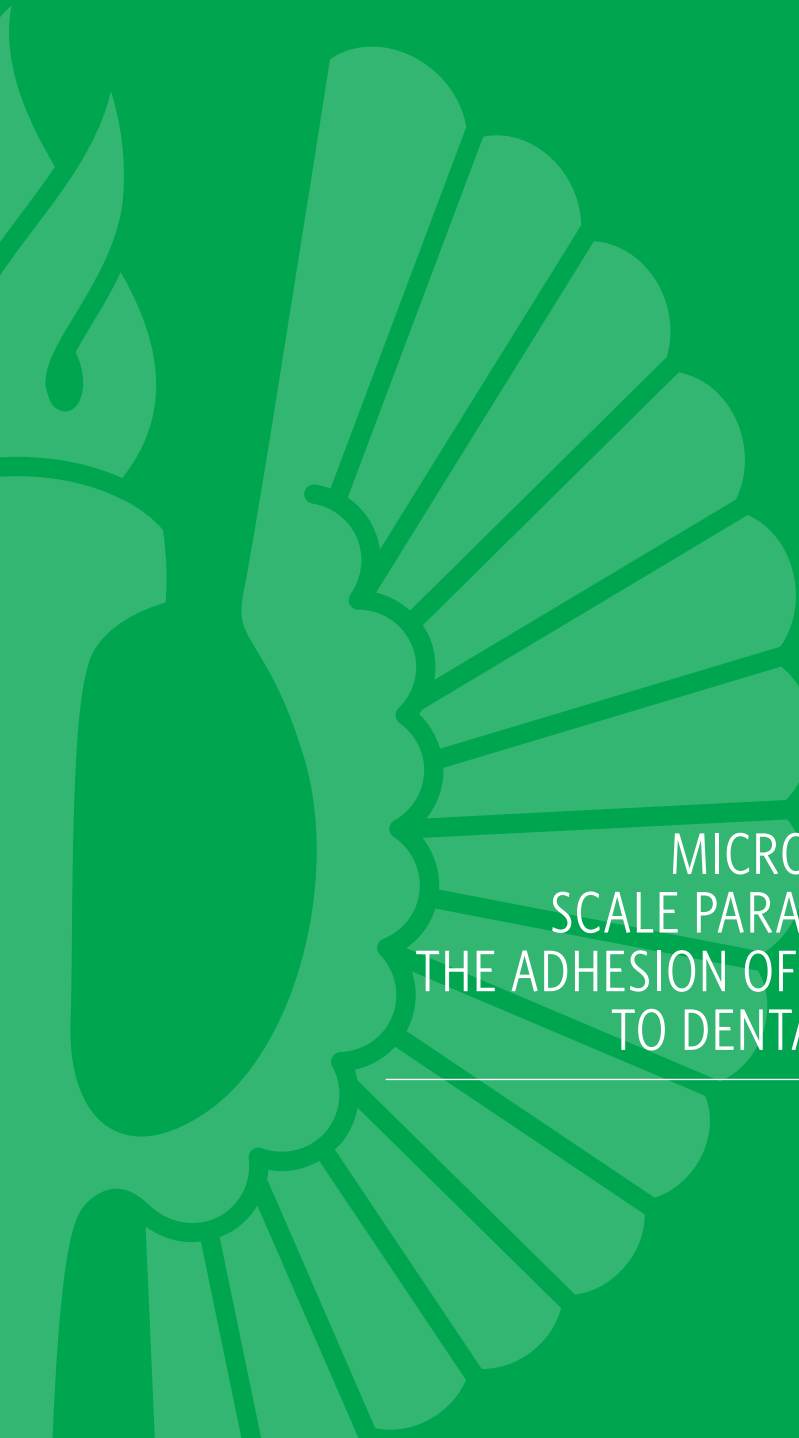




Turun yliopisto
University of Turku

A large, stylized graphic of a flower or sunburst, rendered in a lighter shade of green than the background. It has a central oval shape and radiating, fan-like segments, resembling a sunflower or a stylized flower head.

MICRON AND SUBMICRON SCALE PARAMETERS AFFECTING THE ADHESION OF RESIN COMPOSITES TO DENTAL GLASS CERAMICS

Ravikumar Ramakrishnaiah



Turun yliopisto
University of Turku

MICRON AND SUBMICRON SCALE PARAMETERS AFFECTING THE ADHESION OF RESIN COMPOSITES TO DENTAL GLASS CERAMICS

Ravikumar Ramakrishnaiah

University of Turku

Faculty of Medicine
Department of Biomaterials Science
Finnish Doctoral Program in Oral Sciences
Turku, Finland
and King Saud University
Dental Biomaterials Research Chair
Dental Health Department
College of Applied Medical Sciences
Riyadh, Kingdom of Saudi Arabia

Supervised by

Professor Pekka K Vallittu
Department of Biomaterials Science
Institute of Dentistry
University of Turku
Turku, Finland

Professor Jukka P Matinlinna
Dental Materials Science
Faculty of Dentistry
The University of Hong Kong
Hong Kong SAR, People's Republic of China

Reviewed by

Professor Hidekazu Takahashi
Department of Oral Biomaterials Engineering
Graduate School of Medical and Dental
Sciences, Tokyo Medical and Dental University,
Tokyo, Japan

Professor Morten Rykke
Dental Faculty
Institute of Clinical Dentistry
University of Oslo
Oslo, Norway

Opponent

Professor Ulf Örtengren
Faculty of Medicine,
Institute of Clinical Dentistry
University of Tromsø, Tromsø, Norway

The originality of this thesis has been checked in accordance with the University of Turku quality assurance system using the Turnitin OriginalityCheck service.

ISBN 978-951-29-7313-2 (PRINT)

ISBN 978-951-29-7314-9 (PDF)

ISSN 0355-9483 (Print)

ISSN 2343-3213 (Online)

Painosalama Oy - Turku, Finland 2018

To all my Teachers

*“Thank you for helping me bloom,
You made a wonderful difference in my life”*

ABSTRACT

Ravikumar Ramakrishnaiah

Micron and submicron scale parameters affecting the adhesion of resin composites to dental glass ceramics

University of Turku, Faculty of Medicine, Department of Biomaterials Science, Finnish Doctoral Program in Oral Sciences - FINDOS, Institute of Dentistry, University of Turku. *Annales Universitatis Turkuensis*, Turku, Finland 2018

The adhesion properties of the ceramic restorations play a crucial role in the overall performance and success rate of the treatment. Adhesion is required between the resin cement and tooth substance and indirectly made restoration. The aim of this laboratory study was to investigate the effect of some factors which relate to the bond (adhesion) strength. The study parameters included: 1. The effect of acid etching duration on the surface topography, roughness and wettability 2. The effect of surface neutralization on the wettability of silanes (silane coupling agents), adhesive resin and resin composite cement 3. The degree of resin impregnation into the etched micro-patterns 4. The nano-mechanical properties of the resin-ceramic interface 5. The ceramic-luting cement adhesion (shear bond) strength and 6. The effect of provoked degradation of the interface by exposure to boiling water on nano-mechanical properties and the adhesion strength. Silica based glass ceramics were selected and etching was done with 5% hydrofluoric acid and conditioning was done with two silane coupling agents (experimental and commercial silane coupling agents). Various combinations of silane coupling agents and resin cements were evaluated. Results were statistically analyzed with analysis of variance (ANOVA), the *post hoc* Tukey's test, and regression analysis. Etching results showed a significant change in the surface topography and, increase in surface roughness, and wettability with increased etching duration. Neutralizing the ceramic surface did not show significant effect on wettability of silanes and, adhesive resin and resin composite cement. A combination of primer treatment and application of adhesive resin not only showed better resin impregnation into the etched micro-pores but also had high nano-hardness, modulus of elasticity, and adhesion (shear bond) strength.

Keywords: Dental ceramics; Acid etching; Surface topography; Surface roughness; Wettability; Neutralization; Silane; Adhesive resin; Resin composite cement; Nano-mechanical properties; Resin-ceramic interface; Adhesion strength.

TIIVISTELMÄ

Ravikumar Ramakrishnaiah

Mikrometri- ja submikrometritason rakenteet lasikeraamien ja yhdistelmämuovien rajapinnassa ja kiinnittymisessä

Turun yliopisto, lääketieteellinen tiedekunta, hammaslääketieteen laitos, biomateriaalitieteen oppiaine, Kansallinen suun terveystieteiden tohtoriohjelma – FINDOS, Annales Universitatis Turkuensis, Turku, Suomi 2018

Hammashoidossa käytetään keraamisia materiaaleja epäsuorasti valmistettavissa täytteissä ja kruunuissa materiaalin hyvien ulkonäöllisten ominaisuuksien, biohyteensopivuuden ja eräiden mekaanisten ominaisuuksien takia. Rakenteiden kiinnityksessä käytettävien yhdistelmämuovien tulee tarttua hyvin keraamin pintaan, jotta rakenne toimii hyvin osana restauroitua hammasta. Useiden tekijöiden tiedetään vaikuttavan muovien kiinnittymiseen: keraamin pinnan happosyövytys, pinnan happojäämät, pinnan silanointi ja käytettävän yhdistelmämuovin tyyppi ja koostumus. Tämän tutkimuksen tarkoituksena oli selvittää eräitä lasikeraamin ja yhdistelmämuovin rajapinnan mikrometri- ja submikrometritason rakenteita ja toimintaa tiiviin rajapinnan aikaansaamisessa. Tutkimuksessa selvitettiin erityisesti keraamin happosyövytyksen ajallisen keston vaikutusta pinnan rakenteeseen, pinnan karheuteen ja kostumiseen sekä pinnan neutraloinnin vaikutusta kostumiseen ja yhdistelmämuovien tunkeutumiseen mikroskooppisiin huokosiin keraamin pinnassa. Lisäksi tutkittiin rajapinnan hydrolyyttistä kestävyyttä provosoituissa olosuhteissa kiehuvaan veteen ja hydrolyysin vaikutusta rajapinnan nanomekaanisiin ominaisuuksiin. Lasikeraamin pinnan syövytys tehtiin 5 %:lla vetyfluoridihapolla ja esikäsitellyssä käytettiin kahta erilaista silaaniyhdistettä ja erilaisia yhdistelmämuoveja. Tuloksina raportoituja suureita verrattiin tilastollisesti varianssianalyysillä ja Tukeyn testillä. Korrelaatioanalyysistä tehtiin regressioanalyysillä. Tulokset osoittivat pinnan happosyövytyksen kestolla olevan merkittävä vaikutus pinnan rakenteeseen, karheuteen ja kostumiseen. Etsatun pinnan neutralointi ei vaikuttanut pinnan kostuvuuteen. Silaaniprimerin ja sidosmuovin käyttäminen yhdessä paransivat muovin tunkeutumista pinnan mikroskooppisiin huokosiin sekä paransivat rajapinnan nanomekaanisia ominaisuuksia vaikuttaen myös sidoslujuteen suotuisasti.

Avainsanat: Hammaskeraami; lasikeraami; sidosmuovi; sidostaminen; pinnan karheus; pinnan kostuminen; silaani; yhdistelmämuovi; rajapinta

TABLE OF CONTENTS

ABSTRACT.....	4
TIIVISTELMÄ	5
ABBREVIATIONS	8
LIST OF ORIGINAL PUBLICATIONS.....	10
1 INTRODUCTION	11
2 REVIEW OF LITERATURE	14
2.1 Dental ceramics	14
2.2 Acid etching	18
2.3 Neutralizing agent	19
2.4 Surface topography of etched ceramic.....	20
2.5 Surface roughness (S_a)	21
2.6 Surface wettability.....	21
2.7 Surface neutralization.....	23
2.8 Silane coupling agents.....	24
3 AIMS OF THE STUDY	27
4 MATERIALS AND METHODS.....	29
4.1 Materials.....	30
4.2 Specimen preparation.....	30
4.2.1 Specimen preparation, grouping and etching procedure to determine the effect of etching on surface characteristics (study I).....	30
4.2.2 Specimen preparation and grouping to determine the effect of ceramic surface neutralization on wettability of silane and resin (study II).....	31
4.2.3 Specimen preparation and grouping for micro and nano structural analysis of ceramic-luting resin interface (study III)	34
4.2.4 Specimen preparation and grouping for evaluation of two- step and one-step conditioning system on ceramic-resin cement adhesive interface (study IV)	35
4.3 Methods	37
4.3.1 Scanning electron microscopy (SEM) analysis	37
4.3.2 Surface roughness (S_a) measurement.....	37
4.3.3 Surface wettability measurement.....	38
4.3.4 Nano-indentation.....	38
4.3.5 Boiling water exposure	38
4.3.6 Adhesion testing procedure.....	39

4.3.7	Evaluation of failure mode	39
4.3.8	Statistical methods.....	39
5	RESULTS.....	41
5.1	Acid etching of ceramics	41
5.2	Surface roughness	41
5.3	Surface wettability	42
5.4	surface neutralization.....	43
5.5	Ceramic-resin interface characteristics.....	43
5.6	Shear bond strength	45
6	DISCUSSION.....	46
6.1	The effect of hydrofluoric acid etching duration on the surface micromorphology, roughness, and wettability of dental glass ceramics (study I).....	47
6.2	The effect of surface neutralization on wettability of silane coupling agents and adhesive resin cements (study II)	49
6.3	Micro and nano-structural analysis of dental ceramic and luting resin interface and the effect of water exposure on integrity of cement interface (study III).....	50
6.4	Two-step vs. one-step conditioning systems and adhesive interface of glass ceramic surface and resin systems (study IV).....	53
7	CONCLUSIONS	56
	ACKNOWLEDGEMENTS	57
	REFERENCES.....	58
	ORIGINAL PUBLICATIONS.....	63

ABBREVIATIONS

3-methacryloxypropyltrimethoxy silane

3-acryloyloxypropyltrimethoxysilane

Atomic force microscope

Aluminum

Aluminum oxide

Acidulated phosphate fluoride

Analysis of variance

bis-phenol-A-glycidyl dimethacrylate

bis-1,2-(triethoxysilyl)ethane

Carbon

Calcium

Contact angle

Computer-aided design/Computer-aided machining

Carbon dioxide

Camphorquinone

Energy dispersive X-ray analysis

Federation of European Producers of Abrasives

Fully stabilized zirconia

Gigapascal

Hydrochloric acid

Hydrofluoric acid

Hafnium oxide

Water

Hydroxypropyl methacrylate

Phosphoric acid

Potassium

Potassium and Sodium aluminosilicate

Potassium and aluminum tectosilicate

Potassium oxide

Lithium peroxide

Lithium disilicate

Managing accurate resin curing
Megapascal, N/mm², SI derived unit of tensile strength
Sodium
Ammonium polyfluoride
Sodium chloride
Sodium hydroxide
Nickel chromium
Hydroxyl group
Methoxy group
Potential of hydrogen
Phosphorus pentoxide
Partial stabilized zirconia
Scanning electron microscope
Surface roughness
Measure of skewness or symmetry in roughness
Shear bond strength
Standard deviation
Silicon
Silicon dioxide
The spread of height distribution
Statistical package for social sciences
Maximum surface peak height
Root mean square value of the sampling area
Maximum valley or pit depth
Sum of largest peak height value and largest pit or valley depth
Triethylene glycol dimethacrylate
Tetragonal zirconia polycrystals
Urethane dimethacrylate
Yttrium oxide
Yttria stabilized tetragonal zirconia
Zirconium oxide
Micro liter
Micro meter

LIST OF ORIGINAL PUBLICATIONS

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

- I. Ramakrishnaiah R, Alkheraif AA, Darshan DD, Matinlinna JP, Vallittu PK (2016). Effect of hydrofluoric acid etching duration on surface micromorphology, roughness and wettability of dental ceramics. *Int J Mol Sci* 17(6): 822-839.
- II. Ramakrishnaiah R, Alkheraif AA, Darshan DD, Alghamdi KF, Matinlinna JP, Lung CYK, Sunil C, Vallittu PK (2017). The effect of ceramic surface neutralization on wettability of silane coupling agents and adhesive resin cements. *Silicon* <https://doi.org/10.1007/s12633-017-9670-6>
- III. Ramakrishnaiah R, Alkheraif AA, Darshan DD, Elsharawy M, Matinlinna JP, Vallittu PK (2018). Micro and nano structural analysis of dental ceramic and luting resin interface and the effect of water exposure on integrity of cement interface. *J Biomater Tissue Eng* 8(1): 136-143.
- IV. Ramakrishnaiah R, Alaqeel SM, Alkheraif AA, Darshan DD, Matinlinna JP, Vallittu PK (2018). Two-step vs. one-step conditioning systems and adhesive interface of glass ceramic surface and resin systems. *J Adhes Sci Technol* 32(17):1952-1963.

The original papers have been reprinted with the permission of the copyright holders.

1 INTRODUCTION

Dental ceramics are natural-looking, highly aesthetic indirect restorative materials in modern restorative dentistry (Ozkurt *et al.*, 2011). Ceramics are widely used, and there is a growing interest for their application in various disciplines of dentistry because of their biocompatibility (Chaiyabutr *et al.*, 2008). Development of computer-aided design/computer-aided machining (CAD/CAM) technology has enabled clinicians to deliver high-quality, precise ceramic restorations. Advances in the dental research have led to the development of high strength ceramics with significantly accurate fabrication techniques and predictable clinical results. Newer high strength glass ceramics, such as lithium disilicate, leucite reinforced, and zirconia reinforced glass ceramics are used to restore the high load bearing areas ranging from 400 to 620 MPa with great success (Pallis *et al.*, 2004). Relatively high static strength and excellent aesthetic characteristics have made dental glass ceramics highly preferred materials to restore teeth with various clinical conditions using inlays, onlays, veneers, crowns, and even short and long span fixed dental prostheses. However, there has been concern of long term durability of resin composites to dental ceramics and also to the tooth surface, especially to dentin (Amaral *et al.*, 2011; Arkles, 2011). With ceramics, the most serious clinical concern of bonding is with zirconia and glass ceramics which are known to adhere to resin composites micromechanically and chemically, the latter being of concern in terms of hydrolytic stability.

In dentistry, bonding between two dissimilar materials is achieved by increasing the surface free energy (Matinlinna *et al.*, 2007b). Increasing the surface free energy improves the wettability of the surface for resin cement bonding (Lung *et al.*, 2012) and increases surface roughness (S_a). Increasing the surface free energy by etching exposes hydroxyl ions and makes the ceramic surface more compatible for chemical bonding with luting resin cements via silane coupling agent. Surface free energy is increased by careful surface conditioning of the internal surface of the ceramic restoration and prepared tooth surface. Surface conditioning of dental glass ceramics is a two-step procedure where the ceramic surface is first etched with 5% hydrofluoric acid (HF) for 2–3 min and later the etched surface is treated with a silane coupling agent (Amaral *et al.*, 2006, Amaral *et al.*, 2011). Both procedures, etching and silane application, result in improved wettability of the ceramic surface (Matinlinna *et al.*, 2006b). Furthermore, acid etching selectively dissolves the glassy phase and makes the surface porous for resin cement penetration (mechanical interlocking). This porous surface not only provides more surface area for resin bonding, but also changes the surface topography and forms surface hydroxyl groups (-OH) on the ceramic surface that are

responsible for chemical bonding via silane coupling agents (Lung *et al.*, 2012; Qeblawi *et al.*, 2010).

The dissolving behavior and the microstructure of etched ceramic surface differs between leucite and lithium di-silicate containing glass ceramics. The crystalline leucite dissolves at a faster rate than lithium di-silicate crystals (Swain, 2014). Furthermore, before application of a silane coupling agent, the etched surface needs to be rinsed thoroughly with copious amounts of water to remove all debris such as residual acid and fluorosilicate precipitates (salts) of Na, K, Ca, and Al (Canay *et al.*, 2001). This procedure can be effectively performed by subjecting the ceramic restoration to ultrasonic cleansing before primer application. However, some amount of acid remnants within deep pores and irregularities are expected. These residual remnants continue the surface degradation of ceramic. In addition, a lower pH value of the etched surface will adversely affects the bonding by interfering with the resin cement polymerization (Bottino *et al.*, 2015; Zorzin *et al.*, 2012). That said, an application of a neutralizing agent has been recommended to neutralize the pH of the ceramic surface and also to arrest any further topographical changes by the acid action (Foxton *et al.*, 2003; Zorzin *et al.*, 2012).

After neutralization the ceramic surface is treated with an activated silane coupling agent to provide reliable and durable chemical bonding with resin cement (Della Bona *et al.*, 2002a; Matinlinna *et al.*, 2013). Silane coupling agents are synthetic silicon esters, hybrid inorganic-organo-functional trialkoxysilane monomers and are capable of unifying organic and inorganic materials. In general, silanes have non-hydrolysable groups (such as methacrylate) and hydrolysable groups (such as methoxy, -O-Me), hence they are defined chemically bifunctional (Lung *et al.*, 2012). When reactive silanes are applied over the etched ceramic surface, the hydrolysable alkoxy groups react with exposed hydroxyl groups, and non-hydrolyzable organic groups polymerize with subsequently applied unset resin cement (Matinlinna *et al.*, 2007b). However, silane aided adhesion is prone to hydrolysis and the bonding is usually weakened considerably over time. There are also differences between the conventional 3-methacryloxypropyltrimethoxy silane (3-MPS) and a novel 3-MPS + *bis*-1,2-(triethoxysilyl)ethane (BTSE), in relation to adhesion promotion (Durgesh *et al.*, 2015; Durgesh *et al.*, 2016).

The ultimate high adhesion strength, also called bond strength, is the result of the resin cementing medium. Resin cements are used to bond ceramic restorations to natural tooth substance because of high bond strength, color stability and low solubility in oral fluids. The resin cements can be either filler containing resin composites or unfilled adhesive resin, ideally the resin cement should completely wet the etched surface and flow into the full depth of micro porosities created by

acid etching procedure. Resin cements with low surface tension will have low viscosity and better wettability on the substrates which allow them to flow easily into the micro pores to provide durable bonds (Han *et al.*, 2007).

With this background, it is critically important to obtain durable bonds for durable restorations, therefore it is highly interesting to investigate factors affecting bonding results at micron and submicron level. Several parameters such as surface topography, S_a of etched glass ceramic, surface wettability of etched ceramic surface to silanes and resin cements, effect of surface neutralization, were investigated. Lastly, the resin-cement interface and its hydrolytic stability at elevated temperature, and adhesion strength of ceramic to resin composites and adhesive resins were determined.

2 REVIEW OF LITERATURE

2.1 Dental ceramics

Some of the disadvantages of the metallic restorations such as lack of esthetics, and some allergic reactions to Ni-Cr base metal alloys led to the development of dental ceramics (Tai *et al.*, 1992; Geurtsen, 2002). Dental ceramics are inorganic, non-metallic materials, they are brittle, display high compressive strength, and relatively low tensile strength. However, with the introduction of newer ceramics and fabrication techniques there is significantly improved clinical results. The traditional ceramics is based on clay/kaolin, quartz (silica), and a naturally occurring feldspar which is a mixture of potassium and sodium aluminosilicates ($K_2Al_2Si_6O_{16}$) (Gracis *et al.*, 2015). Dental ceramics can be glass/silica based (containing silica, leucite, lithium di-silicate and zirconia), crystalline (alumina containing) or polycrystalline which contain alumina (Al_2O_3) and zirconia (ZrO_2) (McLaren, 1998; McLean, 2001). Dental ceramics are classified (table 1) based on several criteria including indications, composition, processing method, firing temperature, microstructure, translucency and fracture resistance (Anusavice *et al.*, 2012; Sakaguchi *et al.*, 2011; Helvey, 2016; O'Brien, 2008; McLaren *et al.*, 2009; Martin, 2012). Kelly *et al.* classified dental ceramics based on the glass content as predominantly glassy material, particle filled glasses and polycrystalline ceramics. Gracis *et al.*, proposed a new classification system (table 2) based on the presence of specific attributes in their formulation (Gracis *et al.*, 2015). Most dental ceramics have two phases in the structure, glass ceramics are multi-phase containing principally silica as main ingredient which forms a glass phase and finely dispersed crystals such as leucite which is a mineral composed of potassium and aluminum tectosilicate ($K[AlSi_2O_6]$), lithium di-silicate ($Li_2Si_2O_5$) and ZrO_2 forms crystalline phase. Crystalline ceramics contains a large amount of crystals (85%) such as Al_2O_3 , spinell and ZrO_2 , dispersed in glass phase amounting to approximately 20-25% of the total structure.

Glass based ceramics are made from the materials that contain silicon dioxide (SiO_2) and various amounts of Al_2O_3 . The naturally occurring mineral aluminosilicate which is also called feldspar is modified by different ways to make glass ceramics for dental application. The traditional feldspathic porcelain for dental use contains low to moderate amounts of leucite, whereas the leucite-reinforced feldspathic glass ceramic contains 35% of the leucite crystals. The increase in tetragonal leucite crystals are responsible for high compressive strength and modulus of fracture. Studies have shown that presence of high leucite crystals also increases thermal contraction coefficient, this creates tangential compressive

stresses in the glass matrix around the crystals. These stresses prevent crack propagation by deflecting the crack (Datla *et al.*, 2015).

Table 1. Classification of dental ceramics according to the indication, composition, processing and structure. (Modified from, Anusavice *et al.*, 2012; Sakaguchi *et al.*, 2011; Helvey, 2016; O'Brien, 2008; McLaren *et al.*, 2009; Martin, 2012).

Based on Use or indications	Anterior and posterior crown, veneer, post and core; Fixed dental prosthesis, ceramic stain, glaze
Based on composition	Pure alumina; Pure zirconia; Pure silica glass; Leucite glass ceramic; Lithia based glass ceramic
Processing method	Sintering; Casting; Hot isostatic pressing; Partial sintering; Glass infiltration; CAD-CAM; Copy milling
Firing temperature	Ultra-low fusing; Low fusing; Medium fusing; High fusing
Microstructure	Amorphous glass; Crystalline; Crystalline particles in glass matrix
Translucency	Opaque; Translucent; Transparent
Fracture resistance	Low; Medium; High

Table 2. Classification of ceramics and ceramic-like materials. (Modified from, Gracis *et al.*, 2015).

Glass matrix ce- ramics	Feldspathic	
	Synthetic	Leucite based; Lithium di-silicate and deriva- tives; Fluorapatite-based
	Glass- infiltrated	Alumina; Alumina and magnesium; Alumina and zirconia
Polycrystalline ceramics		Alumina; Stabilized zirconia; Zirconia-toughened alumina; Alumina toughened zirconia
Resin matrix ceramics		Resin nano-ceramic; glass-ceramic in a resin interpenetrating ma- trix; Zirconia-silica ceramic in a resin interpenetrat- ing matrix

MacCulloch first worked on glass ceramics, but further investigations by Grossman and Adair helped to develop tetra silicic fluormica containing ceramic system for dental application (MacCulloch 1968; McLean, 2001; Shenoy *et al.*, 2010). Glass ceramic restorations are formed by the process called ceraming, which means the conversion of glass to a partially crystalline phase. During sintering the heat treatment results in controlled crystallization by nucleation and growth of internal crystals. This said the formed glass ceramic contains a residual glassy phase which is responsible for esthetic properties and an evenly dispersed crystal phase which gives mechanical strength to the ceramic. The crystal phase in the ceramic is formed by 2 stages, in the first stage the glass is heated to a temperature 750° - 850° and maintained for 1-6 hours to form nuclei and later in the second stage the temperature is gradually increased to 1000° – 1150° degree to form crystals.

Polycrystalline ceramics are crystalline in nature based on Al_2O_3 and yttria stabilized tetragonal zirconia (Y-TZP). The flexural strength and fracture toughness are significantly higher than feldspathic, leucite and lithium di-silicate ceramics because of the ability to resist crack propagation; hence they are indicated in high masticatory load bearing areas (Probster *et al.*, 1992; Wall *et al.*, 1992). The absence of glass phase in polycrystalline ceramics make them less translucent and they are impossible to etch with HF. Alumina consists of high grade AL_2O_3 and is used in polycrystalline ceramics to increase the strength and its elastic modulus is highest of all dental ceramics (Guess *et al.*, 2011; Scherrer *et al.*, 2007). The basic ceramic structure consists of partially sintered porous alumina which is later infiltrated with lanthanum molten glass after dry pressing (Al-Wahadni, 1999; Claus, 1990; Probster *et al.*, 1992). The infiltration of molten glass to the core ceramic results in characteristic color, translucency and strength. The strength of the final restoration is significantly higher than the conventional feldspathic porcelain (Giordano *et al.*, 1995).

Zirconia is a white, dense, crystalline oxide of zirconium which is highly biocompatible, manufactured from ZrO_2 and 3-5% of yttrium oxide (Y_2O_3) (Oilo *et al.*, 2008). Pure ZrO_2 is available in three forms: monoclinic which is stable up to $1170^{\circ}C$, above this temperature it will transform into tetragonal, and when temperature exceeds $2370^{\circ}C$ the tetragonal form transforms to cubic. Dental zirconias are classified based on the form as fully stabilized zirconia (FSZ), partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZP) (Chevalier *et al.*, 2009). At present all dental zirconias are TZP type, especially Y-TZP. These are the most advised ceramic for dental applications because of its better mechanical properties such as strength and fracture toughness after machining and sintering, because of the resistance to crack propagation due to the phase transformation (Sailer *et al.*, 2007; Miyazaki *et al.*, 2013). When transformation oc-

curs from tetragonal to monoclinic the volume increases by 4%, this increase in volume closes the cracks and results in increase in fracture toughness. Because of the high strength and opaque nature, this material is used as core structure to support veneer ceramics. It is also used in orthopedic implants as a surface coating material (Guazzato *et al.*, 2004; wang *et al.*, 2008; Denry *et al.*, 2008).

With the introduction of new materials and processing techniques and also due to their inertness, the clinical uses of ceramics in the field of dentistry are steadily increasing. Dental ceramics have a wide range of optical properties and excellent esthetics. Dental ceramics are used as a veneering material for metal ceramic restorations, and the current trend is to develop all-ceramic materials for the fabrication of crowns, bridges, inlays, onlays and esthetic laminate veneers (Figure 1). Ceramics are also used to fabricate ceramic posts, abutments for implant superstructure and implants (Denry *et al.*, 2010).

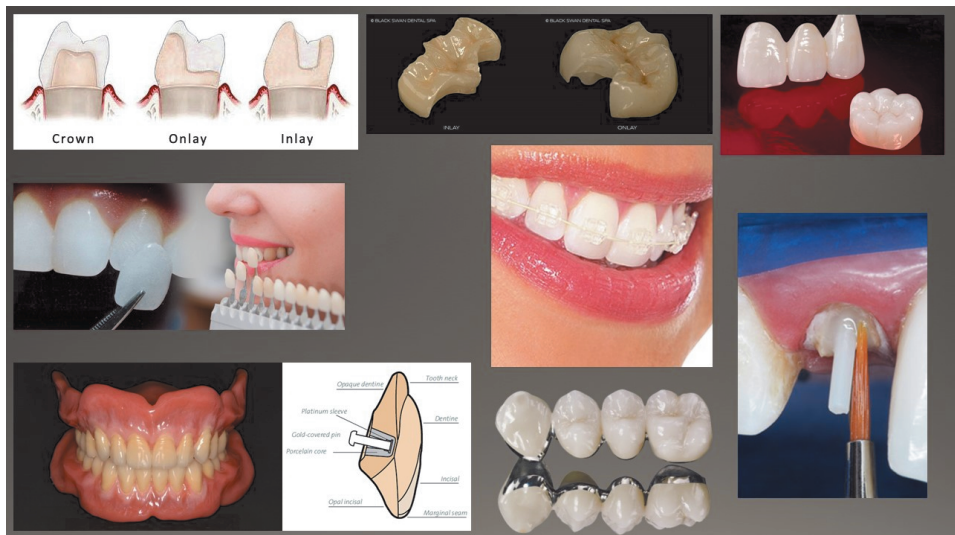


Figure 1. Applications of dental ceramics.

Ceramic inlays are gaining more popularity than composite resin restorations because of their better abrasion resistance, superior biocompatibility and clinically acceptable marginal gaps. Ceramic esthetic veneers (laminate veneers) are furthermore used to cover the unaesthetic facial surfaces of anterior teeth, traditionally laminates were fabricated using feldspathic porcelain. Currently, laminate veneers are also fabricated using lost wax-technique or machined by CAD/CAM technique with high strength ceramics such as leucite-reinforced or lithium disilicate ceramics. Ceramic onlays, crowns and bridges have multiple advantages over metal restorations, such as restoration margins which can be placed supragingivally and still be invisible. The aesthetics is superior to metal ceramic

restorations. No dark areas can be seen at the tooth-restoration margin at the gumline, since the restoration does not contain metal and hardly any postoperative sensitivity is experienced (Shenoy *et al.*, 2010; Denry *et al.*, 2010; Willard *et al.*, 2018; Kelly *et al.*, 2011).

There is an increase in the use of ceramic (zirconia) as abutments for implant superstructures and implants because of their inertness. Ceramic implants can be considered for patients who are allergic to metals. Other advantages of ceramics over metal implants are high durability, improved mechanical properties and lack of corrosion.

In spite of several advantages and wide clinical applications of dental ceramics, ceramic restorations fail as a result of several reasons, however the long term survival rate is high (Schwass *et al.*, 2013; Saridag *et al.*, 2013; Fasbinder 2006; Fernandes *et al.*, 2015). The reasons for the failure are

- Fracture because of crack initiation and propagation in high occlusal load area.
- Chipping as a result of structural failure because of occlusal loading near the wear facets.
- Thermal surface degradation as a result of grain pullout during transformation grain growth of zirconia ceramics.
- Lack of chemical bonding with tooth substance.

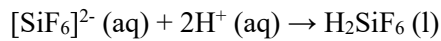
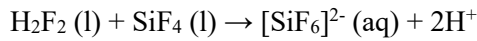
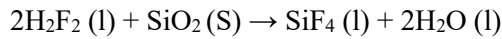
Improving the material properties and finding the reasons for failures of the ceramic restorations have been the great challenges. Advances in dental ceramics will continue in terms of improving structural durability, fabricating veneers and core ceramics separately using CAD/CAM process, and producing CAD/CAM restorations using additive manufacturing technology.

2.2 Acid etching

Acid etching is the procedure of treating the internal surface of the ceramic restoration and prepared tooth surface with a suitable acid (usually mineral acid) to increase the surface free energy (Matinlinna *et al.*, 2007b). In dentistry adhesion between two dissimilar materials is achieved by increasing the surface free energy by application of acid which changes the surface characteristics and by treating the surface with suitable silane coupling agent which improves wettability of the cementing surface to luting resin cements (Lung *et al.*, 2012). It is noteworthy that natural enamel and dentin are etched using 35% phosphoric acid (H_3PO_4)

and silica based glass ceramics like leucite reinforced, lithium di-silicate, and glass infiltrated alumina are etched using 5% or 9.5% HF gel. Etching of internal surface of glass ceramics selectively dissolves glassy phase and increases surface area for resin bonding by creating micro pores. Etching also exposes -OH which are responsible for chemical bonding via silane coupling agent (Matinlinna *et al.*, 2007a).

When etched with HF acid, the silica based ceramic surface forms silicon tetra-fluoride, silicon tetrafluoride reacts with HF and forms a soluble complex called hexafluorosilicate. The hexafluorosilicate reacts with protons to form tetrafluoro-silicic acid which is rinsed off (Basset, 1965; Matinlinna, 2004). The three stages of chemical reaction is:



Kenneth *et al.* studied the long-term survival of ceramic restorations in the human oral cavity using data available for the 1444 restorations. Data showed that the probability of survival of an acid-etched ceramic restoration was 74% at 14.1 years. The long-term survival improved significantly when restorations were acid-etched before luting (Malament *et al.*, 1999). Blatz reviewed the surface treatment modalities for silica based glass ceramics and preferred acid etching with HF solution for strong resin bond (Blatz *et al.*, 2003b). Strong resin bond relies on proper surface treatment procedure with acid. After surface treatment the subsequently applied luting resin cement flow into the micro-pores and provides micro-mechanical retention through resin tags. Researchers also successfully used laser etching technique to create rough surface for lithia-based glass ceramics (Gokce *et al.*, 2007).

2.3 Neutralizing agent

Application of HF acid changes the surface chemistry of the ceramic substrate by forming fluorosilicate products such as F, Si, Al, K, Ca and Na in the etched zone (Canay *et al.*, 2001), which probably may increase the concentration of hydrogen ions (Foxton *et al.*, 2003). Foxton *et al.*, studied the pH of the ceramic surface after treatment with HF and phosphoric acid using scanning chemical microscope based on flat pH imaging semiconductor silicon sensor. The study showed that the pH of the etched ceramic surface increased with increase in the duration of water rinsing times with both acid treatments.

Neutralizing agent is a white odorless powder containing 25-50% sodium carbonate, it is supplied along with the IPS ceramic etching gel (IPS ceramic neutralizing powder™, Ivoclar Vivadent, Schaan, Liechtenstein). The powder is mixed with distilled water and used to neutralize the HF gel after etching ceramic restorations. The mixture can also be used during acid hazard situation when acid gel comes in contact with soft tissues. To neutralize the HF gel, add the neutralizing solution and let it react for 5 minutes. One measuring spoon of IPS Ceramic Neutralizing Powder is suitable to neutralize the quantity of IPS Ceramic Etching Gel required for a large MOD inlay. After the reaction time, pour out the neutralized solution and rinse with copious amounts of water (Ivoclar Vivadent, 2015).

2.4 Surface topography of etched ceramic

Etching of glass ceramics creates numerous micro-pores. There are several studies that have investigated the microstructure and surface topography of the etched ceramic surface. The surface typically shows amorphous micro-structure with numerous porosities due to dissolution of glassy phase and an increase of S_a which is measured by using surface profilometers. The surface topography depends on many factors such as the type of acid used, concentration of acid, duration of acid contact, and type of ceramic (Simonsen *et al.*, 1983; Stangel *et al.*, 1987; Roulet *et al.*, 1995). Prolonged etching and using highly concentrated acids create larger pores and cracks which significantly reduces bond strength (Peumans *et al.*, 2000).

Canay *et al.*, studied the effect of different surface treatments on the surface texture of a feldspathic porcelain. They used acidulated phosphate fluoride (APF) applied for 10 min and HF applied for 1 and 4 min and thereafter characterized the etched surface using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). EDS found crystalline precipitates (salts) of Na, K, Ca, Al on the etched surfaces. The study found a significant difference between the etchants and the time of exposure to the etchant. The sample surface treated with APF appeared relatively smooth and homogenous, and as such, to be insufficient for creating a micromechanical bonding surface in comparison with HF treated specimens. The samples etched with HF revealed an irregular surface showing a three dimensional lattice of voids and channels. The surface micro patterns appeared more pronounced and aggressive with larger voids and deeper channels with increase in HF etching time (Canay *et al.*, 2001).

In addition, Borges *et al.*, compared the changes in surface microstructure of the six different ceramic materials after etching and airborne particle abrasion. This study found a little (silica based glass ceramics) /no (In-ceram™ alumina and In-ceram™ zirconia) changes with grit-blasting (also called airborne particle abra-

sion). HF etching created surfaces with elongated crystals scattered with shallow irregularities to be characterized as honeycomb-like. However, a treatment of alumina and zirconia based ceramics with HF had no effect on surface morphology (Borges *et al.*, 2003) because they hardly dissolve.

The concentration of acid used and the duration of acid contact time on the surface of the ceramic have a direct effect on the S_a and wettability to resins cements. An increase in the concentration and duration increase the S_a and wettability of the ceramic surface. Ersu *et al.*, evaluated the effects of CO₂ laser and conventional surface treatments on S_a and shear bond strength (SBS) of glass-infiltrated alumina-ceramics to dentin. The study reported significantly higher S_a values with sandblasting and CO₂ laser irradiation (Ersu *et al.*, 2009). Zogheib *et al.*, studied the effect of different acid etching times on the S_a and the flexural strength of a lithium di-silicate-based glass ceramic. The roughness values increased with the increase of the etching time. The study also showed that the HF etching significantly reduced the mean flexural strength as the etching time increased (Zogheib *et al.*, 2011b). The study by Ayad *et al.*, also showed similar results when tested on heat pressed ceramics (Ayad *et al.*, 2008).

2.5 Surface roughness (S_a)

The surface roughness (S_a) is the measure of a surface topography of a given specimen surface and it is measured using a contact or a non-contact surface profilometer (Ramakrishnaiah *et al.*, 2016). Contact profilometer contacts the surface of the sample and measures the S_a and is least accurate. The non-contact surface profilometer uses optical device to measure the S_a without contacting the surface.

Indeed, the S_a is a very important parameter in bonding dental restoration to natural enamel, it increases surface free energy and wettability to silane coupling agent and resin cement. Increasing the S_a of the ceramic surface or enamel also increases surface area for resin bonding. Several techniques like air particle abrasion, acid etching, laser etching are recommended to increase the S_a .

2.6 Surface wettability

Surface wettability (generally referred to as hydrophobicity/hydrophilicity) refers to how a liquid deposited on a solid substrate spreads out (Xu *et al.*, 2007; Chen *et al.*, 2015). Improving the surface wettability makes the ceramic substrate surface more compatible to subsequently applied luting resin cements. Depending on the type of substrate, wettability can be characterized as total wetting or partial wetting. When the substrate has strong affinity to liquid, the liquid spreads

completely this is referred as total wetting. In partial wetting the drop will not spread totally, because of cohesive force within the liquid, minimizing its contact with the substrate surface and form an angle between liquid and substrate surface. This angle is called the contact angle (CA) (Figure 2 and 3) (Hirasaki 1991, Yuan *et al.* 2013).

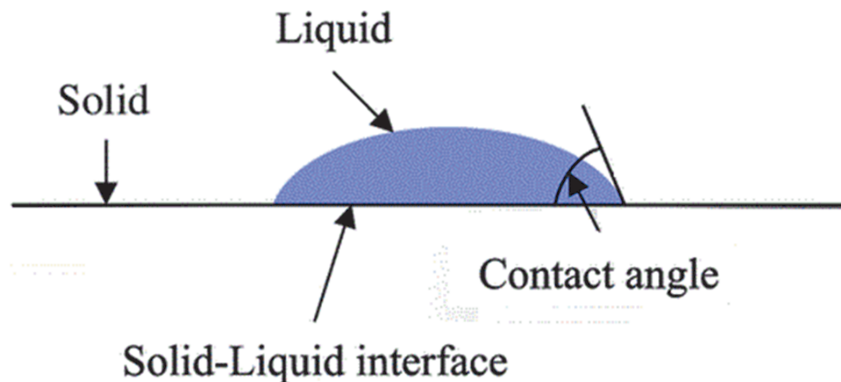


Figure 2. Contact angle (Modified from, Manahiloh *et al.*, 2017)

The contact angle is measured by Young's equation, where γ_{SG} is the solid surface tension, γ_{SL} is the solid and liquid boundary tension, γ_{LG} is the liquid surface tension and $\cos\theta$ is the angle formed.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$$

The CA is the measurement of the surface wettability. In the laboratory, CA is measured through any liquid when it makes contact with a given solid surface by intermolecular interaction. As the tendency of the liquid to spread on the substrate surface increases, the CA decreases. This indicates that the substrate surface has better wettability. Hence CA and wettability are inversely related; a CA of less than 90° is considered as the substrate surface wettability is favorable, and a CA of more than 90° is considered as the wettability is unfavorable. The degree of wettability of the given substrate is determined by the force balance between adhesive and cohesive forces (Sharfrin *et al.*, 1960).

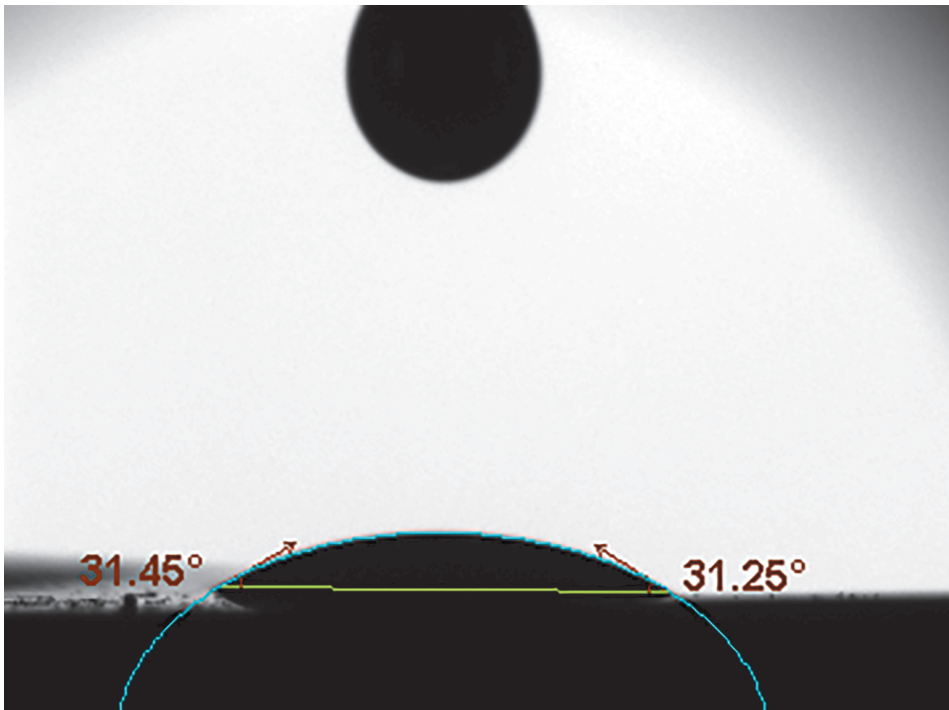


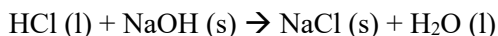
Figure 3. Schematic showing contact angle of a liquid on solid surface.

In dentistry the surface wettability is increased by conditioning the surface of an indirect restorative material and tooth substance. This includes etching, rinsing, neutralizing and application of a silane coupling agent. Etching increases surface free energy: when the surface has high surface free energy, it is clean and it tends to attract the liquid, *i.e.*, a liquid spreads instantly. Wettability also depends on the surface tension and viscosity of the liquid. Surface tension is the energy or work required to increase the surface area of a liquid. It depends on the intermolecular forces between liquid molecules (Moustafa *et al.*, 2009).

2.7 Surface neutralization

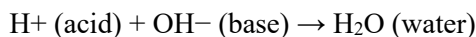
After etching with HF the ceramic surface is washed thoroughly with water to remove residual acid and fluorosilicate precipitates. This procedure can be carried out effectively by subjecting to ultrasonic cleaning before cementation. However, acid action results in formation of fluorosilicate precipitates such as F, Si, Al, K, Ca and Na, which may lower the pH of the etched surface (Canay *et al.*, 2001; Foxton *et al.*, 2003). The acidic cementing surface may interfere with the cement polymerization (Foxton *et al.*, 2003; Saavedra *et al.*, 2009; Bottino *et al.*, 2015; Zorzini *et al.*, 2012).

In general, neutralization between strongly acidic hydrochloric acid (HCl) and strongly basic sodium hydroxide (NaOH) proceeds as:



This product, NaCl (sodium chloride) and H₂O (water), are neutral (pH = 7).

Potential of hydrogen (pH) is a logarithmic scale, which indicates how acidic or alkaline the substance is, measured on a scale from 0 to 14. Acidic substance will have lower pH, *i.e.*, less than 7 and alkaline substance will have higher pH *i.e.*, more than 7. The substances which are neither acidic nor alkaline are called neutral, and their pH will be 7. In relation to acid etching, the acid etched surface will remain acidic (Foxton *et al.*, 2003), hence the manufacturers recommend to neutralize after etching in order not to interfere with polymerization of the luting resin cement. Hence the ceramic surface is treated with neutralizing agent after etching with HF.



However, perhaps surprisingly, Saavedra *et al.*, found conflicting results after neutralization, when they studied the effect of acid neutralization and mechanical cycling on the micro-tensile bond strength of glass-ceramic inlays. They reported a significant reduction in the micro-tensile bond strength in the specimens that were neutralized (Saavedra *et al.*, 2009).

2.8 Silane coupling agents

Silane coupling agents (silanes) are synthetic hybrid inorganic-organic compounds that possess at least one direct –Si-C– bond in their molecular structure. Chemistry of Si with its so-called empty *d*-orbitals provide peculiar chemical properties (Matinlinna, 2010). Silanes are silicon hydrides and silicon esters and their derivatives, and are used as surface modifying agent for adhesion promotion (dental composite fillers) and surface conditioning agent (a coupling agent for composite to conditioned ceramic and composite surface to silica-coated metals and alloys) (Hooshmand *et al.*, 2001). Silanes are non-hazardous, non-cytotoxic and they exhibit moderate thermal stability. In prosthetic dentistry silane coupling agents are routinely used to increase the surface free energy of silica-coated or silica-containing indirect restorations to luting resin cements (Matinlinna *et al.*, 2006b). Generally, silanes used to promote adhesion are organofunctional silanes and silane esters (R-Y-SiX₃, where R is a non-hydrolyzable organic group, Y is a linker, and X is a hydrolysable group). Hence, silanes are primarily used to bond two dissimilar materials, *i.e.*, capable of unifying organic and inorganic materials (Matinlinna *et al.*, 2006a). In general, silanes have non-

hydrolysable groups (such as methacrylate) and hydrolysable groups (such as ethoxy), which is why they are chemically bifunctional (Matinlinna *et al.*, 2007b). When reactive silanes (in a diluted liquid with 1-2% of silane monomer in it) are applied over the etched ceramic surface, the hydrolysable alkoxy groups react with exposed hydroxyl groups, and the non-hydrolyzable organic groups polymerize with unset resin composite cement to provide durable chemical bonds (Matinlinna *et al.*, 2007a; Ramakrishnaiah *et al.*, 2016).

Silanes were first extensively studied in glass fiber reinforced composites for bonding of silanes to glass fiber surface through siloxane bonds (-Si-O-Si) (Plueddemann *et al.*, 1962; Clark *et al.*, 1963; Plueddemann, 1970a; Plueddemann, 1991). Some trialkoxysilanes are used to synthesize particulate filler restorative composites such as Ormocer (Tagtekin *et al.*, 2004). 3-methacryloxypropyltrimethoxysilane, Vinyltrimethoxysilane, vinyltriisopropoxysilane are some of the trialkoxysilanes (Figure 4).

Depending on number of silicon atoms, silanes are named as *monofunctional* (one silicon atom with three alkoxy group), *bisfunctional* (two silicon atoms each with three alkoxy group), *trisfunctional* (three silicon atoms), or as *nonfunctional* silane (contains alkoxy, halogen, aryl or alkyl groups). *Bisfunctional* silanes are also called dipodal silanes. When these silanes are used in combination with other functional silanes, they significantly improve bonding, and hydrolytic stability of composites (Matinlinna, 2004; Jayaseelam *et al.*, 2001, Arkles 2003). The hydrolytic stability of such silanes are said to be 1×10^5 times higher (Matinlinna 2004).

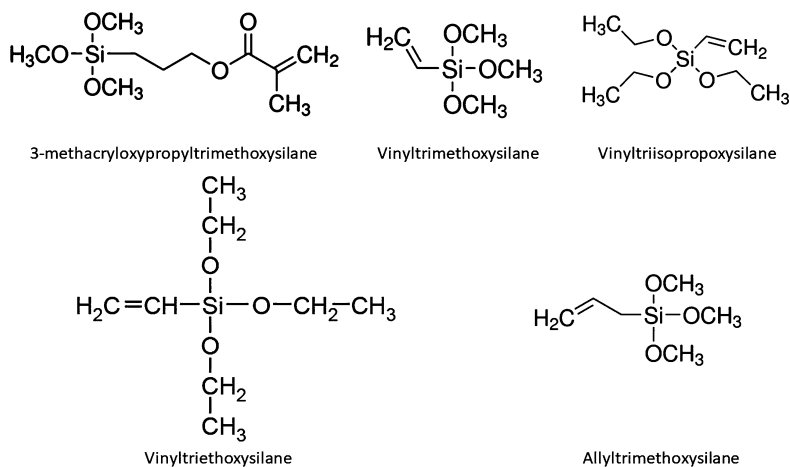


Figure 4. Trialkoxysilanes.

Depending on number of alkoxy groups, silanes are termed as *monoalkoxysilanes* (one alkoxy group), *dialkoxysilanes* (two alkoxy groups) or *trialkoxysilanes* (three alkoxy groups). *Trialkoxysilanes* are hydrophobic and have high stability; hydrophobic silanes are hydrolyzed before deposited on the substrate surface. The hydrolytic stability of the silanes depends on the pH, the ideal pH for the silane deposition onto substrate surface is 4-6. Silane hydrolysis depends on concentration, solution, and temperature (Matinlinna, 2004).

Currently, 3-MPS diluted in ethanol-water solution, ca. 1-2%, pH adjusted to 4-5 with acetic acid is the most commonly used silane-coupling agent in dentistry because of the strong bond forming capacity. However extensive research on other silanes of same chemical type (but with various functionalities) has been carried out (Matinlinna *et al.*, 2005; Matinlinna *et al.*, 2004; Matinlinna *et al.*, 2006a). The novel silane system, *i.e.*, blends consisting of functional silanes such as 3-isocyanatopropyltriethoxysilane (a trialkoxysilane with one organofunctional group), 3-acryloyloxypropyltrimethoxysilane (ACPS), vinylsilane and an isocyanuratesilane blended with a cross-linker silane (BTSE) are said to be more reactive, and hence, have the potential to produce significantly higher adhesion strength and longer adhesion durability. MPS type silanes are also used to bond composite resin to titanium and other metal substrates (Matinlinna *et al.*, 2004).

3 AIMS OF THE STUDY

The modern restorative treatments are now focused more towards the use of novel ceramic restorative materials which are biocompatible and durable. The literature review (Chapter 2) described some of the generally accepted and supported ideas about the purpose of etching and silane application to silica based glass ceramics and tooth substance to promote adhesion of adhesive resins.

This study was designed to investigate critical factors at micron and submicron level. In this study factors such as etching, etching time, neutralization, surface roughness, priming (conditioning), wettability and exposure to water which affect the adhesion of resin composite and adhesive resin to dental glass ceramics, were investigated. The specific aims and hypothesis were:

1. To study the effect of acid etching with HF and etching duration (time) on the surface topography in terms of pore pattern, pore width, and pore depth of silica based glass ceramics. The hypothesis: an increase in the acid etching duration significantly alters the surface microstructure in terms of pore pattern, pore depth and width.
2. To study the effect of etching duration on S_a and wettability of silica-based glass ceramics. The hypothesis was that an increase in the etching time results in increased S_a and wettability of the ceramic surface.
3. To determine the effect of a neutralizing agent on wettability of ceramic surface to experimental and commercially available silane primers, and to determine the effect of a neutralizing agent on the wettability of silane treated ceramic surface to an adhesive resin and to a resin composite cement. The hypothesis was that the residual acid remnants present within deep pores and irregularities after acid etching procedure may lower the pH value of the ceramic surface and, as such adversely affect the ceramic-resin bonding by altering the wettability to silanes and wettability of silane treated ceramic surface to adhesive resin and resin composites.
4. To investigate and evaluate the interface between dental ceramic and resin cements (resin composite and adhesive resin) for the degree of resin impregnation into the etched micro-patterns, and the nano-mechanical properties of the resin-ceramic interface. The research hypothesis was that (1) the resin impregnation by adhesive resin system is better than the resin composite, and (2) the resin tags with better penetration to the micro-patterns are better polymerized (*i.e.*, have higher nano-hardness) at the deepest part of the micro-patterns.

5. To evaluate the effect of accelerated hydrolysis on ceramic-resin interface and nano-mechanical properties. The hypothesis was that silane promoted adhesion tends to hydrolyze over a period of time, thereby weakening the nano-mechanical properties.
6. To evaluate the resin cement bond strength to conditioned ceramics using a two-step and a one-step ceramic surface conditioning system and to compare the adhesion strength of resin composite and adhesive resin. Furthermore, to evaluate effect of water exposure on ceramic-luting cement adhesion strength, as silane promoted adhesion tends to deteriorate over a period of time.

4 MATERIALS AND METHODS

Table 3. Materials used in studies I-IV.

Materials	Studies			
	I	II	III	IV
Ceramics	Celtra™, DeguDent, Hanau, Germany.	IPS e-max™, Ivoclar Vivadent, Schaan, Liechtenstein.	Celtra™, DeguDent, Hanau, Germany.	IPS e-max™, Ivoclar Vivadent, Schaan, Liechtenstein. VITA Mark II™, VITA Zahnfabrik, Bad Sackingen, Germany
	IPS e-max™, Ivoclar Vivadent, Schaan, Liechtenstein.		IPS e-max™, Ivoclar Vivadent, Schaan, Liechtenstein.	
	VITA Mark II™, VITA Zahnfabrik, Bad Sackingen, Germany		VITA Mark II™, VITA Zahnfabrik, Bad Sackingen, Germany	
	VITA Suprinity™, VITA Zahnfabrik, Bad Sackingen, Germany			
	VITA Suprinity FC™, VITA Zahnfabrik, Bad Sackingen, Germany			
Etchant	IPS Ceramic etching gel™, Ivoclar Vivadent, Schaan, Liechtenstein.	IPS Ceramic etching gel™, Ivoclar Vivadent, Schaan, Liechtenstein.	IPS Ceramic etching gel™, Ivoclar Vivadent, Schaan, Liechtenstein.	IPS Ceramic etching gel™, Ivoclar Vivadent, Schaan, Liechtenstein.
				Monobond Etch and Prime™, Ivoclar Vivadent, Schaan, Liechtenstein.
Neutralizing agent	IPS Ceramic neutralizing powder™, Ivoclar Vivadent, Schaan, Liechtenstein.	IPS Ceramic neutralizing powder™, Ivoclar Vivadent, Schaan, Liechtenstein.	IPS Ceramic neutralizing powder™, Ivoclar Vivadent, Schaan, Liechtenstein.	IPS Ceramic neutralizing powder™, Ivoclar Vivadent, Schaan, Liechtenstein.
Silane coupling agents		Monobond Plus™, Ivoclar Vivadent, Schaan, Liechtenstein.	Monobond Plus™, Ivoclar Vivadent, Schaan, Liechtenstein.	Monobond Plus™, Ivoclar Vivadent, Schaan, Liechtenstein.
		MPS+BTSE (experimental silane)		Monobond Etch and Prime™, Ivoclar Vivadent, Schaan, Liechtenstein.
Resin cements		GC G-Cem™, GC Europe N. V, Leu-ven, Belgium	Stick Resin™, Stick Tech Ltd, Finland	Stick Resin™, Stick Tech Ltd, Finland
			Variolink N™, Ivoclar Vivadent, Schaan, Liechtenstein.	Variolink N™, Ivoclar Vivadent, Schaan, Liechtenstein.

4.1 Materials

Most commonly clinically used silica based glass ceramics, etchant, neutralizing agent, and resin cements were selected for the studies. The manufacturers details of all the commercially available materials used in studies I, II, III and IV have been tabulated in Table 3. In study III the wettability of commercial silane on the etched ceramic surface and wettability of commercial resin on silane treated ceramic surface was compared with the wettability of experimental silane and experimental resin. The components used to prepare experimental primer and experimental resin, and other details of the components are mentioned in Table 4 and 5. The ceramic specimens for all the studies were prepared using CAD blocks. Rectangular shaped specimens measuring $15\text{ mm} \pm 0.25\text{ mm} \times 11\text{ mm} \pm 0.25\text{ mm} \times 2\text{ mm} \pm 0.25\text{ mm}$ were used in studies I, II and IV. Cuboidal shaped specimens measuring $7.0\text{ mm} \pm 0.25\text{ mm} \times 5.0\text{ mm} \pm 0.25\text{ mm} \times 4.0\text{ mm} \pm 0.25\text{ mm}$ were use in study III. The ceramic specimens requiring crystallization (IPS e-max™, and Vita Suprinity™) were crystallized after specimen preparation and before etching.

4.2 Specimen preparation

4.2.1 Specimen preparation, grouping and etching procedure to determine the effect of etching on surface characteristics (study I)

Seventy-five specimens were cut from each material using a low-speed, water cooling diamond wheel saw (Model L650, Ladd research industries, Williston, VT, USA). The sectioned specimens were polished under running water up to 1000 grit FEPA (Federation of European Producers of Abrasives) silicon carbide papers in a sequential manner and polished with a polishing liquid in order to remove gross surface scratches and irregularities using Labpol 8-12 (Extec, En-filed, CT-06082, USA). Finally, the specimens were ultrasonically cleaned in distilled water for ten minutes using Qantex 140 (L and R, Kearny, NJ, USA) and then stored in sealed plastic containers.

Fifteen samples from each material were randomly selected and assigned to five study groups: one control group and four experimental groups ($n = 75$). Control group received no etching, the remaining samples of experimental groups B, C, D and E were etched for 20, 40, 80, and 160 s respectively with 5% HF. The etching was done in a fume hood in a well ventilated laboratory environment with all safety measures to avoid any acid hazard. The acid was rinsed with copious amount of water for 30 s after specified duration of etching, neutralized using a neutralizing agent for five min. The specimens were washed in running water for 30 s and ultrasonically cleaned for 5 min using distilled water.

4.2.2 Specimen preparation and grouping to determine the effect of ceramic surface neutralization on wettability of silane and resin (study II)

A total of 40 specimens were cut, polished from 600-grit to 1200-grit (FEPA), and cleaned. All the specimens were etched for 20 s using 5% HF, washed, and dried as described in study I. The specimens were randomly assigned to one control group and one treatment group, each comprising 20 samples. The control group received no treatment (non-neutralized), while the treatment group specimens (neutralized) were placed in a solution containing a neutralizing agent mixed with distilled water in 1:1 ratio for 1 min, rinsed with distilled water for 30 s, and specimens were allowed to dry. The samples of each group were further divided randomly into two subgroups each having 10 samples, and tested to determine the effect of neutralizing agent on wettability of experimental and commercial silane primers. Furthermore, the effect of neutralizing agent on wettability of commercial and experimental silane treated samples to experimental unfilled resin (adhesive resin) and commercial resin cement was tested and compared as described below (Figure 5).

The experimental subgroup a: wettability of the non-neutralized ceramic surface treated with a commercial silane primer (Monobond Plus™) was compared with the wettability of neutralized ceramic surface treated with commercial silane to experimental resin cement. The experimental subgroup b: wettability of the non-neutralized ceramic surface treated with a commercial silane primer was compared with the wettability of neutralized ceramic surface treated with commercial silane to commercial resin cement (GC G-CEM™). The experimental subgroup c: wettability of the non-neutralized ceramic surface treated with an experimental silane primer was compared with the wettability of neutralized ceramic surface treated with commercial silane to the adhesive resin. The experimental subgroup d: wettability of the non-neutralized ceramic surface treated with an experimental silane primer was compared with the wettability of neutralized ceramic surface treated with experimental silane to the adhesive resin.

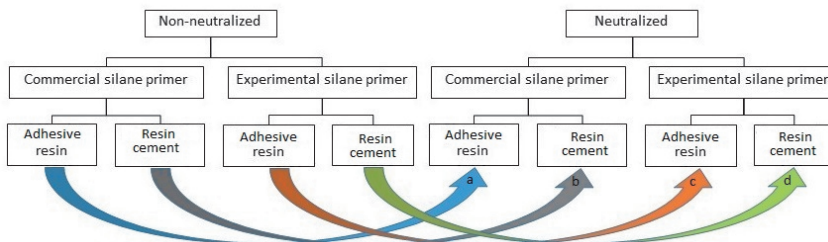


Figure 5. The chart showing the comparison of wettability of resin cements between non-neutralized and neutralized samples. (Copied from, Ramakrishnaiah *et al.*, 2018(a))

4.2.2.1 Experimental silane primer preparation

An experimental silane primer, consisting of 2.0 vol-% of MPS and 2.0 vol-% BTSE in 3 mL abs ethanol, was mixed with 3 mL of 95:5% water-ethanol at pH 4.1, corresponding to a final 1.0 vol% MPS + 1.0 vol% BTSE. This was prepared as described by Matinlinna *et al.* (Durgesh *et al.* 2016; Matinlinna *et al.* 2005). The chemical formulae and the constituents of the experimental primers are shown in Figure 6 and Table 5, respectively.

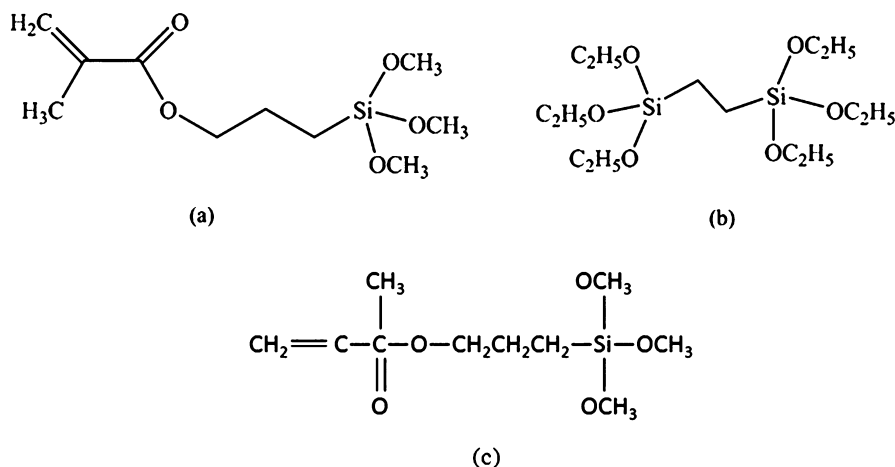


Figure 6. Chemical formulae: the experimental silane: (a) 3-methacryloxypropyltrimethoxysilane (MPS) (b) *bis*-1,2-(triethoxysilyl)ethane BTSE, and (c) Monobond plus. (Copied from, Ramakrishnaiah *et al.*, 2018(a))

Table 4. Experimental silane primer used in the study. (Copied from, Ramakrishnaiah *et al.*, 2018(a))

Name	Silane monomer	Batch no.	Manufacturer
MPS	3-methacryloxypropyltrimethoxysilane <i>i.e.</i> , [3-(trimethoxysilyl)propylmethacrylate]	00901DJ	Sigma-Aldrich, St. Louis, MD, USA.
BTSE	<i>bis</i> -1,2-(triethoxysilyl)ethane	4R-4325	Gelest, Morris- ville, PA, USA.

4.2.2.2 Experimental resin preparation

An experimental adhesive resin consisting of 70.6 wt-% urethane dimethacrylate (UDMA), 27.4 wt-% hydroxypropyl methacrylate (HPMA) and 2 wt-% initiator system camphorquinone (CQ) + *N,N*-cyanoethylmethylaniline (CEMA) was prepared as described by Zhang *et al.* (Zhang *et al.* 2014) The chemical formulae and the constituents of the experimental adhesive resin are shown in Figure 7 and Table 5, and composition of commercial resin cement is shown in Table 6.

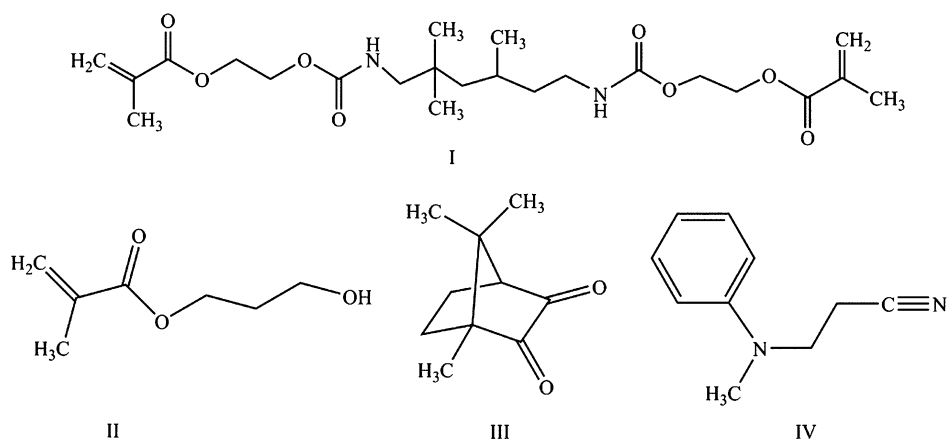


Figure 7. Chemical formulae of the adhesive resin: I. Urethane dimethacrylate (UDMA); II. Hydroxypropyl methacrylate (HPMA); III. Camphorquinone (CQ); and IV. *N,N*-cyanoethyl methylaniline (CEMA). (Copied from, Ramakrishnaiah *et al.*, 2018(a))

Table 5. The components of experimental adhesive resin. (Copied from, Ramakrishnaiah *et al.*, in press)

Name	Components	Purity	Batch no.	Manufacture
UDMA	Urethane dimethacrylate	>90%	X-850-0000	Esstech Inc., Essington, PA, USA
HPMA	Hydroxypropyl methacrylate	>90%	X-796-0000	Esstech Inc., Essington, PA, USA
CQ	(1S)-(+)-Camphorquinone	≥99.0%	A0077555	Accu-Chem Industries, Melrose Park, IL, USA
CEMA	<i>N,N</i> -cyanoethyl methylaniline	≥98.5%	T20100224	Accu-Chem Industries, Melrose Park, IL, USA

Table 6. Composition of resin composite. (Copied from, Ramakrishnaiah *et al.*, 2018(a))

Resin cement	Composition
GC G-CEM™, GC Europe N.V, Leuven, Belgium	Dimethacrylates, 4-META, phosphoric ester monomer, fluoro-aluminio-silicate glass, camphorquinone

4.2.3 Specimen preparation and grouping for micro and nano structural analysis of ceramic-luting resin interface (study III)

Twenty specimens were cut from each ceramic material (IPS e-max™, Vita Mark II™ and DeguDent Celtra™), polished up to 4000-grit (FEPA), and cleaned. All the specimens were etched for 40 s using 5% HF, neutralized, for 1min, washed, and dried as described in study I and study II. The specimens were randomly assigned to two study groups.

Group 1 specimens: the etched surface was treated with a primer, and in the

Group 2 specimens: the etched surface received no primer treatment in order to study the effect of primer application, on penetration of luting resin cements into the etched micro pores.

The specimens of each group were further randomly divided in two sub-groups 1A, 1B and 2A 2B depending on the type of resin applied (Figure 8).

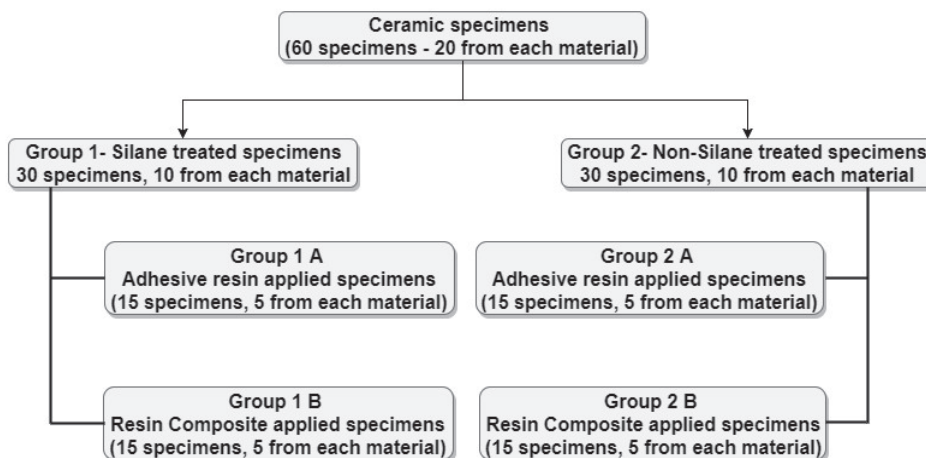


Figure 8. Flow chart of groups and the surface treatments. (Copied from, Ramakrishnaiah *et al.*, 2018 (b))

Adhesive resin was applied on subgroup 1A and 2A surface of specimens and resin composite was applied on subgroup 1B and 2B surface of specimens to

evaluate the difference in terms of penetration of resin into micro pores. After 15 s of impregnation time the resin cement was light cured for 20 s using a light curing unit (Elipar™ Free Light 2, 3M ESPE, Seefeld, Germany) with a wavelength of 420-540 nm and the power of 1505 mW/cm² (MARC-Managing accurate resin curing system, Blue Light Analytics, Halifax, Canada).

The specimens were ground perpendicular to the adhesive interface with water cooling and polished up to 4000 grit FEPA, ultrasonically cleaned and air dried to examine the resin-ceramic interface.

4.2.4 Specimen preparation and grouping for evaluation of two-step and one-step conditioning system on ceramic-resin cement adhesive interface (study IV)

Eighty specimens were cut from each ceramic material (E-max and Mark II), finished, polished up to 4000-grit FEPA, and cleaned.

The specimens of each material were randomly divided into two study groups: group 1 and group 2, both having 40 samples from each material (Figure 9).

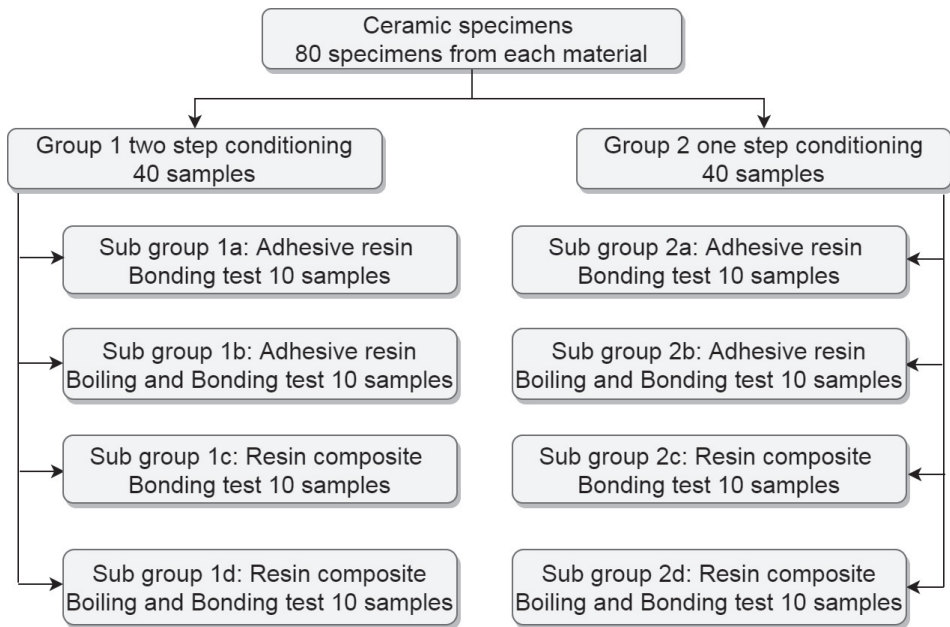


Figure 9. Flow chart of specimen groups. (Copied from, Ramakrishnaiah *et al.*, manuscript)

Group 1: the cementing surface was etched with 5% HF for 40 s and neutralized as described in Studies I, II and III. The cementing surfaces were treated with a commercially available dental silane coupling agent.

Group 2: the cementing surface was treated with the one-step etch and prime liquid with a micro-brush and agitated into the surface for 20 s using slight pressure, and allowed to react for 40 s as described by the manufacturer. Next, the specimens were thoroughly rinsed with water until the green color of etch and prime liquid had been removed. The specimens were ultrasonically cleansed for 5 min as recommended by manufacturer and dried for 10 s with water and oil free air.

The specimens of each group were further divided into 4 subgroups labelled as follows: subgroups 1a, 1b, 1c, 1d, and 2a, 2b, 2c, 2d (n=10), depending on the type of cement applied, and then subjected to exposure in boiling water. Unfilled adhesive resin (Stick resin) was applied on subgroups 1a, 1b, 2a, and 2b; filler containing resin composite (Variolink N) was applied on subgroups 1c, 1d, 2c, and 2d. The specimens of subgroups 1a, 1c, 2a, and 2c were tested for adhesion strength without subjecting to boiling water, and 1b, 1d, 2b, and 2d group specimens were tested for adhesion strength after subjecting to boiling water.

4.2.4.1 Specimen of resin bonded onto ceramic

A split-type stainless steel mold (3.0 mm thick) with a hole at the center measuring 4.0 mm in diameter was designed and prepared (Figure 10). The designed mold was held firmly on the ceramic sample and the hole was aligned exactly on the previously conditioned area, then resin was filled into the hole and carefully condensed with a hand instrument. A microscope glass slide was pressed onto the condensed resin cement. After 15 s of impregnation time the resin cement was light cured as described in study III.



Figure 10. Split stainless steel mold

4.3 Methods

4.3.1 Scanning electron microscopy (SEM) analysis

The gross surface microstructure, width and depth of the pores, after etching the ceramic specimens for different duration were analyzed using SEM at X2000 and X6000 magnification (JSM-6360LV, JEOL, Japan). To measure the pore depth and width, etched samples were fractured vertically from the edge of an unetched surface using a sharp knife with a single hammer impact. The specimens were gold sputter-coated in an argon plasma gold sputter coater (Polaron E-5200, Energy Beam Sciences, Agawan, USA) and the junction of etched surface and the fractured edge was examined. The depth and width of the pores were measured directly in SEM using image measurement software after tilting the specimen by 45 degrees. The ceramic-luting resin interfaces before and after subjecting to exposure in boiling water, were analyzed at a magnification of 1000X magnification.

4.3.2 Surface roughness (S_a) measurement

The no-contact optical profilometer (Bruker Contour GT-K, Bruker, Berlin, Germany) was used to measure the S_a of the ceramic specimens after etching for different time intervals. This system utilizes a nano lens AFM module with a fully automated turret and platform which is programmable in the X, Y, and Z directions. The profilometer delivers a laser light in order to guide the operator to select the test area on the specimen. Measurements of four randomly selected areas on each sample were taken, and their mean was calculated and considered as the final S_a value. To perform the measurement, the sample was placed on the platform in such a manner that the measuring surface was perpendicular to the optical beam. The measurement area of $1.261 \text{ mm} \times 0.946 \text{ mm} \times 500 \mu\text{m}$ in the X-, Y-, and Z-axes were scanned with a resolution of 100 points/mm after the application of a Gaussian regression filter with a short wavelength pass. The long cutoff wavelength was 0.08 mm (X and Y), the short cutoff wavelength was 0.25 mm (X and Y), and the images were captured in 3x optical zoom using integrated "Vision64" software. Several areal surface texture parameter values were measured to characterize the surface topography, which includes S_a (surface roughness), S_p (the maximum surface peak height), S_v (maximum valley or pit depth), S_z (the sum of largest peak height value and largest pit or valley depth), S_q (root mean square value of the sampling area), S_{sk} (the measure of skewness or symmetry in roughness), and S_{ku} (the spread of height distribution). The mean S_a is always considered as standard because this parameter gives the arithmetic mean of the heights and depths of the surface topography of sampling surface.

4.3.3 Surface wettability measurement

In study I the wettability of etched ceramic surface to deionized water was measured. In study II the effect of ceramic surface neutralization to the wettability of an experimental silane primer and a commercial silane primer, and the effect of experimental and commercial silane treated ceramic surface to wettability of experimental and commercial adhesive resin cements were measured by CA measurement using sessile drop technique. In the analysis, the sample was kept parallel to the floor on the adjustable sample holder, a 2 μL drop of respective solution was dispensed onto the sample surface and the measurements were taken using an optical tensiometer connected to a computer. One reading was taken per sample from each group and subgroups. The dynamic CA was measured by using an inbuilt software from the time of initial contact of the test liquid till the droplet attained zero or stable contact angle. The images were captured using a built-in digital camera.

4.3.4 Nano-indentation

The modulus of elasticity and surface nano-hardness exactly at the resin-ceramic interface were measured using a nano-indenter (Bruker NH-2, 1041, Tucson, AZ, USA) equipped with a 3 sided Berkovich diamond indenter tip, one indentation was performed for each sample. During the nano-indentation test, the indenter tip was pressed onto the test surface at interface with preset loading and unloading values. The resin-ceramic interface of all the specimens was evaluated, and the response to the load was recorded as the load-displacement curve (P-h curve) with a high resolution displacement gauge. The test was performed at room temperature in low noise conditions, the loading and unloading rate was set at 0.01 mN/s and 0.02 mN/s, respectively, with a 5 s rest period at the maximum load of 10 mN.

4.3.5 Boiling water exposure

The integrity of resin-ceramic interface and the effect of exposure to boiling water on the nano-mechanical properties at the resin-ceramic interface was evaluated in study III. The effect of subjecting to exposure in boiling water on the adhesion strength of adhesive resin and resin composite was evaluated in study IV. The specimens were kept in water bath and the temperature of the water was gradually increased to 100⁰C and maintained for 24 h using a thermo-cycler machine (SD Mechatronik Thermocycler, Huber, Peter Huber Kaltmaschinenbau, Offenburg, Germany).

4.3.6 Adhesion testing procedure

Traditionally, the shear bond strength is measured by applying force on the specimen directed parallel to the interface and calculated by the formula

$$\sigma_s = F/A$$

Where, A is the cross-sectional area and F is the force (Rasmussen 1996).

In the present study, the shear bond (adhesion) strength (SBS) was determined by bond test as specified by ISO 10477:2004 using the Instron™ universal material testing machine that was connected to a computer (Interface type 8500/8800; Instron™, Canton, MA, USA) at a constant cross-head speed of 1.0 mm/min. The specimens were held in custom made metal holder and the blunt tip of the attachment was exactly positioned on the specimen and the shear force was applied to failure. The SBS was recorded by built-in software integrated with the Instron™ machine in MPa.

4.3.7 Evaluation of failure mode

The cemented areas of ceramic specimens after testing the SBS was evaluated to determine the nature of bond failure by using a light microscope (Nikon™ Sm2-10, Tokyo, Japan) at a magnification of 20x. The nature of failures was classified into four types: Type I, adhesive failure; Type II, cohesive failure in resin cement; Type III, cohesive failure in ceramic; and Type IV, mixed failure.

4.3.8 Statistical methods

The statistical analysis was performed with SPSS (Statistical Package for Social Sciences) 22.0 (SPSS, Chicago, IL, USA) software at a significance level of $p < 0.05$.

In study I the mean S_a and CA were analyzed using the one-way analysis of variance (ANOVA) and the *post hoc* Tukey's test. The linear regression analysis was used to determine the correlation between the etching duration and S_a ; etching duration and CA; S_a and CA.

In study II the analysis of variance was used to compare the mean CA values of silanes and resin cements.

In study III multivariate analysis of variance and a *post hoc test* was used to calculate the difference in the mean values of modulus of elasticity and surface nano-hardness before and after subjecting the specimens to accelerated hydroly-

sis. Regression analysis was performed between the modulus of elasticity and surface nano-hardness.

In study IV analysis of variance, unpaired *t*-test and a *scheffe post hoc test* was used to evaluate the effect of subjecting to exposure in boiling water on adhesion strength and to calculate the difference in the mean values of adhesion strength between two-step and one-step surface conditioning systems.

5 RESULTS

5.1 Acid etching of ceramics

The effect of hydrofluoric acid etching duration on the surface micromorphology, surface roughness, and surface wettability of five dental ceramics was studied in the first part of the study. The control group specimens showed smooth and homogeneous surfaces without any porosity as a result of polishing. In the present study the control group specimen surfaces presented dark and light areas, which represented the glass matrix and crystals, uniformly distributed fluorapatite and zirconia crystals in lithium di-silicate and zirconia-reinforced lithium di-silicate ceramics. The etched surfaces showed significant changes in the surface microstructure depending on the type of the ceramic material with an increase in the etching time. In common, the etched surfaces of all specimens were irregular and were characterized by the presence of numerous micro porosities, grooves, and striations as a result of the dissolution of the glassy phase. The specimens etched for 20 s predominantly showed a glassy phase and isolated small pores with closed and irregular borders measuring 0.37 to 0.84 μm . With an increase in the etching duration to 40 s, a weaker glassy phase (SiO_2 , Li_2O , K_2O , Al_2O_3 , P_2O_5 , ZrO_2 , and HfO_2) around the crystals that has higher solubility to acid action than lithium di-silicate crystal phase, dissolved at a faster rate than the crystals (Li_2SiO_5). This resulted in an increase in the size of the pores, which appeared as elongated grooves. A further increase in the etching duration to 80 s and 160 s resulted in specimens predominantly showing irregularly oriented crystals measuring 2.56 to 2.97 μm and scratch-like gaps because of an extensive loss of the glassy phase and areas with grain pullout in particle filled ceramics (IPS E-maxTM, Dentsply CeltraTM, Vita SuprinityTM, Vita Suprinity FCTM). Specimens of Vita mark IITM (feldspathic porcelain) and Vita Suprinity FCTM (zirconia-reinforced lithium silicate, fully crystallized) showed large cavitations, the dimensions of which increased with an increase in the etching time. Vita mark IITM typically showed a honeycomb-etched pattern because of the absence of crystal phase, which was different compared to other particle-filled ceramic samples. The pore width and depth increased with an increase in the etching time, the depth ranged from 3.89 μm to 5.01 μm , and the width ranged from 3.95 μm to 18.79 μm .

5.2 Surface roughness

Results of the one-way ANOVA for S_a showed a statistically significant difference among the groups. The S_a increased with an increase in etching time in all the materials and experimental groups. The increase in S_a with increase in etching

duration is because of the dissolution of glass matrix. Dentsply Celtra™ and Vita Suprinity FC™ specimens showed the lowest S_a (0.08 ± 0.008) and E-max and Vita mark II™ showed the highest S_a of 0.16 and 0.14 respectively in control group specimens. The S_a values differed from one material to the other, the difference was approximately five times more in Vita Suprinity, and three times more in Mark II and Vita Suprinity FC when compared with E-max suggesting faster degradation of glass matrix.

The S_a of Celtra was 0.14, 0.22, 0.28 and 0.33 in 20 s, 40s, 80s and 160 s respectively.

The S_a of E-max was 0.21, 0.30, 0.56 and 0.65 in 20 s, 40s, 80s and 160 s respectively.

The S_a of Mark II was 0.36, 0.41, 0.59 and 0.60 in 20 s, 40s, 80s and 160 s respectively.

The S_a of Vita Suprinity was 0.46, 0.55, 0.56 and 0.64 in 20 s, 40s, 80s and 160 s respectively.

The S_a of Vita Suprinity FC was 0.26, 0.29, 0.35 and 0.53 in 20 s, 40s, 80s and 160 s respectively.

5.3 Surface wettability

The results of wettability showed a statistically significant difference (a decrease) in CA (an increase in surface wettability) with an increase in the etching time. The samples etched for a longer time (160 s) showed the lowest mean CA, ranging between 6.86 (Dentsply Celtra™) and 27.4 (Vita Suprinity FC™) and the samples etched for shorter time showed high mean CA ranging from 27.95 (E-max) to 74.80 (Mark II). The decrease in CA values varied from one material to another material.

The CA of Celtra was 54.94, 46.06, 24.86 and 06.86 in 20 s, 40s, 80s and 160 s respectively.

The CA of E-max was 27.95, 24.06, 18.00 and 17.53 in 20 s, 40s, 80s and 160 s respectively.

The CA of Mark II was 74.80, 49.06, 30.00 and 22.20 in 20 s, 40s, 80s and 160 s respectively.

The CA of Vita Suprinity was 39.13, 33.27, 27.07 and 20.93 in 20 s, 40s, 80s and 160 s respectively.

The CA of Vita Suprinity FC was 61.13, 48.67, 40.27 and 27.40 in 20 s, 40s, 80s and 160 s respectively.

When comparing the values of S_a and CA, results of regression analysis showed significant dependency on each other in all the materials and at all the intervals.

5.4 surface neutralization

The effect of treating the etched lithium di-silicate ceramic surface with neutralizing agent on wettability of commercial and novel silane coupling agents and, the wettability of resin composite and adhesive resin cements to commercial and experimental silane treated specimens was evaluated in the second part of the study.

There was no statistically significant difference in the CA values between the two experimental groups suggesting that the neutralizing agent had no significant effect on the wettability of the silane coupling agents. Furthermore, the experimental silane primers showed slightly lower mean CA values of 4.531, when compared to the commercial silane primer 4.861 in non-neutralized specimens. However, the difference was statistically not significant. The neutralized specimens showed reduced CA values of 4.821 and 4.491 for commercial silane and experimental silane, respectively.

There was no statistically significant difference in CA values of the adhesive resin and commercial resin cements between non-neutralized and neutralized and, commercial and experimental silane treated specimens. The mean CA of commercial and experimental resins was 31.09 and 18.47, respectively, in commercial silane treated specimens and, 29.30 and 18.26 in experimental silane treated specimens. The results suggest that the neutralizing agent has no significant effect on wettability of adhesive resin cements.

The experimental adhesive resin showed statistically significant lower CA values on both commercial (18.47) and experimental silane (18.26) treated specimens when compared to commercial resin composite in commercial (31.09) and experimental silane (29.3) treated specimens. This might mean that, the experimental resin had better wettability than commercial resin in both commercial and experimental silane treated specimens.

5.5 Ceramic-resin interface characteristics

The third part of the study evaluated the micro and nano-structural characteristics of dental ceramic and resin cement interface for the degree of penetration of resin

cement into the etched micro patterns. The difference in degree of penetration between silane treated and non-silane treated specimens, and difference in degree of penetration between adhesive resin and resin composite were measured. The study also evaluated the nano-mechanical properties at the resin-ceramic interface and the effect of water exposure on integrity of cement interface.

The silane treated specimens with the application of adhesive resin (1A group specimens) showed better penetration of resin into the etched porosities than other group specimens. The specimens with no primer treatment and resin composite applied specimens (2B group) demonstrated visible gaps between ceramic and resin composite in all of the materials.

The specimens showed some degree of resin disintegration at the resin-ceramic interface after subjecting to boiling water, which resulted in increased resin-ceramic gap. The degree of disintegration and gap at the interface varied from one group to the other. The adhesive resin showed the least disintegration (1A and 2A group specimens) compared to the resin composite, furthermore primer treated specimens showed least disintegration (1A group specimens). The specimens with no primer treatment and resin composite applied specimens (2B group specimens) showed the highest resin disintegration.

The results of the nano-indentation study showed that the primer treated specimens with an application of adhesive resin (Group 1A) showed significantly the highest hardness of 2.02 and 0.02 GPa (E_{max}^{TM}), before and after exposure to boiling water, respectively, followed by Celtra (1.96 and 0.02 GPa) and Mark II (1.78 and 0.02 GPa). Group 1A specimens also showed highest modulus of elasticity of 46.07 and 6.14 GPa, before and after exposure to boiling water, respectively, followed by Celtra (45.75 and 6.33 GPa) and Mark II (37.21 and 5.85). All the materials showed low modulus of elasticity and nano hardness in group 2B. In particular, the specimens with no silane treatment and with application of resin composite (Group 2B) had significantly the lowest nano-hardness of 0.30 and 0.01 GPa (CeltraTM), followed by Mark II (0.33 and 0.01 GPa) and E-max (0.35 and 0.01 GPa). Furthermore, the specimens had a modulus of elasticity of 16.59 and 1.25 GPa (MarkTM II) followed by Celtra (17.61 and 1.51 GPa) and E-max (18.05 and 1.49 GPa), before and after exposure to boiling water respectively.

When comparing the materials, E-max showed highest nano-hardness in all the groups except in group 2A. The modulus of elasticity was also high in E-max before subjecting to boiling water exposure. When comparing the resin systems, adhesive resin showed high nano-hardness and modulus of elasticity in all the materials tested. Furthermore, silane treated samples had higher nano-mechanical

properties than non-silane treated samples. Resin composite cement had lowest nano-mechanical properties in non-silane treated samples.

5.6 Shear bond strength

The last part of the study determined the difference in SBS after the ceramic specimens had been conditioned with two-step and one-step conditioning systems. The study also examined the adhesive interface between glass ceramic surface and, adhesive resin and resin composite systems.

Adhesive resin showed the highest SBS values in all the groups, in both E-max and Mark II ceramic materials. The SBS value was high when the specimens were treated with two-step conditioning system after application of adhesive resin (22.05 MPa and 18.65 MPa in E-max™ and Mark II, respectively) followed by group 2a specimens (18.13 MPa and 15.13 MPa in E-max and Mark II, respectively).

Exposure to boiling water significantly reduced SBS in both group 1 and group 2; the reduction in the bond strength was seen with both adhesive resin and resin composite cements. Adhesive resin showed the highest shear bond strength of 6.42 MPa and 5.72 MPa for E-max™ and Mark II™, respectively, with the two-step conditioning system. Resin composite cement showed the lowest values of 3.38 MPa and 3.08 MPa for E-max™ and Mark II™, respectively, with the one-step conditioning system after exposure to boiling water.

Evaluation of mode of failure of each specimen showed that all the specimens showed adhesive failure after exposure to boiling water (1b, 1d, 2b and 2d) in both materials. Seven specimens of E-max™ and 9 specimens of Mark II™ of subgroup 1a (two-step conditioned, adhesive resin) showed cohesive failure in resin cement. The remaining specimens of both materials showed mixed failures. Eight specimens of E-max™ and 6 specimens of Mark II™ of subgroup 2a (one-step conditioning, adhesive resin) showed cohesive failure in resin cement. Most of the specimens in subgroups 1c and 2c showed mixed failures and none of the specimens showed cohesive failure in ceramic. No spontaneous failure was observed.

6 DISCUSSION

Ceramics are natural and inorganic non-metallic materials. They are synthetic or naturally occurring tough, strong and bio inert suitable for placement in living tissues. Ceramics have wide application in medical and dental fields. Ceramics are used as femoral heads and acetabular cups for total hip replacement. In dental medicine feldspathic, alumina and zirconia based ceramics are used as dental implants, implant abutments, and as restorative materials. Nano-structured calcium phosphate ceramics and porous bioactive glasses combined with an organic phase are used as bone fillers and scaffolds for bone substitution in tissue engineering.

Ceramics have a unique feature of creating strong and biologically relevant interface with bone, they promote bone-implant adhesion through osseointegration without fibers soft tissue interface. Hence, their major application in medical field is for total hip or knee joint replacement. Use of ceramics for joint replacement also have advantage of reduced wear rate compared to other metallic materials. Alumina and zirconia based ceramics are prone to form soft tissue interface when used as implant material. Introduction of Y-TZP completely replaced alumina and zirconia based ceramics and became more popular because of their higher fracture toughness and strength. The biomedical grade Y-TZP exhibits excellent mechanical properties because of the characteristic feature of resisting the crack propagation through transformation toughening.

The use of ceramics in dental medicine has a wide application because of their excellent esthetic and optical properties. The color and translucency of the dental ceramics can be modified as required to match the color of the remaining or existing natural teeth for partial tooth restoration or complete tooth replacement. The natural ivory color of the ceramics provides superior esthetics compared to all other restorative materials used in dentistry, including metal-ceramic restorations. Hence, there is growing requirement and vast research in the field of development of all ceramic materials. Dental ceramics have other advantages such as biocompatibility and excellent mechanical properties. However, the lack of chemical bonding with natural enamel and dentin is the major concern in the current clinical dentistry. Hence, the current research was designed to study the effects of the micro and nano-structural characteristics, the surface characteristics and, the silane treatment of the silica based glass ceramics on adhesion of adhesive resin and resin composite.

6.1 The effect of hydrofluoric acid etching duration on the surface micromorphology, roughness, and wettability of dental glass ceramics (study I)

Five commercially available silica based glass ceramics were investigated for effect of etching duration on surface topographical changes and associated changes in surface characteristics. Etching of internal surface before cementation is an imperative step for better clinical performance of ceramic restorations; etching alters surface topography by creating micro- and nano-scale porosities of varying depth and width (Della Bona *et al.*, 1998; Ho *et al.*, 2011). The resultant altered topography increases the surface area for micromechanical bonding (interlocking, retention) with resin composites (Xiaoping *et al.*, 2014; Ren *et al.*, 2013; Colares *et al.*, 2013). However, creating a desired surface topography for durable bonding depends on the concentration of etchant and the etching duration (Zogheib *et al.*, 2011a; Della Bona *et al.*, 2002). Furthermore, the S_a also affects wettability of the ceramic surface to the subsequently applied silanes coupling agent and resin composite.

The present study showed a marked change in the surface micromorphology in terms of pores and grooves pattern, width, and depth. This is considered as critical for bonding ceramics to tooth structure with resin composites. Etching for a short duration of 20 s resulted in the dissolution of the glassy phase predominantly around the crystals and creating small isolated pores and fissures. Etching for 40 and 80 s resulted in the further loss of the glassy phase around the crystals, which exposed the crystal structure. The SEM images presented topographies predominantly consisting of platelet shaped lithium di-silicate and lithium orthophosphate crystals. Prolonged etching for 160 s dissolved the matrix around the crystals, which at this stage appeared as protruding out of the glass matrix, typically elongated, and randomly oriented pillars of plate-like lithium di-silicate crystals measuring 2.56 to 2.97 μm . This suggests that the matrix dissolves at a faster rate than do crystals, and deeper and wider pores are formed when the surface was exposed for longer etching cycles. Acid etching is the most commonly employed technique compared to grit-blasting to improve the bond strength (adhesion strength). Etching increases the surface area by creating micro-pores into which uncured flowable resin penetrates to provide durable micromechanical interlocking (Chen *et al.*, 1982; Stangel *et al.*, 1987). Etching also cleans the surface by removing debris and impurities. However, prolonged etching does not significantly increase the bond (adhesion) strength. Some studies have reported a reduction in the shear bond strength after prolonged acid etching, which may be due to disintegration of the over-etched surface, losing even crystals, making the surface in total weaker, more porous and softer. The reduced bond strength may also be due to wide pores and fissures that offer poor mechanical interlocking

sites than do the smaller pores. Creating an adequately porous surface is a vital step for durable cementation of the indirect restoration, and this can be achieved by etching the surface for appropriate and material specific etching cycles.

Etching porcelain with HF is a gold standard because it creates a rough surface required for micromechanical retention with resin composites (Zogheib *et al.*, 2011; Della Bona *et al.*, 2002; Della Bona *et al.*, 1995). The S_a is a result of the formation of numerous porosities and grooves due to the acid action on the matrix and the crystal structure. The absolute amount of roughness required for ideal bonding is actually not known, but a positive correlation between S_a and etching duration as observed in the present study has been found (Chaiyabutr *et al.*, 2008; Zogheib *et al.*, 2011; Addison *et al.*, 2007; Wolf *et al.*, 1993). However, over etching can lead to the formation of large and deep porosities and may affect the bond strength (Addison *et al.*, 2007; Della Bona *et al.*, 2002; Della Bona *et al.*, 1995). The present study found that the width of the porosities increased at a faster rate than did the depth after having been exposed to longer etching cycles, which resulted in relatively large, wide, and shallow pores. The increase in the pore width is because of the dissolution and disintegration of the weaker glassy phase at a faster rate than the dissolution of the crystal phase. This significant loss of glassy phase weakens the ceramic and affects the bond strength (Della Bona *et al.*, 2002; Addison *et al.*, 2007).

HF is a weak inorganic acid compared to stronger acids like sulfuric and hydrochloric acids. However, HF is strong enough to cause tissue damage, and the damage may go unnoticed until serious damage has occurred. The application of HF and its concentration used in dental office do not have the power to cause death or serious injury, but preventive measures to avoid such acid hazards have been suggested by manufacturers and followed with great caution. HF can cause tissue damage due to corrosive burns from free hydrogen ions or due to chemical burns from tissue penetration of the fluoride. Fluoride ions from HF penetrate the skin and bone and lead to destruction of deeper tissue layers. Most commercial HF used in dentistry are buffered because they are safer. Buffered HF are safer, less corrosive, and are indicated for use in dental offices, where as non-buffered HF is indicated to use only in dental laboratories. HF gels supplied for dental office applications are easy to use as they are supplied as viscous gels are less volatile, and easy to control on the area of application due to visual contrast.

Wettability is another important factor crucial for the ultimate bond strength of ceramics to resin composites. In the present study, the ceramic surface was tested for wettability using deionized water, the rationale behind using hydrophilic water was that the etched ceramic surface is treated first with a hydrophilic activated silane coupling agent before it is bonded with hydrophobic resin composite ce-

ment. The present study suggests a positive correlation between the etching duration and wettability: wettability increased significantly with an increase in the etching time because of an increase in the surface free energy (Matinlinna *et al.*, 2007b). This is usually attributed to the fact that etching removes surface impurities such as oxides and other inorganic and organic debris which makes the surface readily wettable for the subsequently applied silane coupling agent and resin composite cement (Ho *et al.*, 2011). This laboratory study also showed a significant and positive correlation between S_a and wettability. A porous surface with improved wettability allows easy spreading and a reaction of silane and resin composites, thereby resulting in superior adhesion strength.

6.2 The effect of surface neutralization on wettability of silane coupling agents and adhesive resin cements (study II)

The bond between dental ceramic and natural tooth is mainly achieved by luting resin composites, and the bonding mechanism may be enhanced by surface modifications and surface treatment procedures (Zarone *et al.*, 2006; Nagai Taro *et al.*, 2004). Surface free energy of the ceramic and surface tension of the silanes play a vital role in bonding mechanism (interlocking) (Moustafa *et al.*, 2009; Ramakrishnaiah *et al.*, 2016). When the ceramic surface has high surface free energy, it is clean and it tends to attract the applied silane primer. Desirable surface for lithium di-silicate ceramics can be achieved by etching the surface for 20 s with hydrofluoric acid, followed by thoroughly rinsing with water to remove remaining acid (Ramakrishnaiah *et al.*, 2016). Previous studies have reported formation of fluorosilicate crystals as a results of etching ceramic with HF, therefore ultrasonic cleaning was recommended to remove the precipitates which may interfere with bonding mechanism (Saavedra, 2009; Canay *et al.*, 2001; Bottino *et al.*, 2015; Zorzin *et al.*, 2012). However, the pH of the etched ceramic surface remains acidic, therefore, application of neutralizing agent was recommended to neutralize the ceramic surface (Foxton *et al.*, 2003; Canay *et al.*, 2001; Ozcan *et al.*, 2015).

In the present study, the wettability experiment was carried out to determine both surface tension and CA of the silanes. Surface tension is the energy or work required to increase the surface area of a liquid. It depends on the intermolecular forces between liquid molecules, this play an important role in wettability. The silanes used in the present study showed low surface tension ranging from 24.1 ± 3.0 mN/m (the experimental silane primer) to 26.1 ± 3.0 mN/m (the commercial silane primer). This coupled with the low viscosity of the silanes and high surface free energy of surface treated ceramic substrate, resulted in lower CA values. Apart from having low surface tension, the novel experimental silane system has proved to be highly reactive in nature, and hence, significantly able to en-

hance adhesion onto silica-based (etchable) ceramic substrate (Matinlinna *et al.*, 2006b; Durgesh *et al.*, 2016).

A noteworthy finding of this study was that surface neutralization didn't show any significant effect on wettability of ceramic to silane primers. The study also compared the experimental and commercial silane primers (control silane). The results showed lower mean CA values for the experimental silane primer compared to the commercial silane primer. This may be because of lower surface tension of the experimental silane primer (24.1 ± 3.0 mN/m) compared to the control silane (26.1 ± 3.0 mN/m).

The ultimate bond strength of the ceramic restorations depends on several factors such as the surface conditioning, the pH of the surface, coupling agent applied, resin monomer and fillers in the composite. Resin cements of low viscosity are preferred for luting ceramic restorations, the low viscosity resin cements are expected to flow and penetrate the micro-pores, and therefore, viscosity of the resin composite also plays an important role in the ultimate bond strength. In the present study, the experimental unfilled resin showed statistically significant lower mean CA values (i.e., better wettability) than the commercial resin composite, with both the experimental and commercial silane primer. The results of the study also showed that there was no statistically significant effect of neutralizing agent on wettability of resin cements on both experimental and commercial silane treated ceramic specimens. The reason for lower CA values in the UDMA based experimental resin is because of low filler content which makes it less viscous (Han *et al.*, 2007).

Although the effect of neutralizing agent on the surface wettability was not found, the benefit of using neutralizing agent could be in ensuring the proper free radical polymerization of the autopolymerizing, dual-polymerizing and light polymerizing adhesive and cements which in many cases contain basic activator systems. Also, hydrolytic stability of the silane promoted polysiloxane interface between the ceramic and resin material could potentially be improved by neutralizing the ceramic surface after acid etching.

6.3 Micro and nano-structural analysis of dental ceramic and luting resin interface and the effect of water exposure on integrity of cement interface (study III)

The bond strength of cemented ceramic restoration is influenced by several factors, such as the surface characteristics of ceramic, bonding substrate of dentin and enamel, etching, silane application, and type of resin cement used. The bonding cement should also have sufficient cohesive mechanical properties to with-

stand the forces which are transferred to the resin-cement interface. Given this, the current laboratory study was initiated and conducted to evaluate the degree of penetration of resin composite and adhesive resin and the effect of a primer on degree of penetration of two cements. The study also investigated nano-mechanical properties and hydrolytic stability of resin-ceramic interface.

The ability of the luting medium, *i.e.*, adhesive resin and resin composite luting cement, to impregnate micro pores of etched glass ceramics depends on the cement characteristics, such as surface tension, viscosity, hydrophobicity, and filler size and content (Aboushelib *et al.*, 2009). The cement with lower filler content has lower surface tension than cement with higher filler content. Similarly, unfilled adhesive resins will have lower surface tension than filled resin composites. Even so, resin cements with low surface tension will have low viscosity and better wettability on the substrates, such allowing them to flow easily into the micro pores (Han *et al.*, 2007). The results of this study showed higher resin impregnation in primer treated samples, which is mainly because of the ability of the primer to increase the surface wettability of cementing surface as has been found previously (Wei *et al.*, 1993). Primer is a low viscosity solution with usually ca. 99 vol% of ethanol + water, and only ca. 1 vol% of silane. When cured (reacted), silanes form a molecular level 3D polysiloxane network on the surface of ceramic. Methacrylate groups of the silane molecules will turn the ceramic surface to be more hydrophobic and thereby increasing the surface wettability by the resin monomers. The thickness of the siloxane layer on the ceramic surface is dependent on, among others, the concentration of silane in the solution. It has been assessed and reported that a solution of silane of 0.25% with reactive silane on a glass surface, results in the thickness of three to eight molecular layers corresponding thickness of 10 nm. There are two types of bonding of silane coupling agent to ceramics; one is chemisorbed and the other is physisorbed bonding. (Arkles, 2011; Matinlinna *et al.*, 2004; Matinlinna *et al.*, 2004b).

Condensation of the silane molecules after being hydrolyzed to the hydroxyl group covered glass surface, can occur to some extent at room temperature but the condensation reaction is more effective at elevated temperatures. It can be said that the better the degree of cure for the silane is, the better is the stability of the silane promoted adhesive interface (Plueddemann, 1991; Xiao *et al.*, 1998). That said, the extent of the condensation reaction is responsible for the hydrolytic stability of the silane coupling agent promoted adhesive interface. In the current study, the primer consisting of 3-methacryloxytrimethoxy silane (MPS) was used without pre-hydrolyzing the silane. This has become the common way with dental silane primers since introduction of so-called one bottle silane primers. It can be expected that the function of silanes of this kind is predominantly based on improving the surface wettability rather than creating covalent bonds between the

ceramic substrate and siloxane network. It has been demonstrated that water exposure at 37°C for four years of time deteriorate effectively the silane coupling agent promoted adhesive interface (Heikkinen *et al.*, 2013; Guarda *et al.*, 2013). To accelerate hydrolytic deterioration of adhesive interfaces, the test materials can be exposed to boiling water. This study used exposure of the adhesive interfaces to boiling water for the time period of 24 hours (Plueddemann, 1991).

Degradation of the interface between ceramic and resin based material is not only related to the silane coupling agents, but also to the possible hydrolysis of the resin based material. The hydrolytic stability of polymers based on dimethacrylates in the *bis*-phenol-A-glycidyl dimethacrylate – triethylene glycol dimethacrylate (*bis*-GMA-TEGDMA) monomer system is basically caused by their molecular structure where the glycidyl group in the *bis*-GMA molecule protects the molecule from hydrolytic degradation, although degradation to some extent has been also reported (Koin *et al.*, 2008). In fact, the study of this issue by Koin *et al.*, has even more relevance to the present work. They studied hydrolytic stability of particulate filler resin composites where the focus was at the silane promoted adhesive interface of fillers and resin matrix. They concluded that although the overlay of siloxane and the *bis*-GMA-TEGDMA system on the filler particle could potentially degrade at the ester groups adjacent to the aromatic rings or the ester group of the silane coupling agent, no such degradation products were found. This supports the findings of the present study that the *bis*-GMA-TEGDMA based flowable resin remained integrated to the ceramic surface the best after the accelerated hydrolysis test in boiling water. On the other hand, the monomer system of the resin composite Variolink N™ is based on urethane dimethacrylate (UDMA) monomers. It is known that the UDMA based resin composites are also prone to degradation and release of uncured monomers. However, it has also been stated that UDMA molecules are used in dental composites in several forms which may differ in terms of curing rate and degradation properties (Polydorou *et al.*, 2009; Polydorou *et al.*, 2009b).

The quantity and size of filler particles in the resin composites have a strong influence on the viscosity. The size of the micro irregularities (pores) on the surface of etched glass ceramics is from 0.37 to 0.84 µm (Ramakrishnaiah *et al.*, 2016). It is, at least in theory, possible that filler particles close to the opening of the porosity and resin phase may penetrate into the pore. If this was the case, there would be air bubble containing microenvironments under the resin composite layer, and, the molecular oxygen can thus inhibit the free radical polymerization of the resin composite cement (Pilkenton *et al.*, 2011; O'Brien *et al.*, 2006; Vallittu, 1999; Bijelic-Donova *et al.*, 2015). An inadequately polymerized resin system is more prone to degradation and leaching. In the present study, resin

composite exhibited higher gap formation than adhesive resin after being hydrolyzed by exposing the specimen to boiling water.

With regard to results of the nano-mechanical indentation of this study, it needs to be emphasized that the reduction of the mechanical properties is well in line with the aspects discussed above.

6.4 Two-step vs. one-step conditioning systems and adhesive interface of glass ceramic surface and resin systems (study IV)

The present study evaluated and compared the ceramic-resin cement adhesion strength after the ceramic surface was conditioned with the one-step or the two-step conditioning systems. The study also compared the shear bond (adhesion) strength between filler containing resin composite cement and unfilled adhesive resin. In addition, the hydrolytic stability of the silane promoted bonding was evaluated.

The results of the current study showed lower adhesion strength values when the ceramic surface was conditioned with a one-step conditioning system compared to the two-step conditioning system. This is mainly because the one-step conditioning system Monobond™ Etch and Prime contains ammonium polyfluoride (Na_4HF_2) which is a weak acidic salt of HF, whereas in the two-step conditioning system the acid used is 5% HF. Etching using Monobond™ Etch and Prime liquid partially etches the glassy phase in the ceramic and creates lower surface roughness. The low surface roughness adversely affects the mechanical interlocking with resin tags which can be explained because of the poor flow of the resin cements into the micro-pores (Ho *et al.*, 2011). Poor etching also results in an inadequate exposure of hydroxyl ions required for chemical bonding with a silane coupling agent (Matinlinna *et al.*, 2007b). Specimens etched with 5% hydrofluoric acid for 40 s showed higher adhesion strength values because etching with 5% hydrofluoric acid creates S_a values of 0.30 and 0.41 S_a for E-max™ and Mark II™ ceramics, respectively. This sufficiently dissolves the glassy phase for penetration of resin cement and adequately exposes hydroxyl ions on the ceramic surface required for chemical bonding (Ramakrishnaiah *et al.*, 2016). It is noteworthy that inadequate etching also affects the ceramic surface wettability for resin cements. Given this, the lower SBS values could also be obtained because of the inadequate wettability of ceramic surface for resin cements, especially with resin composite which is more viscous than the adhesive resin.

In the current study, adhesive resin cement showed statistically significant higher adhesion strength values compared to resin composite cement. This might be because of the lower viscosity of adhesive resin compared to resin composite (Han

et al., 2007). Adhesive resin is in this case an unfilled resin cement and therefore, has lower surface tension and lower viscosity than the filler containing resin composite cement. Low surface tension and low viscosity enable easy and complete penetration of adhesive resin cement into the micro-pores and provide durable adhesion (bonding) (Zhang *et al.*, 2014). On the other hand, filler containing resin composite cement flows at a lower rate. This said, the degree of flow of the resin composite cement into the micro-pores is influenced by the quantity and size of the filler particles. Resin composite cements with a higher filler content have high viscosity and they flow at a lower rate. This is why it may be possible that the size of the filler particles, which is less than the opening of the micro-pores in the ceramic matrix, are only partially able to penetrate and thereby to contribute to the adhesion strength (Blatz *et al.*, 2003a; Sorensen *et al.*, 1991). In this view, the lower adhesion strength of resin composite cements is maybe because of the partial penetration of cement into the micro-pores.

In this laboratory study bond (adhesion) strength after exposure to boiling water was studied to evaluate the hydrolytic stability of silane promoted adhesion and the resin cement. The boiling water was used in the study to accelerate aging (even though it has no clinical relevance), because silane promoted adhesion tends to deteriorate over a period of time and the resin cement may thereby get disintegrated because of improper curing (Guarda *et al.*, 2013). It has also been demonstrated that the water storage at 37 °C for four years significantly deteriorates silane promoted adhesion (Heikkinen *et al.*, 2013). To accelerate the hydrolytic deterioration, indeed, the test specimens might be subjected to boiling water for 24 h providing some evidence of the adhesion durability (Plueddemann, 1991). In the current study where the specimens were exposed to boiling water to accelerate the hydrolytic deterioration, the results showed lower bond (adhesion) strength of both unfilled adhesive resin and filled resin composite cement, with both E-max™ and Mark II™ ceramic materials. This said, this could be because of the hydrolysis of silane promoted adhesive interface, and, it could also be because of the partial disintegration of the resin composite cement itself. Given that, when observed under the light microscope, all the specimens showed adhesive failure after exposure to boiling water which suggests hydrolytic degradation of the adhesive interface in the specimens.

The results of the failure mode analysis showed that most of the adhesive resin specimens demonstrated cohesive failure in resin cement, when the ceramic surface was conditioned with the one-step and the two-step conditioning system. Furthermore, resin composite cements showed mixed failures when the ceramic surface was conditioned with the one-step and the two-step conditioning system. This might suggest that the traditional two-step ceramic surface conditioning is more effective than the one-step conditioning. From the clinical perspective, the

weakening of the adhesive interface by the provocative conditions, i.e., accelerated aging by using boiling water, might suggest that the silane promoted interface potentially degrades in the oral conditions over time.

Further studies are advised to evaluate the ceramic surface topography after etching with one-step and two-step etching systems.

7 CONCLUSIONS

Effect of acid etching with hydrofluoric acid, some micron and submicron level parameters, silane systems and surface conditioning systems which affect the adhesion of adhesive resins and resin composites were studied. Based on the results of the laboratory studies and stated hypothesis, the conclusions are drawn and presented below:

1. An HF acid etching and an increase in the HF etching duration significantly alters the surface topography in terms of pore pattern, pore width, and pore depth. Etching for longer times results in an increased number and width of the pores, and the width of the pores increases at a faster rate than does the depth.
2. An increase in the acid etching duration significantly increases the S_a and wettability of silica based ceramics. A positive correlation between the S_a and wettability was found; an increase in the S_a improves wettability.
3. The application of a neutralizing agent doesn't affect the wettability of etched ceramic surface to commercial and experimental silane primers, and silane treated ceramic surface to adhesive resin and commercial resin cements. The experimental silane primer showed better wettability than the commercial silane, in both control and neutralized ceramic samples. The experimental resin showed better wettability than the commercial resin composite on both experimental and commercial silane primer treated ceramic samples.
4. A combination of experimental silane treatment and application of adhesive resin showed better resin impregnation into the etched micro-pores. The experimental silane treated specimens with application of adhesive resin showed statistically significant higher nano-hardness and modulus of elasticity.
5. All the specimens showed a statistically significant decrease in nano-mechanical properties after exposure to boiling water. Silane treated specimens with adhesive resin showed least cement disintegration after subjecting to boiling water.
6. The two-step conditioning of the ceramic surface showed higher adhesion strength with both adhesive resin and resin composite cement compared to the one-step conditioning. The adhesion strength of unfilled adhesive resin cement was higher when compared with filled resin composite cements. Exposure to boiling water significantly reduced bond (adhesion) strength of both adhesive resin and resin composite cement. There was no difference in the provocative hydrolysis test between two-step and one-step conditioning systems.

ACKNOWLEDGEMENTS

This PhD study was carried out at the Department of Biomaterials Science, Institute of Dentistry, University of Turku, Turku, Finland, and at the Dental Biomaterials Research Chair, Dental Health Department, College of Applied Medical Sciences, King Saud University, Riyadh, Kingdom of Saudi Arabia, during 2014-2018. It was a part of the BioCity Turku Biomaterials Research Program, Turku, Finland, and Vice Deanship of Research Chairs, King Saud University, Riyadh, Kingdom of Saudi Arabia.

With exaltation, I express my pronounced gratitude to my esteemed supervisor Professor Pekka VALLITTU for giving me an opportunity to study. Sir, with your creative mind you have gifted me a priceless gift, the scientific knowledge and practical skills: without your guidance and support this thesis would not exist. I also thank my co-supervisor Professor Jukka MATINLINNA and Professor Abdulaziz A. ALKHERAIF for the special efforts, constant cooperation, endless support and persistent guidance.

I thank my postgraduate teachers Professor ANILKUMAR GUJJARI who taught me everything about prosthodontics, Professor RAGHAVENDRA for friendly guidance and Professor DHAKSHAYINI for valuable advice.

I would like to warmly thank all my coauthors for their excellent contributions.

My special thanks to all the members of the Dental Biomaterials Research Chair at King Saud University for the great help, technical support, constructive comments, proofreading of my manuscripts, all of which are greatly appreciated.

I own great gratitude to my beloved wife, ARCHANA for her care, love, encouragement and support. I would like to remember my son SAI VIHAAN, the sunshine of my life.

I thank all my friends and family members. I would like to salute to my parents RAMAKRISHNAIAH and RATHNAMMA for the love and affection during all times of my life. I would like to thank my in-laws VENKATESH and VIJAYLAXMI, you have been the driving force. I thank my brothers PRAKASH and NATARAJU, and sister PUSHPALATHA for their support.

The financial support from University of Turku to complete this thesis is greatly acknowledged. I wish to thank Finnish Doctoral Program in Oral Sciences (FINDOS) for the support.

REFERENCES

- Aboushelib MN, Ghoneim M, Mirmohammadi H, Salameh Z. General principles for achieving adequate bond to all ceramic restorations. *J Dent Oral Hyg* 2009;1: 36-41.
- Addison O, Marquis PM, Fleming GJ. 2007. The impact of hydrofluoric acid surface treatments on the performance of a porcelain laminate restorative material. *Dent Mater* 2007;23: 461-8.
- Al-Wahadni. The roots of dental porcelain: A brief historical perspective. *Dental news* 1999;6:43-44.
- Amaral R, Ozcan M, Bottino MA, Valandro LF, Bittoni MA. Microtensile bond strength of a resin cement to glass infiltrated zirconia-reinforced ceramic: the effect of surface conditioning. *Dent Mater* 2006;22:283-290.
- Amaral R, Ozcan M, Bottino MA, Valandro LF. Resin bonding to a feldspar ceramic after different ceramic surface conditioning methods: evaluation of contact angle, surface pH, and microtensile bond strength durability. *J Adhes Dent* 2011;13: 551-60.
- Anusavice K, Shen C, Rawls HR. Phillips' Science of Dental Materials. St louis, Missouri, USA: Saunders, 2012.
- Arkles B. Silane coupling agents: Connecting cross boundaries. Morrisville, Gelest 2003: 1-22.
- Arkles B. Hydrophobicity, hydrophilicity and silane surface modification, Maidstone, UK: Gelest 2011.
- Ayad MF, Fahmy NZ, Rosenstiel SF. Effect of surface treatment on roughness and bond strength of a heat-pressed ceramic. *J Prosthet Dent* 2008;99: 123-30.
- Basset J. Inorganic chemistry A concise text. Oxford, Pergamon press;1965:248-249.
- Bijelic-Donova J, Garoushi S, Lassila LV, Vallittu PK. Oxygen inhibition layer of composite resins: effects of layer thickness and surface layer treatment on the interlayer bond strength. *Eur J Oral Sci* 2015;123: 53-60.
- Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. *J Prosthet Dent* 2003a;89: 268-74.
- Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: A review of the literature. *J Prosthet Dent* 2003b;89: 268-74.
- Borges GA, Sophr AM, de Goes MF, Sobrinho LC, Daniel, Chan DC. Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics. *J Prosthet Dent* 2003;89: 479-88.
- Bottino MA, Snellaert A, Bergoli CD, Ozcan M, Bottino MC, Valandro LF. Effect of ceramic etching protocols on resin bond strength to a feldspar ceramic. *Oper Dent* 2015;40: E40-6.
- Canay S, Hersek N, Ertan A. Effect of different acid treatments on a porcelain surface1. *J Oral Rehabil* 2001;28: 95-101.
- Chaiyabutr Y, McGowan S, Phillips KM, Kois JC, Giordano RA. The effect of hydrofluoric acid surface treatment and bond strength of a zirconia veneering ceramic. *J Prosthet Dent* 2008;100: 194-202.
- Chen TM, Brauer GM. Solvent effects on bonding organo-silane to silica surfaces. *J Dent Res* 1982;61: 1439-43.
- Chen H, Tang T, Amirfazli A. Effects of surface wettability on fast liquid transfer. *Phys Fluids* 2015;27:112102.
- Chevalier J, Gremillard L, Virkar AV, Clarke DR. The tetragonal monoclinic transformation in zirconia: Lessons learned and future trends. *J Am Ceram Soc* 2009;92:1901-1920.
- Chevalier J, Gremillard L. Ceramics for medical applications: A picture for the next 20 years. *J Eur Ceram Soc* 2009;29:1245-1255.
- Clark HA, Plueddemann EP. Bonding of silane coupling agents in glass-reinforced plastics. *Modern Plastics* 1963;40(10):133-196.
- Claus H. Vita In-ceram, a new procedure for preparation of oxide ceramic crown and bridge framework. *Quintessenz Zahntechnik* 1990;16:34-46.
- Colares RC, Neri JR, Souza AM, Pontes KM, Mendonca JS, Santiago SL. Effect of surface pretreatments on the microtensile bond strength of lithium-disilicate ceramic repaired with composite resin. *Braz Dent J* 2013;24: 349-52.
- Datla SR, Alla RK, Alluri VR, Babu JP, Konakanchi A. Dental Ceramics: Part II Recent Advances in Dental Ceramics. *Am J Mater Eng Technol.* 2015;3: 19-26.

- Della Bona A, Anusavice KJ, Hood JA. Effect of ceramic surface treatment on tensile bond strength to a resin cement. *Int J Prosthodont* 2002a;15: 248-53.
- Della Bona A, Anusavice KJ. Microstructure, composition, and etching topography of dental ceramics. *Int J Prosthodont* 2002b;15: 159-67.
- Della Bona A, van Noort R. Shear vs. tensile bond strength of resin composite bonded to ceramic. *J Dent Res* 1995;74: 1591-6.
- Della Bona A, van Noort R. Ceramic surface preparations for resin bonding. *Am J Dent* 1998;11: 276-80.
- Denry I, Holloway J. Ceramics for Dental Applications: A Review. *Materials* 2010;3:351-368
- Durgesh BH, Alhijji SA, Alkheraif AA, Ramakrishnaiah R, Basavarajappa S, Alsharawy M, Matinlinna JP. A novel silane system as a primer for orthodontic bonding—A pilot study. *Int J Adhes Adhes* 2015;62: 101-6.
- Durgesh BH, Alhijji SA, Hashem MI, Alkheraif AA, Malash AM, Darshan DD, Obaid AS, Asmari MA, Matinlinna JP. Evaluation of an Experimental Silane Primer System in Promoting Adhesion Between Orthodontic Bracket and Ceramic. *J Biomater Tiss Eng* 2016;6: 236-45.
- Ersu B, Yuzugullu B, Ruya Yazici A, Canay S. Surface roughness and bond strengths of glass-infiltrated alumina-ceramics prepared using various surface treatments. *J Dent* 2009;37: 848-56.
- Fasbinder DJ. Clinical performance of chairside CAD/CAM restorations. *Journal of the American Dental Association*. 2006;137(9)Suppl:22S-31S.
- Fernandes NA, Zi Vally, Sykes LM. The longevity of restorations -A literature review. *S Afr Dent J* 2015;70:410-413.
- Foxton RM, Nakajima M, Hiraishi N, Kitasako Y, Tagami J, Nomura S, Miura H. Relationship between ceramic primer and ceramic surface pH on the bonding of dual-cure resin cement to ceramic. *Dent Mater* 2003;19: 779-89.
- Geurtsen W. Biocompatibility of dental casting alloys. *Crit Rev Oral Biol Med* 2002;13:71-84
- Gokce B, Ozpinar B, Dundar M, Comlekoglu E, Sen BH, Gungor MA. Bond Strengths of All-Ceramics: Acid vs Laser Etching. *Oper Dent* 2007;32: 173-78.
- Guarda GB, Correr AB, Goncalves LS, Costa AR, Borges GA, Sinhoreti MA, Correr-Sobrinho L. Effects of surface treatments, thermocycling, and cyclic loading on the bond strength of a resin cement bonded to a lithium disilicate glass ceramic. *Oper Dent* 2013;38: 208-17.
- Guess PC, Schultheis S, Bonfante EA, Coelho PG, Ferencz JL, Silva NR. All-ceramic systems: Laboratory and clinical performance. *Dent Clin North Am* 2011;55:333-352.
- Han L, Okamoto A, Fukushima M, Okiji T. Evaluation of physical properties and surface degradation of self-adhesive resin cements. *Dent Mater J* 2007;26: 906-14.
- Heikkinen TT, Matinlinna JP, Vallittu PK, Lassila LV. Long Term Water Storage Deteriorates Bonding of Composite Resin to Alumina and Zirconia Short Communication. *Open Dent J* 2013;7: 123-25.
- Helvey GA. Classifying dental ceramics: Numerous materials and formulations available for indirect restorations. *Compend Contin Educ Dent* 2014;35:38-43.
- Hirasaki GJ. Wettability: Fundamentals and Surface Forces. *SPE Formation Evaluation* 1991:217-226
- Ho GW, Matinlinna JP. Insights on Ceramics as Dental Materials. Part II: Chemical Surface Treatments. *Silicon*, 2011;3: 117.
- Hooshmand T, Daw R, van Noort R, Short RD. XPS analysis of the surface of leucite-reinforced feldspathic ceramics. *Dent Mater* 2001;17: 1-6.
- Ivoclar Vivadent. IPS neutralizing powder safety data sheet. 2015:1-6
- Jayaseelan S, Van Ooij W. Rubber-to-metal bonding by silanes. *J Adhesion Sci Technol* 2001;15(8):967-991.
- Kelly JR, Benetti P. Ceramic materials in dentistry: historical evolution and current practice. *Aus Dent J* 2011;56:84-96.
- Koin PJ, Kilislioglu A, Zhou M, Drummond JL, Hanley L. Analysis of the degradation of a model dental composite. *J Dent Res* 2008;87: 661-5.
- Lung CY, Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: an overview. *Dent Mater* 2012;28: 467-77.
- MacCulloch WT. Advances in dental ceramics. *Br Dent J* 1968; 124: 361-365

- Manahiloh KN, Meehan CL. Determining the Soil Water Characteristic Curve and Interfacial Contact Angle from Microstructural Analysis of X-Ray CT Images. *J Geotech Geoenviron* 2017;143(8): 04017034
- Martin MP. Materials and clinical considerations for full-coverage indirect restorations. *Compend Contin Educ Dent* 2012;33:2-5.
- Matinlinna JP, Laajalehto K, Lassila LV, Yli-urpo A, Vallittu PK. FT-IR and XPS surface characterization of allyltrimethoxysilane and 3-methacryloxypropyltrimethoxysilane mixture adsorbed onto titanium substrate. Boston. USA: CRC Press 2004.
- Malament KA, Socransky SS. Survival of Dicor glass-ceramic dental restorations over 14 years: Part I. Survival of Dicor complete coverage restorations and effect of internal surface acid etching, tooth position, gender, and age. *J Prosthet Dent* 1999;81: 23-32.
- Matinlinna JP, Lassila LV, Kangasniemi I, Vallittu PK. Isocyanato- and methacryloxysilanes promote Bis-GMA adhesion to titanium. *J Dent Res* 2005;84: 360-4.
- Matinlinna JP, Lassila LV, Vallittu PK. The effect of a novel silane blend system on resin bond strength to silica-coated Ti substrate. *J Dent* 2006a;34: 436-43.
- Matinlinna JP, Lassila LV, Vallittu PK. The effect of three silane coupling agents and their blends with a cross-linker silane on bonding a bis-GMA resin to silicized titanium (a novel silane system). *J Dent* 2006b;34: 740-6.
- Matinlinna JP, Ozcan M, Lassila LV, Vallittu PK. The effect of a 3-methacryloxypropyltrimethoxysilane and vinyltriisopropoxysilane blend and tris(3-trimethoxysilylpropyl)isocyanurate on the shear bond strength of composite resin to titanium metal. *Dent Mater* 2004;20: 804-13.
- Matinlinna JP. Silane chemistry aspects in some conventional and novel dental biomaterials (Ph.D. Thesis). Turku, University of Turku, 2004:27
- Matinlinna JP, Tsoi JK, de Vries J, Busscher HJ. Characterization of novel silane coatings on titanium implant surfaces. *Clin Oral Implants Res* 2013;24: 688-97.
- Matinlinna JP, Vallittu PK. Bonding of resin composites to etchable ceramic surfaces - an insight review of the chemical aspects on surface conditioning. *J Oral Rehabil* 2007a;34: 622-30.
- Matinlinna JP, Vallittu PK. Silane based concepts on bonding resin composite to metals. *J Contemp Dent Pract* 2007b;8: 1-8.
- Matinlinna JP, Laajalehto K, Laiho T, Kangasniemi I, Lassila LV, Vallittu PK. Surface analysis of Co-Cr-Mo alloy and Ti substrates silanized with trialkoxysilanes and silane mixtures. *Surf Interface Anal* 2004b;36: 246-53.
- Matinlinna JP, Lassila, LV. Experimental novel silane system in adhesion promotion between dental resin and pretreated titanium. Part II: Effect of long-term water storage: Rapid communication. *Silicon* 2010;2: 79-85.
- McLaren EA, Phone TC. Ceramics in dentistry- Part I: Classes of materials. *Inside Dent* 2009;5:94-103.
- McLaren EA, Figueira J. Updating classification of ceramic dental materials: A guide to material selection. *Compendium* 2015;36:739-744.
- McLaren EA. A-ceramic alternatives to conventional metal ceramic restorations. *Compendium* 1998;19:307-325.
- McLaren EA, White SN. Survival of In-Ceram crowns in a private practice: a prospective clinical trial. *J Prosthet Dent* 2000;83:216-222.
- McLean JW. Evolution of dental ceramics in the twentieth century. *J Prosthet Dent* 2001;85: 61-6.
- Miyazaki T, Nakamura T, Matsumura H, Ban S, Kobayashi T. Current status of zirconia restorations. *J Prosthodont Res* 2013;57:236-261.
- Moustafa N, Aboushelib MG, Hesam M, Ziad S. General principles for achieving adequate bond to all-ceramic restorations. *J Dent Oral Hyg* 2009;1: 36-41.
- Nagai Taro KY. Effect of hydrofluoric acid etching on bond strength of composite luting agent to lithium disilicate ceramic material. *Int Chin J Dent* 2004;4: 100-06.
- O'Brien AK, Bowman CN. Impact of Oxygen on Photopolymerization Kinetics and Polymer Structure *Macromolecules* 2006;39: 2501-06.
- O'Brien WJ. Dental materials and their selection. Chicago: Quintessence, 2008.
- Oilo M, Gjerdet NR, Tvinnereim HM. The firing procedure influences properties of a zirconia core ceramic. *Dent Mater* 2008;24: 471-475.
- Ozcan M. Adhesion of resin composites to biomaterials in dentistry: An evaluation of surface conditioning methods (Ph.D. Thesis). Groningen, University of Groningen 2003.

- Ozcan M, Volpato CA. Surface Conditioning Protocol for the Adhesion of Resin-based Materials to Glassy Matrix Ceramics: How to Condition and Why? *J Adhes Dent* 2015;17: 292-3.
- Ozkurt Z, Kazazoglu E. Zirconia dental implants: a literature review. *J Oral Implantol* 2011;37: 367-76.
- Pallis K, Griggs JA, Woody RD, Guillen GE, Miller AW. Fracture resistance of three all-ceramic restorative systems for posterior applications. *J Prosthet Dent* 2004;91: 561-9.
- Peumans M, Van Meerbeek B, Lambrechts P, Vanherle G. Porcelain veneers: a review of the literature. *J Dent* 2000;28: 163-77.
- Pilkenton M, Jeremiah L, Richard C. Effect of oxygen on the crosslinking and mechanical properties of a thermoset formed by free-radical photocuring. *Journal of Applied Polymer Science* 2011;119: 2359-70.
- Plueddemann EP. Silane Coupling Agents. Springer US: New York;1991.
- Plueddemann EP. Adhesion through silane coupling agents. *J Adhes* 1970a;2(7):184-201.
- Plueddemann EP. Silane coupling agents. New York, Plenum Press, 1991.
- Plueddemann EP, Clark HA, Nelson LE, Hoffman KR. New silane coupling agent for reinforced plastics. *Modern Plastics* 1962;39(8):135-187.
- Polydorou O, Konig A, Hellwig E, Kummerer K. Long-term release of monomers from modern dental-composite materials. *Eur J Oral Sci* 2009a;117: 68-75.
- Polydorou O, Konig A, Hellwig E, Kummerer K. Uthethane dimethacrylate: A molecule that may cause confusion in dental research. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 2009b;91B: 1-4.
- Probster L, Diehl J, Slip casting alumina ceramics for crown and bridge restorations. *Quintessence Int* 1992;23:26-31
- Qeblawi DM, Munoz CA, Brewer JD, Monaco EA. The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement. *J Prosthet Dent* 2010;103: 210-20.
- Ramakrishnaiah R, Alkheraif AA, Darshan DD, Matinlinna JP, Vallittu PK. The Effect of Hydrofluoric Acid Etching Duration on the Surface Micromorphology, Roughness, and Wettability of Dental Ceramics. *Int J Mol Sci* 2016;17: 822.
- Ramakrishnaiah R, Alkheraif AA, Mohammed A, Darshan DD, Kotha SB, Celur SL, Hashem MI, Vallittu PK, Rehman IU. Preliminary fabrication and characterization of electron beam melted Ti-6Al-4V customized dental implant. *Saudi J Biol Sci* 2016;24(4):787-796.
- Ramakrishnaiah R, Alkheraif AA, Darshan DD, Alghamdi KF, Matinlinna JP, Lung CY, Cherian S, Vallittu PK (a). The effect of lithium disilicate ceramic surface neutralization on wettability of silane coupling agents and adhesive resin cements. *Silicon*; <https://doi.org/10.1007/s12633-017-9670-6>
- Ramakrishnaiah R, Alkheraif AA, Darshan DD, Elsharawy M, Matinlinna JP, Vallittu PK (b). Micro and nano structural analysis of dental ceramics and luting resin interface and the effect of water exposure on integrity of cement interface. *J Biomater Tissue Eng* 2018;8:136-143.
- Ramakrishnaiah R, Alaqeel SM, Alkheraif AA, Darshan DD, Matinlinna JP, Vallittu PK. Two-step vs. one-step conditioning systems and adhesive interface of glass ceramic surface and resin systems. *J Adhes Sci Technol* 2018; 32: 1952-1963.
- Rasmussen ST. Analysis of dental shear bond strength tests, shear or tensile? *Int J Adhesion and Adhesives* 1996; 16: 147-154.
- Ren DF, Luo XP. Effect of hydrofluoric acid etching time and resin bonding on the flexural strength of lithium disilicate glass ceramic. *Zhonghua Kou Qiang Yi Xue Za Zhi* 2013;48: 462-6.
- Roulet JF, Soderholm KJ, Longmate J. Effects of Treatment and Storage Conditions on Ceramic/Composite Bond Strength. *J Dent Res* 1995;74: 381-87.
- Saavedra G, Arika EK, Federico CD, Galhano G, Zamboni S, Baldissara P, Valandro LF. Effect of acid neutralization and mechanical cycling on the microtensile bond strength of glass-ceramic inlays. *Oper Dent* 2009;34: 211-16.
- Sailer I, Feher A, Filser F, Gauckler LJ, Luthy H, Hammerle CH. Five-year clinical results of zirconia frameworks for posterior fixed partial dentures. *Int J Prosthodont* 2007;20:383-8.
- Sakaguchi R, Powers J. Craig's Restorative Dental Materials. Philadelphia USA: Mosby, 2011.
- Saridag S, Sevimay M, Pekkan G. Fracture resistance of teeth restored with all-ceramic inlays and onlays: an in vitro study. *Operative Dentistry*. 2013;38(6):626-34.

- Scherrer SS, Quinn JB, Quinn GD, Wiskott HWA. Fractographic ceramic failure analysis using the replica technique. *Dent Mater* 2007;23:1397-1404.
- Schmitter M, Mueller D, Rues S. In vitro chipping behaviour of all-ceramic crowns with a zirconia framework and feldspathic veneering: comparison of CAD/CAM-produced veneer with manually layered veneer. *J Oral Rehabil* 2013;40:519-25.
- Schwass DR, Lyons KM, Purten DG. How long will it last? The expected longevity of prosthodontic and restorative treatment. *New Zealand Dental Journal*. 2013;:98-105.
- Sharfrin E, William ZA. Constitutive relations in the wetting of low energy surfaces and the theory of the retraction method of preparing monolayers. *J Phys Chem* 1960;64:519-524.
- Shenoy A, Shenoy N. Dental ceramics: An update. *J Conserv Dent* 2010;13: 195-203.
- Simonsen RJ, Calamia JR. Shear bond strength of composite bond to etched porcelain. *J Dent Res* 1983;62: 297.
- Sorensen JA, Kang SK, Avera SP. Porcelain-composite interface microleakage with various porcelain surface treatments. *Dent Mater* 1991;7: 118-23.
- Stangel I, Nathanson D, Hsu CS. Shear strength of the composite bond to etched porcelain. *J Dent Res* 1987;66: 1460-5.
- Swain MV. Impact of oral fluids on dental ceramics: what is the clinical relevance? *Dent Mater* 2014;30: 33-42.
- Tagtekin DA, Yanikoglu FC, Bozkurt FO, Kologlu B, Sur H. Selected characteristics of an Ormocer and a conventional hybrid resin composite. *Dent Mater* 2004;20(5):487-497.
- Tai Y, De Long R, Goodkind RJ, Douglas WH. Leaching of nickel, chromium, and beryllium ions from base metal alloy in a fastened oral environment. *J Prosthet Dent* 1992;68:692-697.
- Vallittu PK. Unpolymerized surface layer of autopolymerizing polymethyl methacrylate resin. *J Oral Rehabil* 1999;26: 208-12.
- Van Noort R. Dental ceramics. In: An introduction to dental materials. Hong Kong, Elsevier 2002a:231-246.
- Wall JG, Cipra DL. Alternative crown systems. Is the metal-ceramic crown always the restoration of choice. *Dent Clin Nort Am* 1992;3:765-782.
- Wei M, Bowman RS, Wilson JL, Morrow NR. Wetting Properties and Stability of Silane-Treated Glass Exposed to Water, Air, and Oil. *Journal of Colloid and Interface Science* 1993;157: 154-59.
- Willard A, Chu TG. The science and application of IPS e.Max dental ceramic. *The Kaohsiung Journal of Medical Sciences* 2018; <https://doi.org/10.1016/j.kjms.2018.01.012>
- Wolf DM, Powers JM, O'Keefe KL. Bond strength of composite to etched and sandblasted porcelain. *Am J Dent* 1993;6: 155-8.
- Xiaoping L, Dongfeng R, Silikas N. Effect of etching time and resin bond on the flexural strength of IPS e.max Press glass ceramic. *Dent Mater* 2014;30: e330-6.
- Xiao SJ, Textor M, Spencer ND. Covalent Attachment of Cell-Adhesive, (Arg-Gly-Asp)-Containing Peptides to Titanium Surfaces. *Langmuir* 1998; 14: 5507-5516
- Xu L, Siedlecki CA. Effects of surface wettability and contact time on protein adhesion to biomaterial surfaces. *Biomater* 2007;28: 3273-3283.
- Yuan Y, Lee TR. Contact angle and wetting properties. Springer, Heidelberg 2013: 3-34
- Zarone F, Sorrentino R, Vaccaro F, Traini T, Russo S, Ferrari M. Acid etching surface treatment of feldspathic, alumina and zirconia ceramics: a micromorphological SEM analysis. *Int Dent South Afr* 2006;8: 20-26.
- Zhang M, Matinlinna JP, Botelho MG, Sailynoja ES. Comprehensive properties of a novel fiber reinforced composite with a UEDMA-based resin matrix. *Odontology* 2014;102: 176-83.
- Zogheib LV, Bona AD, Kimpara ET, McCabe JF. Effect of hydrofluoric acid etching duration on the roughness and flexural strength of a lithium disilicate-based glass ceramic. *Braz Dent J* 2011;22: 45-50.
- Zorzin J, Petschelt A, Ebert J, Lohbauer U. pH neutralization and influence on mechanical strength in self-adhesive resin luting agents. *Dent Mater* 2012;28: 672-9.

Annales Universitatis Turkuensis



Turun yliopisto
University of Turku

ISBN 978-951-29-7313-2 (PRINT)
ISBN 978-951-29-7314-9 (PDF)
ISSN 0355-9483 (PRINT) | ISSN 2343-3213 (PDF)