Synthesis of New Silane Coupling Agents with a Trimellitic Anhydride Group and Application as Primers for Ceramics and Alloys

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Received April 20, 2007/Accepted June 6, 2007

With a view to improving the bond strength of resin to dental ceramics and alloys, new silane coupling agents, namely 4-tri-chlorosilylpropyl- and 4-trimethoxysilylpropyl-trimellitic anhydride (4-CSTA and 4-MSTA, respectively), were synthesized. In addition, silane mixtures of 4-CSTA with 3-methacryloxypropyltrimethoxysilane (3-MPS) and 4-MSTA with 3-MPS were used as primers for adhesion of poly (methyl methacrylate) to glass, silver-palladium-gold alloy (Ag-Pd alloy), and cobalt-chromium alloy (Co-Cr alloy). The tensile bond strengths of resin to glass using 4-CSTA+3-MPS and 4-MSTA+3-MPS were 28.5±5.3 and 23.9±8.1 MPa respectively. With the metal alloys, the strengths were 14.8±5.3 MPa for Ag-Pd alloy and 24.7±7.2 MPa for Co-Cr alloy. In the light of these results obtained, it seemed that the mixture of 4-MSTA and 3-MPS was an effective primer for both metals and ceramics.

Keywords: Silane coupling agent, Adhesion, Ceramics, Alloy

INTRODUCTION

In the fabrication of dental prostheses, a wide range of materials — metals, ceramics, and polymers — are used, and many prostheses are made by a combination of these dental materials thereof. For example, porcelain-fused-to-metal crowns consist of metal and ceramics. However, when the crown is damaged, the repair is a challenging uphill task. This is because the crown is small and it constitutes multiple materials. In the case in which the crown is repaired by resin, it is then necessary to use primers which are exclusive for each alloy and ceramic at small parts of the crown.

In the field of dentistry, numerous excellent primers such as 4-META\(^3\), Phenyl-P\(^{2,3}\), and 3-MPS have been developed for a particular material type. Favorable results have been yielded with these primers when used properly. 4-META and Phenyl-P are excellent primers for non-precious alloys, while 3-MPS is a primer for ceramics. However, 3-MPS is a less effective primer for metals, and 4-META and Phenyl-P are less effective for ceramics. In the event where 3-MPS spread over to the metallic part when 3-MPS was applied to the ceramic part for repair, the adhesive strength of resin to the metal might be reduced. Against this backdrop of having to exclusively match a primer to a material type, it would indeed be very ideal and convenient if an effective primer for both metals and ceramics is obtained.

In this study, with a view to obtaining an effective primer for both metals and ceramics, new silane coupling agents with a trimellitic anhydride group were synthesized. The treatment effects of these agents on metal alloys and ceramics was then evaluated and compared.

MATERIALS AND METHODS

Synthesis of new silane coupling agents

Trimellitic anhydride chloride (Tokyo Kasei Kogyo Co., Tokyo, Japan) was recrystallized from an ice-cold mixture of dichloromethane and hexane in a 7:3 volume ratio. Pyridine was distilled at atmospheric pressure in the presence of a small amount of potassium hydroxide. Allyl alcohol was stored in the presence of molecular sieves, and was distilled under reduced pressure before it was used. All reagents except for trimellitic anhydride chloride were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan.

Trimellitic anhydride chloride (0.15 mol), benzene (50 ml), and chloroform (10 ml) were placed in a three-neck 200 ml flask, and the flask was cooled in an ice bath. The mixture of pyridine (0.15 mol) and allyl alcohol (0.15 mol) diluted with benzene (30 ml) was dropped slowly for one hour into the stirred solution in the flask. Reaction mixture was stirred for one day at room temperature, and then for one hour at 50°C. After which, the reaction mixture was filtrated and the solvent evaporated under reduced pressure. Crystalline residue was thereby obtained and recrystallized from hexane. The yield of 4-allyl-trimellitic anhydride (4-ATA) was 73%.

A mixture of hydrogen hexachloroplatinate(IV) hexahydrate (20 mg), 4-ATA (0.0129 mol), trichlorosilane (0.0516 mol), and toluene (10 ml) was sealed in a glass tube and heated for two days at 90°C. After cooling, charcoal was added to the mixture, and the mixture was heated for two hours at 60°C. After cooling, a small amount of toluene was added into the mixture, and then the mixture was filtrated by glass filter under reduced pressure.
A mixture of 4-CSTA (0.0129 mol) and methyl alcohol (0.0516 mol) was placed in a three-neck 100 ml flask, and the flask was cooled in an ice bath. Pyridine (0.0129 mol) diluted with toluene (2 ml) was slowly dropped for twenty minutes into the stirred solution in the flask. After the reaction mixture was filtered and the solvent was evaporated, the residue obtained was distilled for purification (4-trimethoxysilylpropyltrimellitic anhydride, 4-MSTA). All products were identified by IR and NMR. All reagents except for 4-allyl trimellitic anhydride were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan.

Preparation of specimens for adhesion test
Glass plate (Glass), cobalt-chromium alloy (Co-Cr alloy), and dental casting silver-palladium-gold alloy (Ag-Pd alloy) were used as adherends. Glass was a commercial soda-lime glass (3×15×15 mm in length). Co-Cr alloy was supplied by manufacturer (Sankin Industry Co. Ltd., Tochigi, Japan), which was rod-shaped with 6.5 mm diameter and 30 mm length. Ag-Pd alloy (Sankin Industry) was prepared according to manufacturer’s cast specifications, and the size was 3×10×10 mm in length. The adhesive surfaces of all adherends were ground with 1,000-grit silicone carbide waterproof paper under flowing water, and cleaned two times for one minute by an ultrasonic cleaning machine in ion-exchanged water. All adherends were dried in an oven at 60°C and cooled at room temperature.

The chemical formulas of two synthesized primers and seven test primers used in this study are shown in Tables 1 and 3, respectively. Methyl methacrylate (MMA) (Wako Pure Chemical Industries, Osaka, Japan) was used as solvent, and the concentration of the primers was in mass percent (mass%). Ethanol was used as a control. In the case where primer was prepared from silane with alkoxy group, 4-MSTA and 3-MPS, acetic acid (Wako Pure Chemical Industries) of 10 mass% was added to the primer solution and then that was applied to the adherend.

Orthomite SuperBond (Sun Medical Co. Ltd., Shiga, Japan) was used as an adhesive resin, and the bonding procedure was performed as given in a previous literature. However, MMA was not used with the accessory and the commercial product was used without purification. Bonded test pieces were stored in water at 37°C for two days.

Bond strength data were analyzed using one-way analysis of variance (ANOVA). Statistical significance was set in advance at 0.05 probability level. Multiple comparisons were performed using Tukey’s test at α=0.05. Fractured surfaces of the specimens were visually examined with the naked eye, and failure modes were classified as adhesive, cohesive or mixed failure.

RESULTS

Synthesis of 4-CSTA and 4-MSTA
4-CSTA and 4-MSTA were synthesized as light-yellow, viscous liquids with yields of 57 and 79% respectively. Characteristics of the synthesized 4-CSTA and 4-MSTA are summarized in Table 2. In the case of 4-CSTA, 1H NMR chemical shift (δ) of 1.4–4.7 ppm assigned for the propylene chain [6H, −CH2CH2CH2−] that bonded to silicon, and the IR bands of 920 and 1650 cm−1 assigned for the allyl group could not be detected. In the case of 4-MSTA, 1H NMR chemical shift of 3.6 ppm was assigned for the trialkoxy groups [9H, −Si(OC2H5)3] that bonded to silicon, and IR bands of 820 and 1100 cm−1 were assigned for the alkoxy group. They were spectrally identified as new compounds by 1H NMR and IR spectra.

Tensile bond strength measurement
Table 3 shows the tensile bond strengths of the resin to the glass treated with the primers and the failure modes after adhesion test. Bond strength of resin to glass without primer (ethanol treatment) was 4.2±0.6 MPa. Fracture mode was 100% adhesive failure. Bond strength of resin to glass treated with 2% 4-META was 5.8±0.6 MPa. Quite apparently, no treatment effect was rendered by 2% 4-META on glass.

When treated with 4% 4-META+1% 3-MPS (with and without catalyst), 2% 4-MSTA, and 2% 4-CSTA, the bonding strengths of these specimens ranged from 12 to 15 MPa — which were significantly lower than that of 2% 3-MPS. When treated with 1% 4-MSTA+1% 3-MPS and 1% 4-CSTA+1% 3-MPS, bonding strengths were 23.9±8.1 and 28.5±5.3 MPa.
Table 2  Characteristics of the synthesized compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Appearance</th>
<th>Yield (%)</th>
<th>1H NMR spectra (δ, ppm)</th>
<th>IR spectra (neat, cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-ATA</td>
<td>White solid</td>
<td>73</td>
<td>4.7-5.0 [2H, CH₃=CH-CH₂-], 5.2-5.6 [2H, CH₂=CH-CH₂-], 5.8-6.3 [H, CH₃=CH-CH₂-], 8.0-8.7 [3H, phenyl]</td>
<td>920, 1650 (ν,C=C)</td>
</tr>
<tr>
<td>4-CSTA</td>
<td>Light-yellow,</td>
<td>57</td>
<td>1.4-1.8 [2H, Si-CH₂-], 1.9-2.4 [2H, CH₂CH₂CH₂-O⁻], 4.3-4.7 [2H, CH₂CH₂CH₂-O⁻], 8.0-8.7 [3H, phenyl]</td>
<td>Disappearance 920, 1650 (ν,C=C)</td>
</tr>
<tr>
<td>4-MSTA</td>
<td>viscous liquid</td>
<td>79</td>
<td>0.6-0.9 [2H, Si-CH₂-], 1.7-2.2 [2H, CH₂CH₂CH₂-O⁻], 3.6 [6H, (C₆H₅)₃Si], 4.2-4.6 [2H, CH₂CH₂CH₂-O⁻], 8.0-8.7 [3H, phenyl]</td>
<td>820, 1100 (ν Si-OCH₃)</td>
</tr>
</tbody>
</table>

Table 3  Bonding strengths of the resin to glass treated with the primers

<table>
<thead>
<tr>
<th>Primer</th>
<th>Acid catalyst</th>
<th>Strength (MPa)</th>
<th>A/M/C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Non</td>
<td>4.2±0.6</td>
<td>100/0/0</td>
</tr>
<tr>
<td>2% 3-MPS</td>
<td>Added</td>
<td>28.2±3.0</td>
<td>0/60/40</td>
</tr>
<tr>
<td>2% 4-META</td>
<td>Non</td>
<td>5.8±0.6</td>
<td>100/0/0</td>
</tr>
<tr>
<td>4% 4-META+1% 3-MPS</td>
<td>Added</td>
<td>15.2±6.5</td>
<td>0/80/20</td>
</tr>
<tr>
<td>2% 4-MSTA</td>
<td>Added</td>
<td>12.5±2.4</td>
<td>0/80/20</td>
</tr>
<tr>
<td>1% 4-MSTA+1% 3-MPS</td>
<td>Added</td>
<td>23.9±8.1</td>
<td>0/40/60</td>
</tr>
<tr>
<td>2% 4-CSTA</td>
<td>Non</td>
<td>15.4±2.3</td>
<td>0/80/20</td>
</tr>
<tr>
<td>1% 4-CSTA+1% 3-MPS</td>
<td>Non</td>
<td>28.5±5.3</td>
<td>0/0/100</td>
</tr>
</tbody>
</table>

* Values are represented as mean±standard deviation. Identical letters indicate that the mean values are not significantly different in each test group (p<0.05).

* Failure modes: percent of Adhesive failure/Mixed failure/Cohesive failure in adhesive resin.

Table 4  Bonding strengths of the resin to Co-Cr and Ag-Pd alloys treated with the primers

<table>
<thead>
<tr>
<th>Adherend</th>
<th>Primer</th>
<th>Acid catalyst</th>
<th>Strength (MPa)</th>
<th>A/M/C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Cr alloy</td>
<td>5% 4-META</td>
<td>Non</td>
<td>40.4±7.4</td>
<td>0/0/100</td>
</tr>
<tr>
<td></td>
<td>4% 4-META+1% 3-MPS</td>
<td>Non</td>
<td>29.1±6.3</td>
<td>0/20/80</td>
</tr>
<tr>
<td></td>
<td>1% 4-MSTA+1% 3-MPS</td>
<td>Added</td>
<td>24.7±7.2</td>
<td>0/20/80</td>
</tr>
<tr>
<td>Ag-Pd alloy</td>
<td>5% 4-META</td>
<td>Non</td>
<td>28.8±7.2</td>
<td>0/60/40</td>
</tr>
<tr>
<td></td>
<td>4% 4-META+1% 3-MPS</td>
<td>Non</td>
<td>25.7±8.4</td>
<td>0/40/60</td>
</tr>
<tr>
<td></td>
<td>1% 4-MSTA+1% 3-MPS</td>
<td>Added</td>
<td>23.5±6.9</td>
<td>0/40/60</td>
</tr>
</tbody>
</table>

* Values are represented as mean±standard deviation. Identical letters indicate that the mean values are not significantly different in each test group (p<0.05).

* Failure modes: percent of Adhesive failure/Mixed failure/Cohesive failure in adhesive resin.

respectively — which were not significantly different from that of 2% 3-MPS. With these primers, the failure mode was predominantly cohesive failure.

Table 4 shows the tensile bond strengths of the resin to Co-Cr and Ag-Pd alloys treated with the primers and the failure modes after adhesion test. Bond strengths of resin to Co-Cr and Ag-Pd alloys treated with 5% 4-META were 40.4±7.4 and 28.8±7.2 MPa respectively, and they were the highest in each group. Bond strengths
of resin to Co-Cr alloy treated with 4% 4-META+1% 3-MPS without and with catalyst were 29.1±6.3 and 32.6±6.1 MPa respectively. When 3-MPS was mixed with 4-META, the strength tended to be lower. On the other hand, when treated with 1% 4-MSTA+1% 3-MPS, the strengths of resin to Co-Cr and Ag-Pd alloys were 24.7±7.2 and 14.8±5.3 MPa respectively — which were the lowest in each group. With these primers, the failure mode was either 100% cohesive failure or a mixture of cohesive and mixed failures. Adhesive failure was not observed in any of the test pieces.

DISCUSSION

To the end of realizing the desired esthetics or functionality, dental prostheses are fabricated from a combination of various materials such as metal, ceramics, and polymers. An adhesive is then needed to fix the prosthetic appliance to the tooth, and primers which are exclusively suitable for each material were developed. For example, 4-META is an effective primer for non-precious metals[4,5]. It is thought that when the trimellitic anhydride group in 4-META is hydrolyzed, the two resulting carboxyl groups will react with the metal ion of metal surface and calcium ion of tooth surface[8,9]. 3-MPS, on the other hand, is an effective primer for silica-based ceramics. It is said that the hydrolysable alkoxy groups of 3-MPS will react with the silanol groups on silica-based ceramic surface to form siloxane bonds[4,10,11].

Having identified the effective primers for metals and ceramics, the authors thought that a primer that combines both a trimellitic anhydride group and a trialkoxysilyl group in a molecule would be effective for both metals and ceramics. In particular, this primer would be especially useful for adhesion of prosthetic appliances that comprise both metal and ceramic materials, such as in the repair of porcelain-fused-to-metal crowns.

To the end of obtaining an effective primer that combines both a trimellitic anhydride group and a tri-chloro- or trialkoxy-silyl group in a molecule, 4-trichloro-silylpropyl- and 4-trimethoxysilylpropyl-trimellitic anhydride (4-CSTA and 4-MSTA, respectively) were synthesized. However, the synthesized silane coupling agents did not have a double bond for reaction with adhesive resins. On this ground, mixtures of the synthesized silanes and 3-MPS were also prepared and tested as primers for metal alloys and ceramics in this study[11,12]. The proposed reactivity of these mixtures was as follows: the trialkoxy- or trichloro-silyl group would react with the ceramic material, the trimellitic anhydride group with metal, and the methacryloxy group in 3-MPS with the adhesive resin. Bonding in the primer layer would be formed by the siloxane bonds between the synthesized silane and 3-MPS[10].

In this study, it was found that the treatment effect of 2% 4-META on glass was low. This was chiefly because it did not have the groups to react with ceramics. As for glass specimens treated with 2% 3-MPS, 1% 4-CSTA+1% 3-MPS, and 1% 4-MSTA+1% 3-MPS, they showed significantly higher bond strengths than those with other treatments (p<0.05). Conversely, the treatment effects of 2% 4-MSTA and 4-CSTA were inferior when compared with that of 2% 3-MPS. As for the reason, it was because 4-MSTA and 4-CSTA did not have a double bond to react with the adhesive resin.

With Co-Cr alloy, treatment with 5% 4-META yielded 40.4±7.4 MPa, which was the highest value among the different treatments for Co-Cr alloy specimens. Failure mode was 100% cohesive failure in the adhesive resin. Besides, the effect of 4-META on non-precious metals was also excellent. When treated with 1% 4-MSTA+1% 3-MPS, the strength yielded was 24.7±7.2 MPa — which was significantly lower than that of 5% 4-META primer. Failure mode, however, was only 80% cohesive failure in the adhesive resin.

With Ag-Pd alloy, treatment with 5% 4-META for Ag-Pd alloy was 28.8±7.2 MPa — which was not significantly different from those of 4% 4-META+1% 3-MPS primers with and without acid catalyst. On the other hand, strength yielded with 1% 4-MSTA+1% 3-MPS was significantly lower than those of the other primers. However, the failure mode of specimens treated with 1% 4-MSTA+1% 3-MPS was almost the same as those of other primers.

From the results of this study, it could be seen that 3-MPS was a less effective primer for both alloys. However, the addition of 4-MSTA — which comprised the trimellitic anhydride group — seemed to be effective in improving the bond strength to non-precious metals. As for precious metals, the effective metal primer should contain mercapto group as a functional group[14,15].

In this study, we could not synthesize a primer that contained a trimellitic anhydride group, a trialkoxysilyl group, as well as a methacyrloxy group (double bond) for reaction with the adhesive resin. A primer with three functional groups in a molecule would be effective for metals, ceramics, and adhesive resins compared with the silane mixtures in this study.

CONCLUSION

To improve the bond strength of resin to dental ceramics and alloys, new silane coupling agents, namely 4-CSTA and 4-MSTA, were synthesized. Silane mixtures of 4-CSTA with 3-MPS and 4-MSTA with 3-MPS were also prepared as primers for adhesion of poly (methyl methacrylate) to glass, Ag-Pd alloy, and Co-Cr alloy. Tensile bond strengths of resin to glass using 4-CSTA+3-MPS and 4-MSTA+3-MPS as primers were 28.5±5.3 and 23.9±8.1 MPa respectively. With the
dental alloys, bond strengths were 14.8±5.3 MPa for Ag-Pd alloy and 24.7±7.2 MPa for Co-Cr alloy. Based on the results obtained in this study, it seemed that the mixture of 4-MSTA and 3-MPS was an effective primer for both metals and ceramics.

REFERENCES