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Experimental Novel Silane System in Adhesion Promotion between Dental Resin and Pretreated Titanium. Part II: Effect of Long-Term Water Storage

Rapid Communication

Jukka P. Matinlinna · Lippo V. Lassila

Abstract In this study we have assessed the effect of long-term water storage at 37°C on silane-aided adhesion promotion. Five experimental silane blends were evaluated as adhesion-promoters. First, five functional organosilane monomers (silicon esters), 3-acryloxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, *tetrakis*-(2-methacryloxyethoxy)silane and *bis*-[3-(triethoxysilyl)propyl]tetrasulfide, were diluted to 1% (v/v) in 95% ethanol and blended with a non-functional cross-linking silane, *bis*-1,2-(triethoxysilyl)ethane (1%). A commercially available pre-activated silane product was used as the control. After activation by hydrolysis, each primer blend was applied to silica-coated Ti coupons. Stubs of experimental *bis*-phenol-A-diglycidyldimethacrylate (*bis*-GMA)-based resin were bonded by photo-polymerization onto the pretreated Ti coupons. Half of the specimens were stored in deionized water for 6 months and half for 12 months. The primer containing 3-acryloxypropyltrimethoxysilane and *bis*-1,2-(triethoxysilyl)ethane produced significantly higher shear bond strengths than the control silane and other experimental silane primers after both periods of storage.

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1 Introduction

Prosthetic metal and alloy constructions such as substructures for dental bridges and crowns are conventionally pretreated by silica-coating and silanization before veneering or cementation [1, 2]. The promotion of adhesion between dissimilar materials, such as inorganic materials to organic polymers, is carried out with silane coupling agents. They are silicon esters of the type -Si(OR)$_3$ that are synthetic compounds with one or more direct ≡Si-C≡ bonds [3]. Silanization is usually performed with 3-methacryloxypropyltrimethoxysilane in dental laboratories, such as for silica-coated restorations in prosthetic dentistry [1, 2]. Hydrophobic silane monomers first need to be hydrolyzed, usually with acids, but the hydrolytic stability [4] during long-term wet storage of materials that have been bonded with the aid of silanes is an ongoing concern in dentistry.

Blends of organofunctional silane monomers and cross-linking silanes have made it possible for many resin-composites to achieve considerable hydrolytic stability and mechanical strength. The cross-linking silane is usually non-functional (Fig. 1). For example, *bis*-1,2-(triethoxysilyl)ethane, which is a so-called *bis*-functional silane, possesses only hydrolyzable ethoxy groups attached to its two Si atoms. This cross-linking silane is often combined at a 1:5–1:10 ratio with a functional silane monomer [5, 6]. The thickness of the cross-linked siloxane film that forms on the silica-coated substrate strongly depends on the silane concentration [3, 4]. It is widely accepted that an inter-

Fig. 1 Silane coupling agent monomers used in the experimental primers : **a**) 3-acryloxypropyltrimethoxysilane (ACPS), **b**) 3-methacryloxypropyltrimethoxysilane (MPS), **c**) 3-glycidoxypropyltrimethoxysilane (GPS), **d**) *tetrakis*-(2-methacryloxyethoxy)silane (TEXS), **e**) *bis*-[3-(triethoxysilyl)propyl]tetrasulfide (TSEF), **f**) *bis*-1,2- (triethoxysilyl)ethane (BTSE)
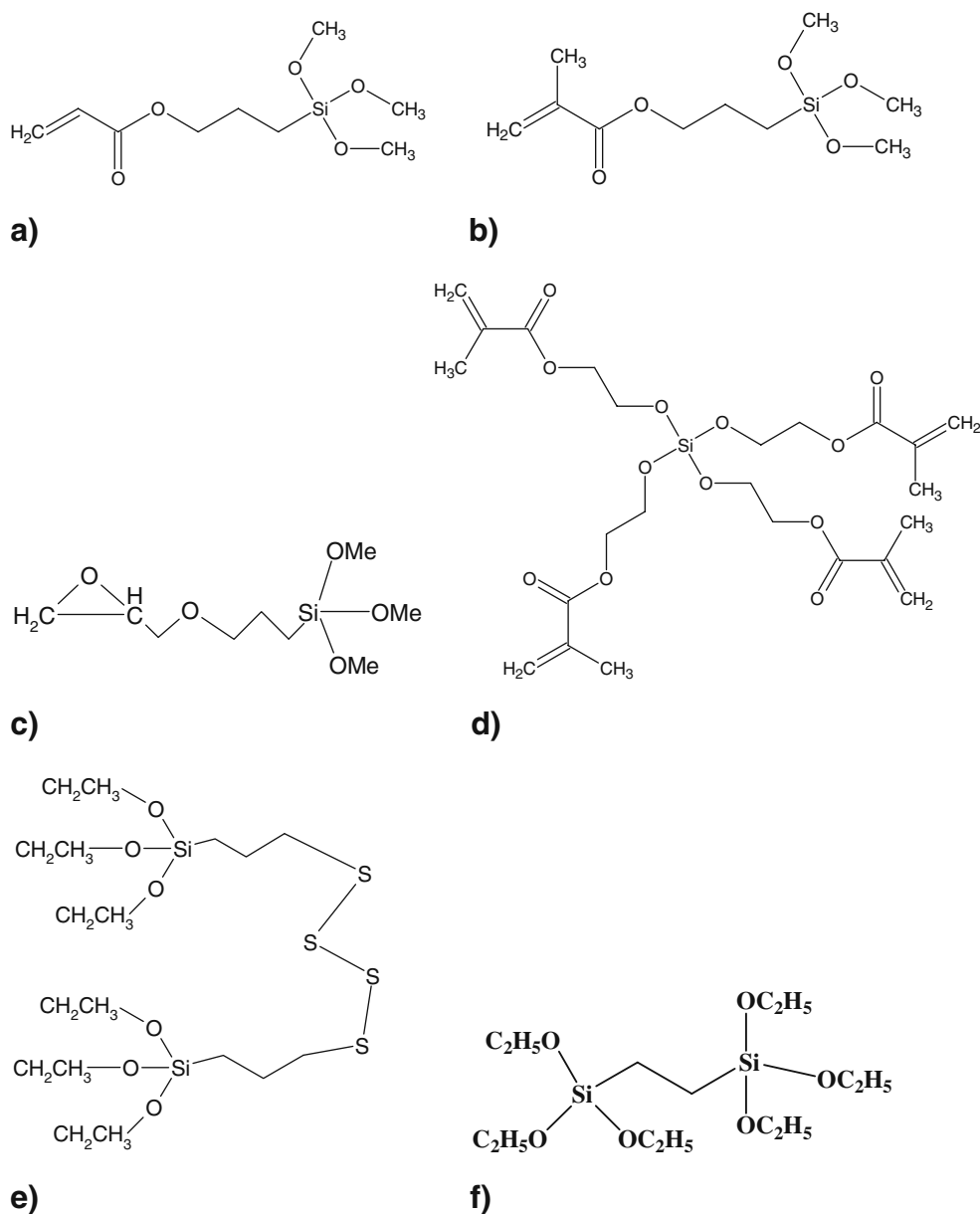
penetrating polymer network [7] forms over the functional silane (Fig. 2).

In this study we have evaluated the effect of long-term water storage on novel silane primer systems that are based on *bis*-1,2-(triethoxysilyl)ethane blended with one of five functional silane monomers (Fig. 1): 3-acryloxypropyltrimethoxysilane [8], 3-methacryloxypropyltrimethoxysilane [9], 3-glycidoxypropyltrimethoxysilane, *tetrakis*-(2-methacryloxyethoxy)silane and *bis*-[3-(triethoxysilyl)propyl]tetrasulfide. A non-filled resin system based on the experimental resin *bis*-phenol-A-diglycidyldimethacrylate (*bis*-GMA) was used in the shear bond strength assay and examination of failure mode [10]. Ti was used as the substrate because it is the biomaterial of choice for crown implants and bridge substructures and its bonding properties have been widely

studied [11–13]. Our hypothesis was that long-term water storage of bonded resin-Ti may weaken the bonding (i.e. shear bond strength) mediated by any of the five experimental functional silane primers.

2 Experimental

The materials used in this study are listed elsewhere [14]. The experimental unfilled resin consisted of 78.4% *bis*-GMA, 19.6% methylmethacrylate, 1.0% 2-(dimethylamino) ethylmethacrylate and 1.0% (±)-camphorquinone, blended together and prepared in polythene syringes, as previously described [8, 9, 13–15]. A sheet of commercially pure grade 2 Ti (Permascand, Ljungaverk, Sweden; >99%) of

Crosslinked, hydrophobic
interpenetrated network

Cross-linking silane →

Silica-coating →
TiO$_2$ →
Ti →
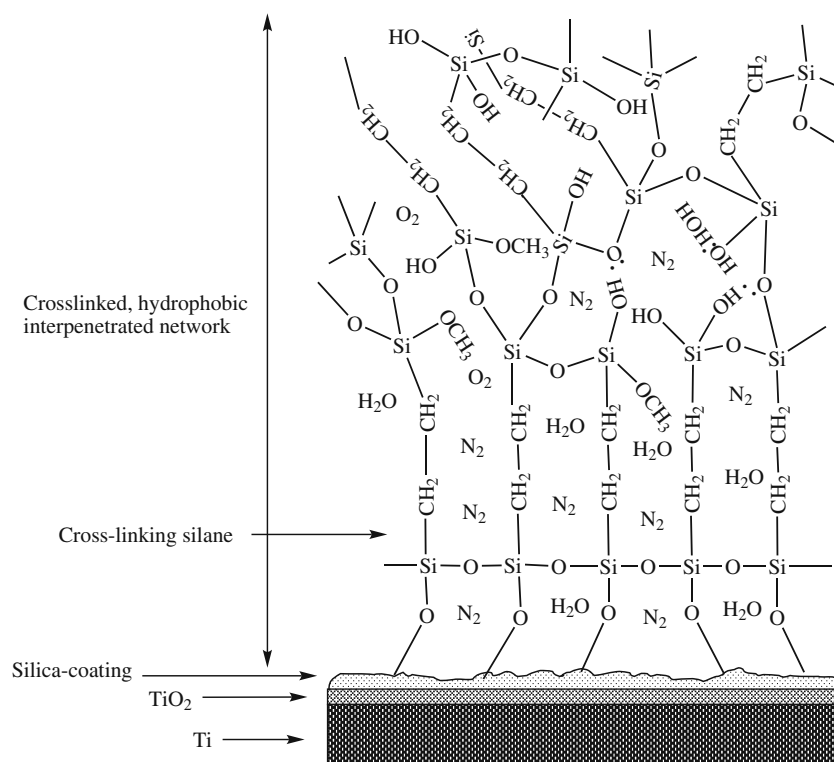
1-mm thickness was cut into coupons of 20 mm by 40 mm ($n=24$). The upper half of the surface was grit-blasted with special silica-coated alumina sand (Rocatec™ system; ESPE, Seefeld, Germany), and the coupons were then cleaned ultrasonically.

Five experimental silane primers were prepared in 95% (v/v) ethanol in deionized water, and adjusted to pH 4.5 with 1 M acetic acid. First, a 1% solution of *bis-1,2-(triethoxysilyl)ethane* was activated by hydrolysis for 23 h at room temperature; then the organofunctional silane was added to reach 1%, and the blends were allowed to hydrolyze for an additional 1 h at room temperature [14]. A commercially available pre-activated silane product was used as the control [2].

The control and five primers were each applied onto 4 randomly selected silica-coated Ti coupons. The experimental resin was applied into polythene molds to form resin stubs with a diameter of 3.6 mm and a height of 4 mm. Five resin stubs were evenly placed on the upper horizontal borders of each pretreated Ti coupon and the stubs were then photo-polymerized. The mold was then carefully removed [14–16]. Half of the specimens (2 coupons for each primer and control) were stored in deionized water for 6 months and half for 12 months in sealed polythene jars, kept in an incubator at a constant temperature of 37 °C.

Shear bond strength testing was performed with a universal material testing machine [16]. Tested specimens were examined by optical microscopy (50–100× magnifi-cation) and their failure mode was assessed: when >66% remained on the Ti substrate, it was cohesive, when >33% but <66% remained, it was mixed failure and when 33% of the resin stub was left on the Ti surface, the failure type was adhesive.

Differences in shear bond strength were assessed with analysis of variance (ANOVA), using multiple comparisons; statistical significance was set at $p=0.001$ [14].

3 Results and Discussion

In this study we have assessed the *in vitro* effects of five experimental silane blends on resin-Ti adhesion after dry storage and two long-term water storage conditions. Long-term water storage in dental materials studies, e.g. for several weeks and several months (even years), is relevant to the clinical situation because dental materials are subject to continuous and constant humidity in the mouth. However, other physiological factors, such as biting forces and pH changes were beyond the scope of this study. The temperature was set at 37 °C±1 °C to simulate the average oral temperature. Deionized water was selected as the storage medium since it is usually used in this type of experiment [8, 9, 11–15]. In some simulations, artificial saliva is used for the same purpose [17]. In general, the water sorption and solubility of resins (and resin-composites) are important issues and concerns in dentistry, because perma-

Fig. 3 Shear bond strength values (in MPa) after four different aging methods: dry storage ("Dry"), thermo-cycling ("TC6000"), 6 months of water storage, and 12 months of water storage. Abbreviations: ESPESil = the control silane, TEXS = *tetrakis*-(2-methacryloxyethoxy)silane, BTSE = 1,2-*bis*-(triethoxysilyl)ethane, ACPS=3-acryloxypropyltrimethoxysilane, MPS=3-methacryloxypropyltrimethoxysilane, GPS=3-glycidoxypropyltrimethoxysilane, TSEF = *bis*-[3-(triethoxysilyl)propyl]tetrasulfide
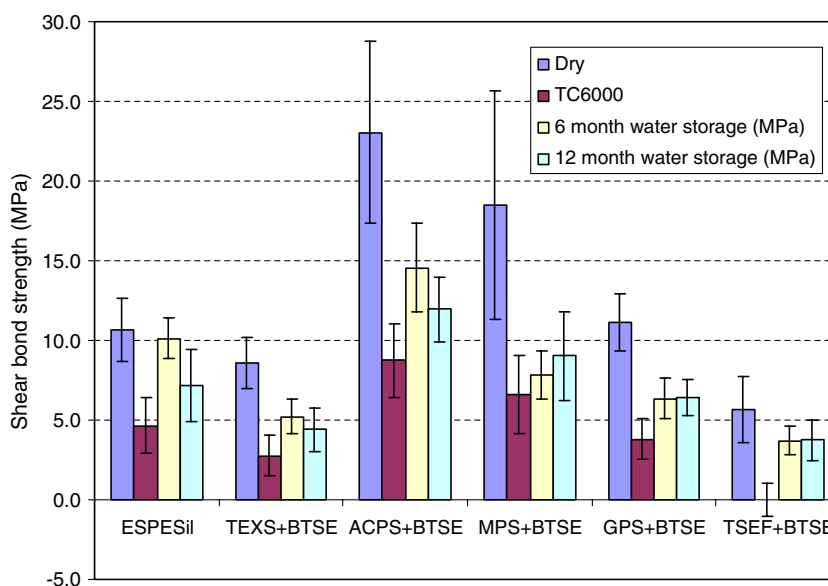
nent restorative materials and luting cements (resins) should have a long service time and they should not dissolve or degrade. The experimental resin type in this study has also been used in some of our previous studies [8, 14, 15, 18–20]. Its solubility and water-sorption properties have been reported recently [15]; hence in this study, we did not make observations about the solubility or sorption properties of the resin or the silica-coated surface.

Compared with the initial values, i.e. data obtained after dry storage, all the shear bond strength values after all artificial wet aging treatments were significantly lower, except for the control (Fig. 3, Tables 1 and 2). The shear bond strength values for the samples treated with control silane or each of the experimental silane primers was significantly higher after 6 and 12 months of water storage than after thermo-cycling. For the *bis*-[3-(triethoxysilyl) propyl]tetrasulfide + *bis*-1,2-(triethoxysilyl)ethane group, all thermo-cycled specimens underwent spontaneous

debonding and had relatively low bonding values that were close to those for the *tetrakis*-(2-methacryloxyethoxy) silane + *bis*-1,2-(triethoxysilyl)ethane group. For 3-acryloxypropyltrimethoxysilane + *bis*-1,2-(triethoxysilyl) ethane, with the highest initial shear bond strength value, a 6-month storage time significantly reduced the highest bonding values (Tables 1, 2, 3, 4 and 5).

It is not surprising that the failure mode analysis after water storage yielded relatively similar results to those achieved after thermo-cycling [14]: for 3-acryloxypropyltrimethoxysilane + *bis*-1,2-(triethoxysilyl)ethane, the failure mode was predominantly mixed, at 60%, with 40% cohesive failure. The control group exhibited a predominantly cohesive failure mode, at 60%, which is in concordance with the group treated with 3-methacryloxypropyltrimethoxysilane + *bis*-1,2-(triethoxysilyl)ethane which showed 50% cohesive and 50% mixed failure (Table 1). Thermo-cycling usually significantly lowers

Table 1 Mean shear bond strength (standard deviation [SD]) after 6 and 12 months of water storage and with the observed failure type ($n=10$ per group)

Silane type	6-month water storage				12-month water storage			
	Shear bond strength (SD) [MPa]	Cohesive failure [%]	Mixed failure [%]	Adhesive failure [%]	Shear bond strength (SD) [MPa]	Cohesive failure [%]	Mixed failure [%]	Adhesive failure [%]
Control ESPE Sil	10.1 (1.3)	60	40	0	7.4 (2.4)	60	40	0
ACPS + BTSE	14.6 (2.9)	40	60	0	12.0 (2.1)	40	60	0
MPS + BTSE	7.8 (1.6)	50	50	0	9.0 (3.0)	50	50	0
GPS + BTSE	6.4 (1.4)	0	0	100	6.4 (1.2)	0	0	100
TEXS + BTSE	5.2 (1.1)	0	0	100	4.4 (1.4)	0	0	100
TSEF + BTSE	3.7 (1.0)	0	0	100	3.7 (1.3)	0	0	100

Abbreviations: see Fig. 3 caption

Table 2 Mean shear bond strength with standard deviation (SD), after all four storage types (*n*=10 per group) [14]

Silane type	Shear bond strength (SD) [MPa]			
	Dry storage Ref. [14]	Thermo-cycling Ref. [14]	Water storage 6 months	Water storage 12 months
Control ESPE Sil	10.6 (2.1)	4.7 (1.9)	10.1 (1.3)	7.4 (2.4)
ACPS + BTSE	23.0 (6.0)	8.7 (2.4)	14.6 (2.9)	12.0 (2.1)
MPS + BTSE	20.0 (6.3)	6.6 (2.6)	7.8 (1.6)	9.0 (3.0)
GPS + BTSE	11.1 (1.9)	3.8 (1.4)	6.4 (1.4)	6.4 (1.2)
TEXS + BTSE	8.6 (1.6)	2.8 (1.4)	5.2 (1.1)	4.4 (1.4)
TSEF + BTSE	6.0 (2.1)	0.0 (0.0)	3.7 (1.0)	3.7 (1.3)

Abbreviations: see Fig. 3 caption

shear bond strength values, as demonstrated in our previous study [18]. Adhesion promotion with 3-glycidoxypropyltrimethoxysilane, *tetrakis*-(2-methacryloxyethoxy)silane and *bis*-[3-(triethoxysilyl)propyl]tetrasulfide blended with *bis-1,2*-(triethoxysilyl)ethane exhibited failure solely at the adhesive interface, although no spontaneous debonding was observed for these groups. Nevertheless, these findings suggest that the bonding was not hydrolytically stable when these three silane blends were used to promote adhesion. Therefore, the *bis*-GMA/MMA resin system exhibits a chemical and/or molecular mismatch with these three experimental primers, such that the primers may have somehow modified the silica-coated Ti surface.

Our statistical analyses (Tables 3, 4 and 5), which included data from our previous publication [14], revealed that the type of functional silane (*p*<0.001) and storage conditions (*p*<0.001) significantly affected the shear bond strength. Acrylate and methacrylate are the most reactive functionalities for silane coupling agents [2–4, 21, 23, 24]. Their blends with the cross-linking silane produced the highest bonding values, compared with values for the control group and the groups using the other three experimental primers. Compared with the control silane, use of 3-methacryloxypropyltrimethoxysilane + *bis-1,2*-(triethoxysilyl)ethane led to a change in bonding strength of +22% after 12 months of water storage and, perhaps surprisingly, −23% after 6 months of water storage, which is not easy to explain. For 3-acryloxypropyltrimethoxysilane + *bis-1,2*-(triethoxysilyl)ethane, the change was +62% after 12 months and +44% after 6 months. Finally, the control and the primers 3-acryloxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and 3-glycidoxypropyltrimethoxysilane blended with *bis-1,2*-(triethoxysilyl)ethane produced under 12 months of water storage shear bond strength values that exceeded the formal minimum threshold of 5 MPa, which is set for prosthodontic materials [16].

In principle, van der Waals forces are strong enough to account for durable bonding between solid material substrates and polymers if the contact is extremely intimate [21]. Perfect contact between the substrate and polymer should lead to bonding so strong that the failure mode should be in the polymer or substrate, which represents cohesive failure. It has been proposed that failures in adhesion are due to the weak boundary layer at the interface [22]. Nevertheless, in practice, surfaces are always rough rather than smooth, and intimate contact between the substrate and resin is virtually impossible.

Silica and silica-coated surfaces are polar and hydrophilic, which makes them prone to spontaneous water adsorption. Accordingly, dilute solutions of activated (hydrolyzed) silanes wet a substrate effectively and displace

Table 3 Statistical analysis of data from this and a previous study [14] using tests of between-subject effects (two-way ANOVA) for the shear bond strength of the experimental silane primers

Source	Sum of squares	df	Mean square	F	p level
Corrected model	13243.801 a	26	509.377	56.625	0.000
Intercept	26046.745	1	26046.745	2895.478	0.000
Silane	7728.802	6	1288.134	143.195	0.000
Storage time	3080.991	3	1026.997	114.166	0.000
Silane * Storage time	1610.356	17	94.727	10.530	0.000
Error	2086.994	232	8.996		
Total	41943.861	259			
Corrected total	15330.795	258			

a. R squared=0.864 (adjusted R squared=0.849)

Silane (I)	Silane (J)	Mean difference (I–J)	Standard error	p value
Control	ACPS + BTSE	−6.022	0.6584	0.000
	MPS + BTSE	−2.156	0.6532	0.019
	GPS + BTSE	1.281	0.6532	0.443
	TEXS + BTSE	3.011	0.6483	0.000
	TSEF + BTSE	4.257	0.6817	0.000

air from its surface, without having to be 100% hydrolyzed [3, 6, 7]. Silane coupling agents exhibit strong adhesion to clean metal, metal oxide, glass surfaces and, in particular, silica surfaces. In general, in reinforced plastics such as resin composites, the silica or glass filler particles are always silanized to maintain their adhesion to the hydrophobic polymer matrix [1–4]. The methacrylate functional silane, 3-methacryloxypropyltrimethoxysilane, is well known as one of the most effective silane coupling agents for bonding glass to polyesters when applied as a dilute solution, e.g. 0.5%–2.0% in water-alcohol blends [23]. It is necessary to emphasize that any silane deposited on a surface should not be considered as an adhesive *per se*, but rather as a means of providing a hydrolytically stable, primed surface of controlled polarity to which the monomers of a resin adhere.

Adhesion of polymers to dissimilar substrates involves a dynamic equilibrium of creating and breaking of adhesion bonds [24]. In addition, resin composites undergo polymerization shrinkage and controlling the filler size and load is one way of minimizing volumetric changes [25]. Ti, the silica-coating layer and the experimental resin have obviously different coefficients of thermal expansion, although these were not measured in this study. On the other hand, the temperature was kept constant. Stresses, such as those in polymerization shrinkage, are not dispersed uniformly in the experimental *bis*-GMA/MMA resin mass. These stresses can initiate cracks in the resin and at certain points in the interface. Therefore, we cannot avoid shrinkage stresses between most mineral surfaces such as those in silica-coated metals and polymers.

Owing to its relatively small size, ambient water can penetrate the resin stub to reach the silica-coated Ti surface (*cf.* Fig. 2). The suggested mechanism [4, 24] is based on capillary migration or filtering through cracks. In other words, water cannot be excluded from the interface between the experimental resin and the substrate. The hydrolytic intrusion of water may also cause a self-healing effect, so that stresses can relax without disrupting the silane-film aided bonding. The reaction is reversible because silanes with silanol groups, ≡Si-OH, can uniquely compete with water on the substrate surface [3–6]. In the siloxane film, the reversible breaking and re-making of bonds, both of hydrogen bonds and of covalent bonds,

occurs through stress deterioration. The latter is promoted by the presence of water at the interface, which supposedly imparts ductility to the experimental *bis*-GMA/MMA resin, in a similar way to how slippage of atom planes at the silica-Ti-surface imparts ductility to Ti and its silica-coating [21–24].

In the first study in our series [14], we discussed the shear bond strength testing and thermo-cycling as an aging method. The authors' opinion is that these testing methods can, and should, be employed in dental materials studies, although it should be borne in mind that they have limitations and that the adhesion results obtained need to be observed critically [26–28].

4 Conclusions

In this second part of our *in vitro* study we have evaluated the adhesion promotion effect of five different experimental primers on a silica-coated Ti surface after two long-term wet storage types, 6 months and 12 months at 37°C. Five functional activated silane monomers were blended with a cross-linking silane. After long-term water storage, the shear bond strength values obtained in the 3-acryloxypropyltrimethoxysilane + *bis-1,2-*(triethoxysilyl) ethane group were the highest among all groups. The study hypothesis was partially proven and significant differences were observed between shear bond strength values obtained with the different experimental primers.

Silane	95% confidence interval	
	Lower limit	Upper limit
ACPS + BTSE	−8.380	−3.664
MPS + BTSE	−4.495	0.184
GPS + BTSE	−1.059	3.620
TEXS + BTSE	0.689	5.332
TSEF + BTSE	1.816	6.699

Abbreviations: see Fig. 3 caption

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