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Long-term bond strength stability of novel organic–inorganic hybrid sol–gel coatings applied to titanium and cobalt-chromium alloys

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ABSTRACT

Water penetration into coating and bonding layers is still considered to negatively affect long-term material stability. This is particularly true when bonding dissimilar materials in applications where water is omnipresent and metal alloys are used. Unfortunately, conventional metal primers still bear a significant risk of continuous bond strength decline, especially after long-term storage in a wet environment.

This study evaluated the impact of various organic–inorganic hybrid sol–gel interlayers on the long-term shear bond strength (SBS) of a bone cement to TiAlNb and CoCrMo alloys. Three *in situ* hydrolyzed alkoxysilanes (3-methacryloxypropyltrimethoxysilane, 1,2-*bis*- (trimethoxysilyl)ethane, 3,3,3-trifluoropropyltrimethoxysilane) and their various combinations were investigated after previous application of titanium-(IV)-tetraisopropoxide (TTP) on grit-blasted metal surfaces. For each silane combination, SBS data were determined followed by statistical evaluation and fracture surface examination.

The novel sol–gel coatings show markedly improved long-term bond strength stabilities after accelerated aging in water (24 h, 80 °C) and long-term immersion in saline solution (365 d, 37 °C). Previous application of TTP on grit-blasted surfaces appeared to be vital for a bond strength improvement of 245 %. Preliminary results in saline solution show an even longer bond strength stability of more than 2 years, which makes these systems particularly interesting for use in biomedical applications.

1. Introduction

Effectively eliminating water penetration into coating layers to prevent moisture-induced surface deterioration and thus avoid subsequent property decline and material failure of the underlying structures in the long term is a general challenge in technical applications [1,2]. Similar deleterious effects of water are well-known in adhesive bonding technology, where bond strength stability may be significantly impaired over time [3]. Hence, water is commonly considered to adversely affect the stability of coating and bonding layers due to hydrolytic degradation [4,5] as well as swelling and plasticization processes [6,7], which often occur simultaneously. While hydrolytic degradation is generally associated with irreversible processes, such as cleavage of chemical bonds, chain scission and mass loss that frequently result in permanent changes of material properties [8,9], swelling and plasticization processes often appear to be repeatedly reversible in artificial restorative materials [10,11] as well as in biological structures [12–14] and may significantly contribute to the stability in wet environment especially in biological adhesive systems [15]. Whether hydrolytic degradation or swelling processes predominate is mainly determined by the chemical composition and structure of the joined materials and the adhesive material itself. Therefore, new artificial adhesive systems need to be specifically designed to fit as closely as possible to the chemical, physicochemical and structural conditions being predefined by the surfaces to be joined [16]. Inspiration for well-considered structure and bonding designs can be gained from a multitude of natural adhesives [17,18].

For a durable bonding of artificial polymer structures, such as poly (methyl methacrylate)-based bone cements [19–21], to biomedical alloys like titanium [22], two design strategies may be pursued in applications where water is omnipresent. One approach is to develop new,

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sophisticated adhesive systems that are fully compatible with a wet environment and can even function in underwater applications [23]. Another strategy is to further develop existing bonding materials, which then provide considerably improved water-resistant or even water-repellent properties to prevent deleterious effects on bond strength stability as much as possible. As an important prerequisite, both concepts may require the presence of sufficiently roughened adhesive surfaces. This can be simply achieved through traditional surface grinding processes using diamond burs or abrasive papers [24] or with modern grit-blasting procedures, which are used in technical [25] and medical applications [26,27]. Unfortunately, however, this kind of surface roughening facilitates water uptake. Although alternative and modern techniques exist for surface treatment to join polymers to metals, either by 'direct surface etching' [28] or by 'laser-assisted metal and plastic joining' [29], the problem of a deleterious water-ingress can not be adequately prevented. A further application of resin-based adhesion promoters therefore appears to be inevitable.

Following the second design strategy outlined above, metal primers for dental applications have previously been considered for improving bond strength stability [30]. These are commercially used at a broader level and are based on pure organic resin components comprising polymerizable methacrylate groups, as well as carboxylic acid, phosphoric acid, and acid anhydride groups [31,32], or belong to the group of silane precursors, such as 3-methacryloxypropyltrimethoxysilane (3-MPS) [27]. Unfortunately, both systems inherently possess more or less hydrophilic material properties and, on their own, were not yet capable of reducing water-induced bond strength declines in the long-term [30,32–34]. Despite this, silane-based chemistry offers a significant opportunity to systematically achieve targeted molecular designs for the more effective introduction of hydrophobic and water-resistant properties, as well as strength, into bonding layers. This is because, from the multitude of different silane precursors available with specific molecular structures and their particular properties, some can be purposefully selected and combined to build up the required bonding characteristics in the final coating application. Specific material properties may be designed at the molecular level. Hence, in recent years, there has been a growing interest in organic–inorganic hybrid sol–gel chemistry [35], which is used in both technical [36] and medical [37,38] applications as well. Highly promising approaches have been reported that utilize these systems to permanently protect vulnerable surface structures, especially those of metals, from detrimental water-induced corrosion processes [39,40]. Nevertheless, little information is available regarding the efficacious use of sol–gel-derived coating and bonding layers to join dissimilar materials in technical [41–43] and medical [38,44,45] applications.

Existing metal primers and silane blends currently used as adhesion promoters exhibit two major problems that should be considered in future developments to prevent systems from suffering from long-term degradation. First of all, grit-blasting with silica or aluminum oxide *per se* generates very hydrophilic surface structures, which later need to be covered as much as possible with adhesion promoter molecules to avoid the existence of free areas where water may be attracted and simply adhered. Often, existing metal primers and previously described coatings are not capable of acting as a tight sealant because their molecular structure is inappropriate for forming stable three-dimensional networks and, with that, impermeable sealings on the entire surface. Secondly, most coating layers contain hydrophilic moieties in their molecular structure, which are necessary to achieve strong adhesion to the polar surface previously activated via a grit-blasting process. This molecular structure is responsible for the fact that polar water molecules may be additionally attracted to the surface. The phenomenon is pronounced in pure silane-based systems, where *per se* free hydroxyl functions may be present due to a ubiquitous equilibrium process between bridged −Si-O-Si- moieties and free Si-OH molecule fragments [46].

To ensure that the two major problems described above do not occur in our investigation, we deliberately decided to implement titanium-(IV)-tetraisopropoxide (TTP) in our study design. It was intended to be used directly after the grit-blasting process to further activate the metal surface. This sol–gel precursor was previously described as introducing distinct water-resistant properties to surface structures [40,47–49] while also improving physical properties [49]. To further develop the water-resistant properties of the newly formulated metal coating, the application of a specifically designed silane blend that completely withstands water penetration, was considered. The combination of 3-MPS with 1,2-*bis*- (trimethoxysilyl)ethane (BTSE) together with heat application for the condensation process appeared to be very suitable because previous investigations had already demonstrated the ability of BTSE to form exceptionally water-repellent, three-dimensional network systems in technical [50,51] as well as medical applications [38,52,53]. Finally, the versatile chemistry of silane-based systems includes fluorinated sol–gel precursors that enable the design of water-repellent coatings. As previously reported, silanes such as 3,3,3-trifluoropropyltrimethoxysilane (TFPS) have been shown to be highly effective in the long term [54,55], and were therefore chosen for the composition of the newly designed sol–gel metal primer in the present study.

Little information is available in the literature about the long-term ability of metal bonding systems to resist the deleterious effects of water steadily penetrating into adhesion layers, which ultimately has a destructive impact if bonding strength decreases by more than 50 %. Therefore, the aim of this *in vitro* study was to investigate the influence of various organic–inorganic hybrid sol–gel coatings based on TTP, BTSE, 3-MPS, and TFPS, which are optimized to function as metal primers, on shear bond strength (SBS) stability and the durability of fixation of a bone cement on TiAlNb and CoCrMo alloys.

The null hypotheses tested were: SBS is independent of (A) the coupling agent, (B) the storage temperature, and (C) the storage time in sodium chloride solution.

2. Materials and methods

2.1. Metal substrates

Using solid femoral stems (Table 1) bar-shaped specimens (20.0 mm x 8.0 mm x 3.0 mm ± 0.1 mm) were prepared for each metal (TiAlNb, CoCrMo) by standard water-jet cutting (Womajet, Daetwyler, Bleienbach, Switzerland; cutting pressure: 350 MPa, feed motion: 200 mm/min, abrasive: water and garnet sand (0.125 mm)) to avoid any thermal impact on surface structures. To guarantee consistent and standardized test surface conditions, all specimens were finally polished using water-cooled mechanical polishing. Successively P800 and P4000 grade SiC paper (Leco Corp., St. Joseph (MI), USA) were used on a plate grinder (400 CS, Exact GmbH, Norderstedt, Germany; speed of rotation: 75 rpm) with a 5 min polishing time for each abrasive paper.

2.2. Surface treatment

All procedures were carried out under an air-conditioned laboratory atmosphere (23 ± 1 °C; 50 ± 5 % relative humidity).

2.2.1. Grit-blasting

Surface treatment was carried out prior to coupling agent application for both metals with a grit-blasting process using Al_2O_3 abrasive particles (Table 1) in combination with a commonly used dental grit-blasting unit (Basic quattro, Renfert GmbH, Hilzingen, Germany). To allow for differences in metal hardness, different grit-blasting pressures were used for TiAlNb (0.4 MPa) and for CoCrMo (0.5 MPa) during the blasting process to achieve similar surface roughness data approaching optimum values for dental (Titanium: 3.0 μm ≤ R_a ≤ 4.5 μm [56]) and orthopedic (Titanium: 1.0 μm ≤ R_a ≤ 2.5 μm [57]) applications. The surface roughness was characterized via R_a, R_z and R_{max} values (Table 2) determined for three independent samples of each metal using an optical profilometer (MicroProf 200, Fries Research & Technology GmbH,

Table 1
Materials used in this evaluation study.

Material	Trade name	Code	Manufacturer	Lot No.
Ti-6Al-7Nb alloy	CLS Spotorno	TiAlNb	Zimmer Biomet Deutschland GmbH, Freiburg, Germany	ISO 5832–11
Co-28Cr-6Mo alloy	Lubinus Classic Plus	CoCrMo	Waldemar Link GmbH & Co. KG, Hamburg, Germany	ISO 5832–4
Reference Metal Primer	Metal Primer Z[#]	MP-Z	GC Corporation, Tokyo, Japan	1902271
Metal alkoxide	Titanium-(IV)-tetraisopropoxide (97 %)*	TTP	ABCR GmbH, Karlsruhe, Germany	1440-S
Silane	3-Methacryloxypropyltrimethoxysilane (98 %)*	3-MPS	ABCR GmbH, Karlsruhe, Germany	1176419
	1,2-*Bis*-(trimethoxysilyl)ethane (96 %)*	BTSE	Sigma-Aldrich Chemie GmbH, Steinheim, Germany	MKBP3281V
	3,3,3-Trifluoropropyltrimethoxysilane (97 %)*	TFPS	ABCR GmbH, Karlsruhe, Germany	1366232
Bone Cement, PMMA-based	Palacos R	n.a.[$]	Heraeus Medical GmbH, Wehrheim, Germany	91664796
Abrasive Al_2O_3	Plurakorund Al_2O_3 250 μm	n.a.[$]	Pluradent GmbH & Co. KG, Offenbach, Germany	20190540
Acetone p.a. > 99.8 %	n.a.[$]	n.a.[$]	Carl Roth GmbH + Co. KG, Karlsruhe, Germany	014349597
Ethylacetate ≥ 99.8 %	Suprasolv	n.a.[$]	Merck KGaA, Darmstadt, Germany	1049789940
1.0 mol/l Hydrochloric acid	Titripur	HCl	Merck KGaA, Darmstadt, Germany	HCl4934557
Distilled water, sterile	Aqua B. Braun	n.a.[$]	B. Braun Melsungen AG, Melsungen, Germany	221428001
0.9 % Sodium chloride solution	Infusion solution	n.a.[$]	B. Braun Melsungen AG, Melsungen, Germany	18511451

[#]Composition from material safety data sheet: Ethanol (90 – 100 %), 10-Methacryloyloxydecyl dihydrogen phosphate (1.0 – 2.5 %).
*Used as supplied by the manufacturer without further purification or distillation.
[$]n.a., not applicable; PMMA, Poly(methyl methacrylate).

Table 2
Mean surface roughness data of metal specimens directly after sandblasting.

	Co-28Cr-6Mo blasted with 0.5 MPa	Ti-6Al-7Nb blasted with 0.4 MPa
R_a [μm]	3.52 ± 0.14	3.88 ± 0.26
R_z [μm]	27.43 ± 1.79	28.46 ± 3.29
R_{max} [μm]	36.39 ± 3.17	37.23 ± 4.42

Bergisch Gladbach, Germany). A 600 μm sensor with a precision of 200 nm and a vertical resolution of 20 nm was used, and the investigated area was 4.00 mm x 1.20 mm in size (sensor frequency 1000 Hz). Surface characteristics were analyzed using Mark III Software (release 3.11.5.2, FRT, Fries Research & Technology GmbH, Bergisch Gladbach, Germany).

2.2.2. Coupling agent application

All chemical raw materials, solvents, and cement components were weighed with an analytical balance (XS205 Dual Range, Mettler Toledo GmbH, Giessen, Germany; accuracy: ± 0.01 mg). Flasks and bottles were closed as soon as possible to avoid extensive contact with humidity.

The commercial metal primer 'MP-Z' was applied onto the specimen surfaces according to the respective user instruction using a dental brush with only one separate layer, followed by gentle air-blowing with oil-free compressed air to remove residual solvents.

In the case of experimental coupling agents, which were used in combination with (TTP), a new 7.5 wt% solution of TTP in ethyl acetate was prepared *in situ* using a 10 ml round-bottom flask with a ground-glass joint to ensure as little air contact as possible. The content of the closed flask was mixed using a magnetic stirrer (MR 3001 K, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) for about 10 s, and a glass pipette was used to apply two drops of the prepared solution in the center of each specimen surface, respectively. Immediately afterwards, every specimen was twisted and waved in the air to homogenously spread the solution on the specimen surface and concurrently evaporate residual solvents. Each specimen was stored at ambient laboratory conditions for 10 min before subsequent silane application (Fig. 1A).

For the silane application, newly prepared solutions of no further purified alkoxysilanes or alkoxysilane mixtures (0.200 g) in acetone (2.00 g; 9.09 wt%) were hydrolyzed *in situ* by adding 0.030 g 0.1 mol/l HCl.[1] In each case, separate 10 ml round-bottom flasks with a ground-glass joint and a magnetic stirrer (MR 3001 K, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) were used. Details of the different experimental coupling agent compositions and the specific silane ratios are listed in Table 3. The freshly prepared and acidified silane solutions were promptly stirred at room temperature for exactly 5 min, and then a glass pipette was used to apply two drops to the center of each separate specimen surface for each metal group. All specimens were immediately twisted and waved in the air to homogenously spread the solution on the surface and simultaneously evaporate residual solvents. Each specimen was stored at ambient laboratory conditions for 30 min before subsequent heat application at 80.0 ± 0.4 °C in an incubator (Thermo Scientific Heratherm, Thermo Fisher Scientific, Waltham (MA), USA), where all specimens were placed on a preheated 15 mm-thick glass plate. After 60 min, specimens were removed from the oven and cooled down to room temperature, immediately followed by the application of bone cement (see Section 2.2.3).

2.2.3. Bone cement application

By means of a modified bonding clamp device (Fig. 2) from the UltraTester™ system (Ultradent Inc., South Jordan (UT), USA) polyoxymethylene (POM) tubes (inner diameter 5.00 ± 0.01 mm, height 8.00 ± 0.10 mm) were used as mold inserts. They were centrally positioned on the respective specimen surface immediately after the coupling agent was applied and tightly fixed by simultaneously screwing both bolts of the bonding clamp device to the same level (Fig. 2) [30]. To avoid overload and tilting of the specimens during the mounting procedure, two aluminum plates (25.0 mm × 15.0 mm × 5.0 mm ± 0.1 mm) covered with a 1.0 mm thick heat-shrink tubing (Bauhaus, Mannheim, Germany) were used as compensation plates (Fig. 2).

Powder and liquid of the high-viscosity bone cement Palacos R (Table 1), typically used for endoprosthetic reconstructions [58], were mixed as recommended by the manufacturer (weight ratio powder/liquid = 2/1) for no longer than 30 s in a Resimix mixing vessel (SCHEU-DENTAL GmbH, Iserlohn, Germany). The resulting dough was directly filled into the mold inserts and immediately pressed onto the specimen surface via a perfectly fitting metal rod (4.95 ± 0.05 mm in diameter), which was concurrently weighted with two 1.0 kg weights (19.62 N) using a parallel press. Chemical curing was performed under ambient laboratory conditions for 15 min without any further treatment of the respective specimen. On a timely basis, 10 specimens from each metal group were stored in the respective storage media described in Section 2.3. Specimens where the bone cement dough was squeezed out between the mold insert and the specimen surface were discarded and then newly prepared to ensure a uniform and consistent bonding surface area for the cement pin (Fig. 1B).

[1] prepared by dilution of 1.0 mol/l HCl.

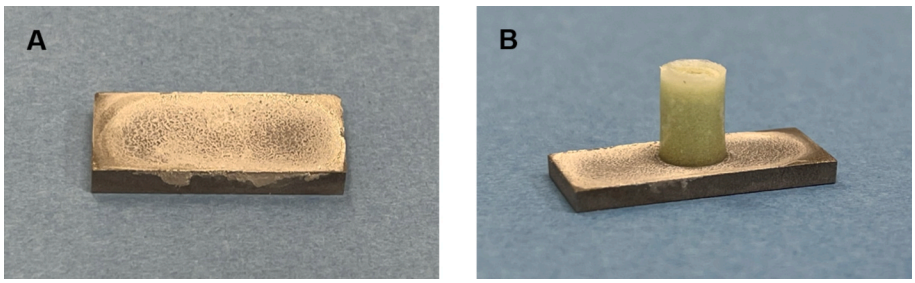


Fig. 1. Exemplary CoCrMo specimen surfaces after (A) TTP application and (B) curing of a bone cement pin.

Table 3
Composition of tested experimental silane coupling agent combinations.

Silane coupling agent	TTP/wt %[#]	3-MPS/ g	BTSE/ g	TFPS/ g	Aceton/ g
TTP/3-MPS	7.5	0.200	–	–	2.0
TTP/3-MPS/BTSE	7.5	0.150	0.050	–	2.0
3-MPS/BTSE	–	0.150	0.050	–	2.0
TTP/3-MPS/BTSE/ TFPS	7.5	0.120	0.040	0.040[§]	2.0

[#] solution in ethyl acetate.
[§] optimal concentration of previously tested various combinations.

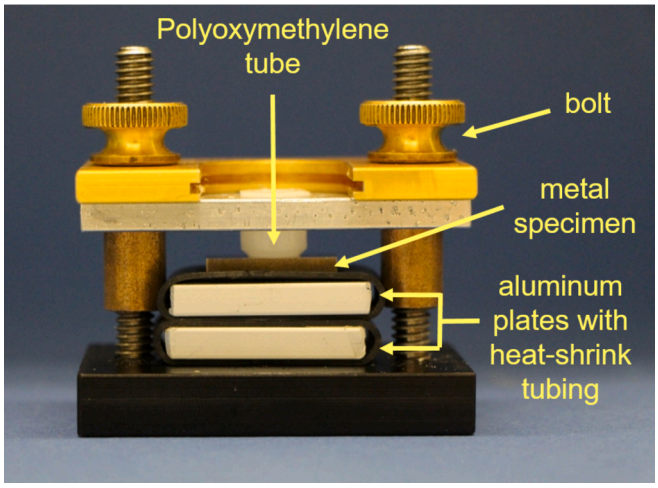


Fig. 2. Modified bonding clamp device from the UltraTester™ system.

2.3. Storage conditions

2.3.1. Short-term storage

For a quick and reliable evaluation of different experimental coupling agent compositions and to determine the effect of their various silane combinations on bond strength data, only TiAlNb surfaces were tested initially. For each series, respectively, 10 specimens were stored 24 h in distilled water using glass vessels at 37 °C and 80 °C. An incubator with 37.0 ± 1.0 °C (Ehret, Emmendingen, Germany) was used to simulate body temperature in a wet environment and a second incubator with 80.0 ± 0.4 °C (Thermo Scientific Heratherm, Thermo Fisher Scientific, Waltham (MA), USA) was chosen to assess the long-term stability of bond strength data after accelerated aging as early described by Plueddemann for 70 °C [59] and in the meantime proven and established for 100 °C [60,61]. Afterwards, specimens were removed one by one from the respective storage medium and dried on filter paper until they were free from visible moisture for no longer than 1 min. Then SBS testing was immediately performed (see Section 2.4).

2.3.2. Long-term storage

To allow for a more realistic assessment of the long-term bond strength stability for each metal group, both TiAlNb and CoCrMo, with 32 specimens each, were investigated after long-term immersion in a 0.9 % sodium chloride solution at 37.0 ± 1.0 °C in an incubator (Ehret, Emmendingen, Germany). After partial storage times of 1 d, 180 d, and 365 d in each case, 10 specimens were removed from the liquid medium, dried on a filter paper until free from visible moisture for no longer than 1 min, and promptly subjected to SBS testing (see Section 2.4). Additionally, for each metal and experimental coupling agent, two intentionally left single specimens were removed from the liquid medium after a further storage time of one year and two years to be tested as described above.

2.4. Shear bond strength testing

An SBS test was chosen for bonding system evaluation, which is also well-established for bond strength testing in dentistry (ISO 10477:2020) [62]. A universal testing machine (Z020, Zwick/Roell, Ulm, Germany) with a 2.5 kN load cell and a crosshead speed of 1.0 mm/min was used to determine the maximum load F_{max} (N) until failure. To be able to report SBS values in MPa according to SBS = F/A the bonding area A (mm^2) of each separate specimen was individually calculated via the diameter (mm) of the respective cement pin using the related software of the testing machine (TestXpert II; release 3.2, Zwick/Roell, Ulm, Germany).

2.5. Failure mode evaluation

After shear bond testing the received fracture surfaces were examined using a digital light microscope (Smartzoom 5, Carl Zeiss Microscopy GmbH, Jena, Germany). Failure modes were recorded by a single calibrated observer. Adopted from Fonseca et al. [63] and his method to divide the fracture surface area into four quadrants for decision-making, failures were classified as pure adhesive fracture (no adhering particles from the opposite side), adhesive with partially cohesive fracture in metal (adhering metal particles on bone cement surface), adhesive with partially cohesive fracture in bone cement (adhering cement clusters and thin bone cement particle layers on metal surface), and finally pure cohesive fracture (complete failure in bone cement pin or metal).

2.6. Statistical analysis

An *a priori* sample size calculation was conducted using G*Power (Version 3.1.9.7, Heinrich Heine University, Düsseldorf, Germany). Based on preliminary experimental data from a previous study [30] – specifically, the comparison of bond strength properties (25.6 ± 2.5 MPa after 24 h vs. 19.6 ± 3.6 MPa after 150 days) – an effect size of d = 1.94 was calculated. With this effect size, a minimum sample size of n = 9 per group was determined to achieve a statistical power of 0.80 at an alpha level of 0.0083 (adjusted using Bonferroni correction for six pairwise comparisons).

Mean values and standard deviations of SBS results in megapascal (MPa) were calculated, and the normality of data distribution was tested

using Kolmogorov-Smirnov and Shapiro-Wilk tests. All statistical analyses were carried out using IBM SPSS Statistics for Windows (version 26.0.0.1, IBM World Trade Corporation, Armonk (NY), USA) at a significance level of $\alpha = 0.05$.

2.6.1. Influence of experimental coupling agents on the shear bond strength of TiAlNb surfaces

After splitting the original data set according to the metal 'TiAlNb' and to the storage time '24 h in distilled water', a 4 × 2 analysis of variance (ANOVA) was conducted with the factors 'coupling agent' (4) and 'storage temperature' (2). Simultaneously, effect sizes (partial eta squared) were calculated. The detailed influence of the independent variable 'coupling agent' on SBS data of TiAlNb surfaces was evaluated by a follow-up one-way ANOVA and *post hoc* comparisons using the Tukey's HSD test in case of homogeneity of variances and the Games-Howell test in case of inhomogeneity of variances. To equally investigate the influence of the independent variable 'storage temperature' on the SBS of TiAlNb surfaces, the Student's *t*-test was applied to determine significant differences between the two temperatures for each separate coupling agent.

2.6.2. Influence of the storage temperature on shear bond strength data and comparison to a reference metal primer

For both investigated metals, the SBS results of the reference 'MP-Z' were compared with those of the two most promising experimental coupling agents by splitting the original data set according to the respective 'metal', the 'storage time of 24 h in distilled water', and the respective 'storage temperature'. Significant differences between the SBS means of different coupling agents were determined by separate one-way ANOVAs with *post hoc* comparisons using Tukey's HSD test in case of homogeneity of variances and the Games-Howell test in case of inhomogeneity of variances. To further evaluate the effect of the independent variable 'storage temperature' in detail, the above data set was split differently according to the 'coupling agent', and the Student's *t*-test was applied to determine significant differences between the two storage temperatures for each separate 'coupling agent'.

2.6.3. Influence of the long-term storage time in sodium chloride solution

After a specific selection of the data sets for both experimental coupling agents and considering the different 'storage times in 0.9 % sodium chloride solution' at 37 °C a 2 x 2 x 3 analysis of variance (ANOVA) was conducted with the factors 'coupling agent' (2), 'metal' (2), and 'storage time in 0.9 % sodium chloride solution' (3). Simultaneously, effect sizes (partial eta squared) were calculated. To further evaluate the influence of the independent variable 'storage time in 0.9 % sodium chloride solution' on the long-term SBS in detail, the original data set was split according to the respective 'metal', 'storage temperature of 37 °C', and the 'coupling agent', followed in each case by a one-way ANOVA with *post hoc* comparisons using the Tukey's HSD test in case of homogeneity of variances and the Games-Howell test in case of inhomogeneity of variances. To further allow a comparison of the long-term SBS means received for both experimental 'coupling agents' at the same 'storage time', the above data set was differently split according to the respective 'storage time' and a Student's *t*-test was used to identify statistically significant differences between both coupling agents.

3. Results

Comparing just the SBS results obtained for all TiAlNb surfaces using a two-way ANOVA, the respective data sets revealed normal distribution and no violation of the assumption of variance homogeneity. Both independent variables 'coupling agent' and 'storage temperature' were statistically significant (Table 4). While the main effect of the 'coupling agent' yielded a remarkable effect size of 0.711, indicating that 71.1 % of the variance in the SBS was explained by the 'coupling agent' (F (3,72) = 59.1, $p < 0.001$), the main effect of 'storage temperature' yielded a lower effect size of 0.137, indicating that only 13.7 % of the variance in SBS was explained by the 'storage temperature' (F (1,72) = 11.4, $p = 0.001$). No significant interaction was found for these two independent variables (F (3,72) = 2.2, $p = 0.096$).

When comparing the long-term SBS results of both metals, determined after storage in sodium chloride solution, a three-way ANOVA revealed a normal distribution and no violation of the assumption of variance homogeneity for all data sets. For both metals, only the independent variable 'storage time' was statistically significant (Table 5), yielding an effect size of 0.219 and thus indicating that 21.9 % of the variance in the SBS was explained by the 'storage time' (F (2,108) = 15.1, $p < 0.001$). The variables 'metal' (F (1,108) = 1.7, $p = 0.192$) and 'coupling agent' (F (1,108) = 1.6, $p = 0.207$), as well as all possible interactions, were not statistically significant (Table 5) and therefore only the main effect was subsequently analyzed in detail.

Table 4
Results from the 4 x 2-ANOVA testing the effect of the factors coupling agent (4) and storage temperature (2) on the shear bond strength on titanium surfaces after storage in distilled water.

Independent Variable	Sum of Squares	*df*	Mean of Squares	*F ratio*	*p value*	Partial Eta squared
Storage temperature	126.5	1	126.5	11.4	0.001	0.137
Coupling agent	1964.6	3	654.9	59.1	< 0.001	0.711
Storage temperature × Coupling agent	73.0	3	24.3	2.2	0.096	0.084

p values < 0.05 designate significant differences.

Table 5
Results from the 2 × 2 × 3-ANOVA testing the effect of the factors coupling agent (2), metal (2) and long-term storage time in sodium chloride solution (3) on the shear bond strength.

Independent Variable	**Sum of Squares**	***df***	**Mean of Squares**	***F ratio***	***p value***	**Partial Eta squared**
Coupling agent	14.1	1	14.1	1.6	0.207	0.015
Metal	15.1	1	15.1	1.7	0.192	0.016
Storage time	265.2	2	132.6	15.1	< 0.001	0.219
Coupling agent × Metal	2.1	1	2.1	0.237	0.627	0.002
Coupling agent × Storage time	48.4	2	24.2	2.8	0.068	0.049
Metal × Storage time	10.5	2	5.3	0.601	0.550	0.011
Coupling agent × Metal × Storage time	1.6	2	0.8	0.091	0.913	0.002

p values < 0.05 designate significant differences.

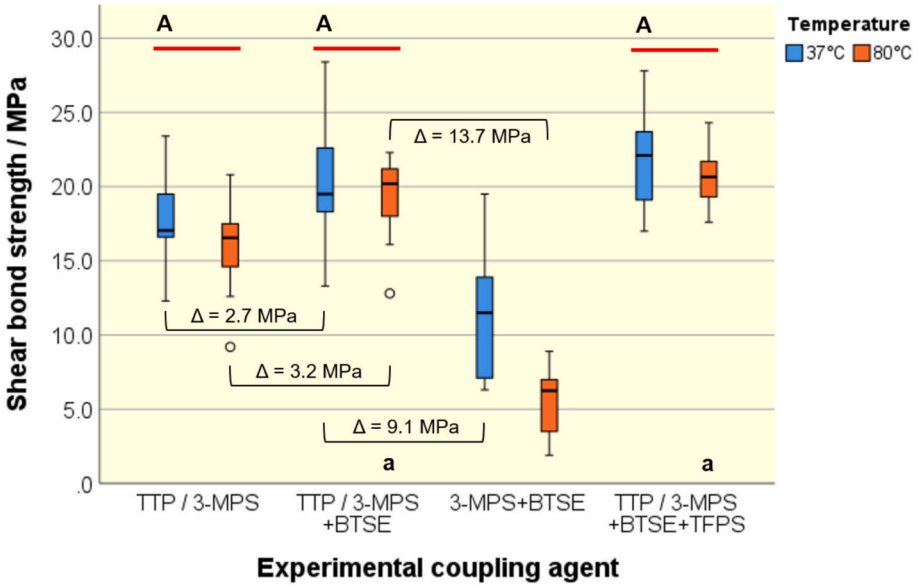


Fig. 3. Shear bond strength results for TiAlNb surfaces arranged according to the coupling agent and storage temperature after storage for 24 h in distilled water. Identical uppercase letters on the same level (on top) represent no significant differences among different coupling agents for the storage temperature of 37 °C ($p > 0.05$). Identical lowercase letters on the same level (below) indicate no significant differences among different coupling agents for the storage temperature of 80 °C ($p > 0.05$). A red bar above boxplots denotes no significant difference between 37 °C and 80 °C storage temperature for the same coupling agent. Circles represent outliers.

3.1. Influence of experimental coupling agents on the shear bond strength of TiAlNb surfaces

Detailed analysis of the calculated means for TiAlNb surfaces via one-way ANOVA and *post hoc* comparisons (Tukey's HSD test) always revealed the lowest SBS data after storage in distilled water for the coupling agent containing no titanate component TTP ('3-MPS + BTSE'), irrespective of the investigated storage temperature ($p < 0.001$; Fig. 3). Conversely, the strength results received for all the other coupling agents, which explicitly contained TTP, always exceeded values of 15.0 MPa for both temperatures and so, in general, were significantly higher ($p < 0.001$).

While for all TTP-containing coupling agents no significant bond strength differences were observed at 37 °C storage temperature ($p > 0.05$; Fig. 3; uppercase letters), divergently, for 80 °C and the same data group the two experimental coupling agents containing BTSE as a cross-linking component revealed significantly higher results than the coupling agent without BTSE ('TTP + 3-MPS'), which showed only 16.0 MPa ($p < 0.05$; Fig. 3; lowercase letters). The two BTSE-containing systems were not significantly different ($p = 0.716$; Fig. 3; same lowercase letters).

All experimental coupling agents that explicitly contained the TTP component showed no significant bond strength differences between the two investigated storage temperatures after storage in distilled water (p

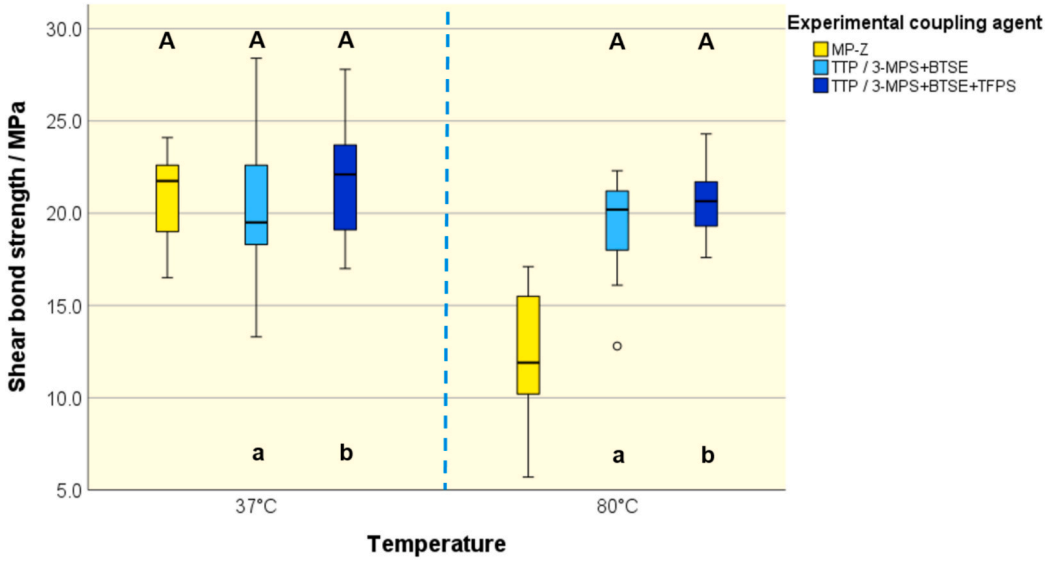


Fig. 4. Shear bond strength results for TiAlNb surfaces arranged according to the storage temperature and coupling agent after storage for 24 h in distilled water. Identical uppercase letters on the same level (on top) represent for each separate temperature no significant differences among coupling agents ($p > 0.05$). Identical lowercase letters on the same level (below) indicate no significant differences among storage temperatures for each coupling agent ($p > 0.05$). Circles represent outliers.

> 0.05; Fig. 3; red bars above boxplots). Conversely, the coupling agent recipe not including TTP ('3-MPS + BTSE') revealed a statistically significant difference between 37 °C and 80 °C ($p = 0.001$; Fig. 3). Hence, for 37 °C a bond strength result of 11.4 MPa was obtained, and for 80 °C, a comparatively low value of 5.6 MPa ($p = 0.001$; Fig. 3).

3.2. Influence of the storage temperature on shear bond strength data and comparison to a reference metal primer

After respective data splitting and further analysis via separate one-way ANOVAs and *post hoc* comparisons (Tukey's HSD test), the following results were obtained for the reference metal primer 'MP-Z' when compared to the two most promising experimental coupling agents 'TTP/3-MPS + BTSE' and 'TTP/3-MPS + BTSE + TFPS'.

While at 37 °C after 24 h, no differences were observed for TiAlNb surfaces between all three comparing coupling agents ($p > 0.05$; Fig. 4 left side; uppercase letters), the storage temperature of 80 °C revealed the significantly lowest bond strength value for the reference material 'MP-Z' (12.2 MPa) when compared to the two experimental coupling agents ($p < 0.001$; Fig. 4 right side; missing uppercase letter), which were not significantly different ($p = 0.614$; Fig. 4 right side; same uppercase letters) and higher than 19.0 MPa. Very similar results were detected for CoCrMo surfaces (Fig. 5). The only exception was the coupling agent 'TTP/3-MPS + BTSE' showing statistically significantly lower bond strength data at the water storage temperature of 37 °C than the reference 'MP-Z' ($p < 0.05$; Fig. 5 left side; different uppercase letters) and at 80 °C no significant difference compared to the reference material ($p = 0.150$; Fig. 5 right side; same uppercase letter).

Compared to the two promising experimental coupling agents, the reference material 'MP-Z' revealed on both investigated metal surfaces a statistically significant decrease for a water storage temperature of 80 °C (about 40 % bond strength reduction) if compared to 37 °C ($p < 0.001$; Figs. 4 – 5; missing lowercase letter). On the contrary, under the same conditions, the two promising experimental coupling agents showed no decline of the SBS values for a storage temperature of 80 °C compared to 37 °C, irrespective of the metal surface tested ($p > 0.05$; Figs. 4 – 5; same lowercase letters).

3.3. Influence of the long-term storage time in sodium chloride solution

SBS data were determined for both experimental coupling agents after storage in 0.9 % sodium chloride solution at 37 °C, and the characteristics concerning the deduced long-term stability evolved in a very similar manner. Despite a long-term storage time of 365 d, all strength results were consistently found to be above 20.0 MPa (Figs. 6 – 7). Even after an extended storage time of 2 and 3 years under identical conditions, two intentionally left single samples of each material category still revealed SBS values exceeding 20.0 MPa after 2 years and 18.0 MPa after 3 years (Table 6).

Compared to the initial strength data determined after one day of storage time, for both coupling agents less than 5.0 MPa bond strength was lost after an overall storage time of 365 d. This result was obtained for both metals, and the differences appeared to be statistically significant ($p < 0.05$; Figs. 6 – 7; lowercase letters), with the only exception being for CoCrMo and 'TTP/3-MPS + BTSE + TFPS' ($p = 0.066$; Fig. 7; same lowercase letters). Finally, during one year of storage time at 37 °C, all statistical comparisons (Student's *t*-test) of bond strength means between both experimental silane blends showed no significant differences irrespective of the storage time and the metal being observed ($p > 0.05$; Figs. 6 – 7; red bars on top). In all cases, after 365 d, no pure adhesive and cohesive fractures were observed. Instead, 95 % of the specimens revealed adhesive with partially cohesive fractures in the bone cement pin (Fig. 8), showing in 76 % of all cases, cement clusters together with thin bone cement particle layers (residues) on the metal surfaces (Fig. 9 A) and with 19 % solely thin bone cement residues (particle layers) (Fig. 9 B). Finally, 5 % adhesive failures with partially cohesive fractures in the metal were detected, with a few metal particles adhering to the bone cement surface (Fig. 10).

Nevertheless, a comparison of the three different storage times revealed a deviant behavior for both experimental silane blends (Figs. 6 - 7). For TiAlNb and the coupling agent 'TTP/3-MPS + BTSE' initially, a minor but statistically significant bond strength decline of about 3.2 MPa was detected after a storage time of 180 d ($p = 0.041$; Fig. 6; no uppercase letter) which subsequently did not undergo further changes even after 365 d ($p = 0.988$; Fig. 6; similar uppercase letters). For the second coupling agent 'TTP/3-MPS + BTSE + TFPS' an inversed behavior was observed. At first, the strength results obtained after 180 d of storage time were not significantly different from the initial data received for 1 d ($p = 0.851$; Fig. 6; similar lowercase letters), but after 365 d had passed, a minor but still significant decline of 2.7 MPa was detected ($p = 0.017$; Fig. 6; no lowercase letter). A very similar long-term behavior was observed for CoCrMo surfaces (Fig. 7) that equally showed for the coupling agent 'TTP/3-MPS + BTSE' no significant bond strength change between the prolonged storage times of 180 d and 365

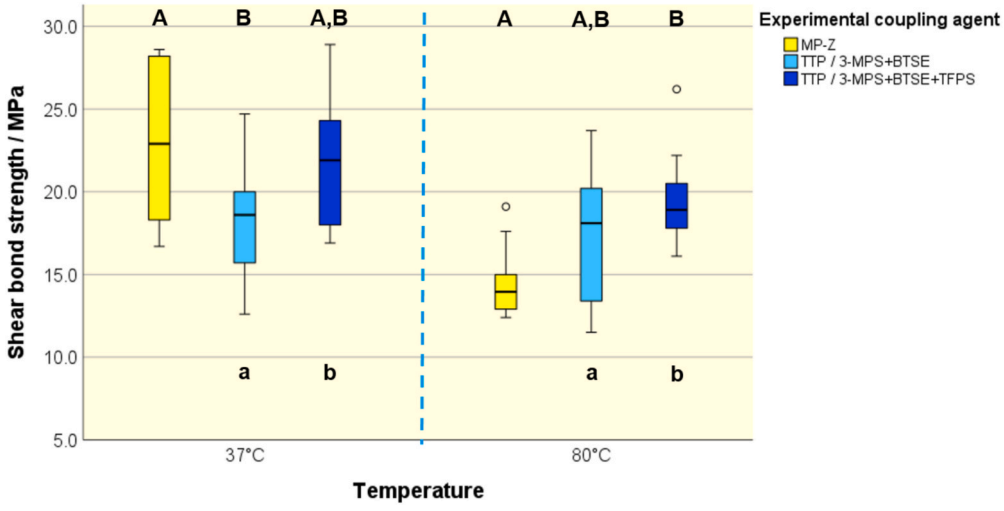


Fig. 5. Shear bond strength results for CoCrMo surfaces arranged according to the storage temperature and coupling agent after storage for 24 h in distilled water. Identical uppercase letters on the same level (on top) represent for each separate temperature no significant differences among coupling agents ($p > 0.05$). Identical lowercase letters on the same level (below) indicate no significant differences among storage temperatures for each coupling agent ($p > 0.05$). Circles represent outliers.

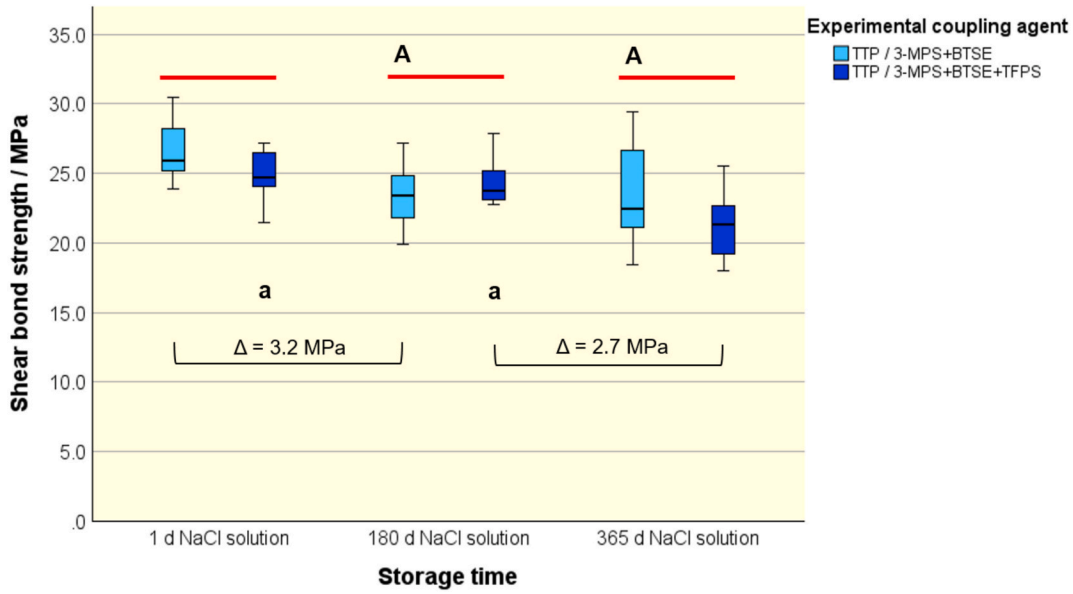


Fig. 6. Shear bond strength results for TiAlNb surfaces arranged according to the storage time in 0.9 % sodium chloride solution and the coupling agent. Identical uppercase letters on the same level (on top) represent no significant differences among different storage times for the coupling agent TTP/3-MPS + BTSE ($p > 0.05$). Identical lowercase letters on the same level (below) indicate no significant differences among different storage times for the coupling agent TTP/3-MPS + BTSE + TFPS ($p > 0.05$). A red bar above boxplots denotes no significant difference between both coupling agents for each separate storage time ($p > 0.05$).

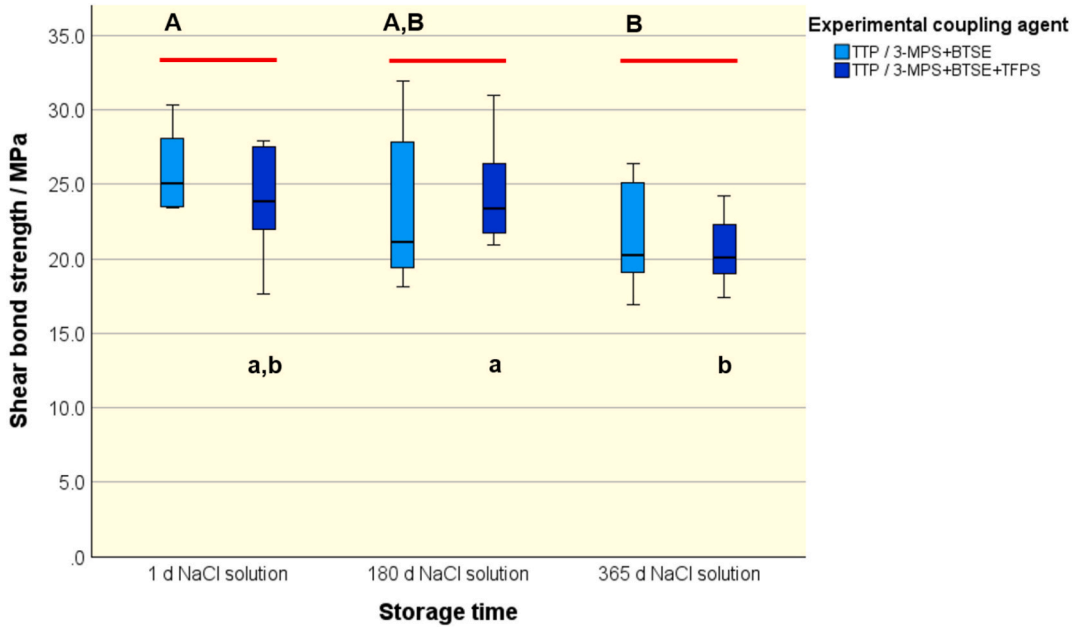


Fig. 7. Shear bond strength results for CoCrMo surfaces arranged according to the storage time in 0.9 % sodium chloride solution and the coupling agent**.** Identical uppercase letters on the same level (on top) represent no significant differences among different storage times for the coupling agent TTP/3-MPS + BTSE ($p > 0.05$). Identical lowercase letters on the same level (below) indicate no significant differences among different storage times for the coupling agent TTP/3-MPS + BTSE + TFPS ($p > 0.05$). A red bar above boxplots denotes no significant difference between both coupling agents for each separate storage time ($p > 0.05$).

d ($p = 0.484$; Fig. 7; similar uppercase letters). But a statistically significant data decline was observed for the system 'TTP/3-MPS + BTSE + TFPS' in the same period of time ($p = 0.024$; Fig. 7; different lowercase letters). Ultimately, after a total storage time of 365 d the CoCrMo data sets for both different coupling agents were not significantly different ($p > 0.05$; Fig. 7; red bar on top) and so were similar to the observations for TiAlNb surfaces (Fig. 6). Both revealed a highly promising outlook to much longer storage times without major strength decrease (Table 6).

4. Discussion

4.1. Influence of experimental coupling agents on the shear bond strength of TiAlNb surfaces

In the literature, silane coupling agents and their various combinations have been described as contributing differently to the improvement of SBS data. These determinations also applied for methacrylate-based polymers on metal substrates and had been previously reviewed [38,45,64,65]. Similarly, in the present study, a significant influence

Table 6
Long-term shear bond strength data on TiAlNb and CoCrMo surfaces for single samples after totally 2 and 3 years storage time in 0.9 % sodium chloride solution at 37 °C.

Experimental coupling agent	Metal surface	SBS 2 years/ MPa	SBS 3 years/ MPa
TTP/3-MPS + BTSE	TiAlNb	26.3	21.2
TTP/3-MPS + BTSE	CoCrMo	24.0	18.6
TTP/3-MPS + BTSE + TFPS	TiAlNb	20.5	17.9
TTP/3-MPS + BTSE + TFPS	CoCrMo	23.5	18.6

and effect of the experimental silane blends on bond strength values was observed ($F(3,72) = 59.1$, $p < 0.001$). Hence, the first null hypothesis that SBS is independent from the 'coupling agent' has to be rejected.

4.1.1. *Influence of TTP in experimental coupling agents*

Previous studies have investigated the influence of titanate coupling agents on the quality of filler surface coatings and thus on the related properties of composites. These revealed significant improvement effects on flexural strength and Young's modulus [66]. Likewise, initial investigations on Kevlar fibers described improving effects on mechanical properties after fibers were treated with various titanate coupling agents such as TTP. The respective fiber-reinforced composites equally yielded higher flexural strength data and, far more importantly, an improved resistance to moisture ingress [67]. In particular, the effect of water uptake is commonly assumed to weaken the adhesion between a composite matrix and its embedded fillers or fibers [68,69] and therefore markedly contributes to a noticeable property decline. Nevertheless, a similar water-repellent effect of TTP and TTP-containing sol–gel films was found to efficaciously protect aluminum alloys [48,49] and other metal surfaces [40] from corrosion processes. Especially on phosphated steel sheets, sol–gel-coated hybrid layers containing a titanate component were reported to be impervious to the diffusion of water and corrosive ions from a 3.5 % NaCl solution [47]. Overall, not only a water-repellent and hence corrosion protective effect could be achieved via the application of TTP. A second result was a significant optimization of adhesion to metal surfaces for blends with an aminopropyltriethoxysilane [49] and 3-MPS, which was patented at an early

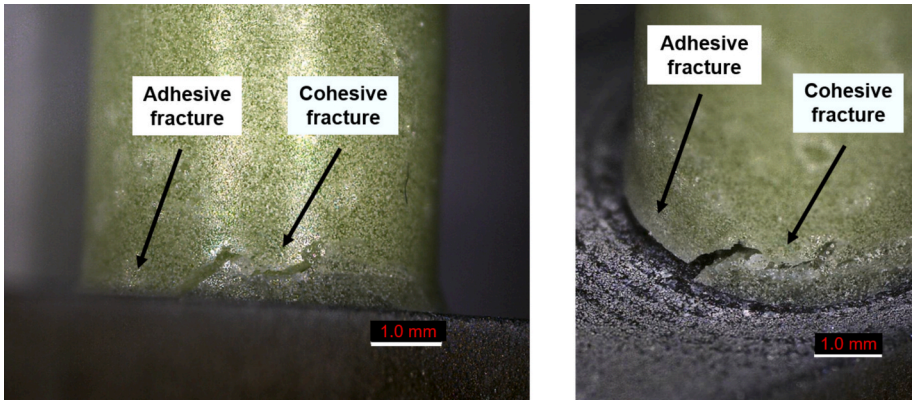


Fig. 8. Representative specimen after shear bond strength testing with partially cohesive fractures in bone cement.

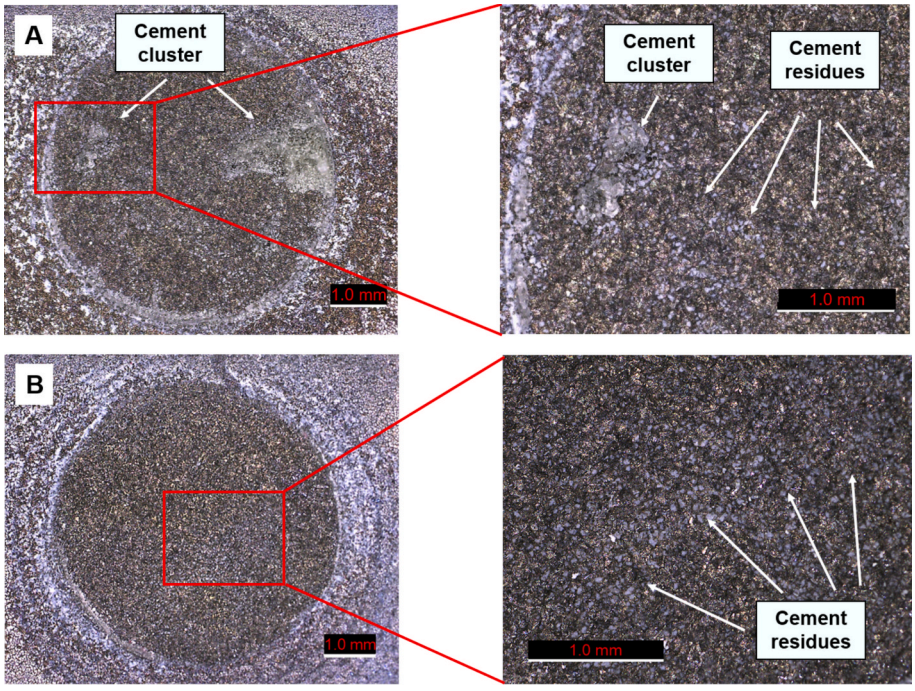


Fig. 9. CoCrMo surfaces after shear bond strength testing. Adhesive failures with mixed cohesive fractures in the bone cement showing (A) cement clusters together with thin cement particle layers (residues) and (B) only thin cement particle layers on metal surfaces.

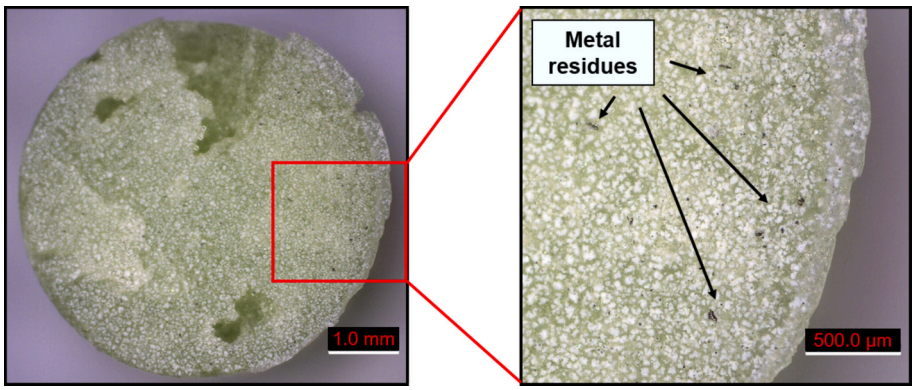


Fig. 10. Representative cement pin surfaces after shear bond strength testing**.** Note metal residues adhering to the cement surface.

stage for dental applications by Göbel (1998) [61].

Very similar results were found in the present study with the use of TTP, where both aforementioned effects substantially improved the bonding properties of methacrylate-based cement pins on implant alloys. After just one day storage time in water (37 °C), significantly increased bond strength data were observed for all silane blends where TTP was previously used as a primary coating on metal surfaces showing mean values always higher than 15.0 MPa (Fig. 3). Conversely, under the same test conditions the markedly lowest strength value of 11.4 MPa was determined for the special silane blend where no TTP was used prior to silane application ('3-MPS + BTSE'; Fig. 3) and where all statistical comparisons revealed differences larger than 5.0 MPa (Fig. 3; missing uppercase letter). Obviously, the improvement effect of TTP on surface structures and its adhesion characteristics, as previously reported in the literature, similarly had a positive effect on the properties of bonding layers investigated on implant alloys in the present study. As previously discussed in detail [47,49], the hydrolysis products of TTP may have contributed to the formation of a strong and more compact three-dimensional Ti-O-Ti and Ti-O-Si network built upon the respective metal surface, thereby imparting strength, hydrophobicity, and ultimately a higher resistance to load impact and water ingress. This effect of TTP was even more evident in the present study, if specimens were stored in water at an elevated temperature of 80 °C to simulate long-term bond strength stability. Hence, while all silane blends applied in combination with TTP as a primary coating again had higher bond strength data than 15.0 MPa, not all were statistically different from their counterparts stored at 37 °C (Fig. 3; red bars above boxplots). Moreover, the analogous silane blend without the TTP-coupling agent revealed an even worse behavior than before, with a mean value of just 5.6 MPa, which is significantly different from the results obtained at 37 °C (Fig. 3; missing red bar). With a bond strength reduction of more than 50 %, this was the lowest result observed in the present study. It clearly corroborates prior observations that a TTP application in hybrid sol–gel interlayers generally enhances water displacement effects on metal surfaces, and therefore might improve bond strength stability in the long term. Unfortunately, it is not yet clear whether this improvement effect of TTP is also dependent on the concentration of its applied solution and the polarity of the solvent used. Answers might be found in future explorations that aim to better understand the effect of TTP surface coatings on bond strength properties.

4.1.2. Influence of BTSE in experimental coupling agents

The cross-linking alkoxysilane BTSE was recently described as an essential component of various silane blends [38,70]. Therefore, its influence on the surface characteristics of coated metals [51,71] and bond strength improvement [72,73] were analyzed in detail. Within various experimental silane blends, Matinlinna was the first to observe a concentration effect of this cross-linking silane on the bond strength quality of a resin-composite cement to silica-coated titanium [74]. As a result, for the mixture of 3-acryloyloxypropyltrimethoxysilane and BTSE, he found an optimal ratio of 1.0 vol% and 0.3 vol% in acidified ethanol–water solution to achieve the highest bond strength data, both in the dry condition and after thermocyling. Later on, he published a paper that reported the highest and a homogenous coverage of titanium surfaces for the same ratio of both silanes, as determined via XPS data [70]. From this observation, he concluded that the existence of a highly cross-linked network covering the respective surface is most likely [70]. In the same study, for the identical silane blend, the lowest surface free energy was calculated via contact angle measurement, indicating a more hydrophobic surface structure for this particular ratio than was found for the original and untreated titanium surfaces. All of this information was taken into consideration when planning the present study. Therefore, a comparable ratio of the chemically related 3-MPS and the cross-linking BTSE was chosen (Table 3) to generate similar surface properties and achieve optimized bond strength data.

As a partial result of the present investigation, a positive effect of BTSE on bond strength properties was observed, clearly corroborating the previously reported findings [74,75]. Accordingly, the experimental coupling agent that did not contain BTSE (namely 'TTP/3-MPS'; Fig. 3) revealed significantly lower bond strength data (20 % reduction) after water storage at elevated temperatures (80 °C) when compared with the two other coupling agents, which both explicitly had TTP and the cross-linking silane BTSE in their compositions (Fig. 3; missing lowercase letter). Hence, the well-known effect of BTSE, which usually contributes to improved cross-linking networks and higher water repellency [76], could be similarly substantiated in the present study on titanium surfaces. The higher resistance and robustness in hot water of such optimized silane blends consisting of TTP, 3-MPS and BTSE (Fig. 3) permit an optimistic outlook for improved bond strength stability in the long term.

Nevertheless, this improvement effect of BTSE appeared to have less influence on the overall bond strength data than the additional application of TTP used as a primary coating (see Section 4.1.1). While BTSE increased the bond strength data by only 2.7 MPa (37 °C) and 3.2 MPa (80 °C) (see differences Δ in Fig. 3), the effect being solely attributed to TTP was found to be 9.1 MPa (37 °C) and 13.7 MPa (80 °C) (Fig. 3). Unfortunately, little information is available in the literature concerning the individual improvement effects of these both sol–gel precursors, especially on bond strength data. Hence, a reliable assessment and comparison of the above findings with data from the literature is not yet possible. However, the individual effects observed in the present study could serve as a valuable source of information in future investigations with new organic–inorganic hybrid sol–gel interlayers. Furthermore, the question arises as to whether similar cross-linking silanes, chemically related to BTSE but with longer alkyl chains or different functional groups between the two trialkoxysilyl groups, may reveal new insights when used in silane blends for improving bond strength. Such investigations may be part of future and ongoing projects.

4.1.3. Influence of TFPS in experimental coupling agents

Several attempts have been made to impede water molecules from penetrating into a bonding layer and hence to avoid property degradation. One common approach to achieving this goal is the use of hydrophobic alkyl silanes, such as BTSE, to form organic–inorganic hybrid sol–gel interlayers with water-repellent effects (see Section 4.1.2). Such hydrophobic properties have been previously assessed via contact angle measurement [70] and may be equally implemented into bonding layers via the selective application of fluorinated silane precursors [77]. The use of fluoroalkyltrimethoxysilanes in specific silane blends for dental applications was previously described by Nihei et al. [54,78] and Suzuki [79] and recently reviewed by Nihei [80]. Preceding and detailed investigations for TFPS independently revealed an optimum concentration of approximately 25 %, resulting in the highest tensile strength data for composite materials, which comprised fillers pre-treated with various silane blends [81]. Similarly, for different fluoroalkylalkoxysilanes a concentration of 20 wt% was found to yield the lowest contact angle (enhanced wetting ability) for dental resin mixtures tested on silane-treated glass surfaces [54,78,79] while concurrently revealing the highest long-term stability of tensile strength data (1800 d, 37 °C, water) determined for composite materials containing various silane blend-treated silica fillers [54]. Preliminary tests for the present study, conducted by Kästingschäfer (2024) with TFPS, similarly corroborated an optimal concentration of 20 wt% but showed no further improvement effects for higher concentrations [82]. Therefore, in the present study, a final concentration of 20 wt% TFPS was also used to ensure ideal surface properties for the following bone cement application.

In the literature, TFPS and its homologous nonafluorohexyltrimethoxysilane, which just bears three further hydrophobic $-CF_2$ groups in the molecular chain, were found to generate significant improvement effects on the long-term stability of composite tensile strength data [54]. Such stabilizing effects of TFPS could likewise be detected in bond strength data for the experimental silane blends investigated in the present study. The respective coupling agent containing TFPS ('TTP/3-MPS/BTSE/TFPS'; Fig. 3) showed the same stability as the related counterpart not comprising this particular silane ('TTP/3-MPS/BTSE') with both blends revealing no statistically significant bond strength degradation after storage in water, even at elevated temperatures of 80 °C (Fig. 3; same lowercase letters). Obviously, the compositions of both silane blends were optimally adjusted to generate a similar water-repellent effect and prevent bond strength data from being continuously degraded. Accordingly, both blends were further examined for their long-term stability behavior after long-term immersion in saline solution (see Section 4.3).

In summary, silane blends comprising fluoroalkylsilane moieties have been mainly described in the literature to reveal improvement effects on water repellency for various filler surface structures, thereby preserving composite properties. However, very little information is available regarding their effects on bond strength data and long-term stability, which were divergently investigated in the present study. This could be because a too-high concentration of fluoroalkylsilanes is capable of provoking very high contact angles (reduced wetting ability) for dental resin mixtures that could markedly impede sufficient adhesion and subsequent chemical bonding of acrylic resins to the respective boundary layer [54]. Therefore, further studies exploring the properties of silane blends containing fluoroalkylsilanes to be used as adhesive promotors are highly recommended to more deeply understand the detailed effects of fluoroalkylsilanes on long-term bond strength stability.

4.2. Influence of the storage temperature on shear bond strength data and comparison to a reference metal primer

Various dental metal primers have been described in the literature that initially improved bond strength data on titanium surfaces but later on revealed strength degradation after either thermocycling [31,32] or following water storage at elevated temperatures [60,61]. These metal primers are based solely on adhesion-promoting, pure organic resin compounds, comprising polymerizable methacrylate groups as well as carboxylic acid, phosphoric acid, and acid anhydride groups. These have intrinsic metal affinity but do not contain any silicon components [31,32]. On the other hand, adhesive systems were reported to be based on pure silicon compounds, such as 3-MPS [60,61]. Similarly, in the present investigation, the storage temperature's significant influence and effect on bond strength results were observed ($F(1,72) = 11.4$, $p = 0.001$). Hence, the second null hypothesis that SBS is independent of the 'storage temperature' has to be rejected.

The effect of temperature on bond strength alteration was most obvious in the present study for the reference metal primer 'MP-Z', which generally yielded significantly lower data sets after water storage at elevated temperatures, independent of the investigated metal surface (Figs. 4 - 5). Therefore, this outcome consequently implies a poorer prognosis for long-term bond strength stability in a wet environment for such primers. Comparable results, which also showed temperature-induced bond strength degradation effects, were previously observed after thermocycling processes in studies investigating similar metal primers routinely used in dental applications [83–85] and in initial investigations on total hip stem alloys [60]. Obviously, persistent water ingress into the respective bonding layer continuously negatively affects the adhesion properties, thus provoking markedly reduced bond strength data. Unfortunately, it is not yet clear whether such water-induced property degradation effects belong solely to irreversible destruction processes with concurrently occurring chemical bond cleavages or whether they may be alternatively related to simple and reversible swelling processes of the polymer-based interlayers. Such water-induced equilibrium effects were recently found in bond strength degradation processes on metal surfaces where epoxide adhesives showed reversible water uptake and reversible plasticization effects, thus resulting in a bond strength recovery after drying [7].

Nevertheless, in the present study, an efficacious elimination of water penetration to the respective bonding surface could be achieved by applying organic–inorganic hybrid sol–gel interlayers comprising BTSE and TFPS as additional silane components. Compared to the reference metal primer ('MP-Z'), the new silane combinations revealed an extraordinary bond strength stability under the same test conditions, preserving the initial high bond strength data received for both investigated metals (Figs. 4 – 5; Identical lowercase letters). Given the fact that even after storage in distilled water at 80 °C no statistically significant strength declines could be observed for both experimental silane blends, there is a reasonable estimation possible that predicts a superior long-term bond strength stability and thus very high survival chances for such bonding layers in medical applications, especially in wet environments. This result clearly corroborates the findings received for the long-term immersion in isotonic saline solution, which are discussed in detail in Section 4.3.

Furthermore, the beneficial effect of both new silane blends in effectively preventing water-induced bond strength degradation has to be compared with the early findings of Göbel [61]. He patented the use of TTP combined with solely 3-MPS to improve bond strength properties on metal surfaces used in dental applications. Although he obtained bond strength data on a high level after a one day storage time in boiling water, prominent strength decreases were nevertheless found in the range of 4.0 to 5.0 MPa for all investigated metal surfaces when the results were compared with initial data sets (loss of about 20 %). Unfortunately, no further detailed information is available to support the reported average values, making a reliable statistical evaluation impossible. Nevertheless, the detection of such lowering effects after high-temperature storage in water could not be substantiated for either of the experimental silane blends in the present study. No statistically significant differences were detected (Figs. 4 – 5; Identical lowercase letters). Obviously, the additional use of BTSE and TFPS in combination with TTP and 3-MPS further increased the water-repellency effect, and

consequently, the bonding layer stability of the new experimental silane blends was improved. This result may be explained simply by the high intrinsic capability of BTSE and TTP to readily build up efficient cross-linking structures on the investigated metal surfaces during the condensation process of the organic–inorganic hybrid sol–gel system. This effect of the highly cross-linked structures is convincingly displayed on the typically received fracture surfaces, which partly show cohesive fractures (Fig. 8) that often reveal cement clusters concurrently remaining on the surfaces (Fig. 9A). Furthermore, simultaneously thin layers of cement residues appear to be firmly bonded to the surfaces to a large extent (Fig. 9B), which are obviously a result of a particular effective bond and cross-linking between metal surface and TTP.

Very little information is currently available in the literature for the particular sol–gel combination of 'TTP/3-MPS + BTSE' having an improvement effect on water-repellency and long-term bond strength stability. This beneficial relationship was first disclosed in the present study, and further investigations based on this particular silane blend are strongly recommended and are currently underway in our lab to assess the effect of various cross-linking silanes and their different concentrations on long-term bond strength stability more broadly.

4.3. Influence of the long-term storage time in sodium chloride solution

In most tests for artificial restorative materials, the important question of hydrolytic stability must be addressed first, especially if metal structures are involved, which may provide a higher risk of corrosion processes. Therefore, simple water-based sodium chloride solutions are frequently used as a storage liquid, which allows an initial and meaningful estimation of material behavior in a corrosive medium. Hence, our previous study also tested bond strength properties after storage in 0.9 % aqueous sodium chloride solution at 37 °C [30]. For the two commercially available metal primers commonly used in dental applications, significantly degraded bond strength was recorded on grit-blasted TiAlNb and CoCrMo surfaces in that investigation after 150 d of storage time. However, when the same storage medium was used in the present investigation, only a very low bond strength decline of less than 3.5 MPa was observed for the new experimental coupling agents after an even longer storage time of 365 d. The decline was much less than in the previous study, but a significant influence and effect of the 'long-term storage time in sodium chloride solution' on bond strength results was still confirmed ($F(2,108) = 15.1$, $p < 0.001$). Consequently, the third null hypothesis that the SBS is independent of the 'long-term storage time in sodium chloride solution' has to be rejected.

A similarly considerable bond strength decline was previously reported by Matinlinna [86] for grit-blasted titanium surfaces after a 6- and 12-month storage time in pure distilled water (37 °C) for a commercially available dental metal adhesive system (Rocatec Plus, ESPE Sil) and various experimental silane blends. The primary difference between this study and the present one was the correlation of long-term storage data in water with results obtained after dry specimen storage. Hence, while Matinlinna observed comparatively large differences of up to 10 MPa and final strength values of less than 12 MPa (partly 50 % bond strength reduction) after a one-year wet specimen storage, the present investigation reveals final strength results still above 20 MPa for both examined metal surfaces with differences between the starting and final values of below 3.5 MPa (only 15 % reduction). Of course, a direct comparison of these absolute bond strength values is not feasible because many factors, such as the differing titanium composition, the grit-blasting process, the silane activation procedure, and specimen storage conditions, may have affected their determination in different ways. Nevertheless, the calculated mean differences and percentage changes in each independent study may allow a trend to be derived, and this could also confirm the existence of the observed bond strength stabilizing effect induced by the innovative sol–gel coatings of the present study.

The remarkably high bond strength values reported in the present study were also verified after two years of storage under the same conditions, with a similarly good prognosis for three years (Table 6). Although Matinlinna already used BTSE as a cross-linking component in his silane blends to introduce enhanced water-repellent properties to the surface structures [86,87], a highly significant bond strength decline was still observed for all his silane blends after long-term water storage. Compared to the present study, this major difference may be unequivocally explained by the additional application of TTP in combination with 3-MPS and BTSE used in the current study, which Matinlinna did not consider during his investigations.

The positive long-term effect of TTP as an integral part of organic–inorganic hybrid sol–gel interlayers can be easily verified by considering once more Fig. 3, where pronounced SBS differences of 9.1 MPa (83 % increase at 37 °C) and 13.7 MPa (245 % increase at 80 °C) between '3-MPS + BTSE' and 'TTP/3-MPS + BTSE' may be solely attributed to the additional application of TTP on the metal surface. Hence, if the same differences, brought about by TTP in the current study, were to be theoretically added to the 12-month bond strength data reported by Matinlinna for 'MPS + BTSE' and 'ACPS + BTSE' [86], bond strength values would have been generated for these systems that very closely resemble the respective dry storage data reported for specimens without water ingress. Thus, it may be speculated that Matinlinna could have similarly achieved no marked decline in bond strength for both of his silane blends if TPP had been used as a pre-coating for his titanium surfaces. Hence, this observation may corroborate the findings of the present study, which demonstrates excellent improvement effects on long-term bond strength stability for TTP pre-coatings.

During the long-term storage test in sodium chloride solution, the comparison of both experimental silane blends in the present study never revealed a statistically significant difference in bond strength, irrespective of the investigated storage time or metal (Figs. 6 – 7; red bars on top). Hence, the question arises as to whether the additional use of TFPS as a water-repellent component in organic–inorganic hybrid sol–gel interlayers is actually appropriate to avoid long-term water ingress into bonding layers, because merely the combination of 3-MPS and BTSE appeared to be sufficient to generate the best possible effect. So, at first glance, it is tempting to generally exclude TFPS from silane blends because an additional beneficial effect on long-term bond strength stability could not be proven, and from an ecological point of view, the ongoing use of TFPS and its related compounds has to be called into question [88,89].

Nevertheless, our study shows a different behavior of both silane systems, which is most apparent on TiAlNb surfaces that revealed lower statistical variances for all three storage times investigated (Fig. 6). Initially, a minor but statistically significant bond strength decline of about 3.2 MPa was detected for 'TTP/3-MPS + BTSE' after a storage time of 180 d, which in contrast did not undergo further significant changes even after 365 d (Fig. 6; similar uppercase letters). An inversed behavior was observed for the second experimental silane blend, namely 'TTP/3-MPS + BTSE + TFPS'. At first, the strength results after 180 d were not significantly different from the initial data set (Fig. 6; similar lowercase letters) but after 365 d of storage time, a minor but significant decline of 2.7 MPa was detected (Fig. 6; no lowercase letter). Both silane blends differ only in the content of TFPS, which obviously induced a more effective prevention of water ingress to the bonding layer in the first half of the storage time. In the second half, the water-induced effect on bond strength decline is realized in a delayed manner. Hence, after 365 d, the measured data ultimately reached the same level as the silane blend, which did not comprise TFPS but, on the contrary, lost an equivalent amount of bond strength (3.2 MPa) much earlier in the first half of the overall storage time. This retarding effect of TFPS or other related fluoroalkylsilanes has not been previously described in the literature. Therefore, the question arises as to whether it is worthwhile developing this further to improve effective long-term resistance against destructive water ingress, or whether, instead, simple alkyl-substituted

silane blends, merely containing BTSE or similar derivatives, provide sufficient protection and stability. Further experiments are strongly recommended and are in progress in our labs.

4.4. Impact on clinical practice

The present study demonstrates a high potential for organic–inorganic hybrid sol–gel coatings to serve as alternative adhesion-promoting layers on metal surfaces in both medical and technical applications. At present, many established adhesive systems commonly used in combination with biomedical alloys still frequently reveal undesired water ingress [38]. Consequently, the long-term service and survival rates of such systems still suffer from concurrently induced multiple property degradation effects [32], especially in medical applications where moisture is omnipresent, leading to swelling processes and material softening. Hence, preserved water-repellent properties in the long run, such as those provided by the surface coatings introduced in the present investigation, are still in great demand and are highly appreciated for reliably impeding the adverse effects of water on long-term stability. Fortunately, organic–inorganic hybrid sol–gel interlayers offer the opportunity to be specifically tailored and designed by using various silane precursors, as demonstrated in the present study. This approach enables the precise adaptation of silane blends to varying surface structures and ensures a perfect fit to the chemical characteristics of potential adherend surfaces. An exemplary system is presented in the present study for poly(methacrylate)-based bone cements often suffering from debonding progression [90], where both experimental silane blends generated exceptionally stable adhesion layers when applied on grit-blasted and TTP-treated metal surfaces. The two interacting process steps of grit-blasting and the immediate application of TTP appear to be crucial factors in achieving long-term property stability. Both can be easily carried out on various substrate surfaces without complex operating procedures. This makes such systems particularly attractive for use in medical applications to generate durable bonding layers on metal surfaces [44], which are often needed in dental prosthetics, endoprosthetics and spinal surgery. However, there is a disadvantage because all surface structures coated with silane blends inevitably need to be activated for several minutes at elevated temperatures (approx. 100 °C) to evaporate residual solvents and water from the condensation process, and, of course, this cannot be realized inside a living body. Nevertheless, a major advantage of organic–inorganic hybrid sol–gel systems is that they provide various opportunities for flexible adjustment to specific surface structures and adhesion problems. Furthermore, recent investigations indicate that silane blends exhibit exceptionally good prognoses, offering superior biocompatibility [91] and bone-like apatite formation capabilities [92].

4.5. Limitations of the present study

An important limitation of the present study is the sole use of a static test procedure to ultimately evaluate the effective long-term bond strength stability of different organic–inorganic hybrid sol–gel interlayers. However, in reality, especially in medical applications, impact loads do not solely affect structures via suddenly appearing mechanical stresses selectively focused on just one single point. In daily practice, stresses may also be transferred continuously via dynamic conversion processes affecting all surrounding structures in the vicinity. Hence, the supplementary use of dynamic test procedures would appear to be very useful to repeatedly stress structures in cyclic fatigue testing to provide a more realistic evaluation of long-term material stability during clinical use. Such test procedures were not used for the present investigation because cyclic test equipment for SBS testing on a small scale was not readily available on the market, and no standardized procedures have been reported yet [93]. Nevertheless, modifiable cyclic test procedures have been recently introduced for some universal testing machines, which, in a further ongoing project, are now adapted in our labs for small-scale applications in cyclic bond strength testing.

A second limitation of the present study is the use of an SBS test to determine bond strength values of different organic–inorganic hybrid sol–gel interlayers. Although several other test procedures, such as tensile bond strength tests, push-out tests, pull-out tests, and lap-shear tests, are available to evaluate adhesive strengths in either micro- or macro-test versions, we decided to use a macro-SBS test, as this procedure remains very popular and is commonly applied in industry and research institutes. It represents an easy and fast method that requires no special know-how and sound expert knowledge for specimen preparation and test procedures. Nevertheless, there are some drawbacks to be considered when interpreting different study results and drawing conclusions from SBS comparisons. Results may vary significantly depending on the size of the bonding area, the elastic modulus of the adhered material, the distance between the load application point and the specimen surface area, the mode of shear force application (knife edges, points, wire loops) and the specimen storage conditions. Hence, for this method, considerable efforts were made to standardize study designs and the reporting of results [94] to facilitate better comparability. This was why we decided to use the experimental setup recommended in ISO 10477:2020 [62] for the present investigation.

Furthermore, a third limitation must be considered. Although an isotonic saline solution was used as a long-term storage liquid in the present investigation to simulate the wet environment in a living body with the aim of further assessing potential corrosion processes on metal surfaces, it remains unclear whether this medium suffices to adequately simulate all possible biological effects induced by natural body liquids such as saliva and synovial fluids, which additionally contain active protein components. Hence, further long-term stability tests in the future may also be conducted using such natural liquids, which are now commercially available. However, the question remains whether these liquids remain stable enough during the entire storage period of months without exhibiting bacteria-induced changes and decomposition reactions at 37 °C. This raises the question of when such liquids need to be replaced to prevent solid residues and incrustations on specimen surfaces, which could negatively impact bond strength testing. Therefore, in this study, an isotonic saline solution was preferred as an initial storage liquid.

Not only the storage liquid itself, but also the storage temperature of the respective liquid, has to be considered as a limiting factor. Besides 37 °C for the long-term immersion test, 80 °C was also used in the present study to assess the stability of bond strength data after accelerated aging during the research phase. The question arises whether the latter conditions are appropriate enough to simulate long-term material behavior instead of using a commonly used thermocycling procedure, which is well-established for dental material testing but still not harmonized [95]. Although thermocycling and its common temperature change between 5 °C and 55 °C has been shown to reveal more obvious effects when detecting bond strength differences between various silane-based adhesion promoters [87] than a sole long-term storage test at 37 °C over several months [86], it was not used as a standard test procedure for long-term simulation in the present study. The reason was its high time-consuming effect during the research phase and the fact that, for the intended use in medical applications, drastic temperature changes were only expected to occur in the oral cavity but not elsewhere in the living body, such as in artificial joints and vertebrae. Furthermore, the dwell time during temperature change may have caused a repeated and uncontrolled loss in water content of the tested coatings, which would not have correctly reflected clinical conditions during long-term use. To minimize the impact of these influences on the long-term bond strength data and to obtain data sets during the research phase in a timely manner, specimens were stored in water at 80 °C for 24 h.

5. Conclusions

The innovative organic–inorganic hybrid sol–gel coating developed

in the present study increased the long-term bond strength stability in water for a poly(methyl methacrylate)-based bone cement adhered to various metal surfaces. Conversely, a commercial metal primer commonly used in dental applications appeared to be exceptionally sensitive to water ingress and therefore exhibited a significant decline in bond strength. By using various sol–gel precursors, the new metal coating was specifically designed to create a tight surface sealing, which protected bonding layers from deleterious water ingress and hydrolytic degradation effects. Different silane blends were selected to create the most effective water-repellent effect.

The application of TTP directly after conventional grit-blasting was demonstrated to be a crucial step in the new process chain of metal surface activation, as it generated a resilient bonding surface comprising a highly cross-linked titanium oxide network. This layer provided a remarkable effect on water resistance while increasing bond strength stability by 245 %. A subsequently applied silane blend containing 3-MPS and BTSE was optimized to ensure strong adhesion to the bone cement and to facilitate the formation of highly cross-linked three-dimensional −Si-O-Si- structures that are far more impervious to water. A blend containing 25 % BTSE improved bond strength stability by 20 %. Further improvements in effects induced by water-repellent silanes, such as TFPS, were not observed. After long-term immersion in isotonic saline solution at 37 °C for more than 365 days, a decline in bond strength of just 15 % was observed. Therefore, such systems are highly interesting for use as adhesion promoters in long-term medical applications, such as dental prosthetics, endoprosthetics, and spinal surgery.

CRediT authorship contribution statement

Thomas Niem: Writing – original draft, Supervision, Project administration, Methodology, Formal analysis, Conceptualization. **Kai Kästingschäfer:** Visualization, Validation, Investigation, Formal analysis. **Markus Rickert:** Writing – review & editing, Resources. **Bernd Wöstmann:** Writing – review & editing, Resources. **Alexander Jahnke:** Writing – review & editing, Methodology, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time, as they also form part of an ongoing study.

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