SURFACE PREPARATION EFFECT ON BONDING TO e. MAX CAD: A FRACTURE MECHANICS APPROACH

by

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DMD, The University of British Columbia, 2011

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Craniofacial Science)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

May 2014

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Abstract

Objective: To assess the effect of surface preconditioning on the short and long term interfacial fracture toughness ($K_{IC}$) of IPS e.max CAD and an adhesive resin luting cement.

Material and Methods: The materials selected for this study were from Ivoclar-Vivadent, Liechtenstein: e.max CAD blocks, Multilink implant, Mono Bond Plus, and IPS Ceramic Etching Gel. Eighty (4x4x4x4 mm) triangular prisms were cut from IPS e.max CAD blocks, crystallized and then randomly assigned to two different surface treatment groups: a) machined, using a 60 µm diamond bur (Henry Schein, Germany) and b) machined, as in group a followed by 20 s 5 % HF acid-etching. After surface treatment, all specimens were silane-treated for 60 s and the cement was used to bond two identical specimens of each group, following the manufacturer’s instructions. All 40 specimens were stored in water at 37 °C until testing. After 24 hours storage, 10 specimens from each group were tested to determine interfacial $K_{IC}$ using a universal testing machine (Instron 4311, Instron Canada, Canada); the other 10 specimens were tested after 60 days water storage. SEM fractographic analysis was performed on representative fractured $K_{IC}$ samples from each group to assess the type of failure, i.e. adhesive, cohesive, or mixed. To determine ARC $K_{IC}$, twenty (4x4x4x8 mm) triangular prisms were prepared using a mould. Half of the specimens were tested after 24 hours storage in water at 37 °C and the other half were tested after 60 days.

The $K_{IC}$ results were analyzed using univariate ANOVA followed, if warranted, by Scheffé multiple means comparisons. The statistical analysis was conducted at $\alpha=0.05$, using SPSS (SPSS for Windows, version 12.0; Chicago, IL).
Results: The machined/etched group had a significantly higher interfacial $K_{IC}$ at 24 hours. Crack propagation occurred through the adhesive resin and the resin-ceramic interface.

Conclusions: The higher $K_{IC}$ was achieved with HF acid etching. Storage in 37 °C water for 60 days led to a deterioration of both cement $K_{IC}$ and cement-mediated interfacial $K_{IC}$.

Clinical significance: IPS e.max CAD/CAM crowns should be etched with HF acid prior to cementation. However, the durability of the bond decreased upon ageing.
Preface

This in vitro study was supervised by Dr. N. Dorin Ruse. The members of the committee were Drs. N. Dorin Ruse and Anthony McCullagh, from the Faculty of Dentistry, and Dr. Tom Troczynski from the Department of Materials Engineering.

Human or animal subjects and bio-hazardous materials were not used in this study; therefore, the ethical approval from the UBC Research Ethics Board was not required.
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Acknowledgements

I would like to express my gratitude to my supervisor Dr. N. Dorin Ruse for his encouragement, patience, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis.

Besides my advisor, I would like to thank the rest of my thesis committee: Dr. Tom Troczynski and Dr. Anthony McCullagh for their insightful comments and being generous with their precious time.

The materials for this study were kindly provided by Ivoclar Vivadent Inc.
Dedication

I would like to dedicate this thesis to my lovely husband, Shahin and my sweet daughter, Paniz. I give my deepest expression of love and appreciation for the encouragement that you gave me.
Chapter 1: Introduction

1.1 Dental Ceramics

Traditional ceramics:

One of the most ancient industries is ceramics. The industry was developed when humans discovered that clay can be formed into objects through mixing with water and then firing. The basic components of traditional ceramics are clay (\(\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O}\)) as a plasticizer, silica (\(\text{SiO}_2\)), and aluminosilicate minerals, or feldspars (e.g.: \(\text{K}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2\)). These components are mixed together to form a paste that is shaped and then fired to make a ceramic object (Shen, Kosma*c et al. 2013).

From a materials science point of view, ceramics are described as heat resistant, non-metallic, inorganic, crystalline solids that are made up from metallic and non-metallic elements (such as aluminum, calcium, carbon, lithium, magnesium, oxygen, potassium, silicon, sodium, tin, titanium, zirconium, etc.) linked by ionic and/or covalent bonds (Anusavice and Phillips 2003). Whereas glasses are non-metallic, inorganic solids in which the elements are heated to fusion then cooled to a rigid solid without crystallization. A combination of ceramic components embedded into a glass matrix is called “porcelain”. In dentistry, the term “dental ceramics” is not clearly defined and is used indiscriminately
(Anusavice and Phillips 2003). In this thesis, the terms ceramic and glass-ceramics are going to be used.

The first presented dental ceramics were glass based ceramics (feldspathic porcelain), which best resemble the characteristics of tooth structure. Dental feldspathic porcelain is a glass-ceramic material, with a feldspathic glass forming the matrix and silica acting as filler. Silica is a high fusing (1710 °C) crystalline material in which the four oxygen atoms of tetrahedral silicate ions (SiO$_4^{4-}$) are shared between adjacent tetrahedra. In feldspars, alumina is incorporated in the structure and since Al is trivalent, for each Al atom present in the network there will be one O atom left unshared on a silicate tetrahedron, which carries a negative charge. To neutralize this negative charge, alkali metals (such as potassium, sodium, and calcium) are introduced. The consequence of this is the interruption of the 3D network structure through breaking down the oxygen-silicon bonds, causing a less cross-linked structure, often amorphous. This new developed open structure has lower strength and fusion temperature (Jones 1998). The drawback of these glass-ceramics is their low mechanical properties (flexural strength from 60 to 70 MPa), which limits their indication to veneering ceramics (Anusavice and Phillips 2003).

Dicor (from Dentsply International) was the first available castable glass-ceramic material for dental use (Anusavice and Phillips 2003). It was made of 55% tetrasilicic fluormica crystals precipitated in 45% glass matrix (Kelly, Nishimura et al. 1996). The lost wax technique was used to make Dicor crowns. The casting was then heated to from tetrasilicic fluormica crystals within the glass matrix to increase the strength and toughness of the glass-
ceramic. This material is no longer used due to the low flexural strength and inability to be stained internally.

**Reinforced glass-cermics:**

Glass-ceramics are partially crystallized glasses which are made by nucleation and crystals growth in the glass matrix phase. When specific composition of feldspar is heated at temperature between 1150-1530 °C, it undergoes partial devitrification (loss of glassy structure following crystallization of the glass) and precipitation of leucite crystals (K₂O·Al₂O₃·4SiO₂) occurs (Anusavice and Phillips 2003).

Leucite improves mechanical properties and increases the coefficient of thermal expansion of glass-ceramics due to its high coefficient of thermal expansion (20-25 x 10⁻⁶/°C) (Deany 1996). To bond veneering ceramics to metal ceramic copings, the coefficient of thermal expansion of the alloy should be slightly above that of the ceramic. When the coefficient of thermal expansion/contraction of the metal is slightly above the veneering ceramic (0.5 ppm/°C), compressive stresses are develop in the veneering ceramic and make it stronger under functional forces (Anusavice and Phillips 2003). In addition, leucite etches at a much faster rate than the glass matrix and this etched pattern produces numerous tiny features for resin cements to enter and create a good micromechanical bond (Kelly and Benetti 2011).

IPS Empress (Ivoclar Vivadent) is a leucite reinforced glass-ceramic which contains about 35% vol% of leucite crystals that increase the resistance to crack propagation. It is available
as press-ceramic ingots or machinable ceramic blocks, which flexural strength of 160 MPa (Anusavice and Phillips 2003).

In the last decade, lithium disilicate (Li$_2$Si$_2$O$_5$) has gained significant attention with regards to its effect on mechanical properties of glass-ceramics. IPS e.max (Ivoclar-Vivadent) is a glass-ceramic containing 70 vol% crystalline lithium disilicate filler (Kelly and Benetti 2011). The volume and shape of crystals increase the flexural strength to approximately 360 MPa, which it is more than double of that of IPS Empress. Lithium disilicate crystals have a low refractive index and, therefore, no adverse effect on the translucency. Dental restorations can be obtained from this material either by pressing or by computer aided designing/computer aided manufacturing (CAD/CAM) technology. Both IPS Empress and IPS e.max glass ceramics are translucent enough to be used for full coronal restorations. However, for the highest esthetic outcome, they can be veneered with feldspatic porcelain.

**Engineering ceramics:**

Engineering ceramics were developed in an attempt to improve mechanical properties of ceramics and they comprise oxides, carbides, nitrides (e.g. Al$_2$O$_3$, SiC, B$_4$C, TiO$_2$, Si$_3$N$_4$, ZrO$_2$, etc.). Among these engineering ceramics, aluminum oxide and zirconium oxide ceramics are routinely used in dentistry.

The concept of adding alumina particles (Al$_2$O$_3$) to feldspatic porcelain to improve physical and mechanical properties was first introduced by McLean (Conrad, Seong et al. 2007). The amount of alumina that can be merged into the feldspatic glass during the pre-fritting
process (combining silica with other oxides) is limited to 40-50 %. An alternative method has been revised in a system called In-Ceram (Vita Zahnfabrik, Germany), in which a pre-sintered alumina framework is infiltrated by feldspathic porcelain through the slip-casting technique. To produce a partially sintered coping or framework, a slurry of highly packed aluminum oxide is applied and sintered to a refractory die at 1120 °C for 10 h to form a porous framework of alumina particles. In the next step, the partially sintered core is infiltrated with glass (by capillary action) at 1100°C for 4 h to remove porosity and to reinforce the slip-cast core. In this way, alumina content could be increased up to 85 % but the produced ceramics are opaque and the copings should be veneered with a feldspathic ceramic for esthetic (Conrad, Seong et al. 2007)

Alumina-reinforced glass-ceramics cores are fabricated either through slip-casting technology or copy-milling technology.

Three core materials were introduced based on slip-casting technology: 1) In Ceram Spinell (ICS), 2) In Ceram Alumina (ICA), and 3) In-Ceram Zirconia (ICZ) (Anusavice and Phillips 2003).

In-Ceram Alumina consists of 70 wt. % alumina infiltrated with 30 wt. % sodium lanthanum glass. It has poor translucency and the strength of around 500 MPa. In an attempt to improve the ceramic translucency, in 1994, In-Ceram Spinell was introduced which contains a mixture of magnesia and alumina (MgAl₂O₃). ICS is twice as translucent as ICA since the refraction index of its crystalline phase is close to that of glass, however, its flexural strength
value (350 MPa) is lower than that of ICA and it is recommended only as core for anterior teeth crowns (Darvell 2009).

In-Ceram Zirconia is another modification of ICA in which 35% partially stabilized zirconia is added to the slip composition to strengthen the ceramic. It has very poor translucency but a high strength of about 700 MPa (Anusavice and Phillips 2003).

Copy-milling technology is applied to produce 20% enlarged model from the scanned working die and dry-pressing technique is used to mechanically compact aluminum oxide powder on the enlarged die. The packed aluminum particles then are sintered at 1550 °C, to eliminate porosity, shrink and make the core to the dimension of the working die. Veneering ceramic is used to complete the crown form. Procera (Nobel Biocare AB, Goteborg, Sweden) is a ceramic coping that contains 99.9% highly compacted aluminum oxide, which was first introduced by Andersson and Oden (Andersson, Razzoog et al. 1998).

Zirconia-based ceramics

Zirconia is a polymorphic material which exists in three phases: monoclinic (up to 1170 °C), tetragonal (between 1170-2370 °C), and cubic (above 2370 °C) (Thompson, Stoner et al. 2011). Zirconia structure is monoclinic at room temperature and is tetragonal at the firing temperature. A unit cell of monoclinic occupies about 4.4% more volume than the tetragonal unit does. Therefore, tetragonal to monoclinic phase transformation involves a 3-5% volume expansion that causes high internal stresses (Conrad, Seong et al. 2007). In the late 1980s, it was found that the tetragonal form can be stabilized at room temperature by incorporating
small amounts (3-8 mass %) of calcium, yttrium(Y-TZP), or cerium. Although it gets stabilized by this method at room temperature, the tetragonal form is "metastable," meaning that energy is trapped inside the material to return it back to the monoclinic phase under localized stress at the tip of the crack; in this case, the 4.4% increase in volume prevents crack propagation (Anusavice and Phillips 2003).

Crystalline ceramics are mostly opaque; therefore these ceramics usually serve as substructure and are veneered by feldspathic glass-ceramics to render them esthetic (Kelly and Benetti 2011).

1.1.1 Bonding Strategies for Dental Ceramic Restorations

In general, three steps are involved in an adhesion procedure: preconditioning, priming, to modify the preconditioned surface and make it compatible with an adhesive, and the adhesive application. The common method for bonding ceramics to composite is through (I) micro-mechanical bonding by grit-blasting or acid etching with HF (preconditioning), and (II) chemical bonding by silane coupling agent (priming) (Noort 2002). A strong resin bond to the ceramic surface is based on chemical bonding and micromechanical interlocking, which requires roughening and cleaning for sufficient surface activation. Grinding using diamond rotary instruments, airborne particle abrasion with aluminum oxide, acid etching (Simonsen and Calamia 1983), and combinations of any of these methods are common treatment options. (Blatz, Sadan et al. 2003).
Modification of the surface topography through etching and airborne-particle abrasion will lead to smaller contact angles and greater wettability (Della Bona, Shen et al. 2004). A liquid can easily spread on the surface of the substrate when the critical surface energy of the substrate is greater than the surface tension of the liquid. Low-energy contaminants, as oil, grease, and proteins, have to be removed prior to bonding (Noort 2002).

1.1.2 Effect of Surface Conditioning Methods on Ceramic - Composite Adhesion

1.1.2.1 Acid Etching

Dental ceramics can be categorized in two main groups based on their reaction to acid etching: acid-sensitive (feldspathic glass-ceramics) and acid resistant (non-feldspathic, engineering type ceramics, such as alumina/zirconia, densely sintered alumina and yttrium-oxide-partially-stabilized zirconia [YTZP]). In acid–sensitive ceramics, surface topography is changed through the selective attack of the hydrofluoric acid, whereas in acid-resistant ceramics, surface topography is not altered following acid-etching (Vanderlei, Passos et al. 2013).

Different etching patterns are produced depending on the ceramic microstructure and composition, type and concentration of the acid, and the acid etching duration (Kupiec, Wuertz et al. 1996). During acid etching, surface defects usually found in the glassy matrix and phase boundaries of heterogeneous ceramic materials are preferentially etched (Della Bona, Shen et al. 2004). The etched ceramic topography depends on the chemical reactivity
of the crystals of single-phase materials that is influenced by crystallographic alignment. In polycrystalline materials, etching features are different. Atoms along the crystal boundaries are more chemically active and dissolve faster than those inside the grains, consequently exhibiting small grooves or linear flaws after etching. Based on the above discussion, it can be concluded that ceramic microstructure and composition are the important aspects in the amount of micromechanical retention created by the etching procedure (Anusavice and Phillips 2003).

Fluoride-containing etchants, such as hydrofluoric acid (HF), ammonium bifluoride (ABF) and acidulated phosphate fluoride (APF) are effective in etching glass-ceramics. Some studies reported lower ceramic-composite bond strengths when APF was used to treat the ceramic surface. It seems that APF creates an inadequate, uneven, micromechanical retentive surface while HF is capable of producing the most prominent etching pattern on acid-sensitive ceramics (Della Bona, Shen et al. 2004). On the other hand, it has been stated that HF etching has a very aggressive effect on the surface of most acid-sensitive ceramics so that porosities are distributed uniformly throughout the ceramic surface. This pattern is more obvious for leucite-based ceramics than for other types of crystalline glass-ceramics (Aida, Hayakawa et al. 1995).

The etching occurs when the ceramic contains silica or silicates. First, an unstable silicon tetrafluoride is produced after acid application (Darvell 2009):

$$2\text{(HF)}_2 + \text{SiO}_2 (s) \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$$
In the second step, silicon tetrafluoride reacts with HF and forms a soluble complex ion, hexafluorosilicate:

\[(\text{HF})_2 + \text{SiF}_4 \rightarrow [\text{SiF}_6]^{2-}(\text{aq}) + 2\text{H}^+\]

Then it reacts with the protons to form tetrafluorosilicic acid that can be washed off with water:

\[\text{[SiF}_6^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{SiF}_6\]

(Darvell 2009)

A micro-retentive surface is the result of this procedure, where the hydrophobic resin can infiltrate and polymerize to create a mechanical bond with the ceramic. The size, number, and scattering of leucite crystals influence the effect of the acid in creating the microprosities. Some low fusing ceramics and glass-ceramics contain only small amounts of leucite crystals, which may prevent the creation of highly-retentive micro porosities after HF acid etching (Kamada, Yoshida et al. 1998).

Etching with HF acid not only creates a micromechanical retentive area but also stimulates hydroxyl group formation on the ceramic surface (Noort 2002). Magne and coworkers also found that hydrofluoric acid treatment could improve the durability of the of resin-silanated glass-ceramics bond. It is probably because of the increase of the area of the chemical adhesion on the rough surface and consequently decreasing the speed of deterioration of the silane coupling agent (Magne, Paranhos et al. 2010).

It has been proposed that silanes could also be used to attach composite resin to porcelain without HF etching, but even though the initial bond strength might be high, deterioration of
the bond over time has been reported with this method. The deterioration of the bond may relate to the development of a multimolecular layer of silane, which is less stable than a monolayer (Hooshmand, van Noort et al. 2002). Therefore, based on the above discussion, acid-sensitive ceramic materials should be etched prior to resin bonding procedure (Kamada, Yoshida et al. 1998; Ozcan, Alkumru et al. 2001).

1.1.2.2 Sandblasting

Sandblasting is the procedure in which the surface is blasted with alumina particles of an average size of 50 µm under an air pressure of 380 KPa for around 10-15 s from a perpendicular short distance (10 mm) from the surface (Lung and Matinlinna 2012). During sandblasting, some alumina particles might be embedded into the surface, which may have a negative impact on the bond strength. The higher the blasting pressure, the higher the amount of the embedded alumina, which could lead to the formation of Al-O-Si bonds after silanization, which are quite unstable and weaker than Si-O-Si bonds (Darvell 2009).

Coarse diamond rotary instruments or intra-oral sandblaster (airborne-particle abrasion systems) have also been used to roughen ceramic surfaces as the first step in the repair of fractured ceramic restorations. It has been revealed that both procedures produce similar topographies, with rotary instruments leaving behind a scalloped-looking surface. These methods are likely to generate more stress and sharp cracks in the ceramic surface and weaken the substrate (Della Bona and van Noort 1995).
The other adverse effect of this method is related to the fact that sandblasting of ceramic restorations has the potential to take away significant amounts of the ceramic structure and could affect the clinical fit of the restoration (Kern and Thompson 1994). A study regarding the effect of sand blasting on various type of ceramics reported a 36-fold loss of glass-ceramics compared with alumina ceramics; as a result, sand blasting of glass-ceramic restorations has been contraindicated (Roulet, Soderholm et al. 1995).

1.1.3 Priming (Silanization)

Primers are the materials which promote adhesion by rendering the surface chemistry of the substratum compatible with the chemistry of the adhesive. Primers have been used in various industries to improve bonding between organic coatings/adhesives and ceramics since the 1940’s. In fact, ceramic primers are silane coupling agents which bond dissimilar materials, organic and inorganic, together. Depending on the microstructure of the ceramic, special ceramic primers are required to bond ceramics to other materials (Matinlinna and Vallittu 2007). This section focuses on glass ceramics silane coupling agents.

Silanes, which are used on glass-ceramics to promote adhesion (surface pre-treatment), are organofunctional trialkoxy silanes, of the general formula M-R-SiX3, where M is a methacrylate group that can co-polymerize with the methacrylate groups of dental adhesives/composites/resins, R is an organic spacer (ethyl/propyl/etc.), and X is a hydrolysable alkoxy group (e.g. methoxy -O-CH3, ethoxy -O-CH2CH3) which permits bonding to hydroxyl groups of activated ceramic surfaces (Matinlinna and Vallittu 2007).
Hydrophobic silanes must first be hydrolysed (activated) and, after application, they condense and deposit onto the inorganic substrate. Water is needed for the silanol conversion (hydrolysis) in which alkoxy groups (-O-R) react with water to produce hydrophilic, reactive, acidic silanol groups, -Si-OH (Darvell 2009).

\[
\text{Si-O-R (solution) + H}_2\text{O} \rightarrow \text{Si – OH (solution) + R - OH}
\]

Trihydroxy silane compound (reactive intermediate product)

When deposited on an inorganic surface, silanol oligomers react with each other, developing branched hydrophobic siloxane bonds, -Si-O-Si- (Noort 2002).

\[
\text{Si – OH (interface) + Si – OH (solution) } \rightarrow \text{ Si - O – Si – (siloxane film) + H}_2\text{O}
\]

Therefore, silanization is the process in which the silanols are absorbed, deposited and polymerized on the substrate surface to create hydrogen bonds and covalent Si-O-Si bonds (Matinlinna and Vallittu 2007). The resin composite contains reactive methacrylate groups which can react with the organofunctional groups of silane (Lung and Matinlinna 2012).

Silane primers can be categorized as: 1) un-hydrolyzed single liquid silane primer, 2) pre-hydrolyzed silane primer that is also single liquid, and 3) two-or three liquid primer with
separate silane coupler in ethanol in one bottle and acid activator (acetic acid) in the other bottle (Chen and Brauer 1982). Lower bond strength has been reported with un-hydrolyzed silane (Aida, Hayakawa et al. 1995) while pre-hydrolyzed primers revealed a higher degree of hydrolysis compared with the two-component primers. It has been shown that stability of pre-hydrolyzed silane primers is insufficient and they have a limited shelf life (Matsumura, Kato et al. 1997). The two solutions primers have longer shelf life and they must be mixed to allow hydrolysis of the silane at a low pH before application (Lung and Matinlinna 2012).

Single- bottle silanes have a limited shelf life and are predisposed to rapid solvent evaporation and hydrolysis, which can render the silane solution ineffective. A good clinical indicator of the effectiveness of a silane product may be the color of the liquid: a clear solution may be indicative of a useful solution, while a milky-looking liquid may reveal that the material had expired. However, clinicians should not rely just on the appearance of the material, since the color does not change in an alcoholic solution (one bottle systems).

The most common silane in dentistry is 3-methacryloxypropyltrimethoxysilane (MPS). It is diluted in ethanol-water, usually pre-hydrolysed (pre-activated), and has a pH of 4-5, which is adjusted with acetic acid. The silane content is 1-5 vol %. MPS is applied to enhance and promote ceramic/metal/composite to composite bonding (Matinlinna and Vallittu 2007; Lung and Matinlinna 2012).

Silanes may be variable chemical structures of 3-trialkyloxysilylpropyl methacrylate (Kato, Matsumura et al. 1996). An understanding of how the silanization process happens on
ceramic surfaces has a significant impact to improve efficiency of silanes. It has been found that three different structures (layers) are produced in the interphase layer after application of a silane on the ceramic surface (Ishida 1985). The outermost layer contains small oligomers that can be rinsed off by water or organic solvents at room temperature. There is another layer of oligomers close to the glass surface, which is hydrolysable and may compromise the bonding of the cement with the ceramic. Removing this layer with hot water is recommended before bonding procedure (Hooshmand, van Noort et al. 2002.). The third layer which is bonded to the ceramic is a monolayer that is attached to the silica phase of the ceramic by covalent bonds and is hydrolytically stable (Barghi, Chung et al. 1999). This layer is providing the actual bond between the ceramics and the adhesive systems. Clinically, it is not possible to prevent formation of the other layers; therefore a few methods have been recommended for removing this unwanted excess silane before the bonding procedure. One method is to use hot air drying (50°C ± 5°C) for 15 seconds to evaporate the solvent after silane application, then rinsing it with hot water (80°C) for 15 seconds, followed by another hot air drying for 15 seconds. This process would remove water and solvent and rinse off any extra silane primer components (Hooshmand, Parvizi et al. 2008).

Removing the excess can be done during the try-in step as well. It is obvious that the try-in step is a contaminant step and usually it is done before silanization. In clinical situations, usually the try-in paste is used on the HF-etched ceramic restoration which is provided by dental laboratories. The HF-treated ceramic surface is hydrophilic and more likely to be contaminated by try-in paste before silanization. The remaining organic pollutants of try-in paste might reduce the bond strength and should be removed prior to the adhesion process.
Solvents, such as acetone or alcohol, or phosphoric acid are recommended for this purpose (Chen and Brauer 1982) & (Barghi, Chung et al. 1999). It has been shown that if the silanization is done before the try-in step, the ceramic surface becomes hydrophobic and the try-in paste can be easily cleaned off by ultrasonic devices, removing the unstable silane layers as well (Manso, Silva et al. 2011).

1.2 Dental Cements

Based on the glossary of prosthodontic terms, a cement is defined as “a binding element or agent used as a substance to make objects adhere to each other, or something serving to firmly unite” and a luting agent is defined as “any material used to attach or cement indirect restorations to prepared teeth” (GPT 2005).

Dental cements are used to maintain appliances, full and partial coverage restorations, and post and cores in a long-lasting stable position. Variable retention mechanisms, such as mechanical, chemical, and micromechanical, are reported based on the nature of the cement and the substrate, but they are typically a mixture of two or three mechanisms (Rosenstiel, Land et al. 1998).

Dental cements should create a strong bond through mechanical interlocking and chemical adhesion, resist dissolution, withstand compressive and tensile functional forces, be biologically compatible, have adequate film thickness and viscosity to ensure complete seating of the restoration, present sufficient working and setting time, and be easy to manipulate (de la Macorra and Pradíes 2002).
Dental cements are classified based on the usage (as liners, bases, luting agents, and restoratives), chemistry (phosphate cements, phenolate cements, polyalkenoate cements, resin cements, and adhesive resin cements); and ability/ inability to provide true adhesion to tooth structure and restorative materials, such as metals and ceramics (adhesive and non-adhesive cements).

The “conventional” or “classical” dental cements set via an acid-base reaction and consist of a powder (as a base) and a liquid (as an acid) which are mixed together to produce a paste. In 1878, zinc phosphate cement (ZPC) was introduced as the first dental luting cement. The powder was composed of 90% ZnO and 10% MgO and the liquid consisted of approximately 67% phosphoric acid buffered with aluminum and zinc. For many years, ZPC had been specified as the most common material in spite of its lack of adhesion, low hardness, and high solubility (Diaz-Arnold, Vargas et al. 1999).

Zinc-polycarboxylate cement was the second luting cement which came to the market to overcome ZPC limitations. The base was zinc oxide and the liquid was composed of polyacrylic acid and water. Although this cement had the capacity to bond to tooth structure (as a result of chelation of the carboxyl groups in the acid with the calcium ions in the apatite of enamel and dentin), it was weak in mechanical and physical properties (Shillingburg and Sather 2012).
Glass ionomer cements (GIC) were developed as the alternative to polycarboxylate cements. The powder is made of calcium fluoroaluminosilicate glass and the liquid is an aqueous solution of copolymers of polyacrylic, itaconic, maleic acids, and tartaric acid. They are sensitive to hydration and dehydration, therefore need protection while setting (Diaz-Arnold, Vargas et al. 1999; Shillingburg and Sather 2012). The main advantages of GIC are their capability to physicochemical bond to tooth structures, have a low coefficient of thermal expansion, and their anti-carcinogenicity through fluoride release. However, their mechanical properties are still low to be used in high stress bearing areas (Rosenstiel, Land et al. 2006).

Resin modified glass ionomer cements (RMGIC) were introduced in 1980 in an attempt to overcome two main weaknesses of GIC, low early strength and high solubility. They are reinforced by resin to improve strength and decrease solubility of the material (Hill and Lott 2011). RMGICs set through a combination of an acid-base reaction, photo and/or chemically activated polymerization.

The other categories of dental cements are resin composite cements. Composite cements, like conventional restorative composites, are made of an organic matrix (i.e.: Bis-GMA, TEGDMA, UDMA) which is reinforced by inorganic fillers. Based on the mode of polymerization, they can be categorized as self-cure (chemically activated), photoactivated, and dual-activated materials. (Kramer, Lohbauer et al. 2000).

Chemically activated resin cements are typically composed of two pastes: one of the pastes contains peroxide (commonly benzoyl peroxide) and the other paste contains a reducing
tertiary amine. The polymerization mechanism of self-cure resin cements is based on the redox reaction of benzoyl peroxide with aromatic tertiary amines (represented by catalyst and base paste, respectively) while in light-cured resin cements, camphoroquinone (CQ) is used as the initiator. In self-cure adhesive cements, the ratio between inhibitors and the amount of peroxide and aromatic tertiary amines controls the working time. Both inhibitors and peroxides are organic compounds subject to deterioration upon storage. As a result, self-cure resin cements have a limited shelf-life and their working/setting time may change depending on storage length and conditions (such as temperature). Deterioration of peroxide may prolong the working and setting time (WT/ST) while degradation of inhibitors may fasten them. However, the consequences of such alterations on the mechanical properties of the resin cements are not known yet (Manso, Silva et al. 2011).

Light cured resin cements have the advantage of the controlled setting/working time since the light is needed to start the polymerization reaction. However, their use is limited to those areas where the light can penetrate to ensure complete cure (e.g.: veneers and very shallow restorations) (Rosenstiel, Land et al. 1998).

Dual polymerizing cements contain both chemical and light polymerizing components found in chemically and light polymerizing systems. They are indicated when the type or thickness of the restoration might prevent light penetration to the interfacial cement. It has been shown that, in dual cure resin cements, self-cure mechanism can be interfered by light-curing and thus the cement cannot reach its maximum mechanical properties (Pegoraro, da Silva et al. 2007).
Therefore, it is recommended that light-curing of dual-cure cements should be delayed as long as clinically possible to let the self-curing process progress to the stage when light initiation no longer interferes with the self-curing mechanism. The delay time between mixing and the light-activation has not yet been reported, but it seems 5 to 10 minutes delay in light curing after mixing does not interfere with the final cure (Anusavice and Phillips 2003). Dual cured resin cements are best used for resin bonding of metal and ceramic restoration.

Regardless of the type of the polymerization reaction, depending on the capability to bond to the tooth structure, three main types of resin cements are available: 1) conventional resin luting cements (RC), which have no inherent adhesion to tooth structure and require a bonding agent, 2) adhesive resin cements (ARC), which have the ability to bond to tooth structure and do not need a separate bonding agent, and 3) self-etching adhesive resin cements (SEARC) which have acidic functional groups (monomers) that simultaneously demineralize, infiltrate, and bond to the tooth structure (dentin and enamel).

Etching and bonding steps are not needed with SEARC since the acidity of the cement is adequate to ensure micromechanical bond with the tooth structure. Using SEARC for bonding ceramic veneers is not recommended since they have lower bond strengths to enamel (Radovic, Monticelli et al. 2008).

Resin-based cements are considered the best choice for cementation of all ceramic restorations as they provide the optimum strength and good micromechanical bonding
capability which is required as the foundation for these otherwise brittle ceramic restorative materials. In addition, they overcome the drawbacks of the former materials, such as solubility, support, and lack of adhesion. However, expansion of resin cements due to water absorption has been reported as a contributing factor in fracture of ceramic restorations (Rosenstiel, Land et al. 2006). Restorative dentistry continually goes through changes and currently no cement could be considered ideal for all applications.

1.3 Principles of Adhesion

The word adhesion derives from the Latin word “adhaerere”, meaning “to stick”. Attachment of one material to another is called adhesion. The adhesive or adherent is the material that bonds two substrates together and the substrate which is adhered to is called the adherend (Anusavice and Phillips 2003).

Adhesion involves intermolecular interactions between atoms/molecules at the interface between two substrates, while cohesion refers to interactions within a material (Marshall, Bayne et al. 2010). Most of the time, the adhesive joint includes multiple interfaces. In dentistry, substrates can be tooth structures (e.g. enamel and dentin) or restorative materials (e.g. composite, ceramic, metal, etc.) and adhesives may involve one interface (e.g. sealant) or multiple interfaces (e.g. ceramic restorations bonded to the tooth) (Baier 1992).

The phenomenon of adhesion has been described through four theories:
1. Mechanical theories - based on mechanical interlock between the adhesive and the surface roughness of the substrate.

2. Absorption theories - include chemical adhesion between the adhesive and substrate.

3. Diffusion theories – which state that adhesion happens due to the interaction between mobile molecules, which is possible at temperatures above the glass transition temperature. It implies that polymers from each side can react with molecules on the other side and the consequence would be joining two units to create one unit.

4. Electrostatic theories – which states that at the interface between a metal and polymer, an electrical double layer is formed, which contributes to bonding (Baier 1992).

In summary, adhesion can be classified into three main types: physical, chemical, and mechanical. Chemical bonds (covalent, ionic, metallic and chelation) are strong while physical bonds (van der Waals forces) are very weak but always exist. The strongest bond is mechanical bond through strong interlocks (Marshall, Bayne et al. 2010).

Irrespective of the type of adhesion mechanism, adhesion needs close contact of the substrates which are to be bonded. It is obvious that adhesion is possible if adhesive can wet the substrates. Wettability of the adherent depends on its surface energy and the surface tension of the adhesive. Roughening the bonding surfaces increases the bonding area and surface energy, while low viscosity of the adhesive enables it to spread into the small irregularities (Summitt 2006).
The most common way to determine the wetting of the surface by an adhesive is by measuring the contact angle, which is the internal angle of a drop of liquid in contact with a solid (Figure 1). Contact angle $>90^\circ$ is considered as non-wetting and $<90^\circ$ as wetting, while a contact angle of $0^\circ$ means spreading and complete wetting (Anusavice and Phillips 2003).

![Figure 1: High and low contact angles](image)

The main goal in all bonding procedures is to promote wetting and spreading through choosing conditions without reducing the adhesive surface tension (Marshall, Bayne et al. 2010). Etching and sand blasting are common methods to alter ceramic surface topography to increase the surface area and energy and to improve the wettability of the ceramic (Della Bona, Shen et al. 2004).

### 1.4 Bond Strength and Interfacial Fracture Toughness of Resin-Ceramic Interface

Adhesive dentistry has undergone significant improvements within the previous decade and the new standards for esthetic restorative dentistry are developed based on biomechanics and stress distribution within the tooth and restorative materials.
Ceramics are considered as the best esthetic material which can match teeth structure and have favorable mechanical and optical properties (Kelly, Nishimura et al. 1996). But these materials are brittle and should be reinforced through bonding systems. The first system was presented by Dr. Charles Pincus in 1938, in which, during filming, porcelain veneers were bonded to teeth of actors/actress with a denture adhesive. It was just a temporary bonding method since no adhesive system was available at that time to securely bond porcelain veneers to teeth. Simonsen and Calamia had a significant role in developing a reliable method to bond porcelain restorations to tooth structure. They discovered that hydrofluoric acid could be used for etching porcelain before cementation (Simonsen and Calamia 1983). It has been proven that certain fluoride containing compounds, such as hydrofluoric acid (HF) or ammonium bifluoride, can create surface texture and roughness on porcelain through selectively removing the glassy matrix (Chen and Brauer 1982). Also, it has been shown that applying a silane coupling agent over the etched ceramic will maximize the bond strength between ceramic and composite (Roulet, Soderholm et al. 1995; Jardel, Degrange et al. 1999). However, according to Aida and colleague, the silane coupling agents made of methacryloxypropylsilane and carboxylic acid could create a strong bond with adhesive resin cements without HF acid etch treatment. They found that the acidic components of the silane system enhanced the adhesion between ceramic and composite resin (Aida, Hayakawa et al. 1995).

The quality and durability of the bond between the ceramic and the tooth has a significant impact on the long term success of bonded ceramic restorations through preventing porcelain
fracture, secondary caries, marginal discolorations (Ayad, Fahmy et al. 2008), and improving retention and marginal adaptation (el-Mowafy 2001).

Dental restorations and adhesive interfaces are susceptible to intraoral stimuli such as temperature changes, functional forces, saliva; and pH changes (Matinlinna and Vallittu 2007). It is essential for in-vitro studies to reproduce conditions resembling the oral environment to provide reliable results on the long-term durability of various bonding methods. Long-term water storage and thermocycling of bonded specimens are well known conditions to mimic aging of the bonding interface. Significant differences between early and late bond strength values have been reported by the studies that use these parameters (Roulet, Soderholm et al. 1995).

To predict the clinical success of resin-bonded ceramic restorations and repaired fractured ceramic restoration, variable bond strength tests, like shear bond test and tensile bond test, have been used. Some concerns have been raised regarding most of these test measurements, which indicate unreliability of such measurements in evaluating the adhesive behavior of bonded dental materials. Olio and colleagues questioned the clinical relevance and precision of the different testing techniques. They argued that although the shear bond and tensile bond tests are the most common testing methods, the result of these tests may not be reliable due to the non-uniform stress distribution (Oilo 1993) Several studies have identified non-uniform stress distribution along interfaces which lead to cohesive bulk fracture inside the cement rather than the interface (Della Bona and van Noort 1995). In fact, the commonly used shear bond test frequently creates fracture at a distance from the resin-ceramic adhesion zone that
may lead to inaccurate assumptions on the quality of the bond. Such errors prevent measurement of interfacial bond strength and limit further enhancements in bonding systems (Della Bona 2009). Weibull scaling analysis of test data with shear bond tests has revealed that the fracture is more related to failure from outer surfaces in tension than interfacial surface in shear. As a conclusion, tensile and shear tests do not resemble intraoral complex loading situations (Kelly, Benetti et al. 2012).

Researchers have assessed similar adhesive systems with different bond test methods to find a reliable test method that creates an uniform stress distribution across the interface (Della Bona and van Noort 1995). The application of fracture mechanics methodology could help overcome these limitations. Fracture mechanics permits measurement of the correlation between material properties such as toughness, stress level, the presence of crack-producing flaws, and crack propagation mechanisms A more reliable way to evaluate the adhesive zone would be to determine the interfacial fracture toughness through crack initiation and propagation within this area (Della Bona and Kelly 2008).

Fracture toughness is described as the resistance of brittle materials to crack propagation from existing defects/flaws under an applied force and is measured in units of stress times the square root of crack length (MPa.m$^{1/2}$) (Anusavice, Phillips et al. 2013). Different tests methods are available to measure the fracture toughness of brittle materials. The chevron-notched short rod (CNSR) test is a very common one and was introduced by Barker in 1979. He prepared the specimens by cutting a chevron notch inside a cylindrical sample of the material, a procedure that is very difficult to perform on brittle materials and especially on
bonded specimens. A new method of determining the fracture toughness of materials and bonded interfaces was introduced by Ruse and colleagues in 1996. It uses a notchless triangular prisms (NTP) specimen (6x6x6x12 or 4x4x4x8 mm), which, when fitted into the holder (Figure 3), reproduces the configuration of the standardized CNSR test. The custom jig (Figure 4) is used to mount the specimen into the holder while a nominated bar is used to space out the specimen holder halves (Ruse, Troczynski et al. 1996). When the specimen is securely mounted into the holder, a defect (~ 0.1 mm deep) is initiated in the middle of one of the edges of the NTP sample or the adhesive interface. The assembly is then tested under tensile mode (at a crosshead speed of 0.1 mm/min) in a universal testing machine (Instron model 4301, Instron Canada, Inc) until fracture or crack arrest (Ruse, Troczynski et al. 1996)

**Figure 2:** Notchless triangular prism (NTP) specimens and holder

**Figure 3:** Notchless triangular prism (NTP) mounting jig
The value for $K_{IC}$ is calculated using the standard formula (Bubsey, Munz et al. 1982):

$$K_{IC} = Y_{\text{min}}^* \frac{P_{\text{max}}}{D\sqrt{W}}$$

Where $P_{\text{max}}$ stands for maximum load recorded during testing, $D$ is specimen diameter, $W$ is specimen length and $Y_{\text{min}}^*$ is the dimensionless stress intensity factor, equal to 28 (Ruse, Troczynski et al. 1996). The value of $K_{IC}$ reveals the capability of a material to resist unstable crack propagation (Della Bona, Anusavice et al. 2006).

The fractured interface may show different modes of failure. The modes of failure are classified as:

Mode 1: interfacial separation at the ceramic–adhesive resin interface. Mode 2: failure initiates at the ceramic–adhesive interface, goes into the adhesive resin and returns to the interface. Mode 3: failure from internal flaw (penny-shape internal crack). Mode 4: failure starts at the ceramic–adhesive interface and propagates through the adhesive resin. Mode 5: failure starts at the ceramic–adhesive interface, goes through the adhesive resin to reach the resin composite–adhesive interface. Mode 1 failure is not common and usually occurs in the course of the specimen cutting. Failure in HF-treated ceramic specimens usually starts as a mode 4 and then it either propagates through the adhesive–resin composite interface (mode 5) or returns to the ceramic adhesive interface (mode 2) (Della Bona 2009).
Light microscopic evaluations cannot provide enough information to define the type of failure of bonded interfaces. The more precise classification of the fracture origin, crack propagation path, and the type of failure can be achieved through fractography. Simply defining the type of failure as adhesive, cohesive or mixed does not provide enough information with regards to the weakness zone of the bond while through fractography, fracture origin can be determined and accurate scientific statement on the mode of fracture can be expressed. Although the mode of failure is an important feature of bond strength tests, this aspect usually is not discussed. A comprehensive assessment of the fracture surfaces can provide information regarding the failure mode of a bonded interface. The fracture behavior of adhesive interfaces is influenced by stress, defects scattering, material properties, and environmental properties. Based on the above discussion, fracture surface description (fractography) combined with fracture mechanics interferences are the important factors to comprehend and predict reliability of the bonded interface (Della Bona, Anusavice et al. 2006).

The cementation method is one of the important features in clinical success of ceramic restorations (Kumbuloglu, Lassila et al. 2005). Durable bonding has been reported for glass-ceramics through etching and silanization (Jensen, Sheth et al. 1989; Sorensen, Kang et al. 1991). However, there is a controversy in literatures with regards to this protocol. One study suggested elimination of hydrofluoric acid etching for the bonding procedure (Aida, Hayakawa et al. 1995), whereas another study found no significant benefit of silane application (Sorensen, Kang et al. 1991). The adverse effects of hydrofluoric acid on ceramics were mentioned by Shimada and colleagues in 2002. They found that insoluble
silica fluoride salts which are produced on the ceramic surface after application of HF acid can interfere with attachment of the resin cement (Shimada, Yamaguchi et al. 2002). In addition higher cohesive failure was reported in the glass-ceramics treated with HF (Clelland, Ramirez et al. 2007).

There is a debate whether new ceramic primers can provide a strong bond to machinable glass-ceramics without the need for ceramic surface treatment through sandblasting or hydrofluoric acid etching (Kamada, Yoshida et al. 1998; Foxton, Nakajima et al. 2003). The effect of the various surface conditioning methods on the quality of the bond between ceramics and adhesive resin cements has been investigated, but no information is available regarding the relationship between the interfacial fracture toughness of the adhesive zone and different surface treatments for e.max CAD ceramics.

1.5 The aim of the study

The aim of this study was to use fracture mechanics methodology to assess the effect of surface preconditioning on the short and long term interfacial fracture toughness ($K_{IC}$) between a lithium disilicate reinforced glass-ceramic (IPS e.max CAD, Ivoclar Vivadent, Schaan Lichtenstein) and an adhesive resin luting cement (Multilink, Ivoclar Vivadent, Schaan Lichtenstein).
Research question:

Which ceramic surface preconditioning produces the most durable interfacial $K_{IC}$ between a lithium disilicate reinforced glass-ceramic (IPS e.max CAD) and an adhesive resin luting cement (Multilink Implant)?

Research hypotheses:

1) There is no difference in interfacial $K_{IC}$ between bonded ceramics preconditioned by machining and those preconditioned by machining plus hydrofluoric acid etching.

2) Storage in the water at 37 °C for 60 days does not affect the interfacial $K_{IC}$ of the adhesive interfaces tested.

3) There is no difference in interfacial crack propagation path between bonded ceramics preconditioned by machining and those preconditioned by machining plus hydrofluoric acid etching.
Chapter 2: Materials and Methods

2.1 Materials

The materials used in this study are listed in Table 1.

Table 1: Experimental materials

<table>
<thead>
<tr>
<th>Glass-ceramic</th>
<th>IPS e.max CAD blocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane coupling agent</td>
<td>Mono Bond Plus (Ivoclar-Vivadent, Liechtenstein)</td>
</tr>
<tr>
<td>Adhesive Resin Cement</td>
<td>A dual-cured Adhesive Resin Cement (Multilink Implant, Ivoclar Vivadent, Liechtenstein)</td>
</tr>
<tr>
<td>Acid etchant</td>
<td>5% hydrofluoric acid (HF) (IPS Ceramic Etching Gel, Ivoclar Vivadent, Liechtenstein)</td>
</tr>
</tbody>
</table>

IPS e.max CAD

IPS e.max CAD is a lithium disilicate (Li2Si2O5) reinforced glass-ceramic, with 3-6 μm long needle-like lithium disilicate crystals occupying ~70 vol%. The blocks are intended to be used in CAD/CAM systems.

The main components of IPS e.max are quartz, lithium dioxide, phosphor oxide, alumina, and potassium oxide (Ivoclar Vivadent 2013). These elements are mixed to produce a glass melt which is poured into a steel mold of a suitable shape. The blocks are cast in one piece which inhibits the development of flaws (pores, accumulation of pigments, etc.) in the body of the block.
The IPS e.max CAD “blue block” is processed in a "soft" intermediate state and has a two-stage crystallization process which produces two crystal types and microstructures. A double nucleation process occurs during the first step of crystallization, where lithium meta-silicate crystals are precipitated. The resulting intermediate lithium meta-silicate crystal structure makes the milling process possible without chipping and excessive bur damage. In this state, it has almost 40% lithium meta-silicate crystals with an average size of 0.5 µm. While the second heat treatment, which is performed after the milling process at around 840-850°C (1544°F) for 20 minutes in a porcelain furnace, the meta-silicate phase is totally dissolved and lithium disilicate crystalizes and the material reaches its final strength of 360 MPa. It must be fired on a silicon nitride firing tray to assure the adequate temperature for crystallization. The final product has 70% lithium disilicate crystals (Ivoclar Vivadent 2013).

**Table 2:** Firing parameters for the crystallization/glaze cycle (Ivoclar Vivadent 2013)

<table>
<thead>
<tr>
<th>Program</th>
<th>Stand-by temperature</th>
<th>Closing time</th>
<th>Heating rate</th>
<th>Holding time</th>
<th>Heating rate</th>
<th>Holding time</th>
<th>Heating rate</th>
<th>Holding time</th>
<th>Heating rate</th>
<th>Holding time</th>
<th>Heating rate</th>
<th>Holding time</th>
<th>Cooling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS Program 1</td>
<td>403°C 757°F</td>
<td>6:00 min</td>
<td>90°C/min 162°F/min</td>
<td>0.10 min</td>
<td>30°C/min 54°F/min</td>
<td>840°C 1544°F</td>
<td>7.00 min</td>
<td>550°C 1022°F</td>
<td>1022°F 1880°F</td>
<td>820°C 1508°F</td>
<td>1508°F 1544°F</td>
<td>700°C 1292°F</td>
<td>20°C/min 36°F/min</td>
</tr>
</tbody>
</table>

**Monobond Plus:**

Monobond Plus is a primer that contains three coupling agents in one bottle to bond composite resin to different material, such as glass-ceramics, polycrystalline ceramics and metals. The three active components (4 wt. %) are a silane (3-trimethoxysilylpropyl
methacrylate), a disulfide methacrylate, and a methacrylate phosphoric acid ester (see Figure 4) all dissolved in ethanol.

![Silane methacrylate](image)

**Silane methacrylate**

![Phosphoric acid methacrylate](image)

**Phosphoric acid methacrylate**

![Disulfide methacrylate](image)

**Disulfide methacrylate**

**Figure 3:** Active components of Monobond plus

The silane methacrylate group is intended to bond to silicate containing materials, the disulfide methacrylate group establishes a bond to gold and noble metals and the phosphoric acid methacrylate group could bond to zirconia, alumina, and base metal alloys. It needs 60 s to react with the surface and the chemical bond between the ceramic and composite luting cement is developed by free methacrylate groups. (Ivoclar Vivadent 2013)
**Multilink Implant adhesive resin cement:**

Multilink Implant is a dual-cure composite resin cement with two components; it is indicated for adhesive cementation of indirect restorations made of metal, metal ceramic, glass-ceramic and oxide-ceramic on implant abutments. The monomer matrix contains dimethacrylate and HEMA. Barium glass, ytterbium trifluoride, spheroid mixed oxide are added as a filler (~ 40 vol %). The size of the filler particles is between 0.25–3.0 μm, with a mean filler size of 0.9 μm.

**Table 3: Multilink Implant components**

<table>
<thead>
<tr>
<th>Base main Components:</th>
<th>Catalyst main components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoxylated bisphenol A dimethacrylate (10-25%)</td>
<td>Ethoxylated bisphenol A dimethacrylate (10-25%)</td>
</tr>
<tr>
<td>2-hydroxyethyl methacrylate (2.5-10%)</td>
<td>2-hydroxyethyl methacrylate (2.5-10%)</td>
</tr>
<tr>
<td>Bis-GMA (2.5-10%)</td>
<td>Bis-GMA (2.5-10%)</td>
</tr>
<tr>
<td>Urethane dimethacrylate (2.5-10%)</td>
<td>Urethane dimethacrylate (2.5-10%)</td>
</tr>
<tr>
<td></td>
<td>Dibenzoyl peroxide (≤ 2.5%)</td>
</tr>
</tbody>
</table>
### Table 4: Physical properties of Multilink Implant (Ivoclar Vivadent 2013)

<table>
<thead>
<tr>
<th></th>
<th>Self-curing</th>
<th>Dual-curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working time (37 °C)</td>
<td>1.5 - 2 min.</td>
<td>-</td>
</tr>
<tr>
<td>Setting time</td>
<td>4 - 5 min.</td>
<td>-</td>
</tr>
<tr>
<td>Film thickness</td>
<td>&lt; 50 μm</td>
<td>&lt; 50 μm</td>
</tr>
<tr>
<td>Water absorption (7 days)</td>
<td>&lt; 40 μg/mm²</td>
<td>&lt; 40 μg/mm²</td>
</tr>
<tr>
<td>Water solubility (7 days)</td>
<td>&lt; 7.5 μg/mm²</td>
<td>&lt; 7.5 μg/mm²</td>
</tr>
<tr>
<td>Radiopacity</td>
<td>350 % Al</td>
<td>350 % Al</td>
</tr>
</tbody>
</table>

**Additional values:**

<table>
<thead>
<tr>
<th></th>
<th>Self-curing</th>
<th>Dual-curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural strength</td>
<td>70 ± 20 MPa</td>
<td>110 ± 10 MPa</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>3500 ± 500 MPa</td>
<td>6000 ± 400 MPa</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>240 ± 20 MPa</td>
<td>280 ± 20 MPa</td>
</tr>
<tr>
<td>Transparency</td>
<td>12 ± 1.5 %</td>
<td>12 ± 1.5 %</td>
</tr>
<tr>
<td>MO 1 and Cat.</td>
<td>2 ± 0.5 %</td>
<td>2 ± 0.5 %</td>
</tr>
<tr>
<td>MO 0 and Cat.</td>
<td>2 ± 0.5 %</td>
<td>2 ± 0.5 %</td>
</tr>
<tr>
<td>Vickers hardness (HV 0.5/30)</td>
<td>-</td>
<td>440 ± 30 MPa</td>
</tr>
</tbody>
</table>
2.2 Methods

2.2.1 Sample Size Calculation

To determine the sample size, the mean and standard deviation was estimated from a similar study by Della Bona et al (Della Bona, Anusavice et al. 2006). The standard deviation and target difference were determined to be 0.07 and 0.01, respectively, at a significance level of 0.05. The Standardized difference was calculated to be 1.4 as follows: (Whitley and Ball 2002)

**Standardized difference:** Target difference/ Standard deviation

Altman nomogram (Altman 1980), was used for the calculation of the sample size using the acquired standardize difference. With the standardize difference 1.4, 80% power and a significant level of 5%, group size was calculated to be 8.

2.2.2 Determination of interfacial fracture toughness for bonded ceramic specimens

Eighty (4x4x4x4) mm triangular prisms were prepared from IPS e.max CAD blocks. Each e.max CAD block was cut into 4 blocks by cutting with an Isomet (Buhler) slow speed saw under water irrigation. A custom-made sample holder (Figure 7) was used to hold and grind the blocks into notchless-triangular prisms (NTP).
Figure 4: Dividing each e.max CAD block to 4 blocks using Isomet slow speed saw

Figure 5: Grinding the blocks into notchless-triangular prisms (NTP)
The adhesive surface of all prisms was ground, under water irrigation, with 60 grit SiC abrasive disks mounted on a grinding machine (Buehler), to reproduce the surface roughness according to the specifications of the Sirona CAD/CAM milling unit (Sirona 2013).

**Figure 6**: 60 grit SiC abrasive disks was used to grind the adhesive surface of the prisms

All prisms were crystallized at 840-850°C (1544°F) for 20 minutes, according to the manufacturer’s recommendation, in an Ivoclar Vivadent furnace.

**Figure 7**: Crystallized specimen and Ivoclar Vivadent furnace
After crystallization, prisms were randomly assigned to two different surface treatment groups before cementation:

A) Machined and silane treated

B) Machined, acid-etched with 5 % HF for 20 s, and silane treated

**Cementation Protocol**

To control the thickness of the adhesive cement, NTP specimens were bonded to each other using a bonding jig (Figures 9 and 10). A “0 µm”-labelled spacer was placed between the sliding halves of the jig while the prisms were brought into contact and secured by the lids on top of them. The “0 µm” spacer was replaced with another one that was 50 µm wider, before applying the adhesive. Thus, the two half-NTP specimens were kept apart at a fixed distance of 50 µm. A layer of the self-cured adhesive cement was placed on both facing ceramic surfaces which were then pushed towards each other and maintained in contact under finger pressure. In this manner, a 50 µm thick layer of cement bonded the two NTP ceramic halves. The cement layer was light-cured (Dentsply Caulk Spectrum 200R Dental Curing Light; 400 mW/cm²) for 60 s from each of the three sides of the triangular prism while finger pressure was maintained.

**Group A: (Machined and silane treated)**

1) Prisms were rinsed and dried with oil free air.

2) A layer of Silane Monobond plus was applied to the adhesive side of the specimens with a micro brush for 60 seconds and then air dried.

3) Multilink implant cement was applied on both prisms from the automix syringe
4) The holder was closed while 50 µ jig was in the middle of the holder

5) All margins were light cured for 20 seconds.

6) Additional curing for 60 seconds was done after removing the bonded prisms from holder.

**Group B: (Machined, acid-etched with 5 % HF for 20 s, and silane treated)**

1) Prisms were rinsed and dried with oil free air.

2) Adhesive side of prisms were etched with 5% hydrofluoric acid (e.g. IPS® Ceramic etching gel) for 20 seconds that is recommended for e max CAD.

3) A layer of Silane Monobond plus was applied to the adhesive side of the specimens with a micro brush for 60 seconds and then air dried.

4) Multilink implant cement was applied on both prisms

5) Holder was closed while 50 µ jig was in the middle of the holder

6) All margins were light cured for 60 seconds.

7) Additional curing for 60 seconds was done after removing the bonded prisms from holder.

![Figure 8: Bonding jig holding the specimens](image-url)
Figure 9: Two half-NTP specimens kept apart by a 50 µm spacer in the bonding jig.

Figure 10: A bonded specimen

Storage Media:

All 40 samples were stored in water at 37°C prior to testing at either 24 h or 60 d.

Figure 11: Specimens in the water storage media
Determination of interfacial $K_{IC}$:

The NTP specimen $K_{IC}$ test was used to determine the interfacial $K_{IC}$ using a computerized universal testing machine (Instron model 4311, Instron Canada, Inc.). A sharp blade was used to create a defect at the level of the adhesive interface, which would serve as an initiation point for crack propagation. The assembly was loaded in tension at a crosshead speed of 0.1 mm/min until fracture or crack arrest. The maximum load at fracture or crack arrest was used to calculate $K_{IC}$ using the following formula:

$$K_{IC} = Y^{*}_{\min} \frac{P_{\max}}{D \sqrt{W}}$$

$P_{\max}$ stands for maximum load recorded during testing, $D$ is specimen diameter, $W$ is specimen length and $Y^{*}_{\min}$ is the dimensionless stress intensity factor, equal to 28 (Ruse, Troczynski et al. 1996).

Figure 12: The notchless triangular prism holder and Instron machine
Scanning electron microscopy:

A Hitachi, S-3000N (Hitachi, Japan) scanning electron microscope (SEM) was used to characterize the surface topography of ceramic specimens before and after crystallization, after HF etching, and after interfacial $K_{IC}$ testing.

Figure 13: Gold plated specimens for SEM

Figure 14: Scanning electron microscope

2.2.3 Determination of $K_{IC}$ of the resin cement

To determine $K_{IC}$ of the luting cement, twenty (4x4x4x8) mm triangular prisms were prepared, using a plastic mold, and stored in 37 °C water for 1 d and 60 d prior to testing.
Figure 15: Fabrication of NTP specimens of the luting cement for $K_{IC}$ test

2.2.4 Statistical analysis

The $K_{IC}$ results were analyzed using univariate ANOVA followed, if warranted, by Scheffé multiple means comparisons. The statistical analysis was conducted at 0.05, using SPSS (SPSS for Windows, version 12.0; Chicago, IL).
Chapter 3: Results

The mean and standard deviation interfacial $K_{IC}$ for two groups at the two time intervals are presented in Table 3 and graphically illustrated in Figure 16. Statistical analysis (summarized in Tables 4 and 5) revealed higher interfacial $K_{IC}$ value at 1 d and 60 d for the ceramics which were machined and acid etched. Both groups showed deterioration of the interfacial $K_{IC}$ during storage, which was more dramatic for the machined-only group.

The most frequent fracture mode was cohesive in the adhesive resin cement for the machined and etched group while it was adhesive for the machined-only group.

Table 5: Results of interfacial $K_{IC}$ tests (Mean ± SD) in MPa·m$^{1/2}$

<table>
<thead>
<tr>
<th>Material/surface preparation</th>
<th>$K_{IC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 d</td>
</tr>
<tr>
<td>IPS e.max CAD machined/silanated</td>
<td>1.09 ± 0.25$^b$</td>
</tr>
<tr>
<td></td>
<td>(10/10)</td>
</tr>
<tr>
<td>IPS e.max CAD machined/ HF acid</td>
<td>1.86 ± 0.24$^a$</td>
</tr>
<tr>
<td>etched/silanated</td>
<td>(10/10)</td>
</tr>
<tr>
<td>Multilink Implant cement</td>
<td>1.76 ± 0.60$^a$</td>
</tr>
<tr>
<td></td>
<td>(10/10)</td>
</tr>
</tbody>
</table>
Figure 16: Box plots of the effect of Time and Surface topography on $K_{IC}$

The results showed that time (1 d and 60 d) and the surface topography had a significant effect on interfacial $K_{IC}$. At 1 d, no significant difference was revealed between the etched/machined group and the cement, while the machined-only group showed significantly lower $K_{IC}$ value compared with the etched/machined and the cement groups. At 60 d, the cement showed higher $K_{IC}$ in comparison to the test groups. In the machined-only group, just 4 of the specimens could be tested, the others having failed during storage (Figure 17).
Figure 17: Deterioration of the bond of the machined-only group during water storage

Table 6: Summary of inter-group and intra-group analysis

<table>
<thead>
<tr>
<th>ANOVA (K_{IC})</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>1.801</td>
<td>2</td>
<td>.900</td>
<td>33.440</td>
<td>.000</td>
</tr>
<tr>
<td>Within Groups</td>
<td>.485</td>
<td>18</td>
<td>.027</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2.285</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Scheffe Multiple Comparisons</th>
<th>(I) surface</th>
<th>(J) surface</th>
<th>Mean Difference</th>
<th>Std. Error</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I-J)</td>
<td>cement</td>
<td>e.max machined/etched</td>
<td>-.15708</td>
<td>.08862</td>
<td>.235</td>
</tr>
<tr>
<td></td>
<td>e.max machined</td>
<td></td>
<td>.53911*</td>
<td>.08493</td>
<td>.000</td>
</tr>
<tr>
<td>e.max etched</td>
<td>cement</td>
<td>e.max machined</td>
<td>.15708</td>
<td>.08862</td>
<td>.235</td>
</tr>
<tr>
<td></td>
<td>e.max machined</td>
<td></td>
<td>.69619*</td>
<td>.09129</td>
<td>.000</td>
</tr>
<tr>
<td>e.max machined</td>
<td>cement</td>
<td>e.max</td>
<td>-.53911*</td>
<td>.08493</td>
<td>.000</td>
</tr>
<tr>
<td></td>
<td>e.max machined/etched</td>
<td></td>
<td>-.69619*</td>
<td>.09129</td>
<td>.000</td>
</tr>
</tbody>
</table>

* The mean difference is significant at the 0.05 level.
Table 7: Summary of inter-group and intra-group comparison analysis at 60 days

<table>
<thead>
<tr>
<th>ANOVA (KIC)</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>.909</td>
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<td>.455</td>
<td>16.362</td>
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<tr>
<td>Total</td>
<td>1.410</td>
<td>20</td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Scheffe Multiple Mean Comparisons</th>
<th>(I) surface</th>
<th>(J) surface</th>
<th>Mean Difference (I-J)</th>
<th>Std. Error</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement e.max etched</td>
<td>.37750</td>
<td>.08101</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cement e.max machined</td>
<td>.48500</td>
<td>.10018</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e.max etched cement</td>
<td>-.37750</td>
<td>.08101</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e.max etched e.max machined</td>
<td>.10750</td>
<td>.10209</td>
<td>.584</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e.max machined cement</td>
<td>-.48500</td>
<td>.10018</td>
<td>.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e.max machined e.max etched</td>
<td>-.10750</td>
<td>.10209</td>
<td>.584</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: The mean difference is significant at the 0.05 level.

The result of this study rejected all hypotheses and showed:

1) There is significant difference in interfacial KIC between bonded ceramics preconditioned by machining and those preconditioned by machining plus hydrofluoric acid etching

2) Storage in water at 37 °C for 60 days affected the interfacial KIC of the adhesive interfaces tested.

3) There is obvious difference in interfacial crack propagation path between bonded ceramics preconditioned by machining and those preconditioned by machining plus hydrofluoric acid etching.
SEM Analysis

Scanning electron microscopic (SEM) characterization of the treated ceramic surfaces of the prisms revealed various morphologies.

SEM micrographs of the ceramic surfaces before crystallization, after crystallization; and after acid etching are displayed in figures 18, 19, and 20. Pores and grooves can be seen in the photomicrographs of the non-crystallized specimens, while these features are not noticeable after crystallization and it seems that the melted superficial ceramic has occluded the roughness created during the milling.

Figures 21, 22, 23, and 24 represent SEM micrographs of fracture surfaces in 1 d and 60 d in both tested groups. In all cases, fractures initiated from the induced defect. Deterioration of the bond occurred following water storage, especially for the machined-only group and the representative SEM photographs showed deterioration of the interfacial bond while it seems that the silane coating still covers the adhesive surface (Fig.22). The adhesive failure mostly occurred for the machined-only group while cohesive failure was most dominant fracture for the machined-etched group at 24 h.
Figure 18: SEM micrographs of a milled specimen before crystallization

Figure 19: SEM micrographs of a milled specimen after crystallization

Figure 20: SEM micrographs of the ceramic surface after acid etching
Figure 21: SEM micrograph of fracture surfaces of machined group

* White squares mark magnified areas.
**Figure 22:** SEM micrographs of fracture surfaces of machined & etched group

* White squares mark magnified areas.
Figure 23: SEM micrographs of fracture surface in 60 d machined group. No cement layer present while silane seems to still cover the ceramic surface.

Figure 24: SEM micrographs of fracture surface in machined &etched group after 60 d. Detaching of the cement layer from the adhesive surface is obvious. (Green arrow)

Figure 25: SEM micrographs of fracture surface of the cement
Chapter 4: Discussion

Long-term success of ceramic restorations is influenced by the quality of the bond between ceramics and tooth structure (Anusavice, Phillips et al. 2013). Various surface preconditionings (i.e.; sandblasting, HF acid etching) and silane coupling agents are routinely used to improve the bond between ceramics and adhesive resin cements. Application of a silane coupling agent onto the preconditioned ceramic surface (HF etched) provides a chemical bond and is a major factor in producing a sufficient bond between the resin and silica-based ceramics (Bailey 1989).

As it was already discussed, tensile and shear bond tests are commonly used to evaluate the quality of the bond, while interfacial $K_{IC}$ test is a more reliable test due to more uniform stress distribution within the adhesive zone. This test also permits determination of the weakest point in the adhesive area, which can then be used for further improvements in substrates conditionings or materials. IPS e.max CAD is a new glass-ceramic which has found significant attention in dentistry during the last decade, but there is no study to show the long-term effect of the existing ceramic surface treatments on the quality of their bond to resin cements.

This study revealed that the interfacial $K_{IC}$ of the IPS e. max CAD glass-ceramic is affected by the type of surface treatment and water storage. The higher interfacial $K_{IC}$ was obtained for the machined-etched group in comparison to the machined-only group.
The bond between ceramic and silane occurs through a condensation reaction in which the silanol group (Si-OH) of the hydrolyzed silane will join the silanol group of the ceramic surface to create a siloxane bond (Si-O-Si) and water as a by-product (Noort 2002). The quality of the bond depends on the availability of Si-OH sites on the ceramic surface. There is a belief that because of the hydrophobicity of the silane, the risk of the hydrolytic deterioration of the bond will decrease and since it produces an organophilic surface for the adhesive, wettability of the ceramic surface will increase (Della Bona, Shen et al. 2004). The results of this study showed hydrolytic degradation of the silane bond due to the gradual water absorption, confirming previously published results (Bailey 1989; Pollington, Fabianelli et al. 2010).

The obtained results from this study may relate to multiple factors: firstly, the silane coupling agent (3-trimethoxysilypropyl methacrylate and methacrylate phosphoric acid ester) used in this study has three active ingredients to bond composite resin to different materials, such as glass-ceramics, metals, and polycrystalline ceramics. There is no evidence regarding compatibility of these components with each other and potential adverse effects of mixing various coupling agents on quality of the bond to ceramics.

Secondly, it may also relate to the fact that adhesive systems are hydrophilic in nature and acidic to some extent; therefore, water penetration may occur, after polymerization, within the adhesive resin and compromise the total bonded area (Carvalho, Manso et al. 2012). Silane coupling agents that contain long hydrocarbon chains (n>10) are more hydrophobic in comparison with those that include short hydrocarbon chains, i.e. pre-hydrolyzed silane
products (Lung and Matinlinna 2012). Ageing techniques, such as water storage and thermocycling, are damaging for the siloxane-ceramic bond. The amount of water absorbed by the composite material has a significant effect on hydrolysis and deterioration of the siloxane film. As composite resin absorbs the water, the bond between silane and composite could fail due to hydrolysis (Roulet, Soderholm et al. 1995).

Thirdly, SEM characterization of machined-only group showed occurrence of the failure at the cement-silane coupling agent interface, which may be indicative of the incompatibility of the adhesive resin cement and the silane.

Fourthly, the SEM analysis of the machined-only specimens before and after crystallization showed that machining opened up the crystal structure of the ceramic, but the irregularities disappeared after heat crystallization. The lack of porosities for micromechanical bonding may necessitate further surface treatment of the ceramic surface after crystallization.

Lastly, by considering the fact that a thin silane coating on the ceramic surface is needed, the cementation strategy should consider the different ceramic microstructures, silane varieties, and mechanisms to decrease the silane coating thickness, such as heat treatment (Della Bona, Shen et al. 2004). Degeneration of the bond may be related to production of a multilayer of silane that is less stable than a monolayer of silane. The thickness of the siloxane film has a significant impact on the behavior of the adhesive zone and it depends on the concentration of the silane solution not the time of the reaction; if it is too thick, it may lead to cohesive failure, while if too thin, it may lead to incomplete coverage of the ceramic surface and
therefore insufficient contact between ceramic surface and a resin composite (Matinlinna and Vallittu 2007).

The thickness of the cement in this study was limited to 50 µm based on the evidence that considerably decreased bond strength of ceramic systems is reported with thicker cement layers (Cekic-Nagas, Canay et al. 2010). It is also a minimal film thickness of 50 µm recommended to increase the support for the ceramic restoration while decreasing the side effects of water sorption and its consequences to the properties of the cement (Manso, Silva et al. 2011).

The interfacial $K_{IC}$ of 24 h machined-etched specimens was similar to that of the 24 h monolithic cement specimens, which, along with the observed cohesive failure through the cement layer, suggest that there are no concerns with regards to sample preparation. But after 60 d water storage, $K_{IC}$ of the monolithic cement samples dropped by almost 50 %. The high $K_{IC}$ obtained for the cement in this study may be related to the deformation of the cement before fracture. It has been shown that absorbed water works as a plasticizer for the cement and may create unsupported areas beneath ceramic restorations and, as a result, increases the chance of fracture of the restorations under functional forces (Ferracane, Berge et al. 1998).

Degradation of the bond during 60 d water storage happened in both groups, which was more dramatic for the machined-only group. This may relate to the weakness of the available silane coupling agents. As it was mentioned by Marshall et al, organo-silane coupling agents
are used to promote chemical adhesion but most of them do not create sufficient chemical bonding and mostly just increase the wettability of substrates (Marshall, Bayne et al. 2010).

The current silane coupling agents are not ideal and can provide the minimum desires in clinical practice with respects to the development of the bond between dental restorative materials and composite resin cements (Lung and Matinlinna 2012). There is a need for improvement with regards to the available silane coupling agents.

In looking at the individual types of indirect restorations that are possible with ceramics and require cementation, it is clear that there must be different cementation recommendations/protocols based on the evidence of mainly in-vitro studies. Although some long-term prospective studies exist on survivability of ceramic restorations, there are clearly many variables that can attribute success or failure of a ceramic restoration, variables that can be better studied under controlled, in vitro studies. Thus, in-vitro study can provide valuable information that must be used in collaboration with clinical studies to provide the clinicians with some sound conclusions about the interplay of ceramics and cements.
Chapter 5: Conclusion

Restorative dental treatments generally include attaching of two non-similar materials. Longevity of ceramic restorations is related to the adhesion of resin cements both to the tooth and ceramic material, therefore, incorrect selection of the (adhesive) resin cement or the possible incompatibility of two parts may lead to failure at the ceramic/cement interface.

Surface conditioning of ceramic restorative materials combined with silanization is considered as a standard protocol in adhesive dentistry. However, the hydrolytic stability of the siloxane bond in the adhesive zone is a major concern. Interfacial $K_{IC}$ test under tensile mode may be preferable to conventional shear or tensile bond strength tests since fracture occurs within the adhesion zone. In this study, the machined-etched group had a significantly higher interfacial $K_{IC}$ at 24 h and 60 d, while the durability of the bond decreased with time in both groups. Crack propagation occurred through the adhesive resin and/or the resin-ceramic interface.

This experimental study showed that 1) roughening the glass-ceramic surface by HF etching and silane coating still yields the highest interfacial $K_{IC}$ for acid-sensitive ceramics in short term, 2) degradation of the bond over time in the oral environment may relate to both the degradation of the cement and to the hydrolysis of the siloxane bond.
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