Storage effect of a pre-activated silane on the resin to ceramic bond

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Summary
Objectives. The purpose of this study was to investigate the process of hydrolysis and chemical stability of a pre-activated silane solution stored for different periods of time. The tensile bond strength of resin composite to ceramic was also evaluated in order to determine the functional effectiveness after storage of the pre-activated silane solutions.

Methods. Silane solutions using γ-methacryloxypropyltrimethoxysilane (γ-MPTS), acetic acid and ethanol were freshly prepared and kept for 15 min, 2 h, 24 h, 1 week, 1 month, 6 months, and 1 year. The solutions were analyzed using a 2000 Perkin–Elmer Fourier transform infrared (FT-IR) spectrophotometer. For the tensile bond strength test, Ni/Cr rods were prepared with ceramic facings polished to 1 μm. Five groups of ceramic surfaces (n = 60) were treated with the pre-activated silane solutions and bonded using a luting resin. The process used to prepare the surfaces prior to bonding consisted of removing unreacted silane by boiling water and then heat treatment. Each group was then subdivided into two groups (n = 30) and stored under two different storage conditions before subjecting to the tensile bond strength test; either (1) dry at room temperature for 24 h or (2) boiling water for 24 h.

Results. FT-IR analysis showed that nearly complete hydrolysis of γ-MPTS has occurred 24 h after mixing, followed more slowly by the formation of siloxane (Si–O–Si) oligomers. The bond strength test results showed that there was no statistically significant difference in the mean tensile bond strength for any of the groups either in dry condition or in boiling water (P > 0.05). The mode of failure for all groups was predominantly cohesive failure within the resin. The silane bond was also capable of resisting hydrolytic attack in boiling water for all the groups.

Significance. From the results of this study it can be concluded that, when using an appropriate silane application technique, the adhesive effectiveness of a pre-activated silane solution based on γ-MPTS, acetic acid and ethanol will not deteriorate when stored for up to 1 year at room temperature.

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Introduction

Silane coupling agents have been extensively used in dentistry with the development of resin composites,
porcelain repair systems and resin-bonded restorations. Micro-mechanical retention can be also created by hydrofluoric acid (HF) etching and/or gritblasting of ceramic surfaces. Establishment of a strong chemical bond between the dental ceramic and resin composite can be achieved by treatment with a silane coupling agent with the general formula \( \text{R-Si-(OR)}_3 \). \(^1\) The organo-functional group (R) is chosen for reactivity with the organic matrix, while the hydrolyzable groups (R') are intermediates in the formation of silanol groups (Si-OH) for bonding to mineral (e.g. ceramic) surfaces. The most commonly used silane in dental applications is \( \gamma \)-methacryloxypropyltrimethoxysilane (\( \gamma \)-MPTS). The choice is based on the compatibility of the methacrylate group with the dimethacrylates used in composite technology. The chemical structure of \( \gamma \)-MPTS is shown in Fig. 1. There is nevertheless still considerable confusion as to the best conditions for presentation, use and storage of silane solutions. Silanes can be presented as single-phase pre-activated solutions or two-component systems that have to be mixed in order to initiate the hydrolysis reaction. Pre-activated silane solutions are composed of three ingredients; silane coupling agent, an acid component and a solvent, usually ethanol.

Fourier transform infrared spectroscopy (FT-IR) is a particularly useful technique to study silane coupling agents as the advantages of infrared spectroscopy in determining chemical and structural information of a compound are well known.\(^3\) Since many functional groups can be identified by their characteristic vibration frequencies, the infrared spectrum could indicate any changes in the compound. Very few studies in the dental literature have investigated the characterization of silane coupling agents by FT-IR. Anagnostopoulos et al.\(^6\) used FT-IR and reported that pre-activated silane primers exhibited a higher rate of hydrolysis than did a two-component primer. With respect to long-term resin/ceramic bond enhancement, a single-component silane primer has been reported to be superior to the two-component system.\(^7\) Yet, the stability of pre-activated silane primers appears to be compromised and shelf life is limited due to the formation of oligomers.\(^8\)

Aida et al.\(^9\) studied the two-component primer systems using FT-IR and also evaluated the adhesion of resin to ceramic with those systems. They concluded that the acid component of the silane system enhanced the formation of siloxane bonds and facilitated the adhesion of resin composite and ceramic. The reaction between methoxy silane (Si-\( \text{OCH}_3 \)) groups of (\( \gamma \)-MPTS) and OH groups of the ceramic surface that forms siloxane bonds is thus initiated and accelerated by acid catalysis. In addition, enhanced bond strengths generated with those types of systems on polished ceramic surfaces led to the conclusion that the hazard of HF acid etching of ceramics could be eliminated. Other studies have also reported increased bond strengths of resin to ceramic using freshly prepared (two-component) silane solutions as opposed to pre-activated silanes.\(^10\)–\(^12\) However, the shear bond strength test design used in these studies may not truly reflect the adhesive characteristics of the bonded interface.\(^13\)–\(^15\) In a previously published study by Hooshmand et al.,\(^16\) a rod-to-rod tensile bond strength test arrangement was used to show that the silane bond to a leucite-reinforced feldspathic ceramic could be improved to such a degree that cohesive failure occurred within the luting resin rather than at the resin-ceramic interface. A freshly prepared silane solution was used which had been left for 2 h for hydrolysis. It was concluded that a durable resin-ceramic bond could be obtained by using an appropriate silane application without the need for HF acid etching the ceramic surface, confirming the earlier observation.\(^9\) The basis for this observation was that the application procedure used had the aim of producing a monolayer of the silane coupling agent by washing away any unreacted silane primer components.

The objective of this study was to test the hypothesis that the chemical stability and bonding efficacy of pre-activated silane solutions would be detrimental over time. The process of hydrolysis and the chemical stability of a pre-activated silane solution stored for different periods of time were investigated using FT-IR. The tensile bond strength of resin to ceramic by the pre-activated silane solutions was also evaluated in order to correlate to the results of the infrared analysis.

**Materials and methods**

**Preparation of silane solution**

A silane solution was prepared, consisting of 2.5% \( \gamma \)-MPTS (Sigma Chemical Co., St Louis, MO), in Analar grade solvents of 2.5% acetic acid, and 95% ethanol by volume (BDH Ltd, Poole, UK). Freshly prepared
samples of the silane solution were kept for different periods of time before analysis as follows; 15 min, 2 h, 24 h, 1 week, 1 month, 6 months, and 1 year.

**FT-IR analysis**

Each solution of silane agent was dropped onto a potassium bromide (KBr) plate. The plate was left for approximately 3 min until the solvent had evaporated. The infrared analysis was performed using a 2000 Perkin–Elmer FT-IR spectrophotometer. All transmission spectra were recorded at 4 cm\(^{-1}\) resolution throughout the range of 4000–400 cm\(^{-1}\). The number of scans used to obtain spectra was one. The infrared spectrum of the neat γ-MPTS was also recorded.

**Tensile bond strength measurement**

Details of the tensile bond strength test method have been published previously.\(^{13,16}\) Briefly, it consists of resin bonding together two Ni–Cr alloy rods (Talladium-V alloy, Talladium Inc., Valencia, CA), which have ceramic facings consisting of a modified leucite reinforced ceramic (Mirage, Myron Inc., Kansas city, KS). In order to create flat surfaces for bonding, the sintered ceramic surfaces were ground on wet 400 and 600 SiC papers. This was followed by polishing with 7.1 μm finish with diamond compounds (Buehler-met AS, Lake Bluff, IL) on a Metaserv grinder-polisher (Buehler, Coventry, UK) at 200 rpm for 5 min using light hand pressure. The specimens were rinsed with distilled water and then cleaned ultrasonically in acetone for 15 min. Five groups of specimens (\(n = 60\)) were treated with silane solutions kept for different periods of time; (A) 15 min; (B) 2 h; (C) 1 month; (D) 6 months; (E) 1 year.

All specimens in each group were bonded by applying the optimized method of silane treatment obtained from the previous study;\(^{16}\) brush application for 60 s, hot air drying at 50 ± 5 °C for 15 s, rinsing with hot water for 15 s and drying again followed by an unfilled resin and then a dual-cured luting resin (Variolink-Vivident, Schaan, Liechtenstein) using an alignment jig. Each group was then subdivided into two groups (each containing 30 specimens) in two different storage conditions. Specimens in one subgroup were kept dry at room temperature for 24 h and the other immersed in boiling water for 24 h to evaluate the hydrolytic stability of the interfacial bond.

The tensile bond strength test was carried out in a tensile testing machine (Model 2000R, Lloyd Instruments Ltd, Warsash, UK) at a cross-head speed of 1 mm/min. The mode of failure was examined under a stereo-zoom microscope at 40 × magnification (Model VMZ, Olympus Optical Co., Tokyo, Japan).

The bond strengths were calculated by dividing the load at failure by the ceramic surface area. Data based on 30 samples in each group were analyzed using one-way ANOVA followed by Tukey’s honestly significant difference (HSD) multiple range test at the 95% level of confidence. A Weibull analysis of the data was also carried out and the characteristic bond strength, Weibull modulus and stress at 5% failure probability were determined.

**Results**

**FT-IR analysis**

**Figure 2** is a transmission spectrum of the neat γ-MPTS as received. The peaks at 2840-3000 cm\(^{-1}\) result...
from carbon-hydrogen stretching vibrations. The strong peak at 1719 cm\(^{-1}\) is the carbonyl C=O stretching mode, while the band at 1638 cm\(^{-1}\) is the vinyl C=C stretching mode. The bands at 1297 and 1325 cm\(^{-1}\) are associated with the ester functionality. The peaks at 1167 and 1192 cm\(^{-1}\) are also due to ester vibrations (C-O-C in the ester group), while the bands at 1089 and 818 cm\(^{-1}\) result from Si-O-CH\(_3\) asymmetric and symmetric stretching vibrations, respectively. The peak at 941 cm\(^{-1}\) originated from the vinyl vibration.

The transmission spectra of the pre-activated silane solution stored for different periods of time are shown in Fig. 3. After 24 h storage, a new broad band started to appear at 3432 cm\(^{-1}\) (assigned to the O-H stretching vibrations of Si-OH and water) and a new shoulder at 1697 cm\(^{-1}\) (assigned to the hydrogen bonded carbonyl with the hydroxyl groups of Si-OH and water) not present at 15 min or 2 h of storage. The intensity of the broad band at 3432 cm\(^{-1}\) continued to increase during the 1 year storage period examined. A drastic reduction in transmission of the 815 cm\(^{-1}\) (assigned to symmetric Si-O-CH\(_3\) stretch), and the 2835 cm\(^{-1}\) symmetric C-H stretch of the SiOCH\(_3\) was also observed after 24 h. The appearance of 902 cm\(^{-1}\) band at 24 h storage is assigned to the stretching mode of the Si-OH group. There was an increase in the intensity of band at 902 cm\(^{-1}\) over time. In addition, the band at 1087 cm\(^{-1}\) region, which can be assigned to the Si-O-Si anti-symmetric stretching mode, became broader over the period of storage which is consistent with the formation of siloxane oligomers.

### Bond strength measurement

Tensile bond strength data for Groups A-E when stored under dry conditions for 24 h at room temperature after resin bonding and the groups placed in boiling water for 24 h after resin bonding are presented in Tables 1 and 2, respectively. There

**Table 1** Mean tensile bond strengths and modes of failure after dry storage for 24 h at room temperature for silane coupling agent solutions stored for various periods of time up to 1 year.

<table>
<thead>
<tr>
<th>Group</th>
<th>Mean (MPa)</th>
<th>SD(^a)</th>
<th>SE(^b)</th>
<th>95% Confidence interval</th>
<th>Range</th>
<th>Adhesive failures</th>
<th>Cohesive failures</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 15 min</td>
<td>30.28</td>
<td>8.6</td>
<td>1.6</td>
<td>27.1-33.5</td>
<td>11.7-48.2</td>
<td>4</td>
<td>26</td>
</tr>
<tr>
<td>B: 2 h</td>
<td>25.7</td>
<td>8.7</td>
<td>1.6</td>
<td>22.4-28.9</td>
<td>13.6-48.9</td>
<td>4</td>
<td>26</td>
</tr>
<tr>
<td>C: 1 month</td>
<td>25.7</td>
<td>10.1</td>
<td>1.8</td>
<td>21.9-29.4</td>
<td>11.4-49.0</td>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>D: 6 months</td>
<td>26.5</td>
<td>11.1</td>
<td>2.1</td>
<td>22.3-30.6</td>
<td>10.8-50.0</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>E: 1 year</td>
<td>30.23</td>
<td>11.7</td>
<td>2.1</td>
<td>25.8-34.6</td>
<td>9.8-54.1</td>
<td>5</td>
<td>25</td>
</tr>
</tbody>
</table>

Vertical line indicates that the values are not significantly different at \( P = 0.05 \) (Tukey-HSD test).

\(^{a}\) Standard deviation.

\(^{b}\) Standard error.
was no statistically significant difference in the mean tensile bond strengths between Groups A and E when stored 24 h under dry conditions. This was also the case when testing the tensile bond strength after exposure to boiling water ($P > 0.05$). However, for each group there was a significant reduction of mean value ($P < 0.05$) after 24 h in boiling water compared with initial mean values in the dry condition. The modes of failure were either adhesive fractures between the ceramic and the luting resin or cohesive fractures of the resin. No cohesive fractures of the ceramic were observed. Adhesive failures were easily identified by the very smooth appearance of the fracture exposing the polished ceramic surface. Residual resin on the ceramic surface could easily be seen due to it being non-reflective as a consequence of its roughness. The mode of failure for all groups in either boiling water or dry condition was predominantly cohesive failure within the resin, in each case being ≥23 out of 30.

Weibull analysis data for Groups A–E in dry condition are given in Table 3. The Weibull curves shown in Fig. 4, have tensile stress plotted on the x-axis and probability of failure on the y-axis. The Weibull moduli for silane solutions stored for Group A (15 min) or Group B (2 h) were higher than the other groups, but were still very low, reflecting the large spread in the bond strength data. The highest tensile stress level at 5% probability of failure (15.20 MPa) was found for Group A. Both Groups A (15 min old silane) and E (1 year old silane) had the highest characteristic bond strength values as shown by the position of the Weibull curves at higher stress levels (Fig. 4).

Table 4 shows the Weibull analysis data for Groups A–E after 24 h in boiling water. The Weibull curves are also shown graphically in Fig. 5. The highest value for Weibull modulus and stress at 5% failure probability was found for the silane solution stored for 1 year (Group E). The Weibull curves for all groups were similar (Fig. 5). Again the Weibull moduli were low, which is characteristic of a defect driven failure process with a wide spread in data.

**Discussion**

The pre-activated silane primers used in dentistry are mixtures of acid, water and a variety of polar and non-polar solvents. The function of the acid is to hydrolyze the silane ester group (-Si-O-CH$_3$) to silanol (-Si-OH)$^{17}$ and the solvent is there to maintain coupling agent solubility until the solution has been applied to the mineral surface. However, with time the silane triols can begin to condense with each other forming dimers, higher molecular weight oligomers, and polymers. In hydrolyzed silane solutions, monomeric or oligomeric silanols may either react to form siloxane bonds (-Si-O-Si) with other coupling agents or surface silanols, or exist as free silanols. It has been suggested that

<table>
<thead>
<tr>
<th>Group</th>
<th>Characteristic bond strength (MPa)</th>
<th>Weibull modulus</th>
<th>Stress at 5% failure probability (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 15 min</td>
<td>33.36 (0.14)$^a$</td>
<td>3.78 (0.09)$^a$</td>
<td>15.20</td>
</tr>
<tr>
<td>B: 2 h</td>
<td>27.95 (0.25)</td>
<td>3.02 (0.12)</td>
<td>10.45</td>
</tr>
<tr>
<td>C: 1 month</td>
<td>28.32 (0.40)</td>
<td>2.47 (0.12)</td>
<td>8.50</td>
</tr>
<tr>
<td>D: 6 months</td>
<td>29.14 (0.42)</td>
<td>2.40 (0.12)</td>
<td>8.45</td>
</tr>
<tr>
<td>E: 1 year</td>
<td>34.18 (0.30)</td>
<td>2.53 (0.08)</td>
<td>10.56</td>
</tr>
</tbody>
</table>

$^a$ Standard errors in parentheses.
the optimum time for adsorption from a silane solution is after hydrolysis and before oligomerization since the silane coupling agents are most effective when adsorbed as monomers.\textsuperscript{18}

In the present study, the infrared spectra of the silane solutions indicated a new broad band at 3432 cm\textsuperscript{-1} (assigned to the O–H stretching vibrations of Si–OH and water) and a new shoulder at 1697 cm\textsuperscript{-1} after 24 h storage, not present at 15 min or 2 h. The new shoulder at 1697 cm\textsuperscript{-1} is assigned to the hydrogen bonded carbonyl with the hydroxyl groups of Si–OH and water as reported by other studies.\textsuperscript{19,20} Carbonyl groups (C\textsubscript{y}O) form hydrogen bonds with OH groups. This is in consistent with the formation of a broad band at 3432 cm\textsuperscript{-1} and increased intensity of the band over time, which is assigned to the O–H stretching vibrations of Si–OH and water. Hydrogen formation as a consequence of hydrolysis shifts the frequency of the C\textsubscript{y}O stretching mode towards lower frequency (from 1717 to 1697 cm\textsuperscript{-1}) as shown in Fig. 3.

In addition, a drastic reduction in transmission of the 815 cm\textsuperscript{-1} symmetric Si–O–CH\textsubscript{3} stretch, and the 2835 cm\textsuperscript{-1} symmetric C–H stretch of the Si–O–CH\textsubscript{3} group after 24 h confirms nearly complete hydrolysis of the solution. On the other hand, the intensity of band at 902 cm\textsuperscript{-1} (assigned to the Si–OH stretching mode) was also increased, again indicating the hydrolysis reaction. The band at 1087 cm\textsuperscript{-1} region (assigned to the Si–O–Si antisymmetric stretching mode) became broader over the period of storage, which is indicative of the formation of siloxane oligomers.\textsuperscript{21}

From the FT-IR analysis, it can be concluded that nearly complete hydrolysis of the experimental solution (γ-MPTS) has occurred 24 h after mixing followed more slowly by the condensation reaction resulting in the formation of siloxane oligomers. This is in agreement with the results of the study by Anagnostopoulos et al.\textsuperscript{6} They showed that pre-activated silanes solution exhibited a higher rate of hydrolysis than did a two-component one. However, the down side is that the formation of oligomers could reduce the effectiveness of the solution in the longer term. Other studies have reported enhanced bond strengths of resin to ceramic using freshly prepared (two-component) silane solutions.\textsuperscript{9–12} In this study, the effectiveness of silane solutions stored up to 1 year on the resin/ceramic bond was evaluated by tensile bond strength measurement. The tensile bond strength test used in this study provided a specimen design with a stress distribution across the interface as near to uniform as is possible. For this reason, the tensile test method is considered to be a more appropriate measurement of the adhesive properties of the resin to ceramic bond than the shear bond strength test.\textsuperscript{13,16}

With regard to the tensile bond strength data, no statistically significant difference in the mean tensile bond strengths for Groups A–E with length of time of silane storage either in dry condition or in boiling water was observed (\(P > 0.05\)). For the dry storage condition, the Weibull analysis shows a more reliable bond strength for Groups A and B as indicated by a higher Weibull modulus but values for \(m\) are still generally very low and unlikely to be

<table>
<thead>
<tr>
<th>Group</th>
<th>Characteristic bond strength (MPa)</th>
<th>Weibull modulus</th>
<th>Stress at 5% failure probability (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 15 min</td>
<td>20.01 (0.13)*</td>
<td>2.65 (0.07)*</td>
<td>6.52</td>
</tr>
<tr>
<td>B: 2 h</td>
<td>15.55 (0.12)</td>
<td>2.62 (0.08)</td>
<td>5.00</td>
</tr>
<tr>
<td>C: 1 month</td>
<td>20.69 (0.16)</td>
<td>2.48 (0.06)</td>
<td>6.24</td>
</tr>
<tr>
<td>D: 6 months</td>
<td>16.22 (0.43)</td>
<td>1.59 (0.08)</td>
<td>2.50</td>
</tr>
<tr>
<td>E: 1 year</td>
<td>20.77 (0.19)</td>
<td>3.02 (0.12)</td>
<td>7.76</td>
</tr>
</tbody>
</table>

* Standard errors in parentheses.
of any significance. The characteristic bond strengths for Group A and E were higher than those of other groups, but again with such a low value for \( m \) this is not of any significance in terms of the relative performance of Groups A–E. In addition, the predominantly cohesive resin failures for all groups in this tensile test design indicate not only that the adhesive interfacial strength exceeds the cohesive strength of the luting resin, but also that the failure process is driven by the same set of random defects within the luting resin layer.\(^{15}\)

The results from the tensile bond strength data after 24 h in boiling water did not give rise to a change from resin cohesive to adhesive interface failures as one might have expected if the interface was susceptible to hydrolytic attack. On the contrary, the mode of failure in all groups continued to be predominantly within the resin. This would seem to confirm the hydrolytic and thermal durability of the silane bond, despite a significant decrease in the mean tensile bond strength values for all groups. Although the boiling water experiment is not representative of any clinical situation, it is an accepted method used by industry for determining the effectiveness of the hydrolytic stability of the silane bond.\(^{22}\) Whereas the resin to ceramic bond strength may have reduced in the presence of boiling water, the observation that cohesive failure of the resin continued to be the predominant mode of failure, indicates that the luting resin was more susceptible to degradation in boiling water than the adhesive interface. Possible reasons for this have been discussed elsewhere.\(^{16}\)

FT-IR analysis showed incomplete hydrolysis of the pre-activated silane solutions when kept for up to 2 h. However, the incomplete hydrolysis of the silane-coupling agent appeared not to have any effect on the tensile bond strength data of specimens treated with silane solutions. Tensile bond strengths after 15 min or 2 h were comparable with those of specimens treated with the silane solution stored for up to 1 year. One possible explanation is that the process of hydrolysis may be occurring after being applied to the ceramic surface due to the acidic character and catalytic effect of a silica rich substrate.\(^{23}\) Thus, it would seem that it is not necessary to wait 24 h before a freshly mixed silane solution can be used.

The importance of the method of silane application (brush application, heat treatment and rinsing with boiled water, hot air drying again and followed by an unfilled resin) as discussed in a previous study\(^ {16}\) should be emphasized. The stability of the ceramic-to-resin bond may not have been achievable with other silane application procedures since it has been shown that it is important that all efforts are made to remove excess silane and with that many oligomers for the prepared surface.\(^ {16}\) The results from this study indicate that by using a silane application technique that removes any unreacted silane from the ceramic surface, a pre-activated silane solution can produce a strong and hydrolytically stable ceramic-to-resin bond from a solution that has been stored for up to 1 year. This may not be true for other bonding procedures of silane solutions. It should also be noted that the concentration of the amount of the silane-coupling agent in the solution used in this study was very low. At higher concentrations of the silane-coupling agent this situation may change due to the increased potential for oligomer formation. Besides, the prepared silane solutions in this study were stored under constant temperature (room temperature) and it is possible that extreme changes of temperature (during transportation) may have adverse effects on the stability of the silane solution.\(^ {17}\) Further work is required to explore these issues.

From the results of this study it can be concluded that, when using an appropriate silane application technique, the adhesive effectiveness of a pre-activated silane solution based on \( \gamma \)-MPTS, acetic acid and ethanol will not deteriorate when stored for up to 1 year at room temperature.

References