

Evaluation of *bis*-GMA/MMA Resin Adhesion to Silica-Coated and Silanized Titanium

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Abstract

The effects of pH value and alcohol solvent type of a silane solution on the bonding of an experimental resin to the silica-coated titanium (Ti) surface were studied. First, Ti surfaces underwent tribochemical Rocatec™ treatment followed by silanization of the surface with 3-methacryloxypropyltrimethoxysilane (MPS). Then, resin stubs based on a mixture of bisphenol-A-glycidyl dimethacrylate and methyl methacrylate were bonded and light-cured onto each silica-coated Ti surface ($n = 6$ per group). Two different solvents for MPS, namely *iso*-propanol (*i*-PrOH)/H₂O and ethanol (EtOH)/H₂O were used, at pH values of 4.5, 5.0, and 5.5, and shear bond strengths were tested both under dry storage conditions and after water sorption induced by accelerated aging (i.e. thermo-cycling). The shear bond strengths were also re-determined after the silane solutions had been stored at 4°C for 15 weeks before the silanization step. For dry samples, the shear bond strengths ranged from 7.5 to 10.6 MPa (ANOVA, $p < 0.05$) when the Ti surface had been silanized with MPS in *i*-PrOH/H₂O, and from 6.5 to 12.4 MPa (ANOVA, $p < 0.05$) when the Ti surface had been silanized with MPS in EtOH/H₂O at pH 4.5. Fifteen weeks of storage of the silane solution increased the shear bond strength of dry samples by *ca.* 1–4 MPa per test group. In contrast, thermo-cycling reduced the shear bond strength in both solvent systems. The weight of the test sample stubs increased by *ca.* 3.5 wt% after 187 days of being subjected to the water sorption test.

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Keywords

Silanes, 3-methacryloxypropyltrimethoxysilane, methyl methacrylate, pH, *bis*-GMA, MMA, Ti, silica-coating

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1. Introduction

Silanes are synthetic hybrid organic–inorganic compounds that are used as coupling agents across organic–inorganic interfaces for bonding dissimilar materials, e.g. paints to metal surfaces [1–3]. In the applications in dentistry and dental technology, silanes are widely used as coupling agents to bond resins to silica-coated metals, ceramics and resin composites [4–7]. When bonding an acrylic resin, the activated alkoxy groups (silanols) in silane molecules react with the metal while the organofunctional group (e.g. the vinyl bond in the methacrylate group) reacts with the monomeric resin matrix. The usefulness of silanes relies on their molecular structure, which contains easily hydrolysable alkoxy groups, such as kinetically favorable methoxy, and organofunctional groups (Fig. 1). The silane molecules first must be activated by hydrolyzing the methoxy groups to become silanol groups [4, 8]. When a hydrolyzed silane is applied onto a metal, the silanol groups will react by forming hydrogen bonds and subsequently covalently bonded siloxane structures are formed on the metal surface. The organofunctional terminal groups of silane molecules can copolymerize with the monomers of the organic matrix by a radical polymerization reaction [9]. By virtue of these chemical reactions, silanes are widely employed in dentistry as coupling agents in practically all resin composite based cements for cementing bridges, metal crowns, onlays, and inlays [4].

Nowadays, there are many commercially available silane products for dental applications [4, 10]. Typically, silane products in dentistry are based on 3-methacryloxypropyltrimethoxy (Fig. 2a), a well-known organofunctional trialkoxysilane. It is normally applied in polar aqueous aliphatic alcohol solutions (e.g. ethanol, *iso*-propanol) or in ethyl acetate, acetone, or even non-polar alkane solvents (e.g. *n*-pentane, *n*-hexane); however, the catalysts needed for activation reactions vary [11]. The concentration of 3-methacryloxypropyltrimethoxysilane (MPS) usually ranges from 1 to 5 vol% in ethanol (EtOH) or *iso*-propanol (*i*-PrOH), both diluted with 5–10% water, but lower silane concentrations are also used [4]. In fact, the low concentration of MPS in solutions is more desirable, because the autopolymerization process of silane molecules can be optimized in diluted solutions. Moreover, low silane concentrations are known to produce thin siloxane films (with a thickness of *ca.* 10–50 nm) that can promote the resin-to-metal bond [12].

In dentistry and dental technology, the biomechanical properties of restorative materials should be close to those of the tooth tissues. Dental materials based on bisphenol-A-glycidyl dimethacrylate (i.e. *bis*-GMA) and triethyleneglycol dimethacrylate (TEGDMA) prepolymers are widely exploited in tooth tissue reconstruction, because the biomechanics and clinical handling properties of *bis*-GMA/TEGDMA-based polymer systems are relatively good [13–15]. Dental resin composite cements containing *bis*-GMA/TEGDMA as the polymer matrix are often called dual-cured resin systems, because polymerization can be initiated either chemically (i.e. peroxide initiated redox polymerization reaction) or by blue light (photo-polymerization) [16, 17]. After the initiation step, the polymerization reaction occurs across the vinyl double bonds of methacrylate groups. The typical final

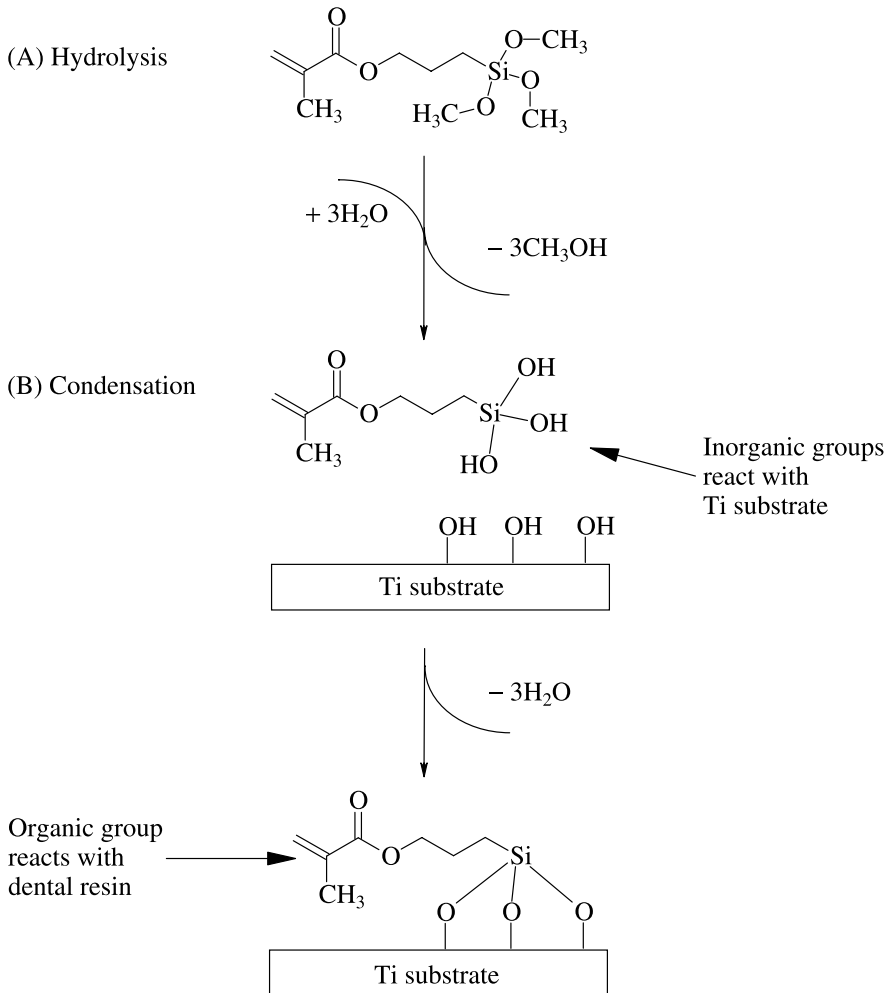


Figure 1. The illustration above shows (A) the hydrolysis reaction of MPS that activates the inorganic groups of the silane molecule and (B) the condensation reaction by which silane is adsorbed onto the surface of Ti substrate.

rate of double bond conversion in dental resin composites is *ca.* 55–75% [18, 19]. As the reaction progresses, the double bonds of methacrylate groups of *bis*-GMA and TEGDMA can also react with the methacrylate group of activated MPS. Thus, *bis*-GMA/TEGDMA resin composites offer the advantages of two relatively easy mechanisms of initiation of polymerization and the possibility of simultaneous covalent bonding of a highly cross-linked network polymer to silanized metal or glass surfaces [4].

Some studies have indicated that silane coupling agents play a key role in adhesion promotion. Several studies have demonstrated the adhesion of methacrylate-based polymers to titanium with the application of MPS [4, 20–22]. Titanium has

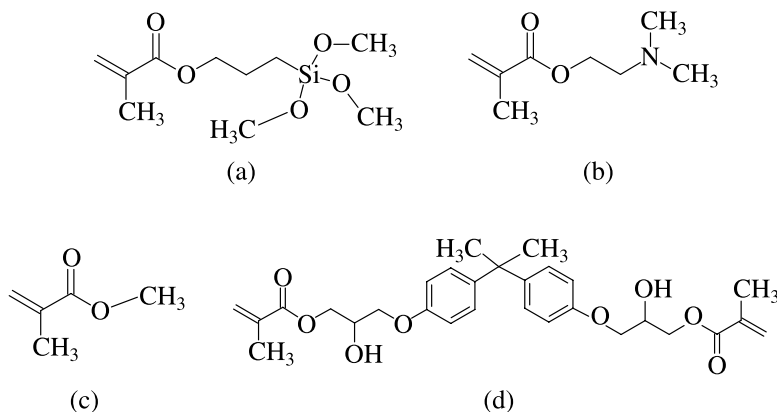


Figure 2. The molecular structures of compounds containing methacrylate group used in the experiments: (a) methacryloxypropyltrimethoxysilane, MPS, (b) *N,N*-dimethylaminoethyl methacrylate, DMAEMA, (c) methyl methacrylate, MMA, and (d) bisphenol-A-glycidyl dimethacrylate, *bis*-GMA.

been used as the substrate of choice because it is potentially a dental biomaterial substructure for crowns, bridges, and in particular implants. In prosthodontics, Ti crowns and bridges are cleaned prior to veneering and cementing by a controlled short-term roughening with sand-blasting and then silica-coated by the tribochemical Rocatec™ or CoJet™ (both 3M Espe) system before silanization [4, 6, 23]. The roughening method, which consist of abrasive blasting with special silica-modified aluminium oxide sand particles, provides micromechanical retention and promotes chemical adhesion, thereby improving the bond strength [21].

A well-known drawback of dental materials based on *bis*-GMA/TEGDMA is incomplete conversion of double bonds. In fact, the cured polymer network can contain up to 6 wt% residual uncured monomers [24]. The release of unreacted monomers, usually mainly methyl methacrylate (MMA), from resin composites may cause allergic reactions in some patients [25]. Another drawback is the tendency of these dental materials to absorb water (i.e. water uptake) in the oral environment. The amount of water uptake by experimental materials is normally determined in conjunction with the shear bond strength measurements, which are often done after alternating thermal stress (i.e. thermo-cycling), in order to try to simulate *in vivo* circumstances [26]. The alternating temperatures during thermo-cycling are typically +5°C for cold exposure and +55°C for hot exposure. The specimens exposed to thermal stress have mostly lower shear bond strength values than those not subjected to thermal stress (i.e. kept in dry storage conditions). It can be summarized that the clinical application of dental materials requires a good knowledge of their various biomechanical properties, such as the bond strength and water uptake in a simulated oral environment.

In this study, surface silanization with MPS was studied to determine the durability of an experimental resin bonded to a Ti substrate. We wanted to understand more about the effects of (a) pH value of the solution, (b) the aliphatic alcohol type

in the solvent, and (c) the hydrolysis time on the bond strength. These aspects have not been widely reported in the dental materials literature. We tested whether solvent and pH could significantly affect the compatibility of the silane molecule in the adhesion promotion system and hence shear bond strength. In this study, experimental silane solutions, with MPS concentrations of 0.01 vol%, were prepared in *i*-PrOH/H₂O or EtOH/H₂O solutions, the pH of which was adjusted to 4.5, 5.0, or 5.5. It has been shown that water sorption affects the long-term stability of dental polymers [27]. Therefore, the water sorption was also determined for the experimental resin employed in the shear bond strength investigation in this study. It was expected that there would be high sorption tendency for water for the experimental resin system.

2. Materials and Methods

2.1. Preparation of Experimental Resin System

The materials used in this study are listed in Table 1. In addition, Fig. 2 shows the molecular structures of compounds used in the experimental resin and silane. The laboratory-made experimental resin contained 78.43 wt% *bis*-GMA and 19.61 wt% methyl methacrylate (MMA). Thereafter, 0.98 wt% of initiator of photo-polymerisation (i.e. camphorquinone) and 0.98 wt% of activator

Table 1.
Materials used in the study

Brand	Abbr.	Manufacturer	Lot number	Type of material
Bisphenol-A-glycidyl dimethacrylate	<i>bis</i> -GMA	Röhms, Germany	T0109/1	Experimental dental resin
Methyl methacrylate	MMA	Fluka, Switzerland	1119540	
Camphorquinone	CQ	Fluka, Switzerland	448343/1	
<i>N,N</i> -Dimethylaminoethyl methacrylate	DMAEMA	Aldrich, Germany	00628MU	
Ethanol (99.5%) ¹	EtOH	Primalco, Finland	160306	Experimental silane solutions (types 1–4)
2-propanol (<i>iso</i> -propanol) ²	<i>i</i> -PrOH	Rathburn, UK	2J06MA	
Acetic acid (glacial, 99.8%)	AcOH	Merck, Germany	K22810463 610	
Methacryloxypropyltrimethoxysilane (98%)	MPS	Aldrich, Germany	S01603-022	
Titanium (c.p. grade 2)	Ti	Permascand, Sweden	ASTM B26589	Metal substrate

¹ In silane solutions of types 1 and 3, the solvent employed was a mixture of ethanol and water.

² In silane solutions of types 2 and 4, the solvent employed was a mixture of 2-propanol and water.

(*N,N*-dimethylaminoethyl methacrylate, DMAEMA) were added to the mixture of *bis*-GMA and MMA. The mixture of experimental resin (Table 1) was prepared within 15–30 min and packed in light protected polyethylene syringes. Thereafter, the resin was stored at +4°C before preparing test specimens.

2.2. Preparation of Experimental Trialkoxysilane Solutions and Their Stability Study

Two experimental 0.01 vol% solutions of MPS were prepared, in which accurate amounts of MPS were dissolved in a solvent mixture of 95 vol%/5 vol% *i*-PrOH and deionized water (Milli-RO Plus 30 water, with a resistivity of 18 M Ω cm, Millipore) or 95 vol%/5 vol% EtOH/deionized water. The MPS was purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany, Lot. S01603-022, purity 98%, unredistilled). Three silane solutions with different pH values were prepared in both alcohols, in which the pH value was adjusted to 4.5, 5.0, or 5.5 with 1 M acetic acid (Merck, Darmstadt, Germany). The carefully sealed silane solutions were allowed to undergo hydrolysis at room temperature for 1 h, before they were employed [10, 11, 21]. These silane solutions were subjected to a stability test before the bonding procedure, i.e. by storing the silane solutions in a carefully sealed container in the dark at +4°C for 15 weeks.

2.3. Grit-Blasting of the Ti Substrate

Titanium used in the studies was commercially pure grade 2 (Permascand Ltd., Ljungavverk, Sweden, Lot. ASTM B26589). Titanium was cut to *ca.* 25 mm \times 55 mm \times 1 mm planar slides ($N = 48$). The surface was finished and polished with silicon carbide (SiC) paper (1200 grit; 0.15 μ m particles). Then, the slides were cleaned for 10 min in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing, Inc., Kearny, NJ, USA) and finally rinsed with ethanol and acetone, in order to remove any grease and other impurities. A part with an area of approximately 10 mm \times 55 mm of each planar Ti surface was silica-coated with a Rocatec™ Junior device (3M Espe, Seefeld, Germany), where the sand employed in Rocatec™ Plus (3M Espe), was 110 μ m aluminum trioxide (Al₂O₃) abrasion particles with uniform silica (SiO₂) coating. Only the above-mentioned area was needed for the resin stubs to be light-polymerized onto surface conditioned (silicatized) and silanized Ti substrates. The silicatization was carried out using a pressure of 280 kPa, for a period of 10 s per *ca.* 1 cm² of the total area to be silicatized, from a perpendicular distance of 10 mm. Prior to silanization, the Ti slides were air-blasted with oil-free compressed air and kept in a desiccator.

2.4. Bonding, Shear Bond Strength Testing, and Silane Solution Stability Evaluation

Table 2 shows the classification of test groups for which the shear bond strengths of resin stubs to Ti were measured. Before the resin was bonded, the Ti slides were silanized at room temperature in the following manner: 2–3 drops of silane solution

Table 2.
Classification of test groups for measuring the shear bond strengths

Group	<i>N</i>	Silane solution	Solvent in the silane solution	pH			Time of hydrolysis
Dry ¹ (60 min)	6	Type 1	EtOH/H ₂ O	4.5	5.0	5.5	60 min
Tc ² (60 min)	6	Type 1	EtOH/H ₂ O	4.5	5.0	5.5	60 min
Dry (60 min)	6	Type 2	<i>i</i> -PrOH/H ₂ O	4.5	5.0	5.5	60 min
Tc (60 min)	6	Type 2	<i>i</i> -PrOH/H ₂ O	4.5	5.0	5.5	60 min
Dry (15 w)	6	Type 3	EtOH/H ₂ O	4.5	5.0	5.5	15 w
Tc (15 w)	6	Type 3	EtOH/H ₂ O	4.5	5.0	5.5	15 w
Dry (15 w)	6	Type 4	<i>i</i> -PrOH/H ₂ O	4.5	5.0	5.5	15 w
Tc (15 w)	6	Type 4	<i>i</i> -PrOH/H ₂ O	4.5	5.0	5.5	15 w

¹ Dry: The shear bond strengths were measured immediately after the preparation of specimens, i.e. in dry conditions.

² Tc: The shear bond strengths were measured after subjecting the specimens to thermal stress, i.e. after thermo-cycling.

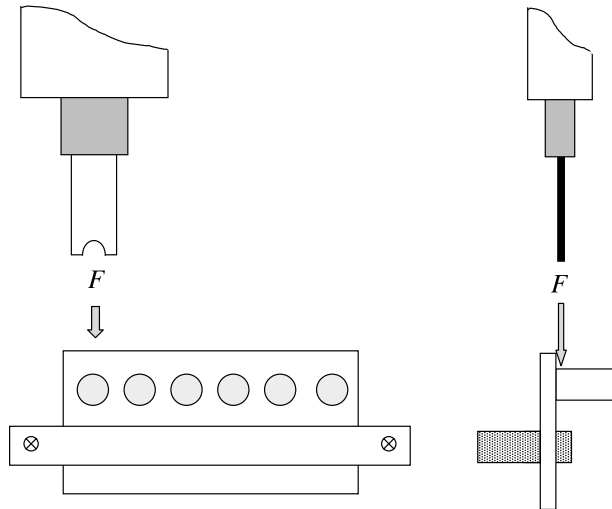


Figure 3. The illustration above shows the test setup for measuring the shear bond strengths of specimens, the system from the front (on left) and from the side (on right).

were brushed onto the substrate (one coat of silane) and allowed to react for 5 min (i.e. visually dry on the surface). Experimental resin was applied as cylindrical stubs ($n = 6$) with a diameter of 3.6 mm and height of 10 mm onto the surface-treated Ti slides. Figure 3 presents the test setup for measuring the shear bond strengths. The resin stubs were light-cured (Optolux 501, SDS Kerr, Danbury, CT, USA) for 40 s

at an average light intensity of 800 mW/cm². For completing the polymerization, the specimens were also cured in a light-curing oven unit (Vision Beta, 3M Espe, Seefeld, Germany) for 15 min in a vacuum. This is a custom procedure carried out at dental laboratories. The molds were then removed carefully by pressing at the same time the cured resin stub with a hand-piece instrument. The shear bond test was conducted for one half of the specimens after a dry storage in a desiccator at room temperature, i.e. in ‘dry storage conditions’ (labeled “Dry”). The other half (labeled “Tc”) were subjected to thermal stress for 6000 cycles at temperatures alternating between +5°C and +55°C with an exposure time of 30 s and a transfer time of 2 s. In addition, after a storage period of silane solutions in the dark at +4°C for 15 weeks, the shear bond strengths were measured once again using the same test setup as described above, to carry out the stability investigation. The silane solutions were allowed to stabilize to room temperature before use. Shear bond strengths were measured with a universal material testing machine (LRX, Lloyd Instruments Ltd., Fareham, UK), using a crosshead speed of 1.0 mm/min. This machine was used according to the recommendation stated in ISO 10477 [28]. The shear bond strength was calculated using NEXYGEN 2.0 software (Nexygen, Lloyd Instruments Ltd., Fareham, UK). The following formula was used to calculate the shear bond strength (σ):

$$\sigma = F/A,$$

where F is the applied load at the failure of the bond during the shear test and A is the cross-sectional area of resin stub.

2.5. Water Sorption Study

The water sorption test was based on ISO 3696:1987 (E) and carried out accordingly [29]. The test specimens ($N = 10$) were stored in contact with 15 ml of deionized Milli-Q water (grade 2) at +37°C in sealed polypropylene flasks for the following time periods: 0, 4, 5, 6, 7, 11, 15, 22, 36, 40, 99 and 187 days. The weight increase was calculated as the weight percentage (wt%) of the original test specimen.

2.6. Statistical Analysis

The mean values for shear bond strength data were analyzed in order to determine the statistical significance of the results using ANOVA. The statistical analysis was performed using SPSS (Statistical Package for Social Science, SPSS Inc., Chicago, IL, USA) software for Windows. The dependent variable (shear bond strength) was discussed in terms of the independent variables (i.e. the pH value and hydrolysis time of silane, alcohol type, and submission of specimens to thermal stress), followed by *post-hoc* test.

3. Results

ANOVA revealed that the independent variables (see Section 2.6) had some effect on shear bond strength. However, one of the independent variables, i.e. subjecting the specimens to thermal stress, had the most significant effect. In dry storage conditions, the shear bond strengths varied between 7.6 and 10.9 MPa (ANOVA, $p < 0.05$), when the Ti-substrate was silanized using MPS in *i*-PrOH/H₂O solution. The highest shear bond strength was obtained (10.9 MPa) at pH 4.5 in *i*-PrOH/H₂O solution, whereas the lowest value was 6.5 MPa at pH 4.5 obtained using MPS in EtOH/H₂O solution. After thermo-cycling, the shear bond strengths of all test groups were reduced in both alcohol/water solution types and at all three pH levels. In the case of 1 h hydrolysis for the silane solution and after subjecting to thermal stress, the shear bond strength was least reduced at pH 4.5 from 6.5 MPa to 6.3 MPa (ANOVA, $p < 0.05$), when Ti-substrate was silanized with MPS in EtOH/H₂O. In the case of MPS in *i*-PrOH/H₂O solution, the shear bond strength least reduced at pH 5.5 (from 7.5 MPa to 5.8 MPa).

Figure 4 shows the results of shear bond strength measurements before and after the stability investigation of different silane solutions. For silane solutions aged for 15 weeks, the shear bond strengths were observed to be numerically higher in both alcohol/water solutions and at each pH level tested. The highest shear bond strength was achieved at pH 4.5 and the lowest at pH 5.5. In the case of MPS in EtOH/H₂O solution, the highest shear bond strength was 12.4 MPa in dry conditions (dry storage) at pH 4.5. In the case of MPS in *i*-PrOH/H₂O solution at pH 5.5 after dry storage, the shear bond strength was the lowest i.e. 8.5 MPa (ANOVA, $p < 0.05$).

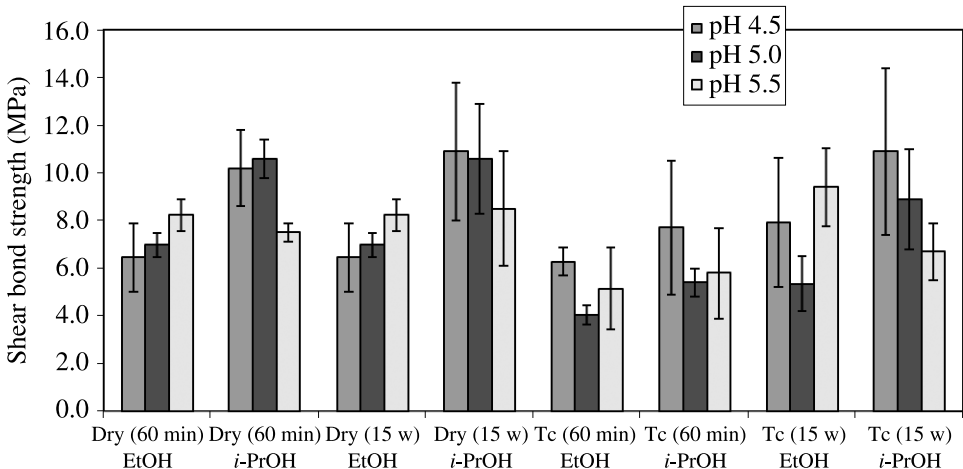


Figure 4. The shear bond strength of the specimens prepared using either ‘fresh’ silane solution, i.e. the hydrolysis reaction time for MPS silane in ethanol (EtOH) and *iso*-propanol (*i*-PrOH) solutions was 1 h, or silane solution after 15 weeks (w) hydrolysis reaction time. The tests were performed either after dry storage conditions (‘Dry’) or after subjecting to thermo-cycling (‘Tc’). Different bars indicate the pH value of silane solution.

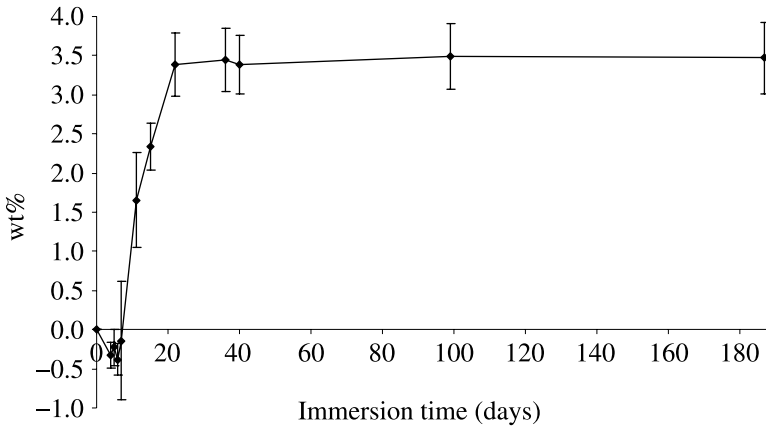


Figure 5. The curve demonstrates the weight increase during the water sorption test for the experimental dental resin.

Thermo-cycling also reduced the shear bond strengths, when 15-week-old silane solutions were employed. However, the shear bond strengths did not decrease significantly at pH 4.5 in the case of MPS in *i*-PrOH/H₂O solution.

Figure 5 shows the change in weight during the water sorption test. After 7-day immersion time, the water sorption first slightly decreased the weight of the specimens (*ca.* 0.4 wt%), because of the release of unreacted residual monomers. After 11-day immersion time, the weight of the specimens increased by *ca.* 1.7 wt%. The saturation point of water sorption was achieved in 22 days, after which the weight of specimens remained constant. At the end of water uptake capacity measurement, the weight of specimens had increased by approximately 3.5 wt%.

4. Discussion

The new information obtained in this study on adhesion promotion with MPS solutions should improve understanding and application of the silane-aided bonding concept. In addition, the ageing time study of experimental silane solutions has some scientific interest, since no inhibitors were used in the experimental solutions to inhibit the hydrolysis of MPS. Previously, it had been reported that the metal cleaning procedure as well as the concentration and pH value of silane affect the formation of silane films *i.e.* silane deposition time and the rate of adsorption onto metals, thus affecting substantially the adhesion promotion performance [3, 12]. Therefore, in this study, the effects of pH and the aliphatic alcohol solvent system used for the bonding capability of the silane molecule between *bis*-GMA/MMA resin system and silica-coated Ti surface were evaluated. Moreover, the effects of subjecting the experimental resin stubs to thermal stress (artificial aging) and the stability of silane solution after 15 weeks aging were studied based on the fact that dilute MPS solutions are known to retain their coupling properties for a long period [30]. 15 weeks correspond to a clinically relevant time period for checking the sta-

bility of experimental silane solutions. There has also been continued interest and demand in developing experimental silane-based adhesion promoters for applications in dentistry and in general in adhesion technology.

The tested silane of interest and choice was MPS (0.01 vol%) in *iso*-propanol (*i*-PrOH)/H₂O or ethanol (EtOH)/H₂O solutions, in which pH had been adjusted to 4.5, 5.0, or 5.5. For one half of the specimens, the shear bond test was conducted after storage in dry conditions at room temperature for 2 h, whereas the other half were subjected to thermal stress (thermo-cycling) to simulate the aging process in oral environment. The other tested materials, Ti and *bis*-GMA/MMA resin, were selected because of their broad utilization not only in dentistry but also in some medical devices [31]. Actually, Ti works excellently as a biomaterial and its surface is easy to modify with silanes, in principle, without [22] or with silica-coating, because of its pre-existing thin oxide layer on its outermost surface [10]. However, silicatization is often recommended prior to silanization in stead of a direct silanization [4, 20, 21]. Although, MPS has shown some preliminary signs of osteoconductive properties but still can be a relevant silane of choice in biomaterials research [32].

In dental laboratories, tribochemical Rocatec™ (3M/Espe) system as a custom pretreatment method is widely employed for metals, amalgams and ceramics [6, 23]. In this study, the Rocatec™ treatment was supposed to produce a relatively uniform and visually rough (Al₂O₃+ SiO₂) outer layer on Ti surface. Figure 3 shows the test setup for measuring the shear bond strength. In terms of tribochemical Rocatec™ treatment, the sandblasting of Ti plates created a microretentive Ti surface. This means that the adhesion of the studied resin system will increase, as Matinlinna and co-workers had previously reported [21, 22]. Therefore, in this study, the failure of the bonds during the shear test was also cohesive in the resin for all specimens. Before the application of the experimental resin onto Ti substrate, the Rocatec™ treated surface was silanized using four different silane solutions (*cf.* types 1–4, Table 2) with controlled pH levels. The pH levels used were based on of the most often used pH values in the literature with MPS. Figure 1 shows two key reactions that are supposed to occur in the silane solution during its hydrolysis [1, 2]. In the first step, the alkoxy groups are hydrolysed resulting in intermediate silanol species. The reaction is relatively fast for the kinetically labile methoxy groups. In the second step, the silanols condense to form hydrogen bonds and siloxane bonds (–Si–O–Si–) to connect the monomer resin phase chemically to the conditioned Ti substrate [4]. In fact, it has been proposed that the pH level may control both the hydrolysis and condensation reactions in dilute silane solutions [33]. In addition, these two primary reactions can also be influenced by other solution variables such as catalyst, silane concentration, and temperature, which are beyond the scope of this study but have been discussed by others [34, 35]. In fact, the hydrolysis of MPS does not require addition of any acids, because the deionized water is slightly acidic, *i.e.* its pH is between 6 and 7. If acid is added to the diluted MPS solutions, the kinetically controlled hydrolysis reaction will be faster and more effective. Therefore,

after 15 weeks, it is most likely that MPS would undergo hydrolysis in pure deionized water, too. This effect will be studied further.

The solvent might affect the siloxane film formation and hence adhesion promotion. Therefore, two aliphatic, “typical” alcohols were employed for comparing the obtained shear bond strengths at three pH values in two hydrolysis and ageing times. However, methanol as the simplest aliphatic alcohol was excluded from the test setup due to its obvious hazards (toxicity). According to the shear bond strength results, *i*-PrOH seems to be a more suitable solvent in conjunction with water for the MPS solution, in particular, if the hydrolysis time is relatively short. An explanation could be the very high surface energy of the Al₂O₃ + SiO₂ coated Ti surface, and lower surface tension of *i*-PrOH resulting in easier wetting as well as slightly slower evaporation of *i*-PrOH (bp. 82°C, STP) compared with ethanol (bp. 79°C, STP). Thus, the ratio between surface tension and viscosity has been reported to be higher for EtOH than *i*-PrOH [36]. Therefore, a binary mixture of *i*-PrOH and water might form a siloxane film more prone to promote adhesion on the outermost surface of the metal substrate. This effect should be investigated further in the future. This research also confirmed that 1 h time period is long enough for activating the inorganic groups in MPS molecule in *i*-PrOH/H₂O.

In dry storage conditions, the highest shear bond strength obtained was 10.6 MPa, comparable to the value obtained with MPS in EtOH/H₂O, where the highest mean shear bond strength was 8.2 MPa (ANOVA, $p < 0.05$). In addition, the lower pH value seems to activate a rapid hydrolysis reaction of MPS in *i*-PrOH/H₂O solution. When silanization was carried out using 15-week-old MPS prepared in *i*-PrOH/H₂O at pH 4.5, the shear bond strengths obtained were slightly higher, even after thermo-cycling. If the stability test storage time had been longer, the bonding capability of MPS might have decreased. We observed that MPS in *i*-PrOH/H₂O already showed some signs of ageing, i.e. initial SiO₂-gel formation. Such gel-like Si obviously makes the coupling properties inferior. To activate the alkoxy groups of MPS in EtOH/H₂O, 1 h hydrolysis time is usually enough [5, 10, 20]. Interestingly, the highest shear bond strength (12.4 MPa) in EtOH/H₂O was obtained at pH 4.5 using a silane solution that had a hydrolysis period of 15 weeks. The hydrolysis in EtOH/H₂O seems to occur at a slower rate by hindering the very rapid condensation of activated silane, which apparently occurs due to the presence of appropriate catalyst [20–22]. Therefore, the reaction activity of MPS in EtOH/H₂O solution may be increased after 15 weeks hydrolysis. This behaviour merits further investigation in the future.

It has been shown that both the shear bond strength and tensile bond strength depend highly on the materials and the geometry of the test arrangement [37]. Moreover, mechanical testing for the strength of a material is a substantially more complicated issue than it appears at first sight. The definition is easy enough: stress at failure but the ultimate question remains: does the testing simulate adequately the real clinical conditions in the oral environment [38]? It can be summarized that in dental materials science, the shear bond strength is a widely used variable for

estimating how strong the union between dissimilar dental materials would be. In this study, the number of specimens in a single test-group was relatively low, i.e. six. Nevertheless, such numbers are statistically relevant and have, in principle, successfully been used in dental materials research and testing previously [20, 39].

The silanization process was based on an aqueous silane solution at controlled pH. Typically, the pH range between 4.5 and 5.5 is commonly used for silane solutions based on published literature [1, 4, 10, 11, 20]. Some investigations have indicated that the pH of an organosilane coupling agent solution can also influence the nature of the various reactions which occur in solutions [35]. In the analysis of data between the groups, there were many independent variables (i.e. the pH and hydrolysis time of silane, alcohol type, and subjecting to thermal stress) as well as their interactions that had some effect on the shear bond strengths. Thermal stress caused the most significant difference between the shear bond strengths of various groups. In addition, the hydrolysis of MPS occurred most readily in the solution containing *iso*-propanol. This study did not find a significant relationship between pH in the range of 4.5–5.5 and shear bond strengths for the two solvent systems tested. Nevertheless, silane solutions with the lowest pH value (4.5) seemed to produce, on average, slightly higher bond strengths than those obtained with silane solutions with higher pH values, in the case of MPS dissolved in *i*-PrOH/H₂O. The tested pH range was selected on the basis of the literature [1, 4, 5] and in the future studies we may widen this range. The polarity of tested alcohol solvents did not differ enough: the polarity index for EtOH is 5.2 and that for *i*-PrOH is 4.0 [40]. Therefore, future studies could assess the effect of lower and higher pH values using other types of alcohols, e.g. 1-butanol or the highly polar, electronegative 2,2,2-trifluoroethanol.

Figure 4 presents the results of thermo-cycling and silane stability (storage) tests. As expected, thermo-cycling produced lower mean shear bond strength values with all silane solutions. According to the literature, thermo-cycling is generally known to decrease the shear bond strengths [10, 20–22, 25]. However, after 15 weeks of ageing, the shear bond strengths were found to be relatively sufficiently high, if MPS in *i*-PrOH/H₂O solution, adjusted at the lowest used pH value, was employed. Interestingly, the shear bond strengths did not decrease significantly after exposure to thermal stress. The relatively rapid hydrolysis of MPS in *i*-PrOH/H₂O solution can thus be considered to occur in stable conditions, if the silane solution is stored carefully in sealed flasks in the dark at +4°C prior to the bonding procedure. In addition, the thermal stress might, to some extent, increase the condensation reaction of this kind of MPS solution. However, this needs to be investigated more precisely to obtain further evidence of this presumption. In the case of EtOH, it was recognised that the age of the silane solution played an important role and had influence on shear bond strength. After subjecting to thermal stress, the highest shear bond strength was obtained at the highest pH value in EtOH/H₂O solution. According to the results of shear bond strengths, the most suitable pH value for activating MPS in

EtOH/H₂O solution was 5.5, whereas the activation in *i*-PrOH/water solution was found to be most effective at pH 4.5.

Water sorption of polymers plays an important role in long-term stability of dental appliances in an aqueous environment [27]. Therefore, it was also relevant to study the diffusion of water molecules into the experimental polymer used in this research. According to the results of water sorption, the weight of specimens first decreased by 0.4 wt% in 7 days. The weight loss most probably indicates that unreacted residual monomers in the polymerized *bis*-GMA/MMA resin were released (this was not detected by chemical analysis, though). In the course of time, the water sorption then stabilized within 22 days, when the weight of specimens had increased by *ca.* 3.5%. After 22 days, the amount of water did not increase during the subsequent period of 165 days. According to the results of this water sorption and bond durability study, MPS in either EtOH/H₂O or *i*-PrOH/H₂O solution, is a suitable promoter in the adhesion of *bis*-GMA/MMA resin to silica-coated Ti substrate, when the pH of silane solution is between 4.5 and 5.5. Moreover, the water sorption of the experimental dental resin was relatively low.

5. Conclusions

Within the limited scope of this pilot study, the following conclusions can be drawn:

- (1) The pH range of 4.5 to 5.5 is relevant to activate MPS in the studied two solvent systems, based on EtOH and *i*-PrOH, and with a final hydrolysis time of 15 weeks.
- (2) In the case of *i*-PrOH/H₂O at pH 4.5, the highest adhesion promotion capacity for MPS was obtained within 1 h. The thermal stress (i.e. aging by thermo-cycling) did not reduce the shear bond strength values significantly, i.e. from 10.2 MPa to 7.7 MPa (ANOVA, $p < 0.05$). In addition, if 15 weeks old silane solutions were used for adhesion promotion, the shear bond strength values did not decrease dramatically, i.e. $\sim 1\text{--}4$ MPa/test group.
- (3) The water uptake of the experimental *bis*-GMA/MMA-based non-filled polymer was *ca.* 3.5 wt% in 187 days.

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