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**BONDING OF COMPOSITE RESIN TO
ALUMINA AND ZIRCONIA CERAMICS
WITH SPECIAL EMPHASIS ON SURFACE
CONDITIONING AND USE OF
COUPLING AGENTS**

by

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To Varpu, Viliina and Viivi

*“If you can't explain it simply,
you don't understand it well enough”*

– Albert Einstein –

ABSTRACT

Timo Heikkinen. Bonding of Composite Resin to Alumina and Zirconia Ceramics with Special Emphasis on Surface Conditioning and Use of Coupling Agents. Department of Biomaterials Science, Institute of Dentistry, University of Turku. *Annales Universitatis Turkuensis*, Turku, Finland 2011.

Dental oxide ceramics have been inspired by their biocompatibility and mechanical properties which have made durable all-ceramic structures possible. Clinical longevity of the prosthetic structures is dependent on effective bonding with luting cements. As the initial shear bond strength values can be comparable with several materials and procedures, long-term durability is affected by ageing. Aims of the current study were: to measure the shear bond strength of resin composite-to-ceramics and to evaluate the longevity of the bond; to analyze factors affecting the bond, with special emphasis on: the form of silicization of the ceramic surface; form of silanization; type of resin primer and the effect of the type of the resin composite luting cement; the effect of ageing in water was studied regarding its effect to the endurance of the bond.

Ceramic substrates were alumina and yttrium stabilized zirconia. Ceramic conditioning methods included tribochemical silicization and use of two silane couplings agents. A commercial silane primer was used as a control silane. Various combinations of conditioning methods, primers and resin cements were tested. Bond strengths were measured by shear bond strength method. The longevity of the bond was generally studied by thermocycling the materials in water. Additionally, in one of the studies thermal cycling was compared with long-term water storing. Results were analysed statistically with ANOVA and Weibull analysis.

Tribochemical treatment utilizing air pressure of 150 kPa resulted shear bond strengths of 11.2 MPa to 18.4 MPa and air pressure of 450 kPa 18.2 MPa to 30.5 MPa, respectively. Thermocycling of 8000 cycles or four years water storing both decreased shear bond strength values to a range of 3.8 MPa to 7.2 MPa whereas initial situation varied from 16.8 Mpa to 23.0 MPa. The silane used in studies had no statistical significance. The use of primers without 10-MDP resulted spontaneous debonding during thermocycling or shear bond strengths below 5 MPa.

As conclusion, the results showed superior long-term bonding with primers containing 10-MDP. Silicization with silanizing showed improved initial shear bond strength values which considerably decreased with ageing in water. Thermal cycling and water storing for up to four years played the major role in reduction of bond strength, which could be due to thermal fatigue of the bonding interface and hydrolytic degradation of the silane coupled interface.

Key words: Adhesion, Alumina, Dental biomaterials, Resin composite, Silicization, Silanization, Thermal cycling, Long-term water storage, Zirconia.

TIIVISTELMÄ

Timo Heikkinen. Yhdistelmämuovin sidostaminen alumiinioksidiin ja zirkoniaan painottaen pintakäsittelyä ja sidostusaineiden käyttöä. Biomateriaalitieteen oppiaine, hammaslääketieteen laitos, Turun yliopisto. Annales Universitatis Turkuensis, Turku, 2011.

Hammaslääketieteelliset kokokeraamiset rakenteet ovat tulleet mahdollisiksi oksidikeraamien biologisuuden ja erinomaisten mekaanisten ominaisuuksien ansiosta. Proteettisten rakenteiden kestävyys on riippuvainen onnistuneesta ja tehokkaasta sementoinnista. Vaikka useiden tuotteiden ja menetelmien takaamat sidoslujuuDET ovat vertailukelpoisia alkutilanteessa, kestävyteen ja riittävään sidoslujuteen vaikuttaa keinotekoinen vanhentaminen. Tämän väitöskirjatYön tavoitteet olivat: mitata yhdistelmämuovin repäisysidoslujutta keraamiin ja arvioida sen kestävyttä; edelleen eritellä sidokseen vaikuttavia tekijöitä painottaen: silikoinnin muoto keraamisella pinnalla; silanoinnin muoto; primerin ja resiinin tyyppi; yhdistelmämuovisementin vaikutus; vedessä vanhentamisen vaikutus sidoskestävyyden arvioimiseksi.

Keraamiset substraatit olivat alumiinioksidi ja yttriastabiloitu zirkonia. Keraamin esikäsitteilytapoihin kuuluivat tribokemiallinen silikointi ja kaksi silaania. Kaupallista tuotetta käytettiin referenssinä. Erilaisia esikäsitteilyresiini- ja yhdistelmämuovisementtikombinaatioita tutkittiin. Sidoslujuus testattiin repäisylujuusmenetelmällä. Sidoksen pitkäikäisyys tutkittiin pääasiallisesti termosyklaamalla. Lisäksi yhdessä osatutkimuksessa pitkäikäisvesisäilytystä verrattiin termosyklaamiseen. Tulokset analysoitiin varianssianalyysillä ja Weibull-analyysillä.

Tribokemiallinen käsittely käyttäen 150 kPa:n ilmanpainetta tuotti 11,2–18,4 MPa:n sidoslajuuden ja vastavasti 450 kPa:n ilmanpaine 18,2–30,5 MPa:n sidoslajuuden. 8000 kerran termosyklaaminen tai neljän vuoden vesihaudesäilytys laskivat molemmat repäisylujuusarvot 3,8–7,2 MPa:iin alkutilanteen vaihdelta 16,8–23,0 MPa:n välillä. Käytetyllä silaanilla ei ollut tilastollista merkitsevyyttä. Ilman 10-MDP:tä sisältäviä primereitä tapahtui spontaania koekappaleiden irtoamista tai repäisylujuusarvot jäivät alle 5 MPa:n.

Johtopäätöksenä tulokset osoittivat parasta pitkäikäisidosta primereillä, joissa on 10-MDP:tä. Silikointi ja silanointi osoittivat alkutilanteessa korkeita sidoslujuusarvoja, jotka pienenevät huomattavasti vesihauteessa vanhennettaessa. Termosyklaus ja vesisäilytys neljän vuoden ajan toimivat pääasiallisina tekijöinä sidoslajuuden vähenemisessä, joka voi johtua termisestä väsymisestä sidostumisalueella ja silaanin sidostumisalueen hydrolyyttisestä rappeutumisesta.

Avainsanat: alumiinioksidi, hammaslääketieteelliset biomateriaalit, pitkäikäisvesisäilytys, sidostaminen, silikointi, silanointi, termosyklaaminen, yhdistelmämuovi, zirkonia.

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ABBREVIATIONS

3-MPS	3-Methacryloxypropyltrimethoxysilane
4-META	4-Methacryloxyethyltrimellitic anhydride
10-MDP, MDP	10-Methacryloyloxydecylidihydrogenphosphate
ACPS	3-acryloxypropyltrimethoxysilane
Al ₂ O ₃	Dialuminium trioxide, alumina
ANOVA	Analysis of variance
Bis-EMA	Bisphenol-A-polyethylene glycol dietherdimethacrylate
Bis-GMA	Bisphenyl-A-glycidylmethacrylate
<i>c</i>	Cubic phase
CAD/CAM	Computer Aided Design / Computer Aided Manufacturing
DMAEMA	2-(Dimethylamino) ethylmethacrylate
EDS	Energy Dispersive X-Ray Analysis
EGDMA	Ethyleneglycoldimethacrylate
FDP	Fixed dental prosthesis
HEMA	Hydroxyethylmethacrylate
ISO	International Standardization Organization
LCTE	Linear coefficient of thermal expansion
<i>m</i>	Monoclinic phase
MEPS	Methacryloyloxyalkylthiophosphate
MMA	Methylmethacrylate
MPa	Megapascal, N/mm ² , SI derived unit of tensile strength
PMMA	Poly(methylmethacrylate)
RDP	Removable dental prosthesis
SD	Standard deviation
SEM	Scanning electron microscope
<i>t</i>	Tetragonal phase
T _g	Glass transition temperature, the temperature at which rubbery polymer chain transforms into glasslike substance
TEGMA, TEGDMA	Triethyleneglycoldimethacrylate
UDMA, UEDMA	Urethanedimethacrylate

VBATDT	6-(N-(4-vinylbenzyl)propylamino)-1,3,5-triazine-2,4-dithione
Y-TZP	Yttria stabilized tetragonal zirconium dioxide
ZrO ₂	Zirconium dioxide, zirconia

LIST OF THE ORIGINAL PUBLICATIONS

This thesis is based on the following original publications, which are referred to in the text by the Roman numerals I-V.

- I Heikkinen TT, Lassila LVJ, Matinlinna JP, Vallittu PK (2007). Effect of operating air pressure on tribochemical silica-coating. *Acta Odontol Scand* 65(4):241-248.
- II Heikkinen TT, Lassila LVJ, Matinlinna JP, Vallittu PK (2009). Thermo-cycling Effects on Resin Bond to Silicitized and Silanized Zirconia. *J Adhes Sci Technol* 23(7-8):1043–1051.
- III Heikkinen TT, Lassila LVJ, Matinlinna JP, Vallittu PK (2009). Dental Zirconia Adhesion with Silicon Compounds Using Some Experimental and Conventional Surface Conditioning Methods. *Silicon* 1(3):199-202.
- IV Heikkinen TT, Matinlinna JP, Vallittu PK, Lassila LVJ (2010). Effect of Primers and Resins on The Shear Bond Strength of Resin Composite to Zirconia. *SRX Dentistry* 2010(2010).
- V Heikkinen TT, Lassila LVJ, Matinlinna JP, Vallittu PK. The Comparison of the Effects of Four Year Water Storage and Thermal Cycling on Shear Bond Strength of Particulate Filler Resin Composite to Ceramics. *Submitted*.

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1. INTRODUCTION

The most common problem a prosthodontic is involved is a missing single tooth or several teeth. This kind of deficiency can be traumatising especially when it occurs on the visible area and more importantly, on shortened dental arch, the risk of traumatic occlusion increases. Nowadays, there is a wide variety of solutions, *e.g.* dental implants, FDPs and RDPs. For a long period of time there have been solutions to replace this kind of deficiencies with metal-alloy-based devices which later on have been developed into two-phase crowns and bridges. The tooth colour and shape has been achieved with composite or porcelain veneers but the underlying metallic shading and darkness have been an aesthetic shortcoming.

The general progress has led to the increasing development of aesthetics and emphasized biocompatibility of materials in prosthodontics. All-ceramic systems in which polycrystalline oxide ceramics and special manufacturing techniques are used to optimize their strength, such as alumina (Al_2O_3) and yttria stabilized tetragonal zirconia (Y-TZP) ceramics, have significantly improved biomechanical properties of ceramics. They can be used in a wide range of clinical applications such as root canal posts, crowns, veneers, inlays, onlays, FDPs, dental implant abutments and also as dental implants (Blatz et al. 2003, Manicone et al. 2007). For clinical applications, such as veneers and onlays, reliable bonding of composite resin cement to the ceramics is important. Hydrofluoric acid etching which is effective in improving the bonding of composite to glass ceramics (Luo et al. 2001, Özcan et al. 2003), cannot improve the bond strength of resin composite to polycrystalline oxide ceramics (Awliya et al. 1998, Sen et al. 2000). However, metallic and oxide ceramic surfaces can be successfully silicized with silica-coating procedure (Kourtis 1997) and then silanized with a silane coupling agent (Matinlinna et al. 2004 a) improving their adhesion to composites.

In dental technology, tribochemical silica-coating or silicatization is a widely used conditioning method for ceramic and metal alloy constructions in fabrication, repair and cementation. Tribochemistry involves creating chemical bonds by applying kinetic energy (Kajdas 2005), *e.g.* in the form of sandblasting, without any application of additional heat or light (Sun et al. 2000). In a so-called cold silicatization method, the en-

ergy needed in the silicization process is transferred to the object material in the form of kinetic energy, which generates frictional heat locally at the impact focus. In average, the temperature may momentarily and focally raise up to 1200°C (Kourtis 1997). Silicization takes place macroscopically, however, without any final change in temperature of the substrate bulk (Kajdas 2005). The system is based on airborne micro-blasting particles, which are especially silica-modified dialuminum trioxide and they provide the ceramics with a reactive silica-rich outer surface prone to silanization for the following resin adhesion. Particle size in the typical process is 110µm (Rocatec™, 3M ESPE, Seefeld, Germany) for the use in dental laboratories and 30µm (CoJet™, 3M ESPE, Seefeld, Germany) for the application of the system in dentist's office (Lorente et al. 2010).

The adhesion of a conventional resin to polycrystalline oxide ceramics with airborne particle abrasion without silicization and additional silanization has been suggested to be inadequate (Schmage et al. 2003). Nonetheless, there are products available based on modern bifunctional resin composites with the methacrylate and organophosphate functionalities that, unlike the conventional resins, do not require silicization and silanization in order to be reactive and effective. By using resin composites with reactive organophosphate monomers, a long-term durable resin bond strength to airborne particle abraded alumina or zirconia can be achieved (Kern and Wegner 1998, Blatz et al. 2004, Yang et al. 2010). Organophosphates have been studied and suggested for cementing in several in vitro studies concerning bonding of resin composites to glass ceramics and oxide ceramics (Kern and Thompson 1995, Borges et al. 2003, Janda et al. 2003, Blatz et al 2003 a&b, Hummel et al. 2004). Bonding procedures based on organophosphates are found to be superior to silicization and silanization without organophosphate cements.

This study was designed to investigate and assess alterations in materials and methods, and clarify the limits of the silicization and silanization methods with alumina and Y-TZP. As part of the investigation into alternative polycrystalline oxide ceramic bonding methods, the aim of the studies was to evaluate in vitro the effect of the operating air pressure of airborne particle silicization, the possibilities of experimental silicization methods, the effect of commercially available silane coupling agents and some experimental silane coupling agents, the effects of primers and the longevity of the bond achieved by silicizing and silanization between oxide ceramics and composite resin.

2. LITERATURE REVIEW

2.1 Polycrystalline oxide ceramics

The contemporary aim of biocompatibility and aesthetics in restorative dentistry has led to the use of polycrystalline oxide ceramics, *e.g.* alumina and zirconia. One of the main shortcomings of metals have been the non-aesthetic appearance of metallic substructures but also some allergenic issues related to noble and base metal alloys, such as Ni-Cr and others with Be content (Tai et al. 1992, Geurtsen 2002). Traditional dental ceramics including feldspathic porcelain primarily comprised an amorphous glass matrix with a crystalline phase as filler. So-called polycrystalline oxide ceramics in dentistry are primarily crystalline in nature (McLaren 1998). These materials are based on crystalline alumina or yttria stabilized tetragonal zirconia (Y-TZP). Some mechanical properties of those materials are presented in Table 1. Special processing techniques in combination with polycrystalline oxide ceramics has made it possible to fabricate FPD frameworks with a flexural strength and fracture toughness that are considerably higher than those of the feldspathic, leucite or lithium disilicate ceramics that have been previously used. The material's ability to resist crack propagation is thus superior to the traditional ceramics (Pröbster and Diehl 1992, Wall and Cipra 1992, Giordano et al. 1995, Seghi and Sorensen 1995). The polycrystalline oxide ceramics used today are based on dialuminum trioxide (alumina) and yttria stabilized zirconium dioxide (zirconia or Y-TZP). They both have beneficial properties such as biocompatibility, color stability, and low thermal conductivity.

Table 1. Mechanical properties of alumina, Y-TZP and Bis-GMA/TGDMA.

	Flexural Strength (MPa)	Hardness (VHN)	Thermal expansion coefficient (K⁻¹)	Elastic Modulus (GPa)	Reference
Alumina	>500	2200	8×10^{-6}	380	(Piconi and Maccauro, 1999)
Y-TZP	900-1200	1200	11×10^{-6}	210	(Piconi and Maccauro, 1999)
Bis-GMA/TEGDMA	60-107	10-22	$2-5 \times 10^{-5}$	0.5-10.5	(Pereira et al., 2005, Sandner et al. 1997)

2.1.1 Alumina

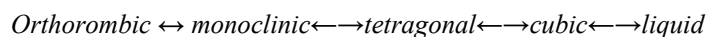
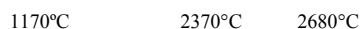
Alumina is the first widely used polycrystalline oxide ceramic material and it has been used to increase the strength of dental porcelains since 1957 (Al-Wahadni 1999). Alumina-based core ceramics consist of a partially sintered porous alumina structure which is infiltrated by molten glass. They are available in two forms: as slip powder used dispersed in water to build up crown copings and FDP cores or as dry pressed material processed for milling FDP frameworks and crown copings. Lanthanum glass is used for infiltration after the final shaping of the structures. The In-Ceram all-ceramic crown system (Vita Zahnfabrik, Bad Säckingen, Germany), introduced in 1989, succeeded in increasing the aluminum oxide concentration up to 70% by presintering a slip-casted aluminum oxide coping and then infiltrating this porous ceramic material with lanthanum glass (Claus 1990, Pröbster and Diehl 1992). This step ensured that the restoration features its characteristic colour, translucency and high final strength. Since postsintering shrinkage does not occur, the dimensions of the substructure remain unchanged during sintering as well as during glass infiltration. Next, the substructures are veneered with dental porcelain to create the appearance of a natural tooth (Vita In-Ceram). Studies have shown that glass-infiltrated alumina has a flexural strength up to four times greater than conventional porcelains, being 236 MPa (Giordano et al. 1995). Long-term follow-up studies were made to determine the longevity of the structures, the suitability and success of the material itself (Wall and Cipra 1992, Pröbster and Diehl 1992, Seghi and Sorensen 1995, Giordano 1995, Neiva G et al. 1998, Wen et al 1999).

Another type of alumina employed a technique where high-purity alumina structures are fabricated using computer-aided design/computer-aided manufacturing (CAD/CAM techniques). The benefit in this case has been described to be the superior flexural strength to glass-infiltrated alumina. For example, Procera AllCeram can reach a flexural strength of 600 MPa whereas In-Ceram reaches the value of 450 MPa, respectively (Schmidseder 2000). The alumina substructures are densely sintered and veneered with dental porcelain. Clinical studies had indicated that such alumina-based crowns may be used as crowns in all locations of the oral cavity (Odén et al. 1998). This technique combined alumina copings with an alumina pontic that is attached to the copings using a specially formulated connecting and fusing material (Odén et al. 1998, Ödman and Andersson 2001, Lang et al. 2004). Another advantage is the superior radiographic contrast of dental ceramics densely sintered pure aluminum oxide in comparison to feld-

spathic porcelain, which is close to the radiographic contrast of dentin. Thus it was possible to diagnose changes in the underlying tooth structure. For example, in 1989 introduced Procera AllCeram crown is composed of a coping of densely sintered high purity aluminum oxide veneered with dental porcelain. A sintering shrinkage is close to 20%, but it is controlled during the manufacturing of the coping. The content of aluminium oxide is 99.9% and the strength for this ceramic material is the highest among all-ceramic restorations used in dentistry (Wagner and Chu 1996, Zeng et al. 1996). An other biomaterial application found in orthopaedics for this type of aluminium oxide was its use as ball and socket replacements of the hip joint (Christel 1992, Odén et al. 1998). The flexural strength of 472-687 MPa and fracture toughness values to 3.84-4.48 MPa m^{1/2} was found according to different studies (Giordano et al. 1995, Ban S 2008). Currently, alumina ceramics are widely used for bearing surfaces in total hip replacements. Their use is based on good strength, modest fracture toughness, high wear resistance, good biocompatibility and corrosion resistance. Unfortunately, significant in-vivo failures have been reported by the orthopaedic community due to the slow crack propagation that leads to failure of the alumina ceramic component with time in service (Aza et al. 2002).

2.1.2 Y-TZP

Zirconia (zirconium dioxide) is a white, dense, crystalline oxide of zirconium. As a biomaterial there are no known adverse reactions reported, on the other hand, long-term clinical studies are yet to be published. Yttria stabilized zirconium dioxide (Y-TZP) is one of the most studied ceramic materials. Crystallographically, pure ZrO₂ has a monoclinic (*m*) crystal structure at room temperature and transitions to tetragonal (*t*) and cubic (*c*) at increasing temperatures:



The volume expansion caused by the tetragonal to monoclinic transformation at elevated temperatures induces critically large stresses, and will cause pure ZrO₂ to crack upon cooling from high temperatures. Some specific oxides may be added to unsintered

zirconia to stabilize the tetragonal and/or cubic phases before firing: magnesium oxide (MgO), yttrium oxide, (Y_2O_3), calcium oxide (CaO), and cerium oxide (CeO_2), amongst others. The lattice transformations of zirconia are so-called martensitic, characterized by being diffusion-free, *i.e.* involving only coordinated shifts of crystal lattice positions versus transport of zirconium atoms. It has been well documented that the $t \rightarrow m$ transformation is an athermal martensitic transformation, associated with a large temperature hysteresis (several hundred K) rather than at a specific temperature and, involving a shape deformation (Evans and Heuer 1980, Jin 2005). This transformation range is bound by the *martensitic start* (M_s) and *martensitic finish* temperatures. Volume changes on cooling associated with these transformations are substantial enough to make the pure material unsuitable for applications that require an intact solid structure. Change in volume is $c \rightarrow t$ approximately 2.31% and $t \rightarrow m$ approximately 4.5%. Sintered structures transforming from t to m on cooling from sintering temperatures (approximately 1300–1500°C) undergo spallation with portions crumbling into multi-grained powders (Kelly and Denry 2008).

Zirconia is very useful in its 'stabilized' stage. In some cases, the tetragonal phase can be metastable, *i.e.* the tetragonal zirconia can transfer to monoclinic stage without any extrinsic factor. If sufficient quantities of the metastable tetragonal phase is present, then an applied stress, magnified by the stress concentration at a crack tip during grinding, airborne particle abrasion or temperature changes can cause the tetragonal phase to convert to monoclinic, with the associated at structural level remarkable volume expansion. This phase transformation can then put the crack into compression, retards its growth and enhance thus beneficially the fracture toughness. This mechanism is known as transformation toughening which significantly extends the reliability and lifetime of products made of stabilized zirconia (Porter et al. 1979, Evans and Cannon 1986, Lughfi and Sergo 2010).

At present the dental ceramic with the most suitable mechanical properties is Y-TZP. Most commonly utilized form of zirconia in dentistry contains 3 mol% yttria (Y_2O_3) as stabilizer (3Y-TZP). The dense radiographic contrast of zirconia is very useful for monitoring marginal adaptation through radiographic evaluation (Manicone et al. 2007). However, the metal-like radiographic contrast to tooth structure prevents cariological diagnostics under the zirconia core. Historically, zirconia was first introduced as a

promising material for fastened hip joint cup coating material in orthopaedic implants because its flexural strength varies between 680-1520 MPa according to different studies and fracture toughness values to 6-8 MPa m^{1/2} (Guazzato et al. 2004, Denry and Kelly 2008, Wang et al. 2008).

However, there has been criticism towards the widely spread use of zirconia as it has been used as an orthopaedic material for over twenty years. The obvious problems with zirconia ageing were noticed with sudden, unexpected and rapid failure rate of some specific femoral heads which took place in 2001. Zirconia manufacturers claimed that this problem was limited under in vivo situation until year 2001 when roughly 400 femoral heads failed in a very short period. It was also claimed that the problem was related on one particular production batch (Chevalier 2006). Even so, if limited in time and number, and clearly identified to be process controlled, these events have had a catastrophic impact for the orthopaedic use of zirconia and some surgeons were taking other solutions in use (Chevalier 2006).

On the one hand, biomedical grade zirconia can show the best mechanical properties of oxide ceramics: this is also due to phase transformation which increases its crack propagation resistance. The stress induces the transformation of metastable tetragonal zirconia grains to the monoclinic phase at the crack tip, and following volume expansion of grains can induce substantial compressive stresses. On the other hand, due to this metastability, zirconia is prone to ageing in the presence of water, hot vapour or in a closed system in particular in contact with body fluids, *e.g.* saliva.

2.2 Mechanics of body ceramics and composite resins

2.2.1 Roughening abrasion and etching

Airborne particle abrasion, *i.e.* sandblasting, of dental materials is often used to clean the substrate surfaces and to achieve both a microretentive topography and increased surface area for bonding. It has been suggested that when using particles of Al₂O₃ for airborne particle abrasion, there are complex reactions on the substrate surface taking place, which consist of the separation and accumulation of certain elements at the substrate surface (Tiller et al. 1985 a, Tiller et al. 1985 b, Özcan and Vallittu 2003, Lorente et al. 2010). The result is an activated and chemically reactive surface which can be

demonstrated by the increased wettability of the material (Tiller et al. 1985 b). Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting, *i.e.* wettability, is determined by a force balance between adhesive and cohesive forces. According to the manufacturers' instructions, many chemical bonding systems either recommend or require airborne particle abrasion of the prosthodontic structure in order to achieve a high bond strength (Özcan and Vallittu 2003, Amaral et al. 2006, Valandro et al. 2006, Yoshida et al. 2006).

The roughening procedure for glass-ceramics and glass-infiltrated ceramics is possible to carry out with acid etching prior to silanizing. Acid-sensitive, glass-based ceramics (feldspathic, leucite and lithium disilicate ceramics) may undergo surface degradation by hydrofluoric acid (HF) gel yielding to a surface roughness that can enhance micro-mechanical bonding. Also, due to its bifunctional characteristics, silane coupling agent on the pretreated ceramic surface may increase the chemical bonding between the ceramic and resin materials (Aida et al. 1995, Özcan and Vallittu 2003, Matinlinna et al. 2004, Della Bona et al. 2004). The bifunctionality means that the silane molecule has two reactive groups. Silanization promotes the wettability of the ceramic surface enabling the resin cement to find close contact with it (Lu et al. 1992, Phoenix and Shen 1995). Moreover, silane coupling agents are able to chemically bond to the silica (silicon dioxide) present in ceramics to the organic matrix of resin cements by means of siloxane bonds (Söderholm and Shang 1993, Matinlinna et al. 2004 a&b, Brentel et al. 2007). However, oxide ceramics are highly inert, acid-resistant materials and require advanced techniques to become prone to silane (Blatz et al. 2003).

2.2.2 Silicatization

There are several alternative ways to silicize (silica-coat) various prosthodontic materials surfaces, *e.g.* restorations, crowns and bridges, in order to clean the surfaces, create a highly retentive surface and foremost, enhance their silanizability and thus promote the proper bonding to the substrate surface. Few techniques can be used at the dentist's office and some are restricted for laboratory or use only. A thermal silica-coating system (Silicoater MD system, Heraeus Kulzer, Wehrheim, Germany) from early 1980's required sandblasting of the metal prior to the silica-coating process. Next, the surface was coated with a liquid of silane which formed at increased temperature silica coating for the sub-

strate in Silicoater MD apparatus. This system had the advantage of avoiding flame adjustment problems (Akisli et al. 2002). Tribochemical silicatization utilizes the same principle with a specifically surface-modified alumina with SiO₂ coating on the surface of the particles. The silica particle diverges and attaches with the surface and intrudes onto it as the particle hits the ceramic surface, thus providing the ceramics with a reactive silica-rich outer surface prone to silanization and the following resin adhesion for cementing with suitable resin composites. The method can be considered as a ceramic coating forming a ceramic interface. Tribochemistry involves creating chemical bonds by applying kinetic energy (Kajdas 2005), *e.g.* in the form of sandblasting, without any application of additional heat or light. The method is capable of silica-coating, *i.e.* silicatizing, of restorations, as well as when using resins with chemically active monomers, *e.g.* organophosphates. The first tribochemical silica-coating system for dental use (Rocatec™ system, 3M ESPE, Seefeld, Germany), introduced in 1989, applied two sandblasting steps to the metal surface prior to the application of silane and resin (Guggenberger 1989). Tribochemical silica-coating using CoJet™ at the dentist's surgery office is a widely used conditioning method in ceramic and metal alloy structure repair and cementing. The system has been criticized for possibility of subcritical crack propagation within zirconia in case the restorations are thin (Zhang et al. 2004 a, Zhang et al. 2004 b, Zhang et al. 2006).

Airborne particle abrasion of prosthodontic materials has the potential to remove significant amount of material which could affect their clinical adaptation. Therefore, the material loss is an important factor that is affecting the clinical fit of restorations (Kern and Thompson 1994). Both morphological and compositional changes in the substrate surface occur through airborne particle abrasion and tribochemical coating procedures (Tiller et al. 1985 b, Pröbster and Kourtis 1991). However, the knowledge of the qualitative and quantitative changes in the surface through these procedures is limited. The reported initial bond strengths for the silica-coating systems are high and appear durable on certain metals surviving severe fastened fatigue (Kern et al. 1990, Hansson and Moberg 1993). In addition, in studies reporting failure modes with silica-coating systems, failures were partly or mostly adhesive, *i.e.* the failure was observed in the interface between resin composite and zirconia surface (Kern et al. 1990, Hansson and Moberg 1993). Therefore, the long-term studies of the effects of various surface treatments is needed to improve our understanding of the bonding mechanisms and failure modes involved (Kern and Thompson 1993).

Silicatization can also be carried out with other methods. Silicoater-technology based on pyrolysis of silanes is used also in the PyrosilPen™-technology which is able to create a silica-rich outer surface on metal or ceramic surface. They are based on a flame from mixture of butane gas and tetraethoxysilane (TEOS) which decomposes in the flame to produce $\equiv\text{Si-O-C}\equiv$ type species. Objects subjected for the flame over a short time, at most optimal 5 s, will be covered by a layer of these fragments which bond adhesively to the substrate surfaces. This surface has glass-like properties and can be successfully silanized, for example, with a widely used 3-methacryloxypropyl-trimethoxysilane (3-MPS) and bonded with a resin composite cement (Janda et al. 2003, Özcan et al. 2008, Rütterman et al. 2008).

2.2.3 Silane coupling agents

Silane coupling agents, *i.e.* silanes, are hydrid inorganic-organic synthetic compounds that are used to enhance the bonding of the resin composite to glass-based fillers and HF-etchable prosthodontic structures or silicatized metals and oxide ceramics, *e.g.* silica-coated surfaces (Matinlinna et al 2004 a). They are trialkoxy silicon esters. On the one hand, silanes can provide in some cases a chemical link, and on the other hand, in their solutions they are understood to promote surface wettability. Silane coupling agents have an organofunctional group that can co-polymerize with the non-reacted carbon-carbon double bonds in monomers of a resin composite. A usually hydrophobic silane compound first must be chemically activated prior to silanizing. Their hydrolyzable alkoxy groups ($-\text{Si-OR}$) need to react in aqueous alcohol solution, at a mildly acidic pH of 4–5 as a catalyst, to form labile reactive silanols, $\equiv\text{Si-OH}$. Hydrophilic silanols condense and deposit and form a hydrophobic siloxane film with the siloxane bonds, $-\text{Si-O-Si-O}$. The siloxane film thickness depends mainly on the silane concentration and reaction conditions and it is usually more than a simple monolayer (Plueddemann 1981, van Ooij and Child 1998).

At the moment, 3-methacryloyloxypropyltrimethoxysilane (also in literature known as 3-methacryloxypropyltrimethoxysilane, 3-MPS, Figure 1) is the most commonly used silane in commercial dental materials (Matinlinna et al. 2004 b, Sideridou and Karabela 2009). Some other silanes of the same chemical type as 3-methacryloyloxypropyl-trimethoxysilane, *i.e.* trialkoxysilanes with one organofunctional group, such as 3- isocyanatopropyltriethoxysilane (Matinlinna et al. 2005), a vinylsilane and an iso-

cyanuratesilane (Matinlinna et al. 2004 b) have been presented and evaluated *in vitro*. 3-Acryloyloxypropyltrimethoxysilane (ACPS, Figure 2) with its acrylate end-group has been studied as a coupling agent in dentistry (Matinlinna et al. 2006) as the terminal acrylate group is more reactive than the methacrylate group. The *in vitro* results have suggested that ACPS and ICS have the potential to produce significantly higher shear bond strength after fastened aging.

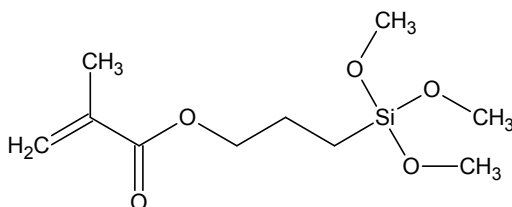


Figure 1. Chemical structure of 3-methacryloxypropyltrimethoxysilane (3-MPS).

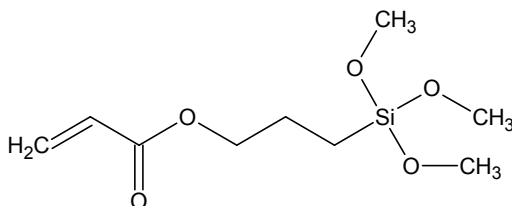


Figure 2. Chemical structure of 3-acryloxypropyltrimethoxysilane (ACPS).

Structurally, both 3-MPS and ACPS share some common properties: the organofunctional groups are connected with a propylene link to the silicon atom, and they have three methoxy groups.

It is widely accepted that a silane coupling agent is effective in promoting a bond between resin composite and glass ceramic although the mechanism of actions of silanes may vary. Some other studies suggest that a porcelain surface does not necessarily need the use of HF acid etching but might be silanized as such, after cleaning (Hooshmand et al. 2004). The use of silane as an organofunctional coupler between polymers and inorganic substances is well known technology in glass fiber laminating applications since early 1960's (Bowen 1962) and also reported in dentistry (Lacy AM et al. 1988). It has

been concluded that heat treatment or acid catalysis of silane increases the bond strength of resin cement to feldspathic ceramics treated with silane coupling agents because of the effective initiation and progress of the formation of siloxane bonds between the silane coupling agent and the glass-ceramic surface (Aida et al. 1995). The results of the *in vitro* study affirm those of previous studies (Bowen 1962, Lacy et al. 1988, Aida et al. 1995). The acidity of the solvent for the silane primer promotes the formation of silanols and thus next the siloxane bonds between the silane coupling agent and ceramic surface, and apparently contributes positively to the bond strength values. This acidic environment may also be attributable to increased wetting at the interface which promotes the condensation of silane monomers/oligomers with the monomers of resin composite (Harada et al. 2000, Shimada et al. 2002).

However, despite of their oxide character, oxide ceramics and metal alloys, both noble and base metal, require silicatization prior to silane treatment in order to be able to form the siloxane film on the substrate surface. Hence, the siloxane bonds of the silane bond indirectly to the silica content on the oxide ceramic surface, not directly into the material. The other end of the siloxane bond forms to the organic matrix of the resin cement to enhance chemical bonding (Stangel et al. 1987, Hayakawa et al. 1992). Zirconia ceramics are not silica based and thus they present a physico-chemical challenge for reliable and durable resin bonding as chemically stable silica-silane bonds cannot be directly established (Ntala et al. 2010).

2.3 Other coupling agents

It is noteworthy that silanes are not the only active materials in primers and silanization is not the only method that is used to promote the long-term durability of the resin composite bond to oxide ceramics. There are, indeed, several primers with reactive monomers that have been evaluated *in vitro* in order to investigate the bond longevity and the capability of the primer to form a chemical bond or, at least, a long-term micromechanical bond to alumina and Y-TZP. There are several products in market aimed at promoting resin oxide ceramic bonding but not all have been found suitable to be used for oxide ceramics. As a result, a massive amount of literature has been published and innovative adhesive strategies combining new surface roughening procedures (Aboushelib et al. 2007, Phark et al. 2009), laser treatments (da Silveira et al. 2005, Spohr et al. 2009),

precipitated and sintered alumina coating on zirconia (Jevnikar et al. 2010) and chemical bonding have been developed and assessed in vitro (Kern and Wegner 1998, Blatz et al. 2004, Yoshida et al. 2004, Yoshida et al. 2006, Atsu et al. 2006, Wolfart et al. 2007, Tanaka et al. 2008, Magne et al. 2010). Blatz et al. compared the bond strengths of different combinations of bonding/silane coupling agents and resin cements to Y-TZP. They concluded that conditioning with a bonding/silane agent that also contains a phosphate ester monomer, 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP, Figure 3), could exhibit superior resin bonding to Y-TZP which was airborne particle abraded with Al_2O_3 particles.

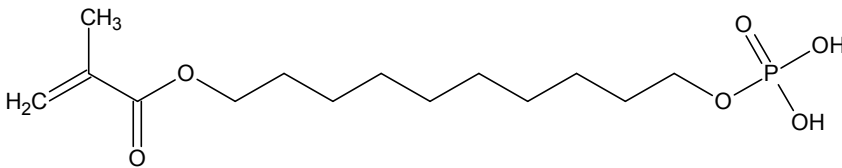


Figure 3. Chemical structure of 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP).

10-MDP containing materials have been suggested for use with oxide ceramics in order to achieve sufficient long-term reliability (Blatz et al. 2004, Yang et al. 2010). It has been shown that even if Y-TZP is bonded using a 10-MDP-containing organophosphate resin without airborne particle abrasion of the surface, specimens demonstrate low bond strength values (Aboushelib et al. 2008). This suggests that without airborne particle abrasion as a pretreatment no beneficial effect can be attributed to the phosphate monomer alone. This conclusion is supported by the observation that when the same bonding resin composite is used on zirconia specimens prepared by using selective infiltration etching (Aboushelib et al. 2008), a significant increase in bond strength can be observed.

A new primer (AZ Primer, Shofu, Kyoto, Japan) containing a phosphonic acid monomer, 6-MHPA (6-methacryloyloxyhexylphosphonoacetate), has been marketed for promoting bonding resin composite cements to alumina and zirconia ceramics. In principle, in vitro investigations are of utmost importance to assist in choosing materials for comparative studies of primers, silanes and resin composite luting cements. Their clinical evaluation can be commenced after preliminary careful comparative studies. Kitayama

et al. concluded that primers containing a silane coupling agent were effective in improving the bonding of resin cements to silica-based ceramic. The primers containing a phosphonic acid monomer or a phosphate ester monomer, including 6-MHPA and MDP, were the most effective ones in improving the bonding of resin cements to zirconia ceramic. Without any primer, the resin cement containing MDP was found to be effective in bonding to zirconia ceramic (Kitayama et al. 2010).

Furthermore, various adhesive monomers, *i.e.* so-called metal primers, have been developed to achieve improved adhesion between resin composite and base or noble metal alloys (Caeg et al. 1990, Yoshida et al. 1993, Gates et al. 1993, Chang et al. 1993, Diaz-Arnold et al. 1995). Initially, metal primers were developed for the repair of fractured metal–ceramic FDPs with metal exposure (Yoshida et al. 2006, Yoshida and Atsuta 1997). The adhesive functional metal primers are based on their affinity to metal oxides that exist on the metal surface and thus they are able to bond powerfully to pure metals and alloys (Ohno et al. 1986, Kojima et al. 1997). In addition to its bulk, Y-TZP surface is covered with a passive oxide film (ZrO_2), analogical similar to the titanium outermost surface (TiO_2). Thus, chemical characteristics of Y-TZP surface are somewhat similar and comparable to those of metal surface with oxide layers. Although it is possible to use a metal primer to increase bond strength between Y-TZP surface and resin cement, available information regarding its effect on the bond strength is limited at the moment. Hence, the objective of this study was to set to evaluate the effect of sandblasting and various selected metal primers on the bond strength between resin cements and Y-TZP ceramics. The null hypothesis to be tested was that there is no significant effect of metal primers on the shear bond strength between resin cements and Y-TZP ceramics after fastened fatigue of the specimens (Yun et al. 2010).

2.4 Resins and resin composites

It has been showed (Uo et al. 2003) that a glass ionomer cement may produce a superior bonding to Y-TZP compared with a phosphate monomer (10-MDP) containing adhesive resin composite. However, some previous studies (Kern and Wegner 1998) showed opposite results and thus 10-MDP containing cement produces a more durable bond after airborne particle abrasion of the Y-TZP surface. 4-META containing adhesive resin (Figure 4) has been pointed out (Dérاند and Dérاند 2000) to have a bond strength superior to 10-MDP-containing resin composite.

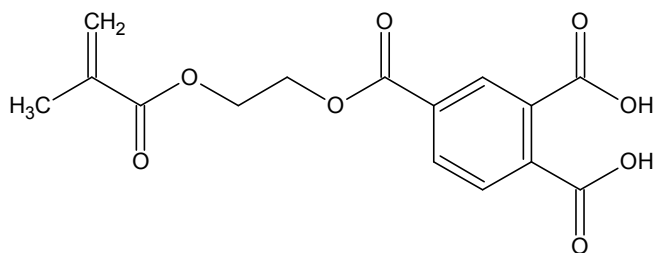


Figure 4. Chemical structure of 4-methacryloxyethyltrimellitic acid (4-META).

An early study suggested the use of either conventional luting cements, *e.g.* zinc phosphate or glass ionomer cements, or resin cements for clinical application as luting cements for bonding ceramics such as alumina or Y-TZP (Kappert and Krah 2000, Lüthy et al. 2006). There is some data suggesting that any kind of resin composite cement bond to Y-TZP might not be capable of sufficient adhesion for Maryland type FPDs (Behr et al. 2010). As one can see the studies can make controversial suggestions depending on the study design. The conclusion is that it is of importance to evaluate carefully the substrates, pretreatments, all the materials used and the presence and the method of fastened fatigue.

Adhesive resins have developed significantly during recent years with new product generations (Watanabe et al. 1994, van Meerbeek et al. 1998). It is widely accepted that the key factors in successful bonding to teeth are micromechanical entanglements of monomer resins to etched enamel and dentin by hybridization and thus marginal seal can be improved considerably (Asmussen et al. 1991, Van Meerbeek et al. 2003, Van Landuyt et al. 2007). As well, there is a notable problem with chemical bonding with resin to Y-TZP as it is an inert, nonreactive and complex surface with Zr atoms on the outer surface. Bond strength tests have always drawn a lot of scientific attention, and that is also the case with evaluating bond strength of different luting materials to Y-TZP. It is also well established that the data obtained from different bond strength tests depend on the actual test setup used and that may differ between individual studies. Therefore, the bond strength data substantially vary among different studies. All these interacting variables, *i.e.* surface pretreatment, silicating, silanes, primers and different resins, make direct comparison between different studies very difficult and ultimately irrelevant (Valandro et al. 2007, Mirmohammadi et al. 2010 b).

In contemporary dental research literature, there can be found several studies suggesting the use of a phosphate monomer containing luting resin which provides significantly higher retention of zirconia ceramic crowns than conventional luting cements (Atsu et al. 2006, Lüthy et al. 2006, Wolfart et al. 2007, Tanaka et al. 2008, Shahin and Kern, 2010). Widely used and suggested use of phosphate monomer composite resin has led to the development of competing products. Due to intellectual property rights (IPR) concerning the structure of MDP-monomer, other manufacturers have produced new phosphate monomers designed not only to bond to zirconia but have also cross-linking branches for bonding the resin matrix as well. One of the recently developed phosphate monomers (RelyX Unicem, Figure 5) has a characteristic of self-etching phosphorylated methacrylates that is designed to bond directly to both enamel and dentin. With two phosphate groups and at least two double bonded carbon atoms, a good bond strength to zirconia plus adequate crosslinking to the resin matrix is possible to achieve.

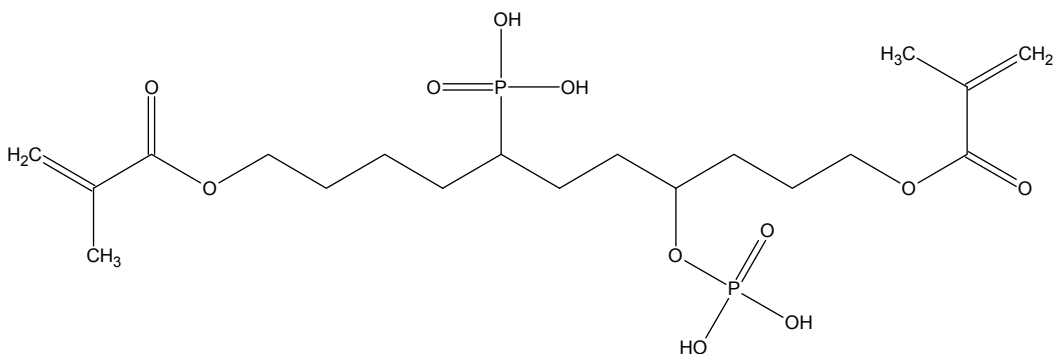


Figure 5. Chemical structure of phosphate monomer used in resin composite RelyX Unicem with self-etching phosphorylated methacrylates.

A recently developed phosphate monomer (RelyX Unicem) has a characteristic of self-etching phosphorylated methacrylates that is designed to bond directly to both enamel and dentin. With two phosphate groups and at least two double bonded carbon atoms, a good bond strength to zirconia plus adequate crosslinking to the resin matrix is possible to achieve. Another new self-etch phosphate monomer (Figure 6) characterized by hydrolytic stability has one phosphate terminal and at least two sites capable of bonding to resin matrix through oxygen bond.

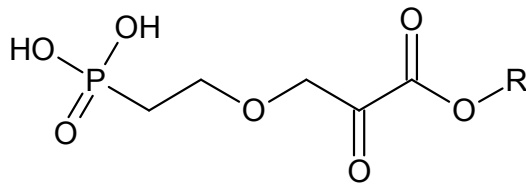


Figure 6. Chemical structure of self-etch phosphate monomer used in resin composite Multilink Automix.

This molecule has a terminal hydroxyl group as a substituent that gives the monomer stability under water and in acidic conditions (Mirmohammadi et al. 2010 b).

A recent *in vitro* study on the differences of the above mentioned phosphate monomer agents suggested that both Multilink and Panavia demonstrated predominantly cohesive failure within resin cement as the surface of zirconia was covered by a layer of resin cement. In contrast, RelyX UniCem revealed predominantly adhesive failure where the surface of zirconia was exposed. Thus, 10-MDP and the reactive molecule used in Multilink Automix could exhibit superior adhesion to RelyX Unicem (Mirmohammadi et al. 2010 b).

2.5 Novel bonding methods

Selective infiltration etching (SIE) is a novel surface treatment developed to transform the non-bonding surface of zirconia into a retentive by promoting the inter-grain nanoporosity. Such porosity forms retentive surface for the microentanglements of the adhesive resin composite to infiltrate and interlock. Y-TZP responds to thermal and mechanical stresses on two basic levels. On a nano-scale level, zirconia crystals have the ability to transform from tetragonal to monoclinic phase when properly stimulated. With volumetric expansion, the generation of compressive fields may prevent propagation of a crack tip. Such properties are the essence of the high fracture toughness of Y-TZP framework materials. On a micro-level, the grains of zirconia are subjected to nano-rearrangement movements, splitting, and sliding in the presence of other (dopant) phases and when heated to a sufficient temperature. Several dopant agents have previously demonstrated the capability to infiltrate the grain boundary region of zirconia and exert high capillary and surface tension forces resulting in structural changes of the surface grains (Abou-

shelib et al. 2006). SIE utilizes a specific glass infiltration agent that is capable of diffusing between the grains and results in nano-inter-grain porosity. After rinsing off this agent, the surface of zirconia can create a nano-mechanical bond with an adhesive resin. In a recent study, the effect of three different surface treatments on the bond strength was investigated: selective infiltration etching, particle abrasion, and coating with MDP monomer. The initial high bond strength was observed for the SIE surface treatment. Additionally, it was the only method capable of maintaining long-term bond strength values after storing in water for four weeks (Aboushelib et al. 2007). The bond strength and interface quality achieved using selective infiltration etching could be further improved with special zirconia primers. Silane coupling agents, *i.e.* silanes, are not able to react directly with the chemically inert zirconia (Kitayama et al. 2010) but they are functional with SIE (Aboushelib et al. 2008), silicating techniques (Matinlinna et al. 2006) and capable of promoting wetting when used with, for example, airborne microabrasion. Such findings directly reflect the need to establish mechanical retention to gain any benefit from the 10-MDP resin composite. These results could be further clarified by subjecting the specimens to thermocycling or long-term water storage (Yang et al. 2010).

2.6 Fatigue of bonding interface

The most common traditional fatigue techniques *in vitro* are water storage and thermocycling. They are fastened aging methods, widely utilized and based on ISO standards for dental materials and can be used separately or combined. For example, short term water storage, such as for three days, can be compared with long time water storage, *e.g.* for six to twelve months. In case of certain prosthodontic materials this can lead to spontaneous dissolution of the bond even without shear bond testing. Having said this, the number of cycles in thermocycling seems to play an important role when considering the durability of the bond. It is obvious that different dental materials behave differently during cycling as well. Thus, within the scope of the literature, it seems important to emphasize the importance of extended cycles. Combined with long-term water storage at 37°C, the method has been recommended for use when evaluating long term stability of the bond (Kern and Wegner 1998).

On the other hand, thermocycling has been criticized in several reports as to what extent it mimics the clinical situation (van Noort et al. 1989). ISO-standard which classifies polymer-based dental crown and bridge materials and specifies their requirements, sug-

gests 6.000 cycles, which may be insufficient for evaluating the long term stability (ISO 10477 Dentistry, 1996). The temperatures, *i.e.* 5°C and 55°C, and dwelling time 20 s used in the several studies have been discussed as well as the meaning of rest time (Gale and Darvell 1999). It is possible that the short transfer time has an effect on the heat conductivity preventing the temperature changes from occurring within the material. Moreover, the specimen size, if relatively bulky, may inhibit the heat transfer and thus the actual, eligible temperature inside a specimen may not be reached (Gale and Darvell 1999). Ceramic materials are well known isolators and insulators. On the other hand, thermal conductivity is strongly dependent on grain size. The average coefficient for thermal conductivity for zirconia is 2 W/mK (Nait-Ali et al. 2006) and for alumina 35 W/mK (Poulier et al. 2007). For PMMA the value is 0.2 W/mK (Hu et al. 2007). Now, as there is no concrete evidence that failures occur because of thermal stresses, every thermocycling test remains somewhat arbitrary and the results tedious to interpret. One possible solution might be a less severe test which would improve discrimination of the failure point as long as the stresses remain below the point that causes immediate collapse. Moreover, the temperature probe might be placed inside the specimen or between the bonded resin composite stub and conditioned zirconia. Then, the actual temperature could be monitored and registered. Nevertheless, the mechanism of the failure caused by cyclic tests, *i.e.* thermal shocks, needs further investigation (Matinlinna et al. 2006). Also, it has never been determined what the relevant factor is: the time at temperature, *i.e.* cumulative duration under stress, or true fatigue. In other words, whether failure occurs due to deformation in one or other of the layers in the bonded structure is unknown. This is obviously dependent on the glass transition temperatures (T_g) of these bonded resin composites which have not been determined or which are not necessarily found in the literature. Such heat flow would lead to collapse in a truly static test at a stress below the ordinary static strength of the bond interface. Thermal cycling testing as such cannot discriminate these issues. If this fact is ignored, this might account for the inconsistency of test results so far reported. The test outcome depends on the stress generated and the failure mechanism. However, due to the mechanism of the failure caused by cycling testing it is necessary to consider other kind of fatigue tests that can be more suitable for clarifying the nature of the failure and the factors leading into it (Soh and Selwyn 1992, Gale and Darvell 1999, Addison et al. 2003).

Initially, there are many bonding procedures capable of establishing a strong bond with Y-TZP and alumina. However, the bond strength should be adequate over years under the relatively aggressive circumstances of the oral cavity, *i.e.* under humidity, temperature shocks, pH fluctuation and mastication forces. In several studies investigating the influence of fatigue, *i.e.* fastened ageing, using water storage and/or thermocycling, fatigue reduction in the zirconia resin bond strength can be observed (Wegner and Kern 2000, Amaral et al. 2008). Bond strength can deteriorate with time, causing loss of retention and increasing microleakage. Two main mechanisms of deterioration of the established bond strength have been proposed: mechanical fatigue and hydrolytic degradation (Kern and Wegner 1998, Lüthy et al. 2006, Bottino et al. 2007, Blatz et al. 2007). Fatigue results from stresses affecting the bond, *e.g.* thermal expansion and contraction. Different linear coefficient values of thermal expansion (LCTE) of resin composite and ceramic may have an effect on the mechanism of failure at the ceramic–resin composite interface. LCTEs of ceramic materials are typically less than LCTEs of resin composite luting cements. This difference causes thermal stresses at the cement–ceramic interface, probably leading to unequal changes in dimensions, and eventually to failure of the bond. The difference between LCTEs is particularly high between ceramics and initially flowable luting cements (Tezvergil 2003, Meric and Ruyter 2008). Contraction of the resin composite, *i.e.* occlusal forces and pre-stress induced by the polymerization shrinkage, cause the same kind of stresses at the ceramic interface (Davidson and Feilzer 1997). Hydrolytic degradation of bonding interface is related to the diffusion of liquids. Diffusion is dependent on time, *e.g.* it takes time that water penetrates the bonding interface and causes chemical breakdown (Ferracane et al. 1995). In case of hydrolytic degradation, the effort should be made to stabilize the bonded interface chemically against the presence of saliva.

Some recent studies have introduced new methods for fatigue testing. A sub-critical fracture load test has been taken in use to evaluate the influence of rotating fatigue on the zirconia resin bond strength, not to find the absolute bond strength values. The test was designed to imitate the chewing function. (Mirmohammadi et al. 2010 a). Recently, micro-rotary fatigue testing was applied to hour glass shaped specimens and it was found that the load at which 50 % of the specimens failed after 100,000 cycles was about 30–40 % lower than the corresponding micro-tensile bond strength (De Munck et al. 2005). Estimations on the chewing strokes per year vary considerably from 100,000

(McCabe et al. 2000) to 1,000,000 cycles annually (Wiskott et al. 1994). The long-term influence of dynamic loading is not known or completely understood and thus further investigations are required to understand the complex interactions and their effects on the performance of zirconia resin bond strength. While deterioration of the established bond strength would not jeopardize the performance of crowns and bridges, reduction of the bond strength may cause higher tendency of debonding failure of adhesive restorations (Mirmohammadi et al. 2010 a).

2.7 Bond tests

As discussed above, it is rarely beneficial to study the initial, unaged situation as there are many factors in the oral cavity affecting the ceramics, the tooth and the adhesion between these structures. A couple of different subcritical fatigue measurement techniques have been suggested to imitate the stresses and loads occurring in the oral conditions and occlusion. A recent study utilized a test where the zirconia-composite resin beams were supported in a cantilever test setup. A constant load was applied on the free terminal of the bars causing stress concentration on the zirconia resin interface. Rotation of the bars was used for even distribution of the stresses at the perimeter of the bonded interface. The specimens were rotated at 1.2 Hz (rps) inducing alternating complex stresses (both compressive and tensile stresses being most detrimental) at the outer surface of the bonding interface of the specimens (Mirmohammadi et al. 2010). Another study dealing with fatigue of zirconia was paying attention to the lifetime measurements. They were performed in the oscillatory bending mode, by applying a cyclic load at the cantilever. A sinusoidal stress with constant maximum level (below the initial sample strength) was applied to the specimen surface at a fixed frequency of 10 Hz. The maximum applied stress was kept constant. Both surfaces of the specimen were alternately submitted to tensile and compressive stresses. The time required for sample failure at these cyclic loading conditions was automatically recorded when no strain was sensed due to specimen breakage. Tests under an aqueous environment were performed by surrounding the sample with a plastic tube filled with distilled and de-ionized water. (Stuart et al. 2007). A method emulating real masticatory functions was used by Uy et al. The location of load application, on the triangular ridge of the buccal cusp at a 135-degree angle, was selected to simulate the occlusal scheme of group function. The load was applied at an angle of 135 degrees to the long axis of the tooth, and a positioning jig

was used to hold each specimen in this orientation. The applied 73.5 N load lies within the range of 70.6 to 146.1 N as reported to be mean masticatory forces. The frequency of the loading device conforms to the masticatory rate of 60 to 120 strokes per minute reported by Graf (Graf 1969) (Uy et al. 2006).

The bonding performance of the adhesive materials can be evaluated by means of various bond tests. In general, tensile bond test and shear bond test have been applied. Due to the improvement of the adhesive capability of the materials, the micro-tensile bond test and micro-shear bond test are becoming more commonly applied for testing the recent adhesive materials. The main purpose of bond tests is recognized as the comparative evaluation of the bonding performance of materials (Tagami et al. 2010).

3. AIMS OF THE STUDY

This study was designed to investigate and to assess adhesion between two oxide ceramics and resin composite. The specific aims and hypothesis were:

1. To investigate the effect of the operating air pressure of airborne particle silicization. The hypothesis was that by increasing the air pressure, the shear bond strength was increased as well.
2. To compare the effect of two different silane coupling agents and fatigue testing on the shear bond strength. The first hypothesis was that acrylate silane (ACPS) is more reactive than methacrylate silane (3-MPS) and therefore could form hydrolytically more stable bonding. The second hypothesis was that thermocycling at $5\pm 1^\circ\text{C}$ and $55\pm 1^\circ\text{C}$ for 15000 cycles weakens the shear bond strength significantly.
3. To evaluate the effect of silicating with some experimental and conventional silicon compounds and conditioning methods. The hypothesis was that conditioning prior to sintering of Y-TZP produces a more reliable bond than conditioning after sintering.
4. To evaluate the effects of various surface conditioning methods and the effects of various selected combinations of coupling agents on the shear bond strength between resin composite and zirconia. The hypothesis was that organophosphates as primers produce superior bonding.
5. To evaluate the effects of three various aging methods and to compare acrylate silane (ACPS) with methacrylate silane (3-MPS) on shear bond strength of particulate filler resin composite to Y-TZP and alumina. The hypothesis was that thermocycling is comparable fatigue method to long-term water storage.

4. MATERIALS AND METHODS

4.1 Materials

4.1.1 Ceramics and coupling agents

The oxide ceramics alumina and Y-TZP chosen for the studies were commercially available products intended for the use in FPDs. The ceramics were either sintered prior to the following treatment or sintered with the following surface treatment material. Materials used have been summarized in Table 2.

In studies I, II, III and V the ceramic surfaces were pretreated with selected silicon-based materials to silicitize the ceramic surface and thus establish a silica-rich outer surface for the following silanization procedure. The commercial products and the preparation of the laboratory-made solutions have been summarized in Table 1.

In the studies all or some groups utilized silane coupling agents (silanes) in adhesion promotion, *i.e.* to create a siloxane layer for the following adhesive treatment. There were two types of silanes involved. As a commercial product and control was used 3-methacryloxypropyltrimethoxysilane (3-MPS, EspeSil, 3M ESPE, Seefeld, Germany) and experimental laboratory-made 3-acryloxypropyltrimethoxysilane (ACPS, laboratory-made, Toray Dow Corning Silicone, Tokyo, Japan). Materials used have been summarised in Table 1.

In Study IV, adhesion promoting coupling agents (Alloy Primer, Kuraray, Osaka, Japan), (Metal Primer, GC, Tokyo, Japan) and (UniFil Bond Primer, GC, Tokyo, Japan) were used in order to investigate their capability to enhance the shear bond strength between oxide ceramics and resin composite. Materials used have been summarised in Table 1.

Table 2. Materials used in the studies I-V.

Study	I	II	III	IV	V
Ceramics	LAVA, 3M ESPE, Seefeld, Germany	Procera Zirconia Nobel Biocare, Göteborg, Sweden	ICE Zirkon, Zirkonzahn GmbH, Bruneck, Italy	Procera Zirconia, Nobel Biocare, Göteborg, Sweden	Procera Zirconia, Nobel Biocare, Göteborg, Sweden
	Procera Alumina, Nobel Biocare, Göteborg, Sweden				
	Procera Zirconia, Nobel Biocare, Göteborg, Sweden				
Silicatizing material	CoJet™ Sand, 3M ESPE, Seefeld, Germany	Rocatec™ Plus, 3M ESPE, Seefeld, Germany	Cab-O-Sil, Cabot GmbH, Hanau, Germany		CoJet™ Sand, 3M ESPE, Seefeld, Germany
			CoJet™ Sand, 3M ESPE, Seefeld, Germany		
			Sodium silicate, Merck KGaA, Darmstadt, Germany		
Coupling agents			Veneering porcelain (ICE Zirkon Keramik Zirkonzahn GmbH, Bruneck, Italy)	Alloy Primer, Kuraray, Osaka, Japan	
				Metal Primer, GC, Tokyo, Japan	
				UniFil Bond Primer, GC, Tokyo, Japan	
Silanizing material	EspeSil, 3M ESPE, Seefeld, Germany	EspeSil, 3M ESPE, Seefeld, Germany	EspeSil, 3M ESPE, Seefeld, Germany	Clearfil Porcelain Bond Activator + SE Bond Primer, Kuraray, Osaka, Japan	EspeSil, 3M ESPE, Seefeld, Germany
		Laboratory-made acrylate silane (ACPS)		UniFil Bond Primer, GC, Tokyo, Japan	Laboratory-made acrylate silane (ACPS)
Adhesion	Multipurpose resin, 3M ESPE, St. Paul, Minn., USA	Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany		Clearfil SE Bond Bond, Kuraray, Osaka, Japan	Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany
				UniFil Bond Agent, GC, Tokyo, Japan	
Resin composite	Filtek Z250, 3M ESPE, Seefeld, Germany	RelyX™ ARC, 3M ESPE, Seefeld, Germany	RelyX™ Unicem, 3M ESPE, Seefeld, Germany	Filtek Z250, 3M ESPE, Seefeld, Germany	RelyX™ ARC, 3M ESPE, Seefeld, Germany
				Gradia Direct, GC, Tokyo, Japan	

4.1.2 Resins and resin composites

In Study I, all the specimens were attached to silicized and silanized surfaces. The preconditioned surfaces were treated with a resin (Multipurpose resin, 3M ESPE, St. Paul, Minn., USA). The resin was photo-polymerized for 10 s (Optilux 501, Kerr, Orange, CA, USA). Resin composite stubs were added on the surfaces (Filtek Z250, 3M ESPE, Seefeld, Germany). The resin composite was photo-polymerized for 40 s.

In Study II, all the specimens were attached to silicized and silanized surface. The preconditioned surfaces were treated with a resin (Adper™ Scotchbond™ 1, 3M ESPE, St. Paul, MA, USA) and the resin was photo-polymerized for 10 s (Optilux 501, Kerr, Orange, CA, USA). Resin composite stubs were added on the surfaces (RelyX ARC, 3M ESPE, Seefeld, Germany). The resin composite was photo-polymerized for 40 s.

In Study III, zirconia in Group 1 was used as intaglio. In Groups 2,3,4,5 and 6 the zirconia surfaces were silicized with an experimental method or tribochemically. In Group 7 a veneering porcelain was fired on the zirconia surface. The surfaces were silanized in Group 5. Resin composite stubs were added on the surfaces (RelyX Unicem, 3M ESPE, Seefeld, Germany). The resin composite was photo-polymerized for 40 s.

In Study IV, the surfaces were preconditioned with primers. The surfaces were treated with a resin (UniFil Bond Agent, GC, Tokyo, Japan or Clearfil SE Bond Bond, Kuraray, Osaka, Japan) and the resin was photo-polymerized for 10 s (Optilux 501, Kerr, Orange, CA, USA). Resin composite stubs were added on the surfaces (Filtek Z250, 3M ESPE, Seefeld, Germany or Gradia Direct, GC, Tokyo, Japan). The resin composite was photo-polymerized for 40 s.

In Study V all the specimens were attached to silicized and silanized surfaces. The preconditioned surfaces were treated with a resin (Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany). The resin was photo-polymerized for 10 s (Optilux 501, Kerr, Orange, CA, USA). Resin composite stubs were added on the surfaces (RelyX ARC, 3M ESPE, Seefeld, Germany). The resin composite was photo-polymerized for 40 s.

Resins and resin composites used have been summarised in Table 1.

4.1.3 Preparation of the specimens

4.1.3.1 Preparation of the specimens in operating air pressure studies (study I)

Seventy-two square-shaped samples (2 mm x 10 mm x 10 mm) of each sintered ceramic were embedded within cylinders (diameter 20 mm, height 10 mm) with an acrylic resin to form one bonding substrate. The resin composite stubs were photo-polymerized on to this surface. The surfaces of the ceramic substrates were examined with a scanning electron microscope (SEM; JEOL Scanning Electron Microscope JSM 5500, PGT Prism 2000-Si(Li) EDS detector, JEOL, Tokyo, Japan). The substrate surfaces were initially wet ground (Struer Lappol, Struers, Copenhagen, Denmark) with silicon carbide abrasive paper of 1000 grit (FEPA standard 42-1984 R 1993, Federation of European Producers of Abrasives). All the substrates were then randomly divided into four groups for tribochemical silicatization, cleaned in a ultrasonic cleaning unit, immersed in 70% ethanol for 10 min, air dried at RT and protected from dust.

The operating air pressures selected in the airborne particle silicatization system (Co-Jet™, 3M ESPE, Seefeld, Germany) were 150, 220, 300 or 450 kPa. Duration of the abrasion was a constant continuous pulse of 10 s and perpendicular distance between the tip of the airborne-particle hand-piece and the substrate was a constant 10 mm, as given in the CoJet™ system instructions. Silica-coated aluminum trioxide particles (Co-Jet™ Sand, particle diameter 30 μm; 3M ESPE, Seefeld, Germany) were applied. All the treatments were carried out by the same operator to keep the experiments comparable with each other. The substrate surfaces were then silanized with a silane coupling agent (EspeSil, 3M ESPE, Seefeld, Germany) containing 3-methacryloxypropyltrimethoxysilane as the active agent. One coat of silane was applied onto the substrate surfaces and covered with a uniform layer of light-polymerizable adhesive resin (3M Multipurpose resin; 3M ESPE, St Paul, Minn., USA) containing bisphenol-A-glycidyl-di-methacrylate (BisGMA) and 2-hydroxyethylmethacrylate (HEMA). The silane coating was allowed to dry for 5 min, as recommended by the manufacturer, and thereafter the adhesive resin was applied and light-polymerized for 10 s (Demetron Optilux, Kerr, Orange, CA, USA). Wavelength maximum of the light was 495 nm and light intensity was 550 mW/cm². A particulate filler resin composite (Z250, 3M ESPE, St Paul, Minn., USA) was applied into polyethylene moulds to form stubs 3.6 mm in diameter and 4.0 mm in height. The stubs were light-polymerized for 40 s and the moulds were removed.

Thermocycling was used as an fastened ageing method: 18 specimens of each group were thermocycled 8,000 times at between 5°C and 55°C (Thermocycling unit 81, custom-made; Biomechanical Testing Laboratory, University of Turku, Turku, Finland).

4.1.3.2 Preparation of the specimens in thermocycling effects studies (study II)

Two groups of Y-TZP (Procera Zirconia, Nobel Biocare, Göteborg, Sweden), consisting of 40 specimens each were prepared. Square shaped pieces (2 mm × 10 mm × 10 mm) of sintered ceramic material were embedded into plastic cylinders (diameter 20 mm, height 10 mm) and filled with an acrylic resin to form the specimen and bonding substrate for the resin composite stubs. The surfaces of the specimens were air particle abraded for 15 s with silica-coated aluminium trioxide particles (Rocatec™ Plus, 3M ESPE, Seefeld, Germany) 110 µm in diameter. An invariable air pressure of 300 kPa was used in conditioning of the surfaces. A distance of 10 mm between the tip of the blasting device and the substrate surface was maintained by securing the blasting device in a mounting jig above the substrate.

For the experimental silane primer, first a 95.0 vol-% ethanol and 5.0 vol-% de-ionized water (milli-Q water, Millipore Corp., Billerica, MA, USA) mixture was prepared. Its pH was adjusted with 1 M acetic acid to 4.5 and then this solvent system was allowed to stabilize for 24 h at room temperature. 1.0 vol-% solution of 3-acryloxypropyltrimethoxysilane monomer was prepared in the acidified ethanol–water solution. The silane was allowed to hydrolyze for 1 h at room temperature as described in literature. Pre-activated 3-methacryloxypropyltrimethoxysilane (EspeSil, 3M ESPE, Seefeld, Germany) was used as a control. Next, the silica-coated surfaces of the first zirconia group, labelled ZA, were silanized with the acrylate silane by applying one coat of experimental silane. The other group, labelled ZM, was silanized with a methacrylate silane (EspeSil, 3M ESPE, Seefeld, Germany). Next, all surfaces in both groups were coated with an adhesive resin (Scotchbond 1, 3M ESPE, Seefeld, Germany) and photopolymerized for 10 s (Optilux 501, Kerr, Orange, CA, USA). Resin composite luting cement (RelyX ARC, 3M ESPE, Seefeld, Germany) stubs (diameter 3.5 mm, height 5.0 mm) were formed by means of a plastic polyethylene mould onto substrates and photopolymerized for 40 s (Optilux 501, Kerr, Orange, CA, USA). The distance between the tip of the photopolymerizer and the stub was controlled by pressing the tip on the plastic mold (height 10 mm). The molds were removed.

The specimens of both groups ZA and ZM were randomly divided into five subgroups. The test specimens ($n = 8/\text{group}$) were thermocycled 0, 1000, 3000, 8000 or 15 000 times between $55\pm 1^\circ\text{C}$ and $5\pm 1^\circ\text{C}$ (Thermocycling unit 81, custom-made, Biomechanical Testing Laboratory, University of Turku, Finland). Duration of exposure to both temperatures was 20 s at a time.

4.1.3.3 Preparation of the specimens in zirconia adhesion with selected silicon compounds studies (study III)

Seven groups of zirconia (ICE Zirkon, Zirkonzahn GmbH, Bruneck, Italy) each consisting of 14 sintered specimens ($n=14$) were prepared in the laboratory. The specimens were ground with 320 grit silicon carbide paper (Struers A/S, Ballerup, Denmark). The square shaped specimens (2 mm x 10 mm x 10 mm) were embedded into acrylic cylinders (diameter 20 mm, height 10 mm) with an acrylic polymer material to form a bonding substrate. Exceptionally, specimens of Group 7 were not embedded until sintering and firing of veneering porcelain on the zirconia. Finally, the substrates were cleaned in 70% ethanol in an ultrasonic device for 300 s.

Group 1 was a reference group with a sintered intaglio zirconia surface.

In **Group 2** the zirconia surface was conditioned prior to sintering with a mixture of 0.87 w-% sodiumsilicate (Merck KGaA, Darmstadt, Germany) and in **Group 3** with 2.50 w-% fumed silica water solution (Cab-O-Sil M-5, Cabot GmbH, Hanau, Germany).

In **Groups 4** and **5** tribochemical silicization by airborne microblasting (CoJet™, 3M ESPE, Seefeld, Germany) was investigated. 450 kPa pressurized air was used in the CoJet™ system to blast silica-modified alumina particles (30 μm , CoJet™ Sand, 3M ESPE, Seefeld, Germany) to silica-coat the substrate surface. Group 5 was additionally silanized (EspeSil, 3M ESPE, Seefeld, Germany).

In **Group 6** the surfaces were pretreated with a mixture of 2.50 w-% fumed silica water solution (Cab-O-Sil M-5, Cabot GmbH, Hanau, Germany) and tribochemically silicized (30 μm , CoJet™ Sand, 3M ESPE, Seefeld, Germany).

In **Group 7** veneering porcelain (ICE Zirkon Keramik, Zirkonzahn GmbH, Bruneck, Italy) was fired on zirconia to form a glass-ceramic layer. The porcelain slurry was first prepared according to the manufacturers instructions and applied with a fine brush as approximately 0.5 mm thin layer uniformly onto the zirconia surface. Then, the specimens were fired with the heat treatment program starting at 400°C with 6 min preheating. The temperature was raised at 55 °C per minute with an applied vacuum (Vacumat 200 Vita Zahnfabrik, Bad Säckingen, Germany). Specimens were kept at the final temperature of 820°C for one minute before cooling started to the RT. No cracking or flawing was observed.

Self adhesive resin composite cement (RelyX Unicem, 3M ESPE, Seefeld, Germany) stubs (diameter of 3.6 mm, height 4.0 mm) were added onto the surfaces of the specimens and photopolymerized for 40 s (Optilux-501, Kerr, Orange CA, USA). Next, the specimens were kept in distilled water for 24 h at room temperature and thermocycled 6,000 cycles between 5±1°C and 55±1°C (Thermocycling unit 8I, custom-made, Biomechanical Testing Laboratory, University of Turku, Turku, Finland). Dwelling time at each temperature was 20 s.

4.1.3.4 Preparation of the specimens in primers and resins study (study IV)

Forty five Y-TZP (Procera Zirconia, Nobel Biocare, Göteborg, Sweden) square shaped sintered specimens (2 mm x 10 mm x 10 mm) were embedded into cylinders (diameter 20 mm, height 10 mm) with an acrylic polymer material (Palapress© Vario, Heraeus Kulzer, Hanau, Germany) to prepare the bonding substrate surface for the resin composite stubs. The substrate surfaces were Au sputter coated and examined with SEM (SEM, JEOL Scanning Electron Microscope JSM-5500, PGT Prism 2000, JEOL, Tokyo, Japan) as intaglio. Substrates were air particle abraded with Al₂O₃ (Korox ® 50, Bego, Bremen, Germany) with a diameter of 50 µm for 10 s with a sand blasting device (Co-Jet™, 3M ESPE, Seefeld, Germany). Air pressure of 450 kPa was used and the perpendicular distance between the tip of the blasting device and the ceramic surface was 10 mm. The surfaces were subsequently examined with SEM.

The specimens were randomly divided into five study groups and surface conditioning was carried out as follows:

Group A: the surfaces were first conditioned with mixture of a silane coupling agent (Clearfil Porcelain Bond Activator, Kuraray, Osaka, Japan) and a primer resin (SE Bond Primer, Kuraray, Osaka, Japan) as the manufacturer recommends. The mixture was applied on the surfaces for 10 s and air-dried for 5 s. Next, a resin (SE Bond Bond, Kuraray, Osaka, Japan) was applied on the surfaces for 10 s, air-dried for 5 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA). Wavelength maximum of the light was 495 nm and the light intensity was 550 mW/cm².

Group B: the surfaces were first conditioned with an alloy primer (Alloy Primer, Kuraray, Osaka, Japan) for 60 s and air-dried. Next, the surfaces were treated in the same way as in Group A.

Group C: the surfaces were conditioned with an alloy primer (Alloy Primer, Kuraray, Osaka, Japan) for 60 s and air-dried. Next, a resin (Scotchbond 1, 3M ESPE, St. Paul MN, USA) was applied on the surfaces for 20 s, air-dried for 5 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA).

Group D: the surfaces were conditioned with a primer (UniFil Bond Primer, GC, Tokyo, Japan) for 20 s and air-dried for 5 s. Next, a resin (UniFil Bond Agent, GC, Tokyo, Japan) was applied on the surfaces for 10 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA).

Group E: the surfaces were conditioned with a metal primer (Metalprimer II, GC, Tokyo, Japan) for 60 s and air-dried. Next, the surfaces were treated in the same way as in Group D.

The air-drying was carried out directly on the zirconia surface with gentle force and rotating movement. The curing light output was calibrated in the beginning of the preparation of each group set with the built-in radiometer of the curing unit (Optilux-501, Kerr, Orange CA, USA).

18 particulate filler resin composite stubs per group were prepared (n=18/group). A stub (diameter 3.6 mm, height 4.0 mm) was bonded to each substrate and photo-polymerized for 40 s (Optilux-501, Kerr, Orange CA, USA). In Groups A, B and C a particulate filler

resin composite (Filtek Z250, 3M ESPE, St. Paul MN, USA) containing *bis*-phenol A polyethylene glycol diether dimethacrylate (BISEMA6), diurethane dimethacrylate, *bis*-phenol A diglycidyl etherdimethacrylate (bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and fillers was used. In Groups D and E a micro-filled resin composite (Gradia Direct, GC, Tokyo, Japan) containing urethane dimethacrylate (UDMA), dimethacrylate and fillers was used.

Thermocycling was used as a custom fastened ageing method. The specimens were thermocycled 8000 times between $55\pm 1^\circ\text{C}$ and $5\pm 1^\circ\text{C}$ (Thermo-cycling unit 8l, custom-made, Biomechanical Testing Laboratory, University of Turku, Turku, Finland). Duration of exposure to both temperatures was 20 s at a time unintermittently. The specimens were kept in distilled water at 37°C for 14 d.

4.1.3.5 Preparation of the specimens for water storage compared with thermocycling study (study V)

Forty-eight Y-TZP (Procera Zirconia, Nobel Biocare, Göteborg, Sweden) and forty-eight aluminium trioxide (Procera Alumina, Nobel Biocare, Göteborg, Sweden) square shaped specimens (2 mm x 10 mm x 10 mm) were embedded into plastic cylinders (diameter 20 mm, height 10 mm) with an acrylic polymer denture base material (Palapress© Vario, Heraeus Kulzer, Hanau, Germany) to leave exposed one bonding substrate for the resin composite luting cement stubs. The substrate surfaces were used as intaglio. Substrates were air particle abraded with silica-coated Al_2O_3 (CoJet™ Sand, 3M ESPE, Seefeld, Germany) with a particle diameter of 30 μm , and for 10 s with a sand blasting device (CoJet™, 3M ESPE, Seefeld, Germany). Air pressure was constant 300 kPa, during operation and the perpendicular distance between the tip of the blasting device and the ceramic surface was 10 mm. Both alumina and zirconia substrates were randomly divided into two sub groups and the ceramic surfaces were treated as follows:

Group AM: the cleaned alumina surfaces were first conditioned with a fresh silane (EspeSil, 3M ESPE, Seefeld, Germany): one coat of silane was spread and allowed to dry for 5 min. Next, a resin (Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany) was applied on the surfaces for 10 s, air-dried for 5 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA). Wavelength maximum of the light was 495 nm and the light intensity was 550 mW/cm^2 .

Group AA: A 95.0 vol.-% ethanol and 5.0 vol.-% de-ionized water (milli-Q water) mixture was prepared. Its pH was adjusted with 1 M acetic acid to 4.5 and then this solvent system was allowed to stabilize for 24 h at room temperature. An experimental silane primer, a 1.0 vol.-% solution of 3-acryloxypropyl-trimethoxysilane (ACPS) monomer was prepared in the acidified ethanol–water solution, in 50 ml polyethylene bottles. The silane was first allowed to hydrolyze for 1 h at room temperature. The alumina surfaces were conditioned with this silane. Next, a resin (Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany) was applied on the surfaces for 10 s, air-dried for 5 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA). Wavelength maximum of the light was 495 nm and the light intensity was 550 mW/cm².

Group ZM: the cleaned alumina surfaces were first conditioned with a fresh silane (EspeSil, 3M ESPE, Seefeld, Germany): one coat of silane was spread and allowed to dry for 5 min. Next, a resin (Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany) was applied on the surfaces for 10 s, air-dried for 5 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA). Wavelength maximum of the light was 495 nm and the light intensity was 550 mW/cm².

Group ZA: A 95.0 vol.-% ethanol and 5.0 vol.-% de-ionized water (milli-Q water) mixture was prepared. Its pH was adjusted with 1 M acetic acid to 4.5 and then this solvent system was allowed to stabilize for 24 h at room temperature. An experimental silane primer, a 1.0 vol.-% solution of 3-acryloxypropyl-trimethoxysilane (ACPS) monomer was prepared in the acidified ethanol–water solution, in 50 ml polyethylene bottles. The silane was first allowed to hydrolyze for 1 h at room temperature. The alumina surfaces were conditioned with this silane. Next, a resin (Adper™ Scotchbond™ 1, 3M ESPE, Seefeld, Germany) was applied on the surfaces for 10 s, air-dried for 5 s and photo-polymerized for 10 s (Optilux-501, Kerr, Orange CA, USA). Wavelength maximum of the light was 495 nm and the light intensity was 550 mW/cm².

The air-drying was carried out with oil-free air directly on the ceramic surface with gentle force and rotative movement for 10 s. Then, the curing light output was calibrated in the beginning of the preparation of each group set with the built-in radiometer of the curing unit (Optilux-501, Kerr, Orange CA, USA). A total 96 particulate filler resin composite stubs were prepared (n=12/group). A stub (diameter 3.6 mm, height 4.0 mm)

were added to each substrate and photo-polymerized for 40 s (Optilux-501, Kerr, Orange CA, USA). A particulate filler resin composite (RelyX Arc, 3M ESPE, Seefeld, Germany) containing bis-phenol A polyethylene glycol diether dimethacrylate (bis-EMA6), diurethane dimethacrylate bis-phenol A diglycidyl ether dimethacrylate (bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and fillers was used.

Thermocycling, long-term water storage and thermocycling combined with long-term water storage were used as fatigue methods. The shear bond strength values were measured initially to form a control group. Then, the specimens were either stored for four years in distilled water $37\pm 1^\circ\text{C}$, thermocycled 8000 times between $55\pm 1^\circ\text{C}$ and $5\pm 1^\circ\text{C}$ (Thermo-cycling unit 8l, custom-made, Turku Clinical Biomaterials Centre-TCBC, University of Turku, Turku, Finland) or first stored in distilled water $37\pm 1^\circ\text{C}$ for four years and subsequently thermocycled 5000 times between $55\pm 1^\circ\text{C}$ and $5\pm 1^\circ\text{C}$. Dwelling time was 20 s at a time.

4.2 Methods

4.2.1 Measurement of shear bond strength

Bond strength were measured as shear bond strengths (SBSs). In order to carry out the shear bond strength test, the test specimens were stored in distilled water (37°C) and then immediately placed in the holder of a universal testing machine (Lloyd Instruments LRX Material Testing Machine, Lloyd Instruments, Fareham, UK) measuring shear bond strength of the resin composite stub to the ceramic material. A cross-head speed of 1.0 mm/min (Lloyd Instruments LRX Material Testing Machine, Lloyd Instruments, Fareham, England) with a parallel knife-edge blade touching the interface of the ceramic and resin composite cylinder was used, and the debonding fracture load was registered. Debonding loads were calculated as shear stress (MPa), *i.e.* by dividing the failure load (N) by the bonding area (mm^2):

$$\tau = F/A$$

where

τ is the shear stress in megapascals (MPa).

F is the failure load in newtons (N).

A is the surface area in squaremillimeters (mm^2).

4.2.2 Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS)

The surface examination was carried out by using scanning electron microscopy. In order to evaluate the fracture surfaces between the ceramics and resin composite, scanning electron micrographs (SEM, JSM 5500, Jeol, Tokyo, Japan) were taken in studies I, III, IV and V. The micrographs were taken after the shear bond strength tests. For the SEM investigations, the specimens were sputter coated with a layer of Au. The SEM connected with a unit for energy dispersive X-ray analysis (EDS detector; JEOL, Tokyo, Japan) EDS was also used for the analysis of the elements of silica residuals on the surface and below.

4.2.3 Assessment of failure mode

In the Study IV, the light microscopy was used to visually determine the failure type of de-bonding as follows: when about 2/3 or more of the resin composite cement was left on the ceramic surface after shear bond strength testing, the failure was designated as “*cohesive*”, and when less than 1/3, “*adhesive*”, respectively. Failure mode was designated as “*mixed*”, when it fell between the limits above.

4.2.4 Statistical methods

In the Study I, two-way analysis of variance (ANOVA, SPSS 10.0, Statistical Package for Social Science, SPSS Inc., Chicago, IL, USA) followed by the Tukey post-hoc test for pairwise comparisons ($p < 0.05$) and Weibull analysis were used as statistical methods. The dependent variable in two-way ANOVA was shear bond strength and independent variables were operating air pressure and ceramic material. Weibull distribution for life data analysis, designed to compute failure probabilities as a function of applied stress, was used to characterize the nature of the shear bond strength by fitting the statistical distribution to life data in order to estimate the failure probability.

In the Study II, two-way ANOVA followed by the Tukey post-hoc test at a significance level ($p < 0.05$) were used as statistical methods. Dependent variable in two-way ANOVA was shear bond strength and independent variables were silane and number of thermal cycles.

In the Study III, the data were analyzed by one-way ANOVA ($p < 0.001$). Dependent variable was shear bond strength and independent variable was the surface treatment method.

Study IV one-way ANOVA followed by Tukey post hoc test ($p < 0.05$) and Weibull analysis were used. Dependent variable in ANOVA was shear bond strength and independent variable was the surface treatment method. Weibull distribution was used to compute failure probabilities as a function of applied stress.

In the Study V the shear bond strength data were analysed with two-way ANOVA followed ($p < 0.001$) using shear bond strength as dependent variable, and silane and fastened fatigue method as independent factors.

5. RESULTS

5.1 Influence of operating air pressure of tribochemical silicatization on shear bond strength of resin composite to polycrystalline oxide ceramics

Shear bond strength of the resin composite to each ceramic material is given in Table 3 and the results of the Weibull analysis in Table 4 for the each operating air pressure. The shear bond strengths of both Y-TZP ceramics (LAVA and Procera Zirconia) increased. LAVA reached initially 12.6 ± 2.6 MPa and with the air pressure of 450 kPa 18.2 ± 3.1 MPa. Procera Zirconia reached initially 11.2 ± 2.1 MPa and with the air pressure of 450 kPa 26.4 ± 2.4 MPa. The shear bond strengths of the aluminum trioxide (Procera Alumina) increased from 18.4 ± 2.4 MPa (air pressure 150 kPa) to 30.4 ± 3.0 (air pressure 450 kPa). Two-way ANOVA revealed that both factors, ceramic material ($p=0.03$) and air pressure ($p<0.001$), had significant effects on bond strength values. There was no interaction between factors (ceramic material and pressure) ($p=0.387$). According to the scanning electron microscope and visual evaluation, all the fractures in every group were *adhesive*. Figures 7, 8 and 9 show the fracture probability of the bond with different shear stress levels. The curves of the fracture probability of both LAVA and Procera Alumina in the groups with the operating air pressures of 150 kPa and 220 kPa cross each other, indicating apparently higher shear bond strength of the lower air pressure group. The groups treated with 300 kPa and 450 kPa air pressure show higher shear bond strengths than the other two groups.

Table 3. Mean shear bond strength (SD) for each material and air pressure.

Air Pressure	Ceramics		
	LAVA	Procera Alumina	Procera Zirconia
150 kPa	12.61 ± 2.64^a	18.37 ± 2.35^a	11.21 ± 2.09^a
220 kPa	13.39 ± 3.98^{ab}	15.56 ± 3.00^{ab}	15.01 ± 3.00^{ab}
300 kPa	17.13 ± 4.92^{ab}	27.09 ± 3.31^{ab}	22.76 ± 2.31^{bc}
450 kPa	18.22 ± 3.11^b	30.49 ± 3.00^b	26.43 ± 2.39^c

Superscript letters indicate homogenous subsets (Tukey, $p<0.05$) between used air pressure within ceramic material.

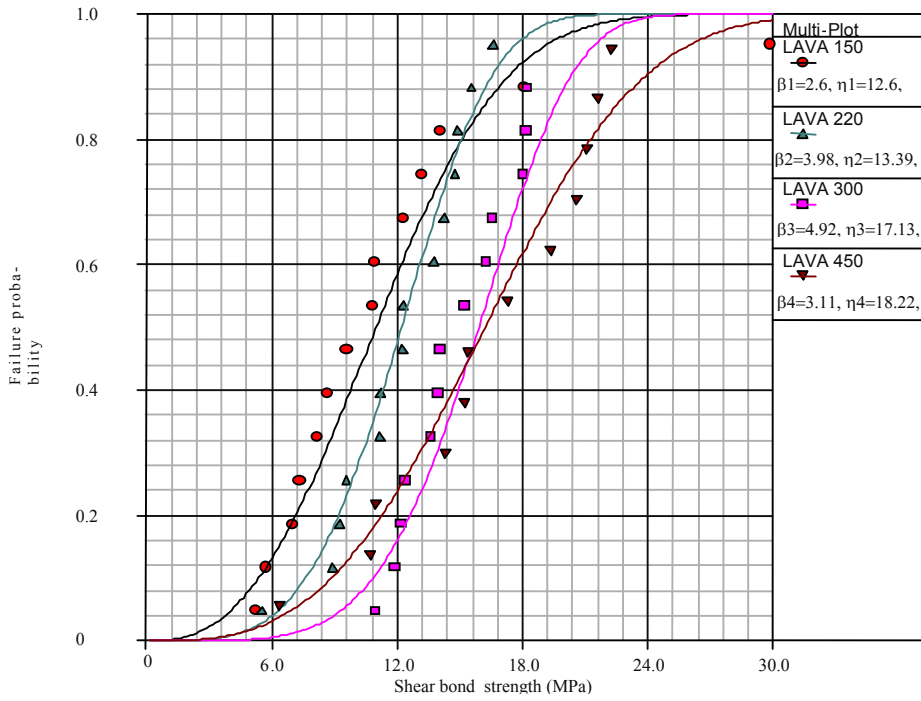


Figure 7. Weibull graphs of shear bond strengths of composite resin to Y-TZP (LAVA) as a function of air pressure of the CoJet™ system.

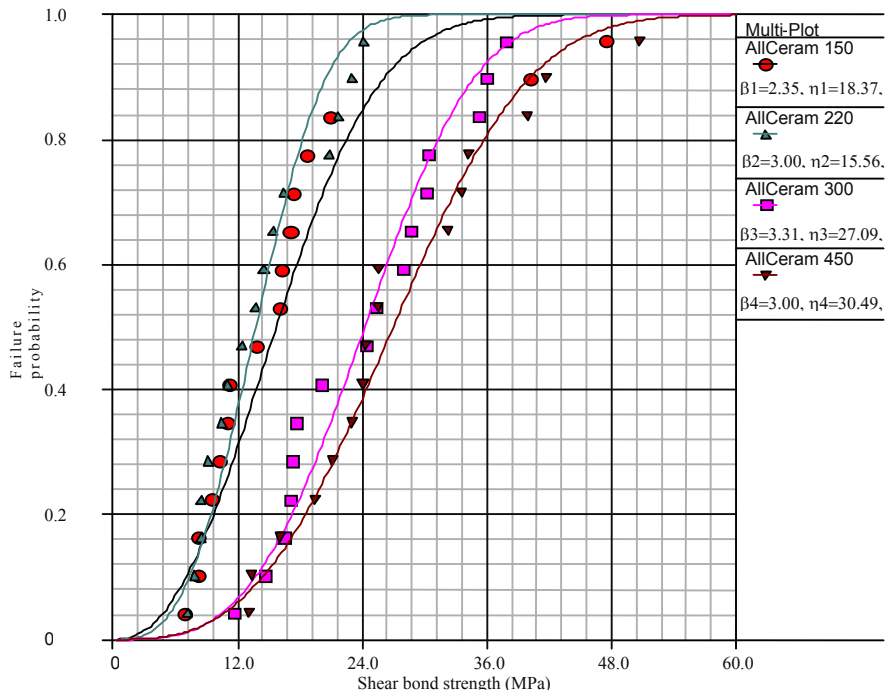


Figure 8. Weibull graphs of shear bond strengths of composite resin to alumina (Procera AllCeram) as a function of air pressure of the CoJet™ system.

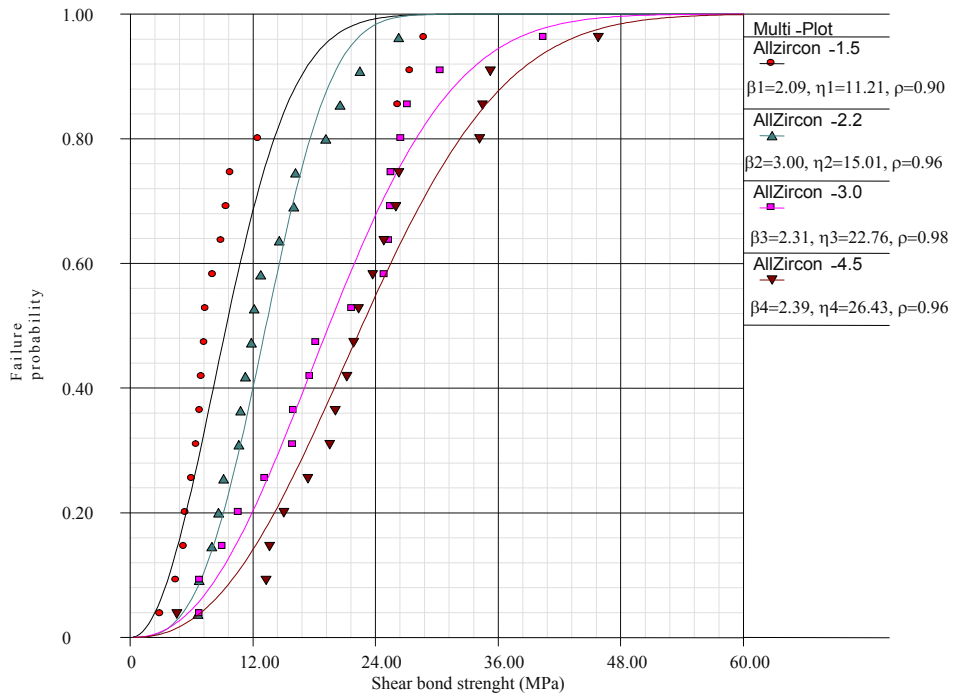


Figure 9. Weibull graphs os shear bond strengths of resin composite to Y-TZP (Procera AllZircon) as a function of air pressure of the CoJet™ system.

Table 4. The results of the Weibull analysis for the shear bond strength and the EDS analysis for silica content on surface of ceramics. Values in parenthesis represent standard deviations.

Air pres- sure (kPa)	Ceramics											
	3M-ESPE LAVA (Y-TZP)				Procera Alumina (Al ₂ O ₃)				Procera Zirconia (Y-TZP)			
	m	Σ	r	SiO ₂ (wt%)	m	σ	r	SiO ₂ (wt%)	m	σ	r	SiO ₂ (wt%)
150	2.64	12.61	0.94	6.60 (0.20)	2.35	18.37	0.91	6.63 (0.25)	2.09	11.21	0.90	3.59 (1.19)
220	3.98	13.39	0.98	6.52 (0.47)	3.00	15.56	0.95	6.52 (0.47)	3.00	15.01	0.96	3.93 (0.51)
300	4.92	17.13	0.87	6.64 (0.78)	3.31	27.09	0.97	8.19 (0.67)	2.31	22.76	0.98	4.66 (0.53)
450	3.11	18.22	0.97	5.80 (0.42)	3.00	30.49	0.98	10.82(0.40)	2.39	26.43	0.96	4.99 (0.59)

5.2 Effect of thermocycling on shear bond strength of resin composite to silicatized and silanized Y-TZP

Mean values of shear bond strengths are presented in Table 5. The shear bond strength values have been presented as a function of thermocycling in Figure 10. Two-way ANOVA revealed that both factors, silane and thermocycling, affected significantly the shear bond strength. There were considerable differences between bond strengths after extended thermal cycles between the two groups. The shear bond strength values in dry condition were considerably higher for both materials than after thermocycling for 1000, 3000, 8000 or 15 000 times. Group ZA (acrylate silane) revealed superior results compared to group ZM (methacrylate silane) prior to 8000 cycles. After 8000 and 15 000 cycles the bond values for group ZA rapidly decreased towards values for group ZM. Group ZM revealed statistically ($p < 0.05$) lower shear bond strength values prior to 8000 cycles compared to group ZA ($p < 0.05$).

Table 5. Mean values of shear bond strengths with standard deviations as a function of thermal cycles. ZA represents group in which Y-TZP was silanized with acrylate silane and ZM group silanized with methacrylate silane.

Group	Thermal cycles (+5± 1°C and +55±1°C)				
	0	1000	3000	8000	15000
ZA	23.0 ±6.7a	20.8 ±5.5ab	13.5 ±7.0b	4.7 ±1.4c	4.7 ±2.7c
ZM	16.8 ±4.2a	10.2 ±5.1bc	6.9 ±4.0bc	4.4 ±1.8c	2.7 ±1.2c
p (within cycles)	0.058	0.002	0.056	0.723	0.105

Same superscript letter within row indicates homogeneous subset (Tukey [$p < 0.05$]).

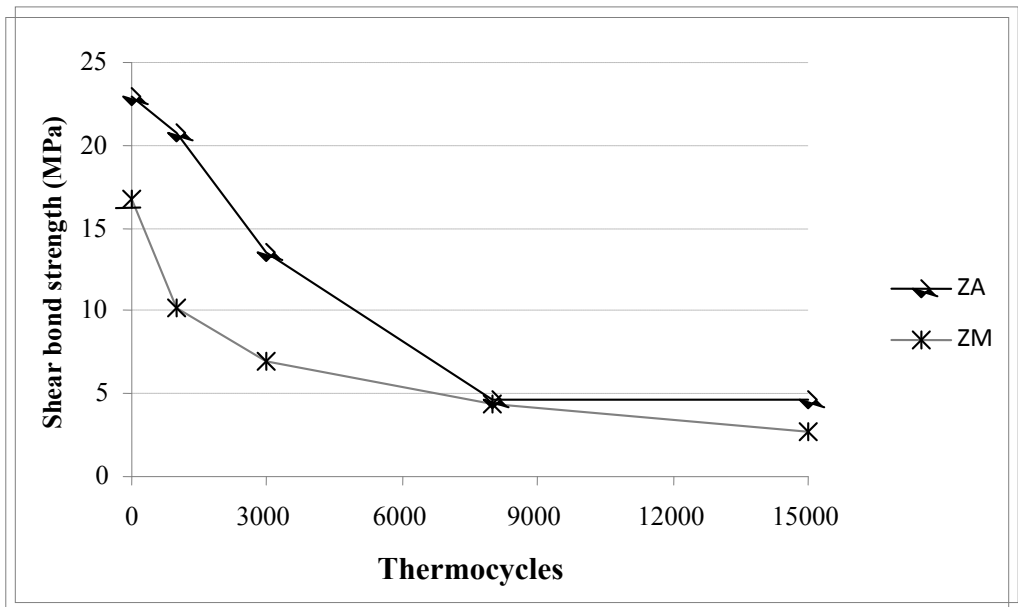


Figure 10. The shear bond strength values as a function of thermocycling. ZA represents group in which Y-TZP was silanized with acrylate silane and ZM group with methacrylate silane.

5.3 Effect of experimental and conventional surface conditioning on shear bond strength of resin composite to Y-TZP

The shear bond strength data are summarized in Table 6. Statistical analysis (ANOVA) indicated significant differences with results achieved by different surface conditioning methods ($p < 0.001$).

Specimens in **Groups 1, 2 and 3** showed spontaneous debonding during water storage. Either unmeasurable or low shear bond strengths could be reached by solely sintering (Group 1: 0 MPa) or by pretreating either with sodium silicate (Group 2: 3.5 ± 1.0 MPa) or 2.5-w% fumed silica water solution (Group 3: 0 MPa).

Groups 4 and 5 were treated with tribochemical silicatization and Group 5 was additionally silanized (Group 4: 10.9 ± 2.9 MPa and Group 5: 18.8 ± 4.2 MPa). Group 5 showed the highest shear bond strength and superior results to the other groups.

Group 6 where zirconia was dipped to mixture of 2.50 w-% fumed silica water prior to sintering and tribochemical silicatization reached 7.6 ± 2.9 Mpa values. Values were higher than in Group 3 (fumed silica water solution prior to sintering) and lower than in Group 4 (tribochemical silicatization).

Group 7 showed moderate shear bond strength (13.7 ± 4.8 MPa). SEM inspection found all the fractures within the fired-on dental porcelain. On the basis of the value nothing can be concluded about the porcelain-zirconia junction.

Table 6. Zirconia surface treatment methods and mean values with standard deviations (SD) of each group (MPa) (a=spontaneous debonding during water storage).

Group	Surface conditioning methods	Shear bond strength (MPa)±SD
1	Normal sintering	a
2	1. Unsintered zirconia dipped to sodiumsilicate 2. Normal sintering	3.5±1.0a
3	1. Unsintered zirconia dipped to mixture of 2.50 w-% fumed silica water 2. Normal sintering	a
4	1. Normal sintering 2. 450 kPa tribochemical silica coating	10.9±2.9
5	1. Normal sintering 2. 450 kPa tribochemical silica coating 3. Silanization	18.8±4.2
6	1. Unsintered zirconia dipped to mixture of 2.50 w-% fumed silica water 2. Normal sintering 3. 450 kPa tribochemical silica coating	7.6±2.9
7	1. Normal sintering 2. Veneering porcelain fired on the zirconia surface	13.7±4.8

5.4 Effect of primer and resin on shear bond strength of resin composite to Y-TZP

The mean values of data of shear bond strengths are presented as a bar diagram in Figure 11. The characteristic Weibull strengths are presented in Figure 12. Statistical analysis (ANOVA) showed that surface conditioning significantly affected the shear bond strength ($p<0.001$).

Group A treated with 10-MDP-containing primer and resin showed improved shear bond strength values (25.8±6.7 MPa). Group B was additionally primed with 10-MDP

containing primer and the shear bond strength was 26.5 ± 8.6 MPa. Group C was conditioned solely with primer containing 10-MDP and the results (16.7 ± 8.5 MPa) were considerably lower compared with Groups A and B. Group D was treated only with methacrylate resin and the results fell considerably (2.6 ± 0.7 MPa). Group E was conditioned with a primer containing thiophosphate (MEPS) and treated with methacrylate resin but could show only poor shear bond strengths (4.2 ± 1.2 MPa).

In Groups A and B the fractures occurred mainly within composite resin and thus were cohesive or mixed. In Group C the fractures were either mixed or adhesive. In Groups D and E the fractures were solely adhesive. The fracture types by groups are presented in Table 7.

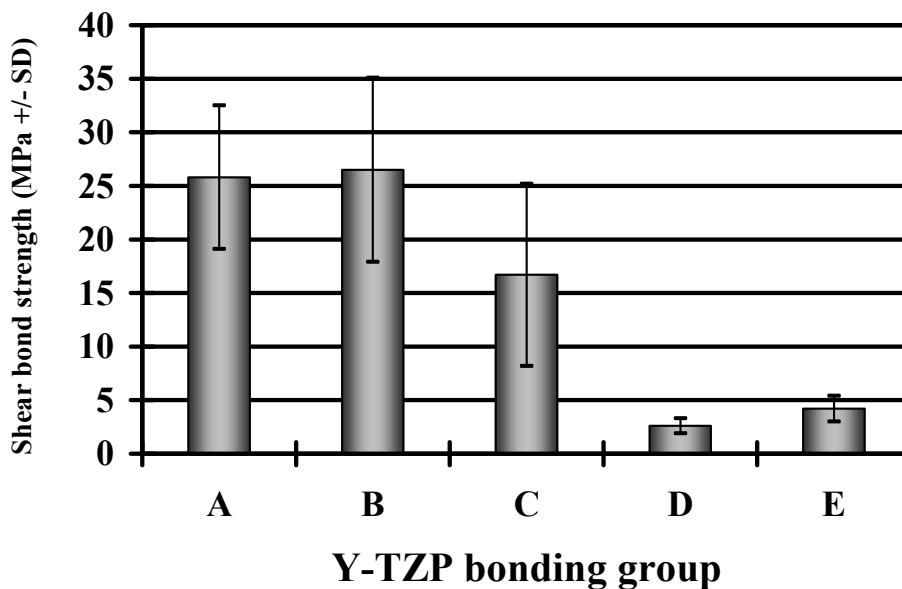


Figure 11. The mean values of data of shear bond strengths.

Group A = silane with organophosphate adhesive, Group B = organophosphate primer with silane and organophosphate adhesive, Group C = organophosphate primer, Group D = methacrylate adhesive, Group E = thiophosphate primer with methacrylate adhesive (n=14).

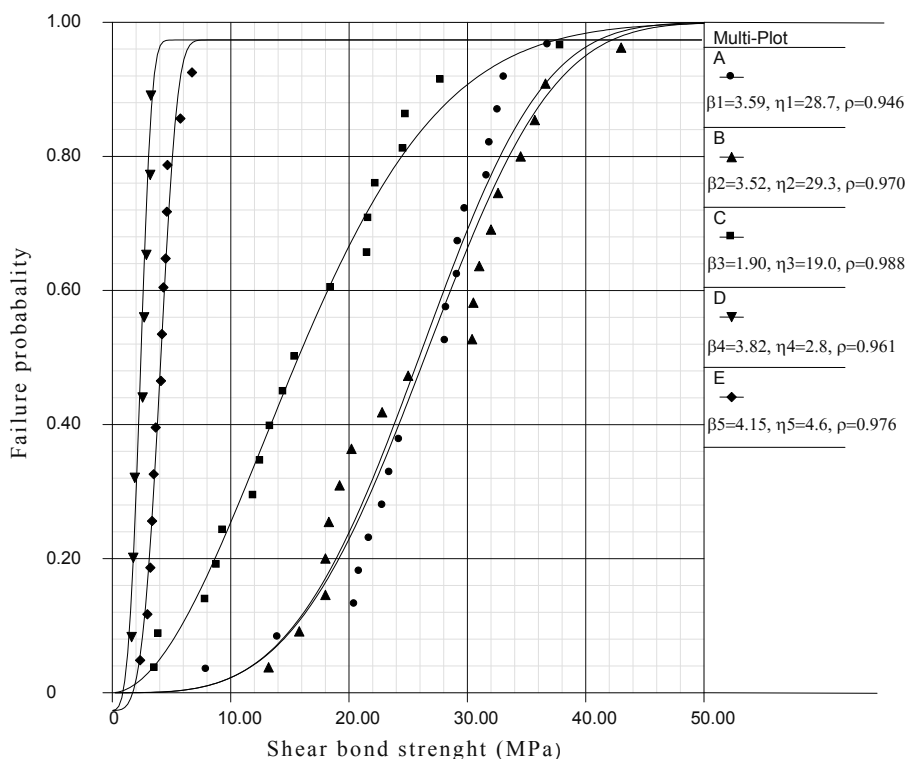


Figure 12. Weibull graphs of shear bond strengths of composite resins to zirconia as a function of various surface conditioning methods. Group A = silane with organophosphate adhesive, Group B = organophosphate primer with silane and organophosphate adhesive, Group C = organophosphate primer, Group D = methacrylate adhesive, Group E = thiophosphate primer with methacrylate adhesive.

Table 7. The fracture types between the resin composite and Y-TZP by groups. Group A = silane with organophosphate adhesive, Group B = organophosphate primer with silane and organophosphate adhesive, Group C = organophosphate primer, Group D = methacrylate adhesive, Group E = thiophosphate primer with methacrylate adhesive

	Cohesive	Mixed	Adhesive
Group A	15	1	2
Group B	13	2	3
Group C	6	1	11
Group D	0	0	18
Group E	0	0	18

5.5 Comparison of the effects of water storage and thermal cycling on shear bond strength of resin composite to polycrystalline oxide ceramics

The mean values of shear bond strengths are presented on Table 8 and as a bar diagram in Figure 13. Control groups were able to show superior results to all the fastened fatigue groups. The shear bond strength values were higher in zirconia groups.

In the water storage and thermocycled groups statistical analysis (two-way ANOVA) did not show any significant difference between groups AM and AA or ZM and ZA ($p=0.763$). All the water storage groups exceeded 5 MPa shear bond strength. Furthermore, there were not considerable differences between the shear bond strengths achieved when comparing alumina and zirconia groups with the same fastened ageing method.

When thermocycling and long-term water storage were combined, the shear bond strength values continued to decrease compared to groups utilizing only thermocycling or water storage. The shear bond strengths were typically below 5 MPa.

Table 8. The mean values of data of shear bond strengths. AA = alumina+ACPS, AM = alumina+3-MPS, ZA = zirconia+ACPS, ZM = zirconia+3-MPS.

Group	n=	Control	8000 thermocycled (TC)	Four years water storage (4Y)	Four years water storage + 5000 thermocycled (4YTC)
AA	24	19.2±4.9	3.8±1.5	5.9±1.6	2.2±0.6
AM	24	17.7±5.1	5.2±2.8	7.2±2.2	2.6±2.1
ZA	24	23.0±6.7	4.7±1.4	6.1±3.0	3.1±1.1
ZM	24	20.5±3.1	4.4±1.8	5.1±0.8	2.6±0.6

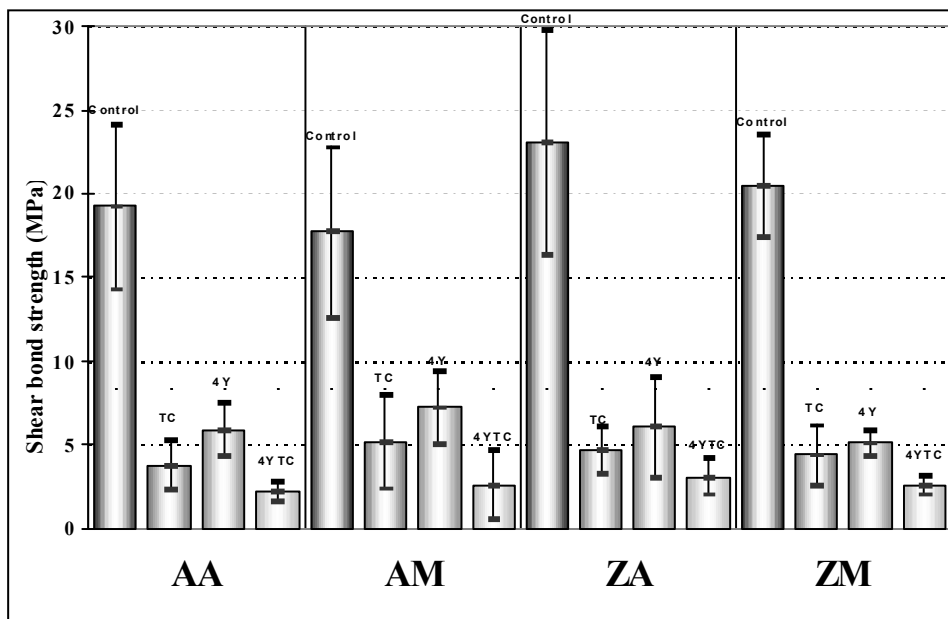


Figure 13. The mean values of shear bond strength by group. AA = alumina+ACPS, AM = alumina+3-MPS, ZA = zirconia+ACPS, ZM = zirconia+3-MPS (n=24).

5.6 Summary of the results of the studies

Study I: The results supported the null hypothesis suggesting that higher operating air pressure increases tribochemically the shear bond strength between ceramics and resin composite.

Study II: The results of the effect of the type of silane indicated contradiction. Initially, the shear bond strength of acrylate silane (ACPS) was superior to methacrylate silane (3-MPS) but when thermocycling was continued the results became close to uniform. However, the results supported the second null hypothesis suggesting that thermocycling at $5\pm 1^\circ\text{C}$ and $55\pm 1^\circ\text{C}$ for 15000 cycles weakens the shear bond strength significantly.

Study III: The results did not support the null hypothesis that conditioning prior to sintering of Y-TZP produces a more reliable bond than conditioning after sintering.

Study IV: According to the results organophosphates used as primers produce superior bonding to other chemical primers. The null hypothesis was accepted.

Study V: The results suggest that long-term water storage is comparable although slower fatigue method to thermal cycling. The nullhypothesis was accepted.

6. DISCUSSION

6.1 Background of the studies

This study was aimed to determine some guidelines for possibilities to bond oxide ceramic to resin composites. It has been suggested that organophosphates are able to form a reliable long-term bond to Y-TZP or alumina with airborne particle abrasion (Kern and Wegner 1998, Blatz et al. 2004, Yang et al. 2010). However, there is a wide selection of materials recommended for cementing Y-TZP without adequate information of their function. Published information may be difficult to interpret. This fact leaves an individual practitioner, who is working with all these contemporary dental biomaterials, on a very thin ice when choosing from the commercial products.

6.2 Tribochemical operating air pressure (study I)

Our *in vitro* study suggests that higher air pressure used in the tribochemical silicatization produces higher shear bond strengths and thus more reliable bond between the resin composite and the ceramic material. SEM imaging revealed increased surface roughness of the ceramic material when higher operating air pressure was used. Higher kinetic energy can explain the simultaneous higher embedding rate of the silica particles. It can be concluded that deeper particle penetration causes a more stable embedding of the silica-coated alumina particles into the ceramic material (Darwell 2000). Furthermore, it is probable that the number of particles blasted and attached to the surface has been higher per time unit with higher operating air pressures. This increases the silicon content on the ceramic surface and also alumina will remain (Matinlinna et al. 2005).

Aluminum trioxide samples exhibited no increase in the bond strength when 150 kPa and 220 kPa air pressures were used. Different behaviour of the materials is probably due to different surface hardness affecting their ability to receive the silica-coating. Alumina surfaces have larger grains, as one can see in the SEM images (Figures 14 and 15). Most probably, higher air pressure caused increased surface roughness and thus increased surface area with more microretention.

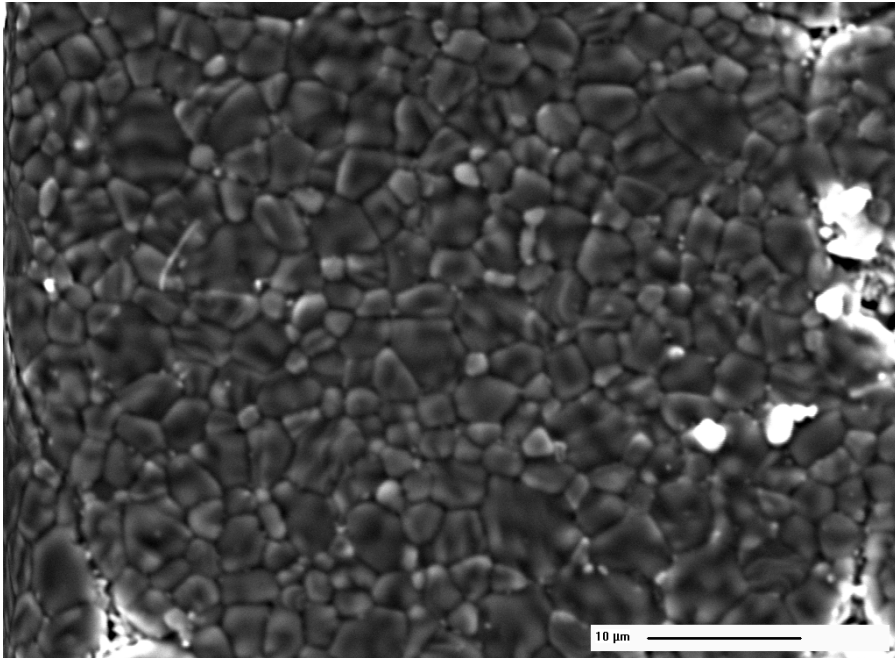


Figure 14. Scanning electron micrograph of the intaglio surface of Procera Alumina (2000x). The measuring bar is 10 μm .

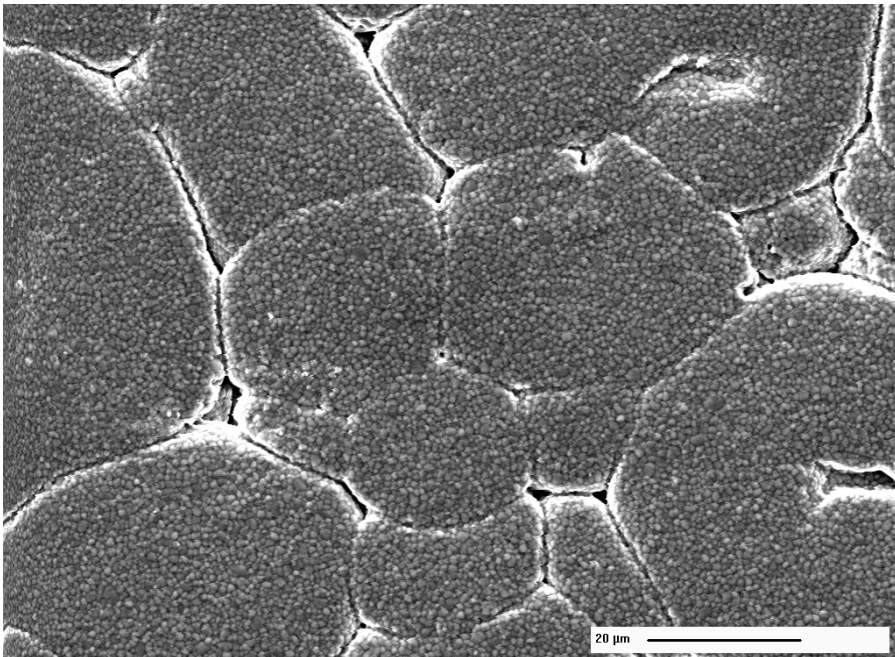


Figure 15. Scanning electron micrograph of the intaglio surface of Procera Zirconia (1000x). The measuring bar is 20 μm .

In the SEM image (Figure 15), Y-TZP surface appears to be more homogenous with irregular grain boundaries and smaller grains. Zirconia also has the ability to transform into another crystallographic form due to mechanical stress, *e.g.* airborne particle abrasion, which causes volume changes in its crystal lattice. The demand for higher operating air pressure seemed to be essential in particular for alumina, which is a harder material than Y-TZP (Prabhu and Bourell 1995, Hah et al. 1995, Kosmač et al. 1999).

It has been demonstrated that shear bond strength values of resin composite luting cement to Procera Alumina substrates are relatively low after thermocycling, *i.e.* a loss of over 50 % of shear bond strength in comparison to the control (Özcan and Vallittu 2003). However, surfaces were silica-coated with the Rocatec system, which uses 110 μm sized silica-coated aluminum trioxide particles instead of the 30 μm particles of the CoJet™ system. Larger-sized hard abrasive particles cause more intensive surface abrasion, because the wear of the surface increases in proportion to the square of the diameter of the abrasive particle (Darwell 2000). Surface roughness achieved by various airborne particle abrasion systems therefore differs as well as the subsequent surface bonding properties (Derand and Derand 2000). The kinetic energy carried by the coating particle creates focally high temperatures (up to 1200°C) as the particle hits the surface. It is important to note that tribochemical silicatizing is still a cold silicization method, *i.e.* without external heat during application, and it does not cause any thermal stress or distortion within the metal framework or the ceramic matrix during the process (Kourtis 1997).

Based on statistical analysis, some defects could be detected in the results of the Weibull analysis for Y-TZP. In Weibull analysis, also called ‘life data analysis’, the attempt is made to make predictions about the life of all samples in the group by fitting a statistical distribution to life data from a representative sample of units (Weibull 1951). The parameterized distribution for the data set can then be used to estimate important life characteristics of the sample such as reliability or probability of failure at a specific time, the mean life and the failure rate. Originally, Weibull distribution was designed to compute failure probabilities as a function of applied stress, and analysis data have been published dealing with the mechanical or adhesive properties of ceramic materials (Robin et al. 2002, Albakry et al. 2004, Fleming et al. 2006).

However, the Weibull analysis was not as uniform and curve-fitted as planned, and might partly have been due to the high standard deviation in the results. Evidently, several reasons, such as operator sensitivity in silicization, silanization, or bonding the resin composite to Y-TZP might have an influence on that. Again, the higher surface hardness of alumina of airborne particle abrasion compared with Y-TZP may have had an influence on the entire conditioning process as well. Weibull analysis has been previously used for characterization of the nature of the shear bond strength by fitting the statistical distribution to life data from each of 12 groups and to estimate the probability of failure (McCabe and Carrick 1986). To our knowledge, so far, no data have been published dealing with the effect of operating air pressure on shear bond strength in dentistry.

6.3 Fastened fatigue effects studies (studies II and V)

These studies of fastened ageing suggested that thermocycling and long-term water storage considerably diminished the shear bond strength values measured between resin composite and tribochemically conditioned Y-TZP. Post-curing due to temperatures during thermocycling has been reported to have an influence on bond strength values, but these studies did not demonstrate any enhanced bonding. Higher degree of monomer conversion of resin composite also increases the glass transition temperature of the polymer by restricting molecular motions of the chains (Meric and Ruyter 2007, Shah et al. 2009). Thus, the thermoset-based polymers containing monomers, such as bis-GMA, TEGDMA, TMDI, DDMA, UDMA, bis-EMA6 used in luting cements, are cross-linked after light-curing and hence in practice more insensitive to post-curing by heat.

An experimental silane primer was utilized in some of these current studies. Specimen groups silanized with an acrylate silane were fabricated, because acrylate silane has been reported to produce higher shear bond strength values than methacrylate silane (Matinlinna et al. 2006). Within these test set-ups it was of great interest to evaluate the long term stability and the effect of type of fastened ageing. Acrylate silane monomer is more reactive, because it does not have the protecting methyl group as methacrylate silane monomer. As activated, hydrolyzed trialkoxy silanes react, they form a complex,

branched, 3D polysiloxane film between ceramic surface and resin composite. The film consists of siloxane, Si–O–Si–, bonds and acrylate/methacrylate groups (Plueddeman 1970, van Ooij and Child 1998). The laboratory-made acrylate silane primer showed superior shear bond strength values initially and after 1000 and 3000 rounds in thermocycling apparatus. However, after 8000 cycles - or four years in storage in 37 °C water bath - both groups exhibited considerable decline in shear bond strength values, as much as 60-85 %. Furthermore, when water storage was combined with thermal cycling the results decreased 85-88 % in shear bond strength compared with the control group. Fastened ageing methods strongly affect the bond between ceramic material and luting cement. Hence, the long-term durability of bond measured *in vitro* is certainly arguable and the feasibility of the method needs critical evaluation.

Conventional shear bond strength test is a widely used typical test for a relatively quick evaluation of adhesion in dentistry. However, it produces a non-uniform interfacial stress at cement–ceramic interface. The specific fracture pattern may cause cohesive failure within the cement or the ceramic, which may lead to erroneous conclusions (Blatz et al. 2003). Different linear coefficient values of thermal expansion (LCTE) of resin composite compared with alumina and zirconia may have an effect on the mechanism of failure at the ceramic–resin composite interface. LCTEs of resin composite luting cements are between 40–60 microstrain/°C (μ -strain/°C) and LCTEs of ceramic materials are typically less than 10 microstrain/°C (μ -strain/°C). This difference necessarily causes thermal stresses at the cement–ceramic interface, probably leading to unequal changes in dimensions, and eventually to failure of the bond. The difference between LCTEs is particularly high between ceramics and initially flowable luting cements, which have lower filler content than conventional restorative filling resin composites in order to improve the flow of the cement and to facilitate the fit of the prosthetic structure (Tezvergil 2003, Meric and Ruyter 2008). Moreover, hygroscopic expansion of luting cements presumably causes extra stresses at the interface of zirconia and cement as the water sorption of the resin composite increases *in vitro* (Sideridou 2008).

According to the results of the studies II and V the effect of different silane primers seems rather irrelevant considering longevity. The acrylate silane did not show any long-term benefits which were observed on shorter water storage conditions or lower

number of thermal cycles. It may be possible to find new chemical combinations, also other than silanes, more favourable and with different functionality for use as a durable substitute for methacrylate-functional silane. The test set-up was divided to two situations, first, by using long-term water storage periods to evaluate the stability of the bonding silane layer to hydrolytic effects. Silane bonds are known to rearrange and reform: hydrogen bonds and covalent bond are understood to be labile in wet conditions. Water is always present at a molecular level in the siloxane film and there is lack of published information on the hydrolytic stability of the siloxane bonding between the materials used in the study (Plueddemann 1970, Matinlinna et al. 2004 a). In the light of the present study, it may be concluded that siloxane film can not resist the effects of water in the long run. Interestingly, there are long-term water storage studies of vinyl silane coupling agents to bond resin composites to glass surfaces (Vallittu et al. 1999, Vallittu 2006). Those studies did not show deterioration of silane promoted adhesion, i.e. siloxane film after 10 years water storage. It is likely that the higher temperature used in copolymerization of silane on glass has led to a more stable siloxane network than the procedure in this study.

Kern and Wegner (1998) used short term water storage and compared it to long time water storage combined with 37.500 thermal cycles. This extraordinary long cycling time led to spontaneous dissolution of the bond even without shear bond strength testing. Different materials seem to behave differently during thermal cycling as well. Thus, within the limitations of these studies, it seems to be necessary to emphasize that thermal cycling till 8.000 rounds, along with long-term water storage at 37°C, can be used to evaluate the long-term stability of the bond. As previously mentioned, thermocycling has been criticized as to what extent it mimics the clinical situation. ISO 10477 prescribes 6.000 cycles, which may be insufficient for evaluating the long-term stability. The temperatures and dwelling times used in the several studies have been questioned as well as the meaning of rest time and the frequency of cycling. While there is no concrete evidence that failures occur because of thermal stresses, every thermo-cycling test remains arbitrary due to the lack of a substituting measurement method.

The drawback of all the in vitro thermal cycling tests is that they are not able to discriminate the type of the failure that causes the collapse of bond to ceramic. It has been suggested that one possibility might be a less severe test which would improve dis-

crimination of the failure point as long as the stresses remain below those causing immediate collapse (Gale and Darvell 1999). However, the mechanism of the failure caused by cycling testing needs further investigation.

6.4 The effects of experimental and conventional surface treating methods studies (studies III and IV)

The studies dealing with different surface treatment methods were carried out in order to compare the effects and possible benefits of some common commercial bonding agents used in everyday practice. Some previously published *in vitro* studies concerning bonding to alumina or zirconia ceramics have been dealing with either the effect of silicized surface achieved with various methods (Kern and Wegner 1998, Janda et al. 2003, Özcan and Vallittu 2003) or the features of different luting cements (Komine et al. 2004, Fleming and Narayan 2003). Different surface pretreatment methods, e.g. airborne particle abrasion, HF etching and tribochemical silica-coating (Bo-Kyoung Kim BK et al. 2005) of the ceramic substrate have been discussed widely as well (Kern and Wegner 1998, Özcan and Vallittu 2003).

The results of the current study suggest that the surface treatment procedure has a considerable influence on bond strength to ceramic material. 10-MDP-containing materials combined with silanization had a better ability to form a stabile bond. Combinations without 10-MDP could not form an acceptable bond to Y-TZP according to the present studies: the bond strengths were abundantly below 10 MPa. Previously, it has been discovered (Taira et al. 1998) that the phosphoric primer (10-MDP) is effective in the bonding of luting agents to cast pure titanium, and further, that a primer containing methacryloyloxy-alkylthiophosphate (MEPS) is also reactive and promotes adhesion. However, the present study cannot suggest the use of MEPS in zirconia ceramics bonding as the material does not promote bonding to Y-TZP unlike 10-MDP. The experimental efforts to coat Y-TZP surface prior to sintering with sodiumsilicate or fumed silica could not show any acceptable shear bond strength. The main problem with previously mentioned agents was probably insufficient surface roughness. On the one hand, this can be partly due to the lower adhesion bonding surface area, due to the surface smoothness and wettability, but on the other hand the sufficient and adequate amount of the silica clearly affects the shear bond strength. Therefore, the air pressure and the du-

ration of airborne particle abrasion affect the sufficiency of the silica amount attached on to the ceramic surface and need further investigations. Furthermore, tribochemical silicatization combined with silanization achieved the highest shear bond strength values. The system is based on air particle abrasion which increases the bonding surface area considerably (Darvell 2000). The abraded surface area was silicatized tribochemically. The silicatization takes place and provides the surface also with an increased surface roughness and a sufficient amount of silica creating the basis for the following silanization with silane. However, pretreating the zirconia surface with fumed silica prior to sintering and tribochemical silicatization did not show any better results compared with tribochemical silicatization after sintering. This is probably due to the lower surface area achieved with the pre-treated zirconia surface which causes lower shear bond strength.

Cohesive fracture in fired-on porcelain group indicates either material defects or limitations of the strength of the veneering porcelain (Guess 2008). It is of further interest to study the bonding capacity of the methods taking place prior to sintering and the effect of higher silicon dioxide concentration of the zirconia surface on the shear bond strength. Advanced methods, *e.g.* selective infiltration etching can be the final answer to more reliable, simpler and faster handling of oxide ceramic prosthodontic structures.

6.5 Clinical considerations

Today, in tooth reconstruction, ceramic restorations are preferred to be utilized in minimal invasive techniques. The retention of the restoration may be insufficient due to the anatomy of the tooth, and therefore the importance of proper wetting followed by adhesive bonding can not be overlooked. A shear bond strength limit of 5 MPa is suggested in ISO standard, but actually 10–13 MPa has been suggested as the minimum for acceptable clinical bonding (Thurmond et al. 1994, Kappert and Krah 2001, Lüthy et al. 2006). Interestingly, almost every system assessed in this study with its short-term static loading tests exceeds this latter limit. The limit proposed by ISO 10477 standard is merely 5 MPa (ISO 10477 Dentistry, 1996) and it is arbitrary in its nature. However, the shear bond strength results may be inferior, when extended thermocycling time is applied. Successful long-term bonding requires proper and deep knowledge over adhesive dental materials as well as control over pre-treatment techniques. The most important individual factor in order to achieve the highest possible shear bond strength is to

choose a reliable bonding system. It may be summarized that such system should include a possibility to achieve a proper airborne abraded ceramic surface, a reliable silicating method, a silane coupling agent, both a primer and an adhesive resin containing 10-MDP as well as a fatigue resistant resin cement.

From the point of view of the clinician, it is noteworthy that the CoJet™ device can be connected to the dental unit by various types of connector. If the Kavo™ type connector is used for the CoJet™ hand-piece, it has to be taken into account that the operating air pressure of a standard dental unit is typically limited up to 250 kPa. This might mean that optimal shear bond strengths cannot be achieved with per today existing standard clinical equipment. The compressed oil-free air for the airborne particle abrasion device can also be taken before the pressure throttle of the dental unit or directly from the compression pump unit to achieve sufficient continuous operating air pressure. According to some recent studies, the effects of airborne particle abrasion have been reported variously as an increase or decrease in flexural strength, depending on the surface damage introduced by the abrasion method used (Guazzato et al. 2005, Curtis et al. 2006, Kosmač et al. 2008).

Another key point of the tribochemical treatment taking place is the aspect of preventing saliva or any other contamination from getting on to the prosthodontic structure during fit-checking, and handling. This is often difficult to carry out and to avoid contamination of the silica-coated surfaces (Yousef 1998). In many cases, the dental laboratory conducts the tribochemical treatment on the ceramic surfaces, but the idea of relying wholly on the laboratory pretreatment may be a serious error source due to the previously mentioned reasons. In addition, all the steps in the surface treatment, including the sufficient operating air pressure, must be carried out meticulously because silicization does not cover the entire treated surface and the silica content rises only moderately (Valandro et al. 2005).

6.6 Suggestions for further research

The inertness of the oxide ceramic surface against chemical treatment has been reported to be the most difficult part of the bonding procedure. Some recently studied etching methods based on silica-coating with Rocatec and followed by selected acid treatments

have modified the surface topography (Lung and Matinlinna 2010). This might give ideas for further conditioning studies. Although an acceptable long-term bond can be created by choosing the materials carefully, it seems, in the light of the literature and the present study, that a chemical bonding procedure is yet to come. Although micromechanical bond seems to be the most reliable guarantee for long-term bonding to zirconia and alumina, especially Y-TZP surfaces are sensitive to mechanical abrasion which can damage the structural stability. Y-TZP has been shown to alter its phase in the presence of water and suitable mechanical irritation. On the other hand, t - m transformation can cause an increase of the strength of the material. The reason is that the t - m transformation induces a local overall compressive stress on the surface, which tends to close a potential advancing crack. Furthermore, the superficial compression must be accompanied by an equilibrating sub-surface tension or the part would not be in mechanical equilibrium. (Lughi and Sergo 2010). Thus, the possibilities of careful and gentle roughening methods of the zirconia surfaces are worth of further interest.

The quest for a chemical agent, a potential new primer formulation, able to form stable and covalent bond to oxide ceramics continues and it will be interesting to see if it affects the longevity: structural stability, bond endurance or microleakage of the ceramic FPDs. Improvement in any of these issues would be of great benefit to oxide ceramic structures directly or indirectly as well as to any other prosthodontic structure.

7. CONCLUSIONS

Based on these five reported and published studies, the main conclusions drawn were:

1. Tribochemical silicating of the oxide ceramics can be affected and operating air pressure has a significant effect on shear bond strength. Silica content on an alumina ceramic surface increases as the operating air pressure increases, whereas results on zirconia surfaces are somewhat controversial. When the air pressure of tribochemical silicating is increased, shear bond strength of the resin composite to zirconia and alumina ceramics increases. The hypothesis was accepted.
2. Silanes have an increasing effect on shear bond strength. Short term hydrolytic stability of acrylate silane is superior to methacrylate silane but long-term results are convergent. The first hypothesis was rejected and the second hypothesis was accepted.
3. An important part of tribochemical silicating is its effect on surface roughness. Without air abrasion the shear bond strength values cannot reach an acceptable bond strength level. This indicates and supports the importance of micromechanical linking on to the surface when bonding to oxide ceramics. The hypothesis was rejected.
4. Organophosphate primers containing 10-methacryloyloxydecyl dihydrogenphosphate (10-MDP) could provide a stable, long-term bond to oxide ceramics. Special attention has to be paid on the proper handling of the materials. The hypothesis was accepted.
5. Four year water storage was concluded to be a comparable fatigue method to thermal cycling and could not show any benefits to thermal cycling. When long-term water storage and thermal cycling are combined the fatigue effect increases. The hypothesis was accepted.

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