Development of a new single-bottle multi-purpose primer for bonding to dental porcelain, alumina, zirconia, and dental gold alloy

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This study investigated the bonding efficacy of a combined primer application which comprised a silane coupling agent, an acidic adhesive monomer, and a dithiooctanoate monomer, as well as the influence of shelf life on bonding. Five experimental primers (coded as Si-P-SS-1 to Si-P-SS-4, and Si-SS as the control) were prepared using 20.0–40.0 wt% 3-methacryloyloxypropyltriethoxysilane (3-MPTES), 0–7.44 wt% 6-methacryloyloxyhexyl phosphonooacetate (6-MHPA), and 0.50 wt% 10-methacryloyloxydecyldisiloxane (10-MDDT). After 24-hour storage at 23°C (Initial) and 2-month storage at 50°C (Aged), tensile bond strengths (TBSs) of a resin cement (ResiCem, Shofu Inc., Kyoto, Japan) to primer-treated porcelain, alumina, zirconia, and Au alloy were measured. With the Initial and Aged primers of Si-P-SS-1 to Si-P-SS-3, there were no statistically significant differences in the mean TBSs (MPa) [porcelain: 21.7–29.2; alumina: 21.4–25.3; zirconia: 20.3–24.5; and Au alloy: 23.4–27.6] among these three primers (p>0.05), but they were significantly higher than that of the control primer (p<0.05). The experimental primers Si-P-SS-1 to Si-P-SS-3 demonstrated good potential as multi-purpose primers: they had good shelf lives as single-bottle primer systems and were thus able to exhibit good bond strength to all the adherends tested after 2-month storage under accelerated aging conditions.

Keywords: Dithiooctanoate monomer, Phosphonic acid monomer, Silane coupling agent, Multi-purpose primer

INTRODUCTION

In today’s esthetic dentistry, there emerges a clinical demand for the development of multi-purpose primers or adhesives which could deliver strong and durable adhesion indiscriminately to a multitude of adherends that coexist in the oral environment, such as dental hard tissues, dental ceramics, dental precious metal alloys, and dental non-precious metals6. For porcelain-fused-to-metal restorations, silica-based ceramics such as feldspathic porcelains and glass ceramics are frequently used to veneer metal frameworks9; for all-ceramic restorations, high-strength ceramic copings are used8. To ensure strong and durable adhesion to a wide spectrum of adherend materials with diverse properties, the inevitable challenge is a multi-purpose primer or adhesive to meet this demand.

Porcelain veneers are steadily increasing in popularity among today’s dental practitioners for conservative restoration of unaesthetic anterior teeth6. Application of a silane coupling agent to a pretreated ceramic surface provides chemical covalent bonding and hydrogen bonding6, thereby providing sufficient bonding between resin and silica-based ceramics5-7. Silane bonding agents usually contain a silane coupling agent and a weak acid, which enhances the formation of siloxane bonds6. However, conventional single-bottle products have a limited shelf life and are susceptible to rapid solvent evaporation and hydrolysis, making the silane solution useless8.

Developments in core materials such as lithium disilicate, alumina-based ceramics (alumina), and zirconia-based ceramics (zirconia) have allowed more widespread application of all-ceramic restorations over the past 10 years9. Due to zirconia’s favorable esthetic characteristics, mechanical properties, and biocompatibility, zirconia-based ceramic systems have become increasingly popular in dentistry, with yttrium tetragonal zirconia polycrystal (Y-TZP)-based materials emerging as the most recent core material of choice for all-ceramic fixed partial dentures (FPDs)10. Establishing a strong and stable bond with zirconia has proven to be difficult11. However, a resin containing a phosphoric acid monomer, 10-methacryloyloxydecyl dihydrogen phosphate (MDP), was found to exhibit durable bonding to zirconia ceramic after the latter was subjected to air particle abrasion (110 µm Al2O3 at 2.5 bar)12. The range of clinical indications for CAD/CAM-fabricated, densely sintered, high-purity aluminum oxide ceramic restorations (Procera AllCeram, Nobel Biocare, Goteborg, Sweden) has recently expanded to laminate veneers13 and resin-bonded FPDs14. A strong and durable resin bond to the restorative materials and supporting tooth structures would thus ensure the clinical success of these all-ceramic restorations15. For the bonding of resin composite veneering materials to precious metals and alloys, the prime focus is still on sulfur-containing adhesion-promoting monomers (adhesive monomers), which are able to chemically interact with metal atoms on the surfaces of precious metals9,17. This phenomenon is attributed to the chemical adsorption of organic sulfur compounds on...
precious metal surfaces and formation of monolayer films by a spontaneous assembly of organic thiol-like molecules
d). A ternary combination of silane coupling agents, acidic adhesive monomers, and sulfur-containing monomers enabled multi-purpose primers to exhibit outstanding adhesion to a variety of substrates, ranging from porcelain and zirconia to dental precious and non-precious metal and alloys. However, the development of single-bottle (one-pack) multi-purpose primers remained a challenge, because of hydrolysis of silane coupling agents and a limited shelf life of single-bottle formulations. In the pursuit of a multi-purpose primer, we have developed several kinds of acidic adhesive monomers bearing the carboxylic acid group (-COOH) or its anhydride group and the phosphonic acid group [-P(O)(OH)]
for bonding to dental precious metals and alloys, we have developed dithiooctanoate monomers.

The first aim of the present study was to investigate the effects of experimental primers containing a silane coupling agent, an acidic adhesive monomer, and a dithiooctanoate monomer on bonding to dental porcelain, alumina, zirconia, and Au alloy. In this study, “Excess degree of silane (EDS)” was defined as the amount of silane coupling agent in excess of the amount of acidic adhesive monomer. The second aim of the present study was to investigate the effect of EDS on shelf life by evaluating the bonding abilities of the primers after 2-month storage at 50°C through an artificial aging test.

The null hypotheses tested in this study were: (1) a ternary combination of 3-MPTES, 6-MHPA, and 10-MDDT would not contribute to increasing the bond strength to dental porcelain, alumina, zirconia, and Au alloy; and (2) an excess amount of silane coupling agent against the acidic phosphonic acid monomer would not affect the shelf life of multi-purpose primers after storage under accelerated aging conditions.

MATERIALS AND METHODS

Preparation of adhesive monomers
A silane coupling agent, 3-methacryloyloxypropyltriethoxysilane (3-MPTES), was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). An acidic adhesive monomer, 6-methacryloyloxyhexyl phosphonoacetate (6-MHPA), and a dithiooctanoate monomer, 10-methacryloyloxydecyl 6,8-dithiooctanoate (10-MDDT), were synthesized using the respective methods previously reported. Figure 1 depicts the chemical structures of 3-MPTES, 6-MHPA, and 10-MDDT used in this study.

Preparation of adherends
A total of four ceramic and metal adherends were employed in this study for bond strength evaluation. Three kinds of ceramic adherends were used: porcelain (Vintage Halo, Shofu Inc., Kyoto, Japan), alumina oxide (Al2O3; Japan Fine Ceramics Co., Ltd., Sendai, Japan), and zirconium oxide (ZrO 2 containing 3 mol% Y2O3; Japan Fine Ceramics Co., Ltd., Sendai, Japan). The metal adherend used was Au alloy (Super Gold Type 4, Shofu Inc., Kyoto, Japan), of which the composition

![Chemical structures of 3-MPTES, 6-MHPA, and 10-MDDT](image)
(mass%) was Au (70), Cu (13), Ag (10), Pt (1), Pd (4), and others (2).

For the porcelain adherends, they were disk-shaped plates of 15 mm diameter × 5.0 mm height produced using a vacuum electric furnace for firing porcelain (Twin Mat, Shofu Inc., Kyoto, Japan). For aluminum oxide, zirconium oxide, and Au alloy adherends, they were square-shaped plates of 15×15×2 mm dimensions.

Preparation of experimental single-bottle multi-purpose primers

Table 1 shows the compositions of the five experimental primers prepared in this study. The code names Si-P-SS-1 to Si-P-SS-4 indicated thus: Si for Silane (3-MPTES), P for Phosphonic acid derivative (6-MHPA), and SS for cyclic disulfide compound (10-MDDT). Si-SS was prepared as a control primer which contained 3-MPTES and 10-MDDT only. All prepared primers (5.0 g) were placed in black plastic containers. The EDS value (=Silane wt%/Acid wt%) indicates how many times the amount of 3-MPTES was higher than that of acidic 6-MHPA. As shown in Tables 1 to 3, the EDS values ranged from 4.0 to 62.5 for the primers of Si-P-SS-1 to Si-P-SS-4. Si-SS was without 6-MHPA content and hence had no accompanying EDS value.

Artificial aging test

To evaluate the shelf lives of the prepared single-bottle primers, an artificial aging test was conducted in this study. Prepared single-bottle primers in black plastic containers were stored under two conditions: Initial versus Aged. Under the Initial condition, the storage duration was 24 hours at 23°C. Separately under the Aged condition, primers in black plastic containers were stored under an accelerating aging condition of 50°C for 2 months.

Tensile bond strength measurement

Tensile bond strengths (TBSs) of both the Initial and Aged primers were measured. To prepare the bonding surfaces of all the adherends, a flat surface of each adherend plate was polished under running water using silicon carbide papers #240 and #600 to obtain a smooth surface. After air abrasion treatment (50 µm alumina beads; Shofu Hi-alumina, Shofu Inc., Kyoto, Japan) under a pressure of 0.25 MPa, the smooth surfaces were ultrasonically cleaned and air-dried. An experimental primer was applied on the bonding surface of each type of adherend plate using a small brush. After left to stand for 30 seconds, each bonding surface was dried using an air syringe until fluidity of the adhesive composition disappeared.

A cylindrical stainless cobalt-chromium (Co-Cr) alloy (Cobaltam, Shofu Inc., Kyoto, Japan) bar of 5.0 mm diameter × 10.0 mm height was used as the TBS test jig. To prepare the jig’s bonding surface, it was also subjected to air abrasion (50 µm alumina beads; 0.25 MPa pressure), followed by ultrasonic cleaning and air-drying.

A dual-curing resin cement (ResiCem, Shofu Inc., Kyoto, Japan) kneaded into a uniform paste was placed between the bonding surfaces of an adherend and the Co-Cr bar for bonding of these two adherends. Excess cement was removed using a small brush, and photopolymerization with a visible light curing unit (Shofu Grip Light II, Shofu Inc., Kyoto, Japan) was focused at the cement margin for 10 seconds. All bonded specimens (n=7 in each group) were immersed in water at 37°C for 24 hours. After water storage, the bonded specimens were subjected to a tensile bond test using a universal testing machine (Model 5543, Instron Co., Norwood, MA, USA) at a crosshead speed of 1.0 mm/min. TBS testing was conducted at 23±1°C.

Failure mode analysis

After TBS testing, the debonded specimen surfaces were examined using a stereomicroscope (Leica DM IL, Leica Microsystems Japan, Tokyo, Japan) at ×20 magnification. The failure modes were classified as follows: Interfacial failure “I”, defined as the fracture which occurred at the bonded interface between adhesive and adherend; Cohesive failure “C1”, defined as the cohesive fracture in adhesive resin; Cohesive failure “C2”, defined as the cohesive fracture in adherend; and Mixed failure “M”, defined as the failure mode in which both interfacial and cohesive failures coexisted on the debonded surfaces.

After examining all the debonded specimens, the failure modes of specimens in each group were identified as I/M/C1/C2 (=Interfacial failure/Mixed failure/Cohesive failure in adhesive resin/Cohesive failure in adherend) and numbered accordingly.
Statistical analysis
Statistical analysis was performed for the TBS data of all the five experimental primers. One-way analysis of variance (ANOVA) was performed to determine the existence of significant differences in TBS among the different types of experimental primers for each adherend. Statistical significance was set in advance at the 0.05 probability level. Multiple comparisons were performed using Student-Newman-Keuls test at α=0.05.

RESULTS

Tensile bond strength
Table 2 presents the effects of five experimental primers on the TBS of a dual-curing resin cement (ResiCem, Shofu Inc., Kyoto, Japan) to four kinds of sandblasted adherends.

After “Initial” storage of the primers, results showed that there were no statistically significant differences in TBS among the four experimental primers of Si-P-SS-1 to Si-P-SS-4 to the four adherends (p>0.05). After “Aged” storage, the TBS of Si-SS was significantly lower than that of the other primers for all adherends. The TBS of Si-P-SS-1 to Si-P-SS-4 increased significantly after aging, whereas the TBS of Si-SS decreased significantly after aging.

Table 2 Effects of the storage conditions of experimental primers on tensile bond strength to porcelain, alumina, zirconia, and Au alloy

<table>
<thead>
<tr>
<th>Primer code</th>
<th>Primer aging condition</th>
<th>Tensile bond strength [mean (standard deviation, SD) MPa]</th>
<th>Porcelain</th>
<th>Alumina</th>
<th>Zirconia</th>
<th>Au alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-P-SS-1 [62.5]</td>
<td>Initialθ</td>
<td>21.8 (4.3)a</td>
<td>25.2 (4.8)a</td>
<td>20.3 (4.9)a</td>
<td>24.6 (4.5)a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Agedφ</td>
<td>21.7 (4.5)a</td>
<td>21.4 (4.6)a</td>
<td>23.6 (4.6)a</td>
<td>23.4 (4.7)a</td>
<td></td>
</tr>
<tr>
<td>Si-P-SS-2 [16.1]</td>
<td>Initial</td>
<td>26.9 (5.6)a</td>
<td>23.9 (4.8)a</td>
<td>21.9 (4.8)a</td>
<td>25.4 (4.9)a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>25.0 (4.4)a</td>
<td>22.9 (4.0)a</td>
<td>21.4 (4.5)a</td>
<td>26.9 (5.8)a</td>
<td></td>
</tr>
<tr>
<td>Si-P-SS-3 [5.4]</td>
<td>Initial</td>
<td>29.2 (5.2)a</td>
<td>22.4 (4.8)a</td>
<td>24.5 (4.9)a</td>
<td>26.8 (5.5)a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>23.1 (4.5)a</td>
<td>23.3 (4.2)a</td>
<td>20.8 (4.2)a</td>
<td>27.6 (5.7)a</td>
<td></td>
</tr>
<tr>
<td>Si-P-SS-4 [4.0]</td>
<td>Initial</td>
<td>20.4 (3.4)a</td>
<td>20.8 (2.7)a</td>
<td>19.7 (2.5)a</td>
<td>19.6 (3.6)a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>8.7 (1.5)b</td>
<td>20.3 (2.4)a</td>
<td>19.2 (2.2)a</td>
<td>19.2 (3.5)a</td>
<td></td>
</tr>
<tr>
<td>Si-SS [-]</td>
<td>Initial</td>
<td>9.1 (1.5)b</td>
<td>10.2 (2.3)b</td>
<td>6.5 (1.3)b</td>
<td>11.6 (1.5)b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>8.8 (1.3)b</td>
<td>8.9 (1.5)b</td>
<td>6.6 (1.5)b</td>
<td>11.0 (1.2)b</td>
<td></td>
</tr>
</tbody>
</table>

n=7.
EDS*: Same definition as described for Table 1.
Initialθ: Experimental single-bottle primers stored at 23°C for 24 hours.
Agedφ: Single-bottle primers stored at 50°C for 2 months.
Groups from the same adherend column that are identified with the same superscript letter are not significantly different (p>0.05).

Table 3 Failure modes of specimens after tensile bond strength testing to porcelain, alumina, zirconia, and Au alloy using the five experimental primers

<table>
<thead>
<tr>
<th>Primer code</th>
<th>Primer aging condition</th>
<th>Failure mode§ of fractured surfaces after debonding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Porcelain</td>
</tr>
<tr>
<td>Si-P-SS-1 [62.5]</td>
<td>Initialθ</td>
<td>0/5/2/0</td>
</tr>
<tr>
<td></td>
<td>Agedφ</td>
<td>1/5/1/0</td>
</tr>
<tr>
<td>Si-P-SS-2 [16.1]</td>
<td>Initial</td>
<td>0/4/2/1</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>0/3/2/2</td>
</tr>
<tr>
<td>Si-P-SS-3 [5.4]</td>
<td>Initial</td>
<td>0/4/1/2</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>0/5/2/0</td>
</tr>
<tr>
<td>Si-P-SS-4 [4.0]</td>
<td>Initial</td>
<td>2/5/0/0</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>7/0/0/0</td>
</tr>
<tr>
<td>Si-SS [-]</td>
<td>Initial</td>
<td>5/2/0/0</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>6/1/0/0</td>
</tr>
</tbody>
</table>

n=7.
EDS*, Initialθ, Agedφ: Same definitions as described for Tables 1 and 2.
Failure mode§: Number of specimens for I (Interfacial failure)/M (Mixed failure)/C1 (Cohesive failure in adhesive)/C2 (Cohesive failure in adherend).
storage, there was also no significant degradation in TBS among the four primers of Si-P-SS-1 to Si-P-SS-4 ($p<0.05$) to all the adherends, except in the bonding of Si-P-SS-4 to porcelain ($p<0.05$).

Si-P-SS-1 to Si-P-SS-4 showed significantly higher TBSs ($p<0.05$) to porcelain, alumina, zirconia, and Au alloy than the control primer of Si-SS which did not contain 6-MHPA — be it after “Initial” or “Aged” storage of the primers. However, an exception was found in the bonding of Si-P-SS-4 to porcelain after “Aged” storage, which was not significantly different from that of Si-SS ($p>0.05$).

**Failure modes**

Table 3 presents the failure modes of the specimens after TBS testing. After “Initial” storage, majority of the failure modes of Si-P-SS-1 to Si-P-SS-4 were mixed and cohesive failures for all the four types of adherends, without any interfacial failure. After “Aged” storage, majority of the failure modes of Si-P-SS-1 to Si-P-SS-3 were mixed and cohesive failures for all the debonded specimens — except for the debonded specimens of porcelain with Si-P-SS-4, which showed interfacial failure after “Aged” storage. For the control primer Si-SS, majority of the failures were interfacial and mixed failures without cohesive failure after “Initial” and “Aged” storage.

For primers Si-P-SS-1 to Si-P-SS-3 (EDS: 5.4–62.5), accelerated aging at 50°C for 2 months did not result in bond strength degradation to all the adherends. However, primer Si-P-SS-4 (EDS: 4.0) showed significantly degraded bond strength to porcelain ($p<0.05$) after 2-month aging at 50°C.

**DISCUSSION**

In the present study, a new single-bottle multi-purpose primer containing a silane coupling agent, a phosphonic acid monomer, and a dithiooctanoate monomer was developed. Its formulation stability as a single-bottle system comprising a ternary combination of adhesive monomers was assessed by evaluating its bonding performance to four types of adherend materials.

For bonding to ceramic substrates, silane coupling agents — such as 3-MPTES — are bifunctional molecules that bond silicon dioxide with the OH groups on silica-based ceramic surfaces. In a silane coupling reaction, the trialkyloxysilyl group [-Si-(OR)$_3$] of silane coupling agents is hydrolyzed in acid solutions to form reactive silanols [-Si-(OH)$_3$]. Partial condensation reaction follows and oligomers are formed, which are adsorbed on silica-based ceramic surfaces by hydrogen bonding. Dehydration condensation, which is applied using heat treatment, then causes covalent chemical bonds to be formed between silanes and silica-based ceramics. It was also reported that when silane coupling agent was used in combination with an acidic compound, bond strength to porcelain was influenced by the acidity of the acid compound.

After “Initial” storage, Si-P-SS-1 to Si-P-SS-4 — which contained a ternary combination of 3-MPTES, 6-MHPA, and 10-MDDT — showed significantly higher TBSs ($p<0.05$) to porcelain, alumina, zirconia, and Au alloy than the control primer of Si-SS which did not contain 6-MHPA. Correspondingly, fracture mode analysis revealed a lot of mixed and cohesive failures for Si-P-SS-1 to Si-P-SS-3 after “Initial” storage, without any interfacial failures. On the other hand for Si-SS, it was predominantly interfacial failures for all the adherends with a few mixed failures. These results suggested that a ternary combination of a silane coupling agent (3-MPTES) and two kinds of adhesive monomers for precious and non-precious metals (6-MHPA and 10-MDDT) were must-have components for multi-purpose primers. Therefore, the first null hypothesis — which stated that a ternary combination of 3-MPTES, 6-MHPA, and 10-MDDT would not contribute to increasing the bond strength to dental porcelain, alumina, zirconia and Au alloy — was rejected.

Another formulation stability challenge posed by single-bottle multi-purpose primers pertains to the shelf life. In the present study, we sought to extend the shelf life by introducing an excess amount of silane coupling agent against that of the acidic adhesive monomer, such that the amount of 3-MPTES used for all the experimental primers was 20 or 40 wt%. Besides, the parameter EDS ($=$Silane wt%$/\text{Acid wt%}$) was used in this study to establish a relation between an excess amount of silane coupling agent and the shelf life of primer. All the experimental primers were stored under an accelerated aging condition of 50°C for 2 months. This was because it was thought that reaction among the co-existing primer ingredients caused the primer composition to degrade, and a high temperature would help to accelerate the reaction. The storage temperature of 50°C was selected because it was estimated that temperature could climb to 50°C during transport of primer products in midsummer season.

Results showed that Si-P-SS-1 to Si-P-SS-3 (EDS: 5.4–62.5) were not degraded after 2 months of accelerated aging storage at 50°C. In sharp contrast, with or without aging, Si-SS which did not contain 6-MHPA showed significantly lower bond strengths ($p<0.05$) to all the adherends tested than the primers of Si-P-SS-1 to Si-P-SS-3. These results proved that acidic adhesive monomers were required to enhance the formation of siloxane bonds between a silane coupling agent and a silica-based ceramic to achieve firm adhesion.

In the case of the artificially aged primer of Si-P-SS-4, it exhibited a significantly lower bond strength of 8.7 MPa to porcelain as compared to its “Initial” bond strength of 20.4 MPa ($p<0.05$), although it contained 6-MHPA. It was thought that hydrolysis with an acidic compound caused the silane coupling agent to degrade. The case of Si-P-SS-4 revealed that the degradation of bond strength to porcelain of single-bottle primers was strongly correlated with the EDS of primers. However, it remained unclear why EDS ranging between 5.4 to 62.5 contributed to the shelf life of single-bottle primers, whereas EDS 4.0 produced degraded bond strength to
porcelain after accelerated aging storage. Nonetheless, it was clear that the EDS value influenced the shelf life of single-bottle multi-purpose primers. Therefore, the second null hypothesis—which stated that an excess amount of silane coupling agent against the acidic phosphonic acid monomer would not affect the shelf life of multi-purpose primers after storage under artificial aging conditions—was rejected.

A critically important finding in this study was that single-bottle multi-purpose primer systems could be realized with an excess amount of silane coupling agent against that of acidic adhesive monomer. On the mechanism of formulation stability achieved in this study, we hypothesized that a trace amount of silane coupling agent was hydrolyzed in a trace amount of water originally contained in acetone and ethanol. Consequently, the water-depleted primer served as an ideal storage environment for the formulation despite a duration of 2 months under 50°C and with both silane coupling agent and acidic adhesive monomer coexisting in a single bottle.

In commercially available silane coupling agents, the silane group typically used is the trialkyloxysilyl group. Alcohol (R-OH) compounds formed as a product of the hydrolysis of silane coupling agents are derived from the [-Si-(OR)3] group. In the case of 3-MPTES, its triethoxysilyl group [-Si-(OCH3)3] in the structure can produce ethanol after hydrolysis, while 3-methacryloyloxypropyltrimethoxysilane (3-MPTMS) with a trimethoxysilyl group [-Si-(OCH3)3] will produce methanol. In light of human health and safety considerations, 3-MPTES was selected for this study. Based on these same considerations, hydrophilic solvents acetone and ethanol—rather than hydrophobic solvents—were used in this study, as hydrophobic solvents are supposedly more toxic than hydrophilic ones.

Establishing a strong and stable bond with zirconia has proven to be difficult[13]. However, it was reported that stable bond strength was achieved on silica-coated yttrium-oxide-partially-stabilized zirconia (YPSZ) ceramics by tribochemical modification with a combined yttrium-oxide-partially-stabilized zirconia (YPSZ) that stable bond strength was achieved on silica-coated porcelain after accelerated aging storage. Nonetheless, it was clear that the EDS value influenced the shelf life of single-bottle multi-purpose primers. Therefore, the second null hypothesis—which stated that an excess amount of silane coupling agent against the acidic phosphonic acid monomer would not affect the shelf life of multi-purpose primers after storage under artificial aging conditions—was rejected.

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In commercially available silane coupling agents, the silane group typically used is the trialkyloxysilyl group. Alcohol (R-OH) compounds formed as a product of the hydrolysis of silane coupling agents are derived from the [-Si-(OR)3] group. In the case of 3-MPTES, its triethoxysilyl group [-Si-(OCH3)3] in the structure can produce ethanol after hydrolysis, while 3-methacryloyloxypropyltrimethoxysilane (3-MPTMS) with a trimethoxysilyl group [-Si-(OCH3)3] will produce methanol. In light of human health and safety considerations, 3-MPTES was selected for this study. Based on these same considerations, hydrophilic solvents acetone and ethanol—rather than hydrophobic solvents—were used in this study, as hydrophobic solvents are supposedly more toxic than hydrophilic ones.

Establishing a strong and stable bond with zirconia has proven to be difficult[13]. However, it was reported that stable bond strength was achieved on silica-coated yttrium-oxide-partially-stabilized zirconia (YPSZ) ceramics by tribochemical modification with a combined application—and hence cooperative interaction—of a hydrophobic phosphonic acid monomer MDP and a silane coupling agent[27]. A recent study[28] also reported that a commercial metal primer containing MDP adhesive monomer (Alloy Primer, Kuraray Medical, Tokyo, Japan) showed effective and durable shear bond strength (SBS) between a tri-n-butylborane (TBB)-initiated acrylic resin and a commercial zirconia-based ceramic (Katana, Noritake Dental Supply, Aichi, Japan). Apart from MDP adhesive monomer, it was reported that 6-MHPA in a commercial metal primer (AZ Primer, Shofu Inc., Kyoto, Japan) contained MDP adhesive monomer (Alloy Primer, Kuraray Medical, Tokyo, Japan) contains 6-MHPA, and 10-MDDT interacted independently and respectively with zirconia-based ceramic and Au alloy in this study.

This phenomenon of independent interactions of sulfur-containing monomers and acidic adhesive monomers has been leveraged for the production of metal primers by commercial manufacturers. Metal Link Primer (M.L. Primer, Shofu Inc., Kyoto, Japan) contains both 6-MHPA and 10-MDDT. In a recent study by Okuyama[32] et al., the effects of three commercial metal primers on the bonding of a methyl methacrylate (MMA)-polymethyl methacrylate (PMMA)/tri-n-butylborane oxide (TBBO) resin to four pure metals and two dental alloys were investigated. After 2,000 times of thermal cycling, the highest SBSs of 33.5 MPa to pure Au and 33.3 MPa to high-gold-content alloy were achieved with M.L. Primer. Although these SBS values[32] were higher than the TBS values obtained in the present study, the differences were thought to be caused by the differences between shear and tensile bond strength testing methodologies.

Research efforts expended in and results reaped from this study—which investigated the effects of a primer comprising a ternary combination of 3-MPTES, 6-MHPA, and 10-MDDT on bonding to porcelain, alumina, zirconia, and Au alloy—eventually culminated in three inventions entitled “(Meth)acrylic ester derivatives”[29], “A composition for metal adhesion”[33], and “One-pack type dental adhesive composition”[40]. In this series of studies on multi-purpose adhesives and primers, our next target is to design a multi-purpose light-curing adhesive. The effect of this novel adhesive on the bonding of a prosthetic light-curing resin composite to dental ceramics and precious metal alloys shall be investigated and assessed.
CONCLUSIONS

Based on the findings in the present study, the following conclusions were drawn:

1. Experimental primers Si-P-SS-1 to Si-P-SS-3 exhibited good bond strength to porcelain, alumina, zirconia, and Au alloy—a clear indication of their potential as multi-purpose primers for diverse adherends.

2. A ternary combination of 3-MPTES, 6-MHPA, and 10-MDDT contributed to increasing the bond strength to dental porcelain, alumina, zirconia, and Au alloy.

3. EDS (Excess degree of silane) values of 5.4 to 62.5 provided primers Si-P-SS-1 to Si-P-SS-3 with a stable shelf life as single-bottle primers, thus enabling them to maintain high bond strength to porcelain after storage under accelerated aging conditions.

REFERENCES


