Effect of different surface treatments on the repair strength of a nanofilled resin-based composite

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The purpose of our study was to re-evaluate the effects of surface treatment on the bond strength of repaired methacrylate-based dental composite materials including nanofillers (Ceram X, Dentsply). The microtensile bond strengths were measured before or after thermo-mechanical fatigue simulation. The treatments were as follows: (1)No treatment (negative control), (2)Bonding agent, (3) Acetone, (4)Acetone+Bonding agent, (5)Silane, (6)Silane+Bonding agent. In the digitized SEM image of the polished aged specimens without any surface treatment, the percentage of the visible fillers relative to the whole image was calculated. Before and after fatigue, no significant differences could be observed among the different pretreatment groups. Fatigue increased the microtensile strength values of Acetone and Silane groups. The digitized SEM image reveals that 11.5% of the exposed surface could be identified as uncovered filler surface. None of surface treatments (acetone, silane and bonding agent) contributed to increase the tensile strength of repaired composite samples including nanofillers.

Keywords: Adhesion, Resin composite, Microtensile bond strength, Silane, Bonding agent
treatments with bonding agents, silane solutions and acetone improved the microtensile bond strength of repaired dental composites to aged dental composites.

MATERIALS AND METHODS

The materials used in this study are shown in Table 1. The experimental design is outlined in Fig. 1.

Preparation of aged composites

The method of preparation of aged composites is illustrated in Fig. 1a. Resin composite blocks (6×6×5 mm) were prepared from a methacrylate-based dental composite (Ceram X duo/Shade D3, Dentsply, Konstanz, Germany) in accordance with the manufacturer’s instructions for use in transparent vinyl polysiloxane matrices. The composite was carefully condensed with a clean filling instrument in order to avoid contamination and/or entrapment of voids. The composite blocks were cured with a halogen light device (Astralis 10, Program; High Intensity, Ivoclar Vivadent, Schaan, Liechtenstein). Irradiation was performed for 20 s on one composite

<table>
<thead>
<tr>
<th>Brand name</th>
<th>Composition</th>
<th>Batch no.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceram X duo: shade D3</td>
<td>Resin: Methacrylate-modified polysiloxane, Dimethacrylate resin, Filler (~57 vol.%): Barium-aluminium-borosilicate glass, Methacrylate functionalised silicon dioxide nano filler, Ethyl-4(dimethylamino)benzoate, Initiator, Stabilizer</td>
<td>0907002281 Dentsply, Konstanz, Germany</td>
<td></td>
</tr>
<tr>
<td>Ceram X duo: shade E1</td>
<td>(Methacrylate-based dental composite)</td>
<td>0712000617 0802001502 Dentsply, Konstanz, Germany</td>
<td></td>
</tr>
<tr>
<td>Xeno V (Bonding agent)</td>
<td>Bifunctional acrylic amides, Acidic acrylic amide, Functionalized phosphoric acid ester, Acrylic acid, Water, Tertiary butanol, Initiator, Stabilizer</td>
<td>0903000340 Dentsply, Konstanz, Germany</td>
<td></td>
</tr>
<tr>
<td>3M ESPE Sil (Silane coupling agent)</td>
<td>Ethyl alcohol, 3-methacryloxypropyltrimethoxysilane, Methyl ethyl ketone</td>
<td>307985 3M ESPE, Seefeld, Germany</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1    Experimental design (details in the text).
surface and another five surfaces of the specimens that were in contact with the surface of the mold, in order to ensure uniform and complete polymerization. Each specimen was removed from the molds and further light-cured on each surface for 20 s.

The substrate specimens were boiled in water for 24 h to age the material. The aged surfaces of the specimens were wet-ground flat with 320-grit silicon carbide grinding paper corresponding to the roughness obtained by diamond bur grinding10-12, and then the specimens were ultrasonically cleaned for 3 min.

Bonding procedure
Specimens were randomly distributed into six groups. Each group differed in the surface treatment that preceded the repair procedure (Fig. 1b). The surface treatment procedures were:

- **Group 1**: No treatment was applied to the repair-surface. This group served as the negative control group.
- **Group 2**: Bonding agent (Xeno V, Dentsply, Konstanz, Germany) was applied, air-dried and cured for 20 s with the halogen light device.
- **Group 3**: Acetone (Acetone SAV, SAV LP, Feldkirchen, Germany, Batch no. 0000021253) was applied for 1 min and air-dried.
- **Group 4**: After the application of acetone as described in Group 3, a bonding agent was applied as described in Group 2.
- **Group 5**: Silane coupling agent (3M ESPE Sil, 3M ESPE, Seefeld, Germany) was applied, air-dried and gently air-dried.
- **Group 6**: After the application of a silane coupling agent as described in Group 5, a bonding agent was applied as described in Group 2.

Following the surface treatment, new resin composite (Ceram X duo, shade E1) was bonded onto the samples using transparent vinyl polysiloxane matrices (Fig. 1c). The composite blocks were cured with the halogen light-curing device for 20 s on one side. This group served as the negative control group.

Resin composite blocks without repair
Resin composite blocks (6×6×10 mm) were prepared as the positive control group from Ceram X duo (shade E1) without layering. The composite blocks were bulk cured with the halogen light-curing device for 20 s on one composite surface and another five surfaces of the specimens that were in contact with the surface of the mold. Each specimen was removed from the molds and further light-cured on each side for 20 s. The specimens were stored in distilled water at 37°C for 24 h.

Specimen forming
Each specimen was secured with a thermoplastic impression compound (Impression Compound Red Stick, KerrHawe, Bioggio, Switzerland) on an epoxy resin block, which was mounted on a cutting machine (Isomet Low Speed Saw, Buehler, Lake Bluff, IL, USA)(Fig. 1e). By means of a water-cooled diamond blade, each specimen was serially sectioned to obtain multiple beam-shaped sticks with dimensions of approximately 1.0×1.0×10 mm, according to the non-trimming technique10. For about one-half of its length, each stick was composed of the aged composite material. The remaining half consisted of the repairing material. More than 25 sticks were prepared for each group.

Microtensile bond strength test
Each specimen was secured at the ends with cyanoacrylate adhesive (UHU, UHU, Bühl, Germany) to a jig designed to transmit purely tensile forces to the specimen when mounted on a tensile testing machine, which was optimized for the microtensile test (MTD-500, SD Mechatronik, Feldkirchen-Westerham, Germany) (Fig. 1f). The test was conducted at a cross-head speed of 1 mm/min until failure. The load at failure was recorded in N, and the specimen’s fragments were carefully removed from the fixtures with a scalpel blade. The cross-sectional area at the site of fracture was measured to the nearest 0.01 mm with a digital caliper (Mitutoyo ID-U1025, Mitutoyo, Kawasaki, Japan) in order to calculate the bond strength at failure in MPa.

The microtensile bond strength was subjected to a comparative analysis by means of one-way ANOVA at a significance level of p<0.05. The data with and without the fatigue simulation were separately evaluated with one-way ANOVA. Significant differences between the groups within the same one-way ANOVA test were further analyzed using Scheffé’s method (significance level of p<0.05). Furthermore, the Weibull moduli (m) for microtensile bond strength data were calculated. The Weibull modulus was a measure of variability of the results and was found by linear regression on a plot of In ln(1/(1−failure probability)) against ln(microtensile bond strength).

The fractured specimens were examined visually with an optical microscope (Stemi SV11, Zeiss, Jena, Germany) at 50× magnification to determine the macroscopic failure modes, which were classified as cohesive (within either the aged or the new resin composite), adhesive or mixed.

Scanning electron microscope (SEM) analysis
Arbitrarily selected specimens were evaluated in a SEM. Two types of evaluation were performed in the SEM:
first, the untreated composite surface was analyzed to determine the percentage of uncovered filler surface in relation to the whole surface; second, the fracture surface after testing was evaluated to get an impression of the failure modes.

The aged specimens without any surface treatment were polished with 320-grit silicon carbide grinding paper, rinsed with distilled water, air-dried and sputter-coated with gold (Polaron Range SC7620, Quorum Technologies, West Sussex, United Kingdom). The specimens were observed in the SEM (SUPRA 55VP, Zeiss, Oberkochen, Germany) at an accelerating voltage of 10 kV and a magnification of 20,000×. In the digitized SEM image, the percentage of uncovered filler surface in relation to the whole surface was calculated with image processing software (ImageJ, Wayne Rasband, Maryland, USA). First, the visible fillers, which were not covered by matrix, were interactively marked with the mouse tool and the marked area was automatically calculated in the program ImageJ. Second, the whole image was marked and the whole area was calculated in the same way. The marked area of all fillers was summarized, and the percentage relative to the whole image was computed.

After testing, a few specimens that were classified as having an adhesive failure mode based on the evaluation with a light microscope were arbitrarily selected from the repaired group with acetone and bond (Group 4). The fracture surfaces of these specimens were evaluated in the SEM at a magnification of 5,000×.

RESULTS

The results of the microtensile bond strength tests are summarized in Table 2. The tensile strength of unrepaired Ceram X (positive control group) was 43.4±9.5 MPa.

In general, before thermo-cycling and mechanical loading, all repaired groups had 25–30% lower microtensile bond strengths when compared to the unrepaired control group. All differences were significant (p<0.05, one-way ANOVA, Scheffé).

Before fatigue simulation, nearly all repaired groups achieved microtensile bond strength data within a very narrow range (27–30 MPa) of microtensile strength. One group had a much lower strength value (Group 3, 21.6 MPa), but the difference was not significant (p>0.05, one-way ANOVA, Scheffé).

After fatigue simulation, again, no significant differences could be observed between the different pretreatment groups (p>0.05, one-way ANOVA, Scheffé).

It is interesting to note that thermo-cycling and mechanical loading significantly increased the microtensile strength values of two groups that involved the application of only a solvent-containing pretreatment (Groups 3 and 5) (p<0.05, t-test). As soon as the bond was applied (Groups 4 and 6), no significant differences could be observed. The two groups without such a solvent-containing pretreatment (Groups 1 and 2) had nearly the same strength values before and after fatigue simulation. Weibull plots of the microtensile bond strengths are shown in Fig. 2. Before fatigue simulation, the Weibull modulus of Group 1 was 3.9, which is similar to the Weibull modulus of the Without Repair control group (m=4.1, Fig. 2a). The Weibull moduli of Group 3 (m=2.7) and Group 5 (m=2.4) were lower compared to the specimens without repair. The application of the bonding agent did not increase the Weibull moduli in the other groups without fatigue simulation (Fig. 2b, Group 2: m=2.8; Group 4: m=3.1; Group 6: m=2.8). After fatigue simulation, however, the Weibull moduli of all groups improved and achieved almost the same value as the positive control group without repair (Fig. 2c, Group 1: m=3.6; Group 3: m=3.6; Group 5: m=3.3; Without Repair: m=4.1, Fig. 2d, Group 2: m=3.4; Group 4: m=4.0; Group 6: m=3.5).

The digitized SEM image reveals that 11.5% of the exposed surface could be identified as uncovered filler surface (Fig. 3). Mostly the large fillers are visibly uncovered, and nearly all smaller fillers are covered by matrix. The gaps around some fillers were observed (arrows in Fig. 3).

SEM images of the fracture surfaces are shown in Fig. 4. In one specimen, on the surface of the repair composite, both bonding agent and fillers are visible (Fig. 4Aa). On the surface covered with bonding agent, hackle that indicates the direction of crack propagation can be observed (black arrows in Fig. 4Aa). The surface of the aged composite is covered with bonding agent (Fig. 4Ab). In the bonding layer, concave area where the filler was removed (white arrow) and hackle (black arrows) can be observed in Fig. 4Ab. In another specimen, the surface of the repair composite is covered with bonding agent (Fig. 4Ba). The surface of the bonding agent exhibits fillers that were pulled out from the composite (box) and concave areas that correspond to large fillers on the aged composite side (white arrows). On the inside of one of the v-shaped structures, a hackle is visible (black arrow) in Fig. 4Ba.

**Table 2 Microtensile bond strength of new resin composite to aged resin composite (MPa)**

<table>
<thead>
<tr>
<th>Fatigue</th>
<th>Group 1 (X, SD)</th>
<th>N</th>
<th>Group 2 (X, SD)</th>
<th>N</th>
<th>Group 3 (X, SD)</th>
<th>N</th>
<th>Group 4 (X, SD)</th>
<th>N</th>
<th>Group 5 (X, SD)</th>
<th>N</th>
<th>Group 6 (X, SD)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before fatigue</td>
<td>29.7 (9.3)a</td>
<td>25</td>
<td>29.9 (14.0)a</td>
<td>25</td>
<td>21.6 (8.3)a</td>
<td>25</td>
<td>29.9 (10.3)a</td>
<td>25</td>
<td>27.4 (9.9)a</td>
<td>25</td>
<td>29.4 (11.1)a</td>
<td>25</td>
</tr>
<tr>
<td>After fatigue</td>
<td>30.5 (8.8)a</td>
<td>25</td>
<td>30.5 (11.6)a</td>
<td>27</td>
<td>28.5 (9.0)a</td>
<td>25</td>
<td>33.4 (9.0)a</td>
<td>26</td>
<td>33.2 (10.3)a</td>
<td>25</td>
<td>32.1 (9.6)a</td>
<td>33</td>
</tr>
</tbody>
</table>

Significant differences are visualized with different letters; capitals within a column, small letters within one row.

X=mean value; SD=standard deviation of the mean

N=number of specimens
In this case, no bonding agent remnants are visible. It is rather easy to bond to fresh composite, which is covered by an oxygen inhibition layer, because a covalent bond is established between the uncured surface layer and the newly applied composite material. Aged composite materials lack this zone, which means that other variables are more important for connecting the new materials with the aged composite. Several techniques are recommended for improving the bond strength to aged methacrylate-based composites, like (1) micromechanical locking to a rough surface, (2) forming an interpenetrating network without direct chemical linkage between the aged and the new matrices, or (3) forming a chemical bond to the surface of exposed glass fillers.
In this study, three different surface treatments were applied according to these alternatives: creating a surface similar to that produced with a medium- to fine-grained diamond (roughening), using the organic solvent acetone (forming a potential interpenetrating network) or applying silane to the surface (creating a chemical bond to the filler surfaces). These conditions were modulated by using the same groups with or without a bonding agent. In addition, the durability of the bond was challenged by fatigue, so another set of these surface pretreatments was investigated after thermo-cycling and cyclic mechanical loading.

In Table 2, it seems that fatigue simulation has an influence on the bond strength. In contrast to common experience, the absolute bond strength values were not lower after fatigue loading. Indeed, the bond strength values of two groups were significantly higher after fatigue loading. One can only speculate about the reasons for this observation based on the current data. It is plausible, for example, to assume that thermo-cycling induced additional post-curing of the dentin bonding agent and the repair composite. We would also assume that, at the same time, crack growth due to fatigue might reduce the bond strength. The overall positive effect of fatigue-loading on bond strength might just be an effect of the current settings, which means the combined effects of fatigue and post-curing due to thermo-cycling. The Weibull modulus (m) is a measure of variability of the results of microtensile bond strength data. High value of the Weibull modulus indicates narrow variation in the data, namely, the increase of the Weibull modulus means that the variation reduces. The improvement of the

![SEM images of the fracture surfaces at 5,000× magnification.](image)

(A) Mixed failure in the bonding agent. (a) The fracture surface of the repair composite. Remaining bonding agent remnants (white arrows) and hackle that indicates the direction of crack propagation (black arrows) can be observed. (b) The fracture surface of an aged composite. Concave area where the filler was removed (white arrow) and hackle (black arrows) can be observed. FAI=fracture area at the interface between the composite and the bonding agent. (B) Adhesive failure at the interface between the bonding agent and the aged composite. (a) The fracture surface of the bonding agent. Fillers that were pulled out from the composite (box) and concave areas that correspond to large fillers on the aged composite side (white arrows) can be observed. On the inside of one of the v-shaped structures, a hackle is visible (black arrow). (b) The fracture surface of an aged composite.
Weibull modulus in all groups after fatigue simulation also looks like a positive influence of post-curing. For future studies, it is suggested either to increase the number of load cycles or to allow prolonged post-curing for the unloaded specimens to test the implied hypotheses concerning the influence of fatigue on bond strength.

The use of dentin bonding as another modulator had several motivations. Clinically, it is not possible to prevent the contamination of the composite surface with a dentin bonding agent when the repair is partially limited by tooth tissue. Bonding agents, on the other hand, are low-filled composites that are not optimized for strength. In spite of their beneficial property of an excellent wetting capacity for all surfaces, this limited mechanical strength could limit the repair strength as well. Our data prove that all repaired groups had lower strengths than the material samples without any repair (positive control group). When we focus on the mean bond strength values in our study, the application of Xeno V had nearly no additional benefit. The Weibull modulus did not show any differences after applying the bonding agent. Ceram X can be classified clinically as an easy-to-sculpture composite, and, on the other hand, this makes it easier to adapt it to the repair surface. However, higher filled or less sculptable composite materials might benefit more from the application of a bond agent.

When the different surface pretreatments (roughening vs. application of acetone or silane) are analyzed in more detail, the surface-roughening-only groups establish the baseline for the repair groups, as all aged composite surfaces were roughened in the same manner. On a 5% level, no significant differences could be found between the groups concerning the bond strength, which means that neither acetone nor silane had either positive or negative effects. The Weibull moduli of the groups with only acetone or silane were lower than the Weibull modulus of the group with only surface roughening, which suggests that the application of acetone or silane caused this variation.

Balkenhol et al.7) reported that repair liquids based on Bis-GMA/TEGDMA with acetone are best suited for conditioning the aged surfaces of temporary crown-and-bridge materials to enhance bond strength. They suggest various mechanisms by which acetone could contribute to this phenomenon: (1) acetone reduces the viscosity of the liquid and is a good carrier for monomers; (2) acetone is a good solvent and tends to solubilize PMMA-polymer surfaces; (3) acetone vaporizes and prevents water molecules from surface quickly. In our study, we did not mix the dentin bonding agent with acetone but instead applied the acetone separately. The composition of dentin bonding agents is fine-tuned by dental manufacturers and therefore should not be deliberately changed during clinical use. Dental composites like Ceram X are highly crosslinked, which makes it less probable that acetone can solubilize the surface to enhance the formation of an interpenetrating network with the subsequently applied bonding agent. Therefore, the only potential benefit of acetone could be to vaporize and prevent water molecules from surface quickly. Looking at the absolute data for the acetone groups (Groups 3 and 4), we can see that the highest and the lowest bond strength values are present in the acetone groups. This wide range of results means that acetone might add a kind of technique sensitivity to the procedure, as was reported for acetone-based dentin bonding agents. The Weibull moduli do not confirm this interpretation, however. Another explanation might be that acetone can be considered as a negative factor of polymerization, which is in accordance with the results for the groups with only acetone (Group 3) before and after fatigue simulation. Actually, when we use especially a one-bottle one-step adhesive system including acetone or alcohol as a solvent, it is recommended to remove the solvent carefully for polymerization. It was assumed that since acetone as a negative factor of polymerization volatilized by thermo-cycling, the bond strength values significantly increased after fatigue simulation. In addition, as stated above, thermally induced post-curing also might have an influence on the increased values after fatigue simulation probably. In the case of the additional dentin bond application, the solvents of the dentin bonding agent (water and tert butanol) and the additional air-drying of the dentin bonding agent might have already compensated for the negative influence of acetone in the group without acetone treatment. In general, acetone does not increase the bond strength during composite repair and therefore cannot be recommended for intraoral repair.

The modern composite materials that can be used for anterior and posterior restorations all have highly optimized filler systems. Roughly 50 vol% of a composite is fillers. Therefore, it is a common interpretation that after roughening a composite, 50% of the surface should be filler surface. This is the reason why the application of silane is advocated for the repair of composite materials. Silanes are molecules with two functional groups: silanol groups react with the inorganic filler particles, and organofunctional groups react with the methacrylate groups in the resin matrix. Thus, silane has been used in composite materials since their inception as the coating on filler particles that binds them to a resin matrix. Furthermore, a covalent bond may be established during repair between the new monomers and the inorganic filler particles of the aged composite after applying silanes to the surface. The strength of filler particle/matrix interface in a resin composite has been found to affect both the crack propagation behavior and the appearance of the fracture surface. In the case of poorly-bonded particles, the cracks propagating through the composite are attracted to the equator of the particle. The fracture surface therefore consists of the surfaces of debonded particles. In the case of well-bonded particles, since the maximum stress is in the matrix, the cracks propagate through the matrix above or below the particles leaving a layer of resin covering the particles. In our study, the surface treatment with silane was not effective aside from just roughening the surface. The SEM evaluation of the ground composite surface and the subsequent image analysis revealed that only 11.5% of
SEM evaluation in future studies. The Weibull graphs of microscope is rather limited and should be replaced by adhesive/cohesive classification with a light microscope. This clearly shows which would have been classified as adhesive failure possibilities can be differentiated in the SEM, all of which are classified as adhesive failure mode (Fig. 5a). Four different fracture modes (b) Cohesive failure within the bonding layer. (c) Mixed failure. (d) Adhesive failure at the side of the new composite.

Fig. 5 Potential locations and failure patterns of the repaired samples within a bonding agent. (a) Adhesive failure at the side of the aged composite. (b) Cohesive failure within the bonding layer. (c) Mixed failure. (d) Adhesive failure at the side of the new composite.

the exposed surface could be identified as uncovered filler surface (Fig. 3). It was mostly large fillers that were visibly uncovered. Smaller fillers could be identified based on their shape, but nearly all of them were covered by matrix. It might be caused by well-bonded and small filler particles of Ceram X. Even if the large fillers contribute to the covalent bonding of repair monomers, not all of them are necessarily attached to the surface, as they could have already been loosened by grinding during surface roughening, which is visible as the gaps around some fillers on the SEM images (arrows in Fig. 3). This finding can probably be generalized to all composite materials with similar filler systems as Ceram X. In addition, contaminated dentin or enamel surfaces by silane solutions may decrease the bond strength during the repair process. Therefore, if we can omit the silane treatment, it might be one of the advantages on repair work.

The possible fracture patterns within a bonding agent at the repair interface are drawn in Fig. 5. The SEM images in Figs. 4A were classified as mixed failure mode (Fig. 5c), and the images in Figs. 4B were classified as adhesive failure mode (Fig. 5a). Four different fracture possibilities can be differentiated in the SEM, all of which would have been classified as adhesive failure when using an optical microscope. This clearly shows that the adhesive/cohesive classification with a light microscope is rather limited and should be replaced by SEM evaluation in future studies. The Weibull graphs of some groups exhibited dog-leg curves, which are usually interpreted as two different failure modes. We could not find a relation between the classification based on the light microscope and the Weibull curve in those groups. Unfortunately, the fractography of all samples based on SEM images was not part of the current protocol, but the results clearly indicate that the SEM should be preferred over the light microscope. The use of the SEM might have made it easier explain the two failure modes indicated by the Weibull analysis. Furthermore, hackles (Figs. 4A, 4Ba) or v-shaped structures (Fig. 4Ba) can be observed on SEM images. Hackle indicates the direction of crack propagation. The v-shaped structures in Fig. 4Ba originate at boundary interface and the cracks deflect into the bonding layer. The tip of the v shows the direction of the crack propagation. Therefore, SEM image might indicate much information for analyzing the crack propagation.

In conclusion, with this composite neither acetone nor silane contributed to an increase in the tensile strength. The application of a subsequent layer of a low-viscosity dentin bonding agent also did not enhance the bond strength additionally. If it is possible to omit the surface treatments by acetone or silane solutions, this would avoid the contamination of dentin or enamel by them during the repair process.

REFERENCES