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Effect of temperature on the silane coupling agents when bonding core resin to quartz fiber posts

Francesca Monticelli^{a,*}, Manuel Toledano^b, Raquel Osorio^b, Marco Ferrari^a

^a Department of Restorative Dentistry and Dental Materials, University of Siena, Policlinico Le Scotte, Viale Bracci, 53100 Siena, Italy

^b Department of Dental Materials, School of Dentistry, University of Granada, Spain

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ABSTRACT

Objectives. To evaluate the effect of different silane agents and air-drying temperatures on bond strength of translucent quartz fibre posts to composite resin.

Methods. The post surface was etched with 10 vol% hydrogen peroxide for 20 min. A two-liquid coupling agent containing 4-methacryloxyethyl trimellitate anhydride (4-META) and γ -trimethoxysilyl propyl methacrylate (γ -MPTS) and two pre-hydrolyzed single component silanes containing 3-methacryloxypropyltrimethoxysilane (3-MPS) and glycid-oxi-propyl-trimethyl-oxi-silane (GPS), respectively, were used for treating the fiber posts. Two different post-silanization drying temperatures were applied (21 and 38 °C). A dual-cure composite resin (Core Paste XP) was selected to build-up the core around posts, obtaining cylindrical specimens that were serially cut in beams and subsequently loaded in tension (μ TBS) at a cross-head speed of 1 mm/min until failure. Bond strength data were statistically analyzed by two-way ANOVA and Student–Newman–Keuls tests ($\alpha = 0.05$).

Results. Warm air-drying determined significantly higher bond strengths ($p < 0.001$) for glycid-oxi-propyl-trimethyl-oxi-silane (11.6 MPa) and 4-methacryloxyethyl trimellitate anhydride/ γ -trimethoxysilyl propyl methacrylate silane (11.7 MPa). These two systems exhibited lower bond strengths (6.9 and 8.8 MPa, respectively) than 3-methacryloxypropyltrimethoxysilane (11.0 MPa) when dried at 21 °C. No statistical differences were recorded for 3-methacryloxypropyltrimethoxysilane when drying at 21 or 38 °C.

Significance. The composition of the silane coupling agent in terms of acidic content, solvent rate or degree of hydrolysis may influence resin/post bond strength when dried at 21 °C. Drying at 38 °C most likely facilitates the evaporation of solvents present in the silane agent, resulting in increased bond strength of the composite resin to the fiber post.

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1. Introduction

Several studies suggested the use of silane coupling agents in coating applications to promote adhesion between inorganic surfaces and polymeric molecules [1,2].

Organosilanes have the formula $R'-Si-(OR)_3$ with an organic functional group (R') and three alkoxy groups (R): the chemi-

cal reaction begins with the hydrolysis of the alkoxide groups (R) into silanols (SiOH) that may condense forming siloxane bonds [2,3].

Many factors (pH, presence of solvents, molecule size, etc.) may exert an influence in the way silane molecules can absorb, condense or interact with the substrate, influencing coupling effectiveness [4,5].

* Corresponding author. Tel.: +39 0338 4623264; fax: +39 0577233117.

E-mail address: francescamonti@hotmail.it (F. Monticelli).

To accelerate the mechanism of chemical interaction between the silane and the inorganic surface, the reaction may be catalyzed by acid treatment or heating [6,7]. Heat treatment of silanated glass is routinely performed in the glass industry to maximize bond strength [8]. Silane has been proven to increase ceramic-composite bond strength during luting procedures or when repairing chipped ceramic restorations [9–11]. Drying with hot air increases the effectiveness of some silane coupling agents when bonding ceramics to composite resins [7,12].

High temperature silane heat treatment (70–80 °C) is not feasible for chair-side procedures, but a stream of warm air (38 °C) may be used for this purpose [7].

Fibre posts are extensively used in combination with composite resins to directly restore endodontically treated teeth [13,14]. The efficacy of silane coupling agents increasing bond strength between fiber post and composite core restorations have been recently reported [15–18]. However, no information is available concerning the possible influence of different silane coupling agents' composition or silanizing modalities on post/composite bond strength. In particular, the possible influence of heating on the condensation reaction of silane molecules on the post surface is still unknown. The aim of the study was to determine the effect of warm air drying and different silane coupling agents on the achieved bond strength between fiber posts and resin composite.

The null hypothesis is that silane composition and air-drying temperature do not influence the microtensile bond strength between fiber post and composite resin.

2. Materials and methods

Thirty quartz fiber posts, with a maximum diameter of 1.80 mm in the cylindrical coronal portion and 1.0 mm at the radicular end (DT Light Post #2, batch no.100US0311A, RTD, St. Egéve, France) were used for this study. DT Light posts are made of unidirectional pre-tensed quartz fibers (60%) bound in an epoxy resin matrix (40%).

The posts were etched in 10 vol% hydrogen peroxide solution (Panreac Química, Barcelona, Spain) for 20 min at room temperature [19]. They were rinsed with tap water and ultrasonically cleaned for 10 min in deionised water (P Selecta S.A. Abrera, Barcelona, Spain), subsequently immersed in 96% ethanol and dried with an air stream.

Six experimental groups ($n=5$) were formed and three different silane coupling agents were used: a pre-hydrolyzed silane coupling agent containing 3-methacryloxypropyltrimethoxysilane (3-MPS) (Monobond-S, batch no. E53184, Ivoclar-Vivadent, Schaan, Liechtenstein); a two-component silane coupling agent containing 4-methacryloxyethyl trimellitate anhydride (4-META) and trimethoxysilyl propyl methacrylate (γ -MPTS) (Porcelain Liner M, batch no. GF1, Sun Medical Co. Ltd., Japan); a pre-hydrolyzed silane coupling agent containing glycid-oxi-propyl-trimethyl-oxi-silane (GPS) (Porcelain Silane, batch no. 4101PFS, BJM Lab, Or-Yenuda, Israel) at two different air-drying temperatures (21 and 38 °C). The tested materials were applied following manufacturers' recommendations. The composition and application mode of the tested materials are described in Table 1.

pH measurements were performed for all tested silane coupling agents with a digital pH-meter and a glass electrode calibrated with standard buffer solutions (Micro pH 2000, Crison Instruments, Alella, Spain).

After etching and silanizing the post surface, composite build-up was performed following a technique previously described by Goracci et al. [15] and using a dual-curing resin composite (Core Paste XP, batch no. 030653101, Dent Mat, Santa Maria, CA, USA). Core Paste XP is a low viscosity core material and contains glass fillers in a methacrylate matrix. Samples were stored 24 h at room temperature before testing.

Microtensile test specimens were prepared by sectioning each sample with a diamond saw under water cooling (Isomet 4000, Buehler, Lake Bluff, IL, U.S.A.). A medium of 29 beams of 1-mm in thickness were tested for each group. For the microtensile bond strength test, each beam was glued with cyanoacrylate (Zapit, Dental Ventures of America, Corona, USA) to the flat grip of a testing device (Bencor, Multi-T, Danville Engineering, San Ramon, CA, U.S.A.) and loaded in tension at a cross-head speed of 1 mm/min until failure (Instron Model 4411, Instron, Canton, MA, U.S.A.). The modes of failure were evaluated after testing under a stereomicroscope (Olympus SZ-CTV, Olympus, Tokyo, Japan) at 40 \times magnification. Failure modes were classified as adhesive (at the post/core interface), cohesive (within the resin composite) or mixed (combination of the two modes on the same surface).

Interfacial bond strength values were expressed in MPa using a mathematical formula previously described by Bouillaguet et al. [20]. Data were analyzed by two-way ANOVA

Table 1 – Silane coupling agent compositions and procedures tested in the study

Material	Composition	Application
Monobond-S (Ivoclar-Vivadent, Schaan, Liechtenstein), pH \approx 3.8	3-MPS (1%), ethanol/water-based solvent, acetic acid	Apply with a brush; leave undisturbed for 60 s; gently air-dry
Porcelain Liner M (Sun Medical Co. Ltd., Japan), pH \approx 4.5	Liquid A: MMA, 4-META (10%); liquid B: MMA, γ -MPTS (10%)	Apply with a brush; gently air-dry
Porcelain Silane (BJM Lab, Or-Yenuda, Israel), pH \approx 1.8	GPS (3%), ethanol-based solvent	Apply with a brush; gently air-dry

3-MPS: 3-Methacryloxypropyltrimethoxysilane; MMA: methyl methacrylate; 4-META: 4-methacryloxyethyl trimellitate anhydride; γ -MPTS: trimethoxysilyl propyl methacrylate; GPS: glycid-oxi-propyl-trimethyl-oxi-silane.

Table 2 – Mean (standard deviation) of microtensile bond strength values (MPa) and percentage of failure mode obtained for each tested group

	21 °C			38 °C		
	Mean (S.D.)	Adhesive (%)	Cohesive (%)	Mean (S.D.)	Adhesive (%)	Cohesive (%)
Porcelain Liner M	8.8 (3.1) ^{a1} , n=30	90	10	11.7 (2.7) ^{c2} , n=27	97	3
Porcelain Silane	6.9 (2.0) ^{b1} , n=30	90	10	11.6 (2.8) ^{c2} , n=30	100	–
Monobond-S	11.0 (2.9) ^{c2} , n=28	100	–	11.4 (2.5) ^{c2} , n=30	97	3

Superscript letters show differences within the same column and numbers within the same row ($p < 0.05$).

to evaluate the effect of the factors (silane composition and air-drying temperature) on the dependent variable (microtensile bond strength). Interactions were included in the analysis. Multiple comparisons were performed with Student–Newman–Keuls test. Statistical significance was set at $\alpha = 0.05$. The sample size was calculated to ensure a power of 0.8 in the statistical analysis.

3. Results

Mean microtensile bond strength values are shown in Table 2. Bond strength was influenced by the air-drying temperature ($p < 0.001$), and by the application of different coupling agents ($p < 0.001$) on the bond strength. Interactions were also significant ($p < 0.001$). 3-MPS performed similarly, regardless of air-drying temperature. If dried at 21 °C, GPS and 4-META/ γ -MPTS silanes exhibited lower bond strengths than 3-MPS. Similar results were attained for all coupling agents when dried at 38 °C. GPS and 3-MPS had a similar acidic pH (4.5 and 3.8, respectively), while 4-META/ γ -MPTS silane recorded a lower value (1.8).

The distribution and percentages of failures are described in Table 2. A percentage of adhesive failure between 90 and 100% was recorded in all tested groups.

4. Discussion

The use of different air-drying temperatures on the silanated posts and the different composition of the silane coupling agents affected the bond strength of composite to fiber posts. Thus, the null hypothesis is rejected.

Silane enhances post-resin bond strength by promoting the wetting of the etched post surface and facilitating the diffusion of the fluid composite resin into the retentive spaces among the exposed fibers [19]. When silane is applied on the post surface and dried, two phases are created [21,22]: an outermost physisorbed layer with few siloxane bonds and a hydrolytically stable chemisorbed layer on the post surface [2,7].

Further reactions between silane molecules and the organic surface (fiber posts) have been proven to occur, enhancing condensation and providing a more tightly packed configuration of the coupler molecules on the post surface [2,23].

Two different silane agents were tested in this study: two single-phase pre-activated solutions based on different silane molecules (3-MPS and GPS, respectively) and a two-component system. In the latter, hydrolysis occurs when

mixing the silane coupler (γ -MPTS) with the acidic monomer (4-META) just before its application [24,25]. Pre-activated silane solutions are expected to exhibit a higher rate of hydrolysis compared to the two-component systems in which an incomplete reaction may eventually take place if the solvent is not completely evaporated, affecting bond strength [8,25].

3-MPS and GPS are considered neutral silanes with a similar degree of coupling power: under mildly acidic concentration, they condense rapidly to reach an equilibrium composition in a short time [7].

GPS silane is appropriate for epoxy resin coupling: however, its application on the post surface has been proven to decrease bond strength at least if dried at 21 °C [26].

Pre-activated silane primers have a limited shelf-life due to the rapid formation of oligomers [2,8]. At high silane concentration (3% GPS in the tested silane) the potential of oligomer formation increases: moreover, the physisorbed silane tends to form a weak boundary layer onto the quartz fibres that may act deficiently in the post/composite interface, causing a lubrication effect [2,5,27]. It explains the lower μ TBS attained by the pre-hydrolyzed GPS-based silane when compared to 3-MPS silane when dried at 21 °C. The results from this study indicated that by using a GPS coupling on the post surface, 38 °C air-drying is advisable to facilitate solvent removal and to achieve chemical stability [28].

Silane coupling is considered a technique-sensitive step. Among the factors affecting its effectiveness, solvent evaporation plays an important role: a small amount of solvent may be beneficial in promoting silane wetting, but an incomplete removal may compromise coupling [29]. Ethanol evaporates easily without affecting the reactivity of silane, especially in pre-hydrolyzed coupling agents [7,30]. However, if evaporation is not completed at 21 °C, warm air-drying may help ethanol and other by-product evaporation, facilitating the elimination of the detrimental outer physisorbed silane layer [31]. The higher bond strength results achieved for GPS dried at 38 °C may confirm this aspect. Ethanol/water-based silanes had a more stable behavior, probably due to the mixing ratio of the two solvent components [32]. At the two selected temperatures, no significant differences in the evaporation rate of water are expected to occur. Higher values may facilitate water removal and could increase bond strength.

The selection of a warm air stream rather than heat treatment, seems to be more effective in bonding to polymers and it may be considered a clinically-feasible chair-side procedure to overcome some of the problems related to silane composition and/or application [6,7,21]. Some results recently achieved on ceramics seem to confirm this aspect, in particular for the

two-component systems that have been proven to be more sensitive to heating [8,21].

Pre-hydrolysed MPS silanes yielded a more stable bond to the post surface as shown by the higher bond strength achieved, regardless of the drying temperature [33]. The hydrolysis and condensation reactions as well as the thickness of the siloxane film are pH dependent [2]. The hydrolysis rate increases at higher pH. In this sense the durability over time of the GPS silane bond (pH around 4.5) may be questionable [34].

The presence of acetic acid in the 3-MPS tested silane solution may guarantee pH stability and effectiveness [34].

Despite a significant increase in bond strength after warm air-drying, the failure mode registered in the all tested groups was predominantly adhesive, revealing the relative weakness of the post/composite bond. Chemical adhesion between methacrylate-based resin composites and fiber posts cannot be completely obtained by silane [19]. Further studies should be performed to evaluate the possibility of combining silane solutions and bonding agents to improve bond strength and stability of silane coupling during aging.

5. Conclusions

Air-drying at 38 °C promotes the condensation process of the silane on the post surface and removes some of the loosely absorbed molecules probably by simple evaporation. Water-based silane coupling solutions were shown to be less influenced by air-temperature during drying.

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