resin, i.e., the area of cohesive failure, was reduced as the number of thermal cycles increased. Fig. 2 shows an example of the surfaces of debonded Ag alloy specimens after the tensile test, which were butt-jointed together with the adhesive resin containing EP8VB. The relative proportion of the area of cohesive failure changed in proportion to tensile bond strength at a rough estimate, thereby demonstrating directly the long-term durability of resin bond against water.

Changes of the area of cohesive failure after tensile testing for Au alloy, Pd alloy, and Ag alloy are exhibited graphically in Figs. 3, 4, and 5 respectively. For Au alloy, the mean percentage of the area of cohesive failure ranged from 93.5% to 39.5%; for Pd alloy, from 95.8% to 40.7%; and for Ag alloy, from 92.7% to 45.8%. Further, the mean percentage of the area of cohesive failure at 0 thermal cycle varied from 89.2% (Ag alloy; EPCHMA) to 95.8% (Pd alloy; EP8VB) as shown in Figs. 3 and 4.

Fig. 2 The surfaces of Ag alloy specimens butt-jointed together with the adhesive resin containing EP8VB and debonded by tensile test.

Fig. 3 The relative proportion of the area of cohesive failure after tensile testing for Au alloy as a function of the number of thermal cycles.

Fig. 4 The relative proportion of the area of cohesive failure after tensile testing for Pd alloy as a function of the number of thermal cycles.
The area of cohesive failure for the adhesive resin with 5VS was markedly reduced as the number of thermal cycles increased.

For Pd alloy, the change in the relative proportion of the area of cohesive failure with the number of thermal cycles after tensile testing revealed that thirane monomers – EP8MA, EP8VB, EPCHMA, and EP2BMA – showed approximately the same results one with another. The retention rates of cohesive failure after 4,000 thermal cycles were 70.7% (EP8MA), 76.3% (EP8VB), 74.9% (EPCHMA), and 73.4% (EP2BMA), when compared with the mean percentages of the area of cohesive failure at the initial stage, i.e., 0 thermal cycle. For Au alloy, more excellent durability against water was noted of thirane monomers, except for EPCHMA, where the retention rates for EP8MA, EP8VB, and EP2BMA were 82.1, 83.6, and 84.5% respectively. In the case of Au alloy, the retention rates of these three monomers based on area of cohesive failure demonstrated a similar trend to that based on tensile bond strength, where they showed the best performances in all the experimental conditions and the values of retention rate increased in the order of EP8MA< EP8VB< EP2BMA as mentioned above. For Ag alloy, distinct differences in bonding durability against water among the thirane monomers were observed as the number of thermal cycles increased. After 4,000 thermal cycles, the mean percentages of the area of cohesive failure were 60.9, 68.5, 46.1, and 55.4% for EP8MA, EP8VB, EPCHMA, and EP2BMA respectively.

**DISCUSSION**

Adhesion promoting monomers for precious metals – such as 5VS, EP8MA, EP8VB, EPCHMA, and EP2BMA – were synthesized based on the molecular design of the adhesive monomer. 5VS is a crystalline solid and classified under the tautomer type according to the molecular design\(^8\). 5VS has a short connecting group and a styrene structure for the polymerizable double bond\(^9\). 5VS possesses an acidic nature, and is therefore effective for both base and precious metals. The thirane monomers, EP8MA, EP8VB, EPCHMA, and EP2BMA, are colorless liquids at room temperature and belong to the precursor type of the molecular design. The thirane derivatives exist as a stable sulfide in solution, and the episulfide ring is cleaved on the surface of a precious metal resulting in the formation of structures analogous to the mercapto group adsorbed on a precious metal\(^8\). Both EP8MA\(^{10}\) and EP8VB\(^{12}\) have a long alkylen chain, an octamethylene group, as a connecting group. Further, EP8MA and EPCHMA possess a methacryloyl group for polymerizable double bond, while EP8VB possesses a styrene structure. The structural feature of EPCHMA\(^{20}\) is a bulky thirane moiety containing a di-substituted three-membered ring with a short connecting group. EP2BMA\(^{27}\) is a bifunctional methacrylate which acts as a crosslinking agent, and has branched connecting chain.

The molecular weights of 5VS, EP8MA, EP8VB, EPCHMA, and EP2BMA are 260.32, 256.41, 318.48, 198.28, and 356.44 respectively. Therefore, the percentages by weight of the adhesive monomer in MMA liquid were 2.56, 2.52, 3.11, 1.96, and 3.47 wt% respectively. The concentration of the adhesion promoting monomer in MMA liquid of the adhesive resin was adjusted to a considerably higher value compared with dental precious metal primers\(^{12}\), since the adhesive monomer of primer is localized at the adhesion interface only while that of adhesive resin is dispersed throughout the resin layer. Generally speaking, the experimental adhesive resins corresponded to Super-Bond C&B in which 5 wt% of 4-META\(^{18}\) was replaced with 1.0 mol% of adhesion promoting monomer for precious metals.

The most remarkable differences in water durability of adhesive monomers were observed for Au alloy as the number of thermal cycles increased. The thirane monomers, EP8MA, EP8VB, and EP2BMA, were previously utilized in primers which contained 1 mol% thirane in ethanol\(^{20}\). Precious metal alloys treated with the primer were butt-jointed together with MMA-PMMMA/TBBO resin, and changes in tensile bond strength of the resin bond with thermal cycling were determined in the same manner as above. The retention rates of tensile bond strength after 4,000 thermal cycles for EP8MA, EP8VB, and EP2BMA were 85.3, 89.5, and 82.8% respectively, when Au alloys were treated with thirane primers\(^{20}\). Thus, the incorporation of the thirane monomer into the adhesive resin considerably lowered
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the retention rate of tensile bond strength with the exception of EP2BMA, when compared with their application as a primer. There seems to be two major reasons for their advantageous application as a primer. The largest cause is the spontaneous evaporation of solvent during surface treatment, which concentrates an adhesive monomer on an adherend surface and promotes the formation of tight self-assembled structures on the adherend substrate, thereby resulting in a higher bonding durability against water. The other factor is that the mechanical properties of the cured matrix resin are not affected by adhesive monomers, since the copolymerization of matrix monomers with adhesive monomers generally leads to reduction of mechanical strength because of the weakness of cured adhesive monomers. This hypothesis explains well the relatively low retention rates of adhesive resins containing EP8MA or EP8VB as compared with the corresponding primers. On the other hand, the adhesive resin with EP2BMA reinforced the cured matrix resin by cross-linking and compensated the disadvantage of less ordered, self-assembled structures. This helps to explain why in the case of EP2BMA, there was only a small difference in the retention rate of bond strength between an adhesive resin and a primer.

The tensile bond strengths of resin bond to Pd alloy exhibited a trend approximately similar to that of Au alloy in their changes with the number of thermal cycles, although the bond strengths after 4,000 thermal cycles were less than 30 MPa for all adhesive resins. The decrease in bond strength of the adhesive resin with 5VS was markedly distinguished from that of the adhesive resins with thirane monomers, and there was a striking similarity in the declining bond strengths to Pd alloy among the thirane monomers. EPCHMA retained a fairly good bond strength to Pd alloy, i.e., 27.9 MPa, even after 4,000 thermal cycles as compared to its performance with other precious metal alloys. This specific affinity of EPCHMA toward Pd alloy was also observed previously where 1.0 mol% of EPCHMA in either ethanol or benzene was utilized as a primer for precious metal alloys. This might be due to the enhanced stereoselective cleavage of thirane ring in EPCHMA caused by the reaction with Pd substrate, although details of the mechanism are unknown at present.

For all precious metal alloys, the reduction in tensile bond strength between 2,000 and 4,000 thermal cycles was insignificant. However, for Ag alloy, the reduction in bond strength between 0 and 2,000 thermal cycles was significant for all adhesive resins, thus indicating that the water durability of resin bond to Ag alloy was the lowest of all the precious metal alloys. Though Ag can be classified as a precious metal in a general sense, the surface of Ag is easily oxidized by water as well as by oxygen in the air. Indeed, Ag alloy specimens that were spontaneously debonded during thermal cycling sometimes revealed an oxidized layer on the surface. Thus, Ag alloy is susceptible to oxidation reaction when compared with Au alloy or Pd alloy. On this basis, the long-term durability against water of resin bond to Ag alloy is considered to be somewhat inferior to that of Au alloy or Pd alloy, since impurities on the adherend surface inhibit the adsorption of adhesive monomers on precious metal substrates.

Evaluation of water durability of resin bond to metal adherend by relative proportion of cohesive failure is superior to that by the tensile bond strength method. This is because the former evaluation method allows observation of the actual phenomenon at the adhesion interface, since water molecules which diffuse from the periphery toward the center along the adhesion interface cause the resin bond to deteriorate. This relative proportion of cohesive failure does not depend on the cohesive strength of the resin, but on interfacial durability against water. Therefore, relative proportion of cohesive failure serves as a convenient evaluation criterion for bonding durability against water when adhesive resins with different monomer compositions are compared, as was the case in the present study.

The mean percentage of the area of cohesive failure was not even 100% at 0 thermal cycle, and the debonded specimens exhibited partial interface failure to a certain degree at the peripheral region of the adhesion interface even before thermal cycling. This phenomenon appeared to be caused by an incompletely polymerized resin layer — which was due to the inhibition reaction by oxygen in the air, since excess resin outside the circumference of cylindrical adherends was removed before the adhesive resins were cured.

The appearance of debonded surfaces generally changed from an almost complete cohesive failure at the initial stage to cohesive failure mixed with a certain degree of interface failure at the latter stage of thermal cycling. Since failure mode itself after the tensile test did not change very much with thermal cycling, the percentage value of the area of cohesive failure plays an important role in evaluating the long-term water durability of resin bond to precious metal alloys. As shown evidently in Figs. 3, 4, and 5, the deterioration of resin bond to a precious metal alloy by the penetration of water was most remarkable for 5VS adhesive resin regardless of the adherend. The poor long-term performance of 5VS resin could most probably be explained by the fact that MMA was not a suitable solvent for the tautomerization of thione-thiol type, and that the thiol-type tautomer of 5VS reacted readily with free radicals — thereby inhibiting the activation of the adhesive species.

It is rather difficult to obtain long-term water...
durability to Ag alloy due to its susceptibility to oxidation as compared with Au alloy or Pd alloy. On this note, the obtained results for Ag alloy should be considered high. Based on the surface analysis of debonded Ag alloy specimens, bonding durability against water was improved in the order of EPCHMA<EP2BMA<EP8MA<EP8VB, which was consistent with bond strength results.

As shown in Figs. 3, 4, and 5, the rate of penetration of water molecules along the adhesion interface gradually decreased as the number of thermal cycles increased. This observation apparently indicated that the distribution of bond strength was not uniform, whereby the central region of adherend surface had a higher bond strength than the peripheral region. As a result, bonding durability against water improved towards the center of the cured adhesive resin. This is because the central region of adhesive resin inserted between two adherends has some advantages over the peripheral region in the curing process. Polymerization is usually initiated around the center of resin, and consequently, the residual or internal stresses due to polymerization shrinkage in the cured resin decreases. Moreover, the interior of applied adhesive resin is not sensitively and adversely affected by the oxygen in the air or by the evaporation of volatile monomers from uncovered surface, thereby enjoying a higher conversion than the peripheral region. These factors were considered to be the dominating causes for the slowing down of the rate of water penetration with thermal cycling. Of course, other factors stemming from postpolymerization and/or non-uniform distribution of thermal stress during thermal cycling were also conceivable causes. The deterioration of resin bond to precious metal alloys due to water penetration unexpectedly continued to proceed gradually at the stage of 4,000 thermal cycles, as shown in Figs. 3, 4, and 5. Whether this deterioration makes any further progress in the subsequent stage – after 4,000 thermal cycles – cannot be known until long-term bonding durability test with extended thermal cycling is performed, since the detailed mechanical and physicochemical properties of the adhesive resins are not yet clarified.

CONCLUSION

The long-term water durability of resin bond to precious metal alloys using adhesive resins containing adhesion promoting monomers for precious metals, 5VS, EP8MA, EP8VB, EPCHMA, and EP2BMA, was evaluated by tensile test and debonded surface analysis. The obtained results indicated that the deterioration of resin bond to precious metal alloys due to water penetration was influenced by both the adhesive monomer and precious metal alloy. The highest bonding durability against water was recorded for the adhesive resin containing EP8VB, where mean tensile bond strengths for Au alloy, Pd alloy, and Ag alloy exceeded 27 MPa even after 4,000 thermal cycles. The excellent long-term bonding durability against water of adhesive resins with EP8MA, EP8VB, or EP2BMA was clarified through debonded surface analysis based on an area of cohesive failure after tensile testing. Thus, the long-term durability test revealed the applicability of EP8MA, EP8VB, and EP2BMA as an adhesive monomer component of adhesive resin formulations.

REFERENCES


