Silanising agents promote resin-composite repair

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**Objective:** The aim of this study was to investigate the effect of silane in the repair of old and new resin-composite restorations. **Method:** Part 1: repair of old composite was performed on 60 resin-composite substrates that were 6 years old and were made of six different brands of composite. Three experiments were performed. In the first experiment, the substrates were ground flat and composite was fixed to the surface with bonding agent without silane (i.e. Clearfil Bond SE only, the control). Shear bond strength (SBS) was tested according to ISO/TS 11405 after thermocycling. In the second experiment, the same 60 substrates were ground again and treated with bis-silane a 2-part silane mixed shortly before application before applying bonding agent (Clearfil Bond SE plus silane) and repair composite before SBS testing. In the third experiment, the same substrates were ground again and a one-step bonding product containing silane (Scotchbond Universal bond containing silane) was used for the repair procedure before SBS testing. Part 2: to evaluate the repair of newly made composite restorations, 66 composite substrates were made and stored in water for 2 months. The specimens were divided into three groups and were tested using the same protocols as used to evaluate repair of old composite. **Results:** Mean SBS (± standard deviation), in MPa, for repair of old composite was 6.2 ± 4.0 (Clearfil Bond SE only, control), 14.8 ± 7.8 (Clearfil Bond SE plus silane) and 15.3 ± 5.6 (Scotchbond Universal bond with silane), whereas for new composite mean SBS was 15.4 ± 8.6 (Clearfil Bond SE only, control), 23.4 ± 8.3 (Clearfil Bond SE with silane) and 23.7 ± 5.8 (Scotchbond Universal containing silane). A significant difference was observed between the control and the test groups with silanising agents, both in Part 1 (P < 0.001) and in Part 2 (P < 0.005). **Conclusion:** Silanising agents increase the bond strength of the resin composite repair.

**Key words:** Composite repair, silanising, resin-based fillings, bonding agents, ageing, shear bond strength

**INTRODUCTION**

One of the reasons for using resin-based composite restorations is that they are repairable¹ and they represent the modern philosophy of ‘Minimal Intervention Dentistry’²,³. Composite restorative materials have been through tremendous development over the last decades concerning material strength, handling properties, aesthetic features and longevity⁴,⁵. Still, the main reasons for restoration failure are caries and fractures⁶–⁹, posing the question to the clinician: repair or replace. The remaining composite restoration may have been in the oral environment for a long, and often unknown, period of time, and the dental clinician is often unaware of the product used to create the initial restoration. Despite these facts, the dentist may find it desirable, or even favourable, to keep all or part of the old restoration in place¹⁰. The reasons may be financial, in that a small filling represents a lower cost, or practical, in order to make the procedure more conservative by sacrificing less of the adjacent sound tooth tissue and/or to simplify the replacement restoration. Simpler restorations may be time saving and enhance moisture control. The treatment goals are long-lasting restorations of good quality, and repair of resin-based composites is reported to have a favourable outcome for the longevity and quality of the restoration without compromising sound tooth tissue more than necessary¹¹–¹³.

Regarding bonding to dentin and enamel, the use of bonding agents in the repair of composite restorations is an established procedure. There is strong evidence for increased bond strength *in vitro* between new and old composite when using dentin-bonding agents in the repair procedure¹²,¹⁴–¹⁷. In addition, other pretreatments have been suggested to improve composite-to-composite bonding, but it has not been possible to identify an optimal procedure¹⁸. In this study we are specifically investigating the effects of using silane in composite repair because old composite consists of inorganic filler particles that should be resilanised to improve bonds to organic monomers in the repair material.
Silanising agents are important in all composite technology as coupling agents\(^1\). They link inorganic filler particles to organic resin polymers. The use of silanising agents in combination with bonding agents has been discussed and investigated lately\(^1\), and at least one company (3M ESPE, St Paul, MN, USA) has recently incorporated a silanising agent in their newest bonding agent. This prompted an evaluation of the importance of silanising agents in composite repair.

The following null hypothesis was proposed: the use of additional silaniser has no effect upon bond strength when repairing a composite restoration.

**MATERIALS AND METHODS**

**Part 1: Test of old composite repair**

The materials used are given in Table 1. The methacrylate-based composites selected were the most commonly used products in Norway in 2006. Test substrate bases were made by packing composite in copper rings (8 mm diameter, 10 mm height), placed on a mylar strip on a table. The composite cylinders were light-cured in increments of approximately 2 mm, from the top of the cylinder, according to the manufacturer’s specifications, using a Demetron VCL 400 halogen curing lamp (Kerr Hawe, Orange, CA, USA) with an irradiance of 859 mW/cm\(^2\), as measured by the Norwegian Radiation Protection Authorities (Østeraas, Norway). After curing, the copper rings were carefully split with a carbide disk and removed. Ten test substrates were produced of each composite resin product, in total 60 substrates. These were made in July 2008, and have been stored in distilled water at room temperature since production and after use in a composite repair study in 2008/2009\(^1\).

The old test substrates were used three times for testing the following three different bonding procedures before repair: (1) Clearfil Bond SE without sialising agent (CB) (control); (2) Clearfil Bond SE with bis-silane pretreatment (CB+SA); and (3) Scotchbond Universal, containing silanising agent (SBU).

The aged composite cylinders were wet-ground manually with grinding paper (Fepa P #500, silicon carbide, waterproof; Struers, Copenhagen, Denmark) to imitate preparation with a superfine diamond bur and to minimise the potential of micro-mechanical interlocking. The ground surface was dried by air blowing for 10 seconds and was masked with plastic tape with a circular aperture of 3 mm in diameter.

The bonding agent was applied according to the manufacturer’s specifications. After bonding application the repair composite was fixed to the old substrate using the equipment described in ISO/TS 11405:2003\(^2\) and light-cured (Elipar S10 LED curing lamp, irradiance: 1150 mW/cm\(^2\); 3M ESPE). All test specimens were thermocycled (5000 cycles/5–55 °C) before measuring shear bond strength (SBS), according to ISO/TS 11405: 2003\(^2\), as previously described\(^1\). All the substrates were again ground flat, as described above, before procedures 2 and 3, respectively.

**Part 2: Test of new composite repair**

Sixty-six new test substrates were made, as described above, from the material of choice (Filtek Supreme XTE) at the student training clinic, University of Oslo. After 60 days in water storage, the new substrates were divided into three groups of 22. This number was chosen for statistical strength as there should be at least 15 specimens in the sample. They were tested using exactly the same protocol as used for repair of old composite.

**Statistics**

The Student’s \(t\)-test for two-tailed samples was performed to compare the results for each treatment procedure.

**Table 1 Materials used in the study**

<table>
<thead>
<tr>
<th>Material</th>
<th>Lot</th>
<th>Repair composite</th>
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<tbody>
<tr>
<td><strong>Old substrates</strong></td>
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<tr>
<td>Filtek Z 250 (3M ESPE, St Paul, MN, USA)</td>
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<td>Filtek Supreme XTE (lot nos N510285 and N486561; 3M ESPE)</td>
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<td><strong>New substrates</strong></td>
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<tr>
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<td>Lots N510285 and N486561</td>
<td>Filtek Supreme XTE (lot nos N510285 and N486561; 3M ESPE)</td>
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<tr>
<td>Bonding agent</td>
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<td>Clearfil SE Bond (Kuraray Noritake Dental Inc., Okayama, Japan)</td>
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</tr>
<tr>
<td>Scotchbond Universal (3M ESPE)</td>
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<td>Silanising agent</td>
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<tr>
<td>Bis-Silane (Bisco Inc., Schaumburg, IL, USA)</td>
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RESULTS

The results of the repair experiments are given in Figures 1–3. The bond strength when repairing old composite was significantly lower than that when repairing new composite ($P < 0.01$). The use of silanising agents significantly improved the bond strength in composite repair ($P < 0.01$) and the increase in bond strength was greater when repairing old composite substrates. The increase in repair strength of old substrates was approximately 139%, compared with that of newly made substrates, which had an increase, in our study, of approximately 51% (Table 2). Binding between Silorane and methacrylate (MA)-based composites gave poorer results than binding between MA-based composites (data not shown), probably because of differences in composition.

DISCUSSION

The results of this in vitro investigation (Figures 1–3) show a clear difference in SBS between repair with and repair without silanising agents ($P < 0.01$) for both old and new composite, confirming the results of previous studies\textsuperscript{21,22}. However, the SBS in the repair interface is significantly weaker than the inherent

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Test results (MPa)</th>
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<tr>
<td>Part 1: Repair of old substrates</td>
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<tr>
<td>1</td>
<td>CB no silane (control)</td>
</tr>
<tr>
<td>2</td>
<td>Silane + CB</td>
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<tr>
<td>3</td>
<td>SBU (containing silane)</td>
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<tr>
<td>Part 2: Repair of new substrates</td>
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</tr>
<tr>
<td>1</td>
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</tr>
</tbody>
</table>

Values are given as mean ± standard deviation.

* Statistically significant difference from the controls ($P < 0.001$).

†Statistically significant difference from the controls ($P < 0.005$).

Table 2 Shear bond strength after repairing old and new composite substrates

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strength of the composite itself. A preliminary test was performed on 15 new substrates (Figure 3). There was no significant difference between repair strength using a separate silanising step (CB+SBU) and using a bonding agent containing silane (SBU) ($P > 0.7$). The latter even had a smaller standard deviation, indicating a more predictable outcome. Both methods of silanising are easy to handle chair side, and require no extra equipment. The conclusion of these findings is that the null hypothesis has to be rejected.

It should be noted that these tests, repair of both old and new composite, were performed 14 days after the bonding procedure followed by thermocycling (5000 cycles/5–55 °C), and they cannot predict the long-term stability of the repair.

It is unclear if the favourable effects of silane are long lasting. The main problem with silanes is their long-term hydrolytic instability, which causes hydrolysis, splitting the Si–O cation bridges over time. When repairing a restoration, all surfaces are covered with at least one single sheet of water molecules, which may not be the ideal condition. The bonding strength will partly become dependent on hydrogen bonds and molecular attraction forces, such as Van der Waals forces, and not the stronger covalent or ionic types. For this reason, the bonding between the silaniser and old composite is always vulnerable to hydrolysis of the relatively weak bonds. Hydrolysis leads to degradation of the interface bonding. The content of hydrophilic monomers, such as 2-hydroxyethyl methacrylate (HEMA), in the bonding agent is of importance for the water content in the repair area. HEMA attracts water and keeps it there, thereby increasing hydrolytic reaction. The stoichiometric configuration of the molecules, especially the silanes, may, on the other hand, prevent water movement and sorption in the area, making an impact on the long-term stability. Much research remains to be completed in this field.

SBU was tested in this study. It contains prehydrolysed silanes, which are reported by the manufacturer to be stable for at least 1 year of storage, and both priming and bonding chemicals are contained in this one mixture. In this short-term test, the silanes performed well. The success of SBU lies in its ability to split off hydroxyl groups and form oxygen bridges to surface cations. The complex chemistry is not publicly available (propriety information), but the product showed remarkably good results in this short-term study. The performance over a longer period of time remains to be seen as it has only been commercially available for a few years. Scepticism of simplified systems is still connected to the problems concerning evaporation of solvents and hydrophilic monomers, causing water sorption and hydrolysis, when all the ingredients are mixed in one bottle.

The good results for SBU may be a result of the presence of another recognized ingredient, 10-methacryloyloxydecyl dihydrogenphosphate (10-MDP), a 10-carbon phosphorylated acidic monomer that shows very good ability to form stable bonds to cations. However, CB also contains MDP. When CB was used with additional silane, the test results were significantly better than those obtained for CB without extra silane, indicating a positive effect of the silaniser. We chose two bonding agents containing MDP to avoid confounders. Likewise, we chose #500 grinding paper to minimise the micro-mechanical interlocking effects at the bonding interface.

One might speculate that the positive effect on SBS when using silanes was a result of resilanising of the filler particles at the prepared restoration surface, improving the bond between the filler particles in the old composite and the resin matrix in the repair composite. The possibility of obtaining a chemical bond between the resins in the old substrate and the bonding agent decreases with time. The resin no longer has free radicals available for bonding and polymerisation, owing to a half-life of approximately 48 hours and a slow chemical aftercure combined with hydrolysis of the available double bonds, leaving the resin without the possibility to form new bonds. The much higher percentage increase of the repair strength for old composite (140%), compared with the increase of repair strength for new composite (50%), and that all the failures for repair of the old composite were of the adhesive type, strengthen the idea that silane has a strong ability to form siloxane bonds to filler particles in composite also when the composite is old. The improved effect of silane in old composite substrates may reflect the fact that hydrolytic degradation is higher in older specimens, which was also observed as reduced strength in the material over time.

Another property of silanes, which may be beneficial to bond strength, is their ability to change surface energy in order to enhance wetting of the surface of inorganic materials, which is essential for the intimate contact needed between different materials to obtain good bonding.

To put the silane test into perspective, it is of interest to compare the bond strength to composite with bond strength to dentine. We have no proof that silanes form bonds to cations in organic substrates such as collagen/dentine. To investigate the role of silanes when bonding composites to dentine, preliminary tests demonstrated no difference in bond strength between bonding with and without silanising agents (data not shown).
CONCLUSION

Composite repair with the use of a silanising agent performed significantly better than repair without a silanising agent. Bonding to older composites gave poorer results, but repair of old restorations is still recommended.

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Silanising agents and composite repair


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