COMPARISON OF ADHERENCE OF SELF-CURED ADHESIVE RESIN CEMENT TO LITHIUM DISILICATE CERAMICS AND CERAMIC RESIN COMPOSITES USING FRACTURE MECHANICS

by

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Abstract

Objective: The goal of this study was to apply fracture mechanics methodology to assess the effect of surface preconditioning on the short and long term adherence between a widely used adhesive resin cement (RelyX Ultimate, 3M ESPE) and recently introduced CAD/CAM materials: two ceramic resin composites (Lava Ultimate – 3M ESPE and Enamic – Vita-Zahnfabrik) and a ceramic (IPS e.max – Ivoclar-Vivadent).

Materials and Methods: Sixty specimens were prepared from each e.max and Enamic, and 120 specimens were prepared for Lava Ultimate. Ceramic resin composite blocks samples were prepared by wet cutting and grinding. Ceramic samples were prepared using the lost wax procedure and pressing. Enamic and e.max bonding surfaces were treated with hydrofluoric acid. Lava Ultimate received two surface treatments: sandblasting and Rocatec soft. All samples were bonded using an adhesive and resin cement and stored in water at 37°C. After 24h storage, half of the specimens from each group were tested to determine the interfacial $K_{IC}$ using an Instron universal testing machine; the remaining specimens were tested after 60d storage. Scanning electron microscopy fractographic analysis was performed on representative fractured samples from each group to determine the mode of failure. To determine the adhesive resin cement $K_{IC}$, twenty specimens were prepared using a mold. Half of the specimens were tested after 24h storage in water at 37°C and the other half were tested after 60d storage. The $K_{IC}$ results were analyzed using two-way ANOVA followed by Scheffé multiple means comparisons.
**Results:** Lava Ultimate had a significantly higher interfacial $K_{IC}$ at 24h when compared to Enamic and e.max. For Lava Ultimate, crack propagation occurred cohesively through the adhesive resin cement. In Enamic and e.max samples, crack propagation occurred cohesively within the adhesive layer. Only Enamic showed a significantly higher interfacial $K_{IC}$ at 60d, compared to the other groups. Lava Ultimate and e.max interfacial $K_{IC}$, and cement $K_{IC}$ showed lower values at 60d.

**Conclusion:** For Lava Ultimate, surface silicatisation seems to be a more effective surface treatment compared to only sandblasting. For Enamic and e.max, the application of silane coupling agent and adhesive contained in one solution does not seem to be effective.
Preface

This in vitro study was supervised by Dr. N. Dorin Ruse. The members of the committee were Drs. N. Dorin Ruse and Caroline Nguyen, 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 Ethics Board was not required.
Table of Contents

Abstract................................................................................................................................. ii
Preface................................................................................................................................. iv
Table of Contents ................................................................................................................ v
List of Tables ........................................................................................................................ viii
List of Figures ....................................................................................................................... ix
Acknowledgements ............................................................................................................ xii
Dedication ............................................................................................................................. xiii
Chapter 1: Introduction ...................................................................................................... 1
  1.1 Computer-Aided Design / Computer-Aided Manufacturing ........................................ 1
      1.1.1 History.................................................................................................................... 1
      1.1.2 Advantages of CAD/CAM Technology................................................................. 2
      1.1.3 Disadvantaged of CAD/CAM Technology........................................................... 3
  1.2 Dental Biomaterials ..................................................................................................... 3
      1.2.1 Dental Ceramics................................................................................................. 4
          1.2.1.1 History......................................................................................................... 4
          1.2.1.2 The Etched and Bonded Ceramics.............................................................. 5
          1.2.1.3 The Non-etched Ceramics........................................................................ 7
      1.2.2 Ceramic Resin Composites................................................................................ 9
  1.3 Bonding to Dental Materials...................................................................................... 10
      1.3.1 Conditioning ....................................................................................................... 11
          1.3.1.1 Sandblasting ............................................................................................. 11
1.3.1.2 Surface Silicatisation ................................................................. 12
1.3.1.3 Acid Etching ................................................................................. 13
1.3.2 Priming ......................................................................................... 14
1.4 Testing of Adhesion ........................................................................ 16
1.4.1 Bond Strength Testing ................................................................. 16
1.4.2 Fracture Mechanics .................................................................... 19
1.5 Clinical Significance ....................................................................... 21

Chapter 2: Research Protocol .................................................................. 22
2.1 Specific Aims .................................................................................... 22
2.2 Research Hypotheses ....................................................................... 22

Chapter 3: Materials and Methods ............................................................ 23
3.1 Materials ......................................................................................... 23
  3.1.1 Lava Ultimate ............................................................................... 23
  3.1.2 Enamic ......................................................................................... 24
  3.1.3 IPS e.max ................................................................................... 26
  3.1.4 IPS Ceramic Etching Gel ............................................................ 26
  3.1.5 Scotchbond Universal Adhesive .................................................. 27
  3.1.6 RelyX Ultimate ........................................................................ 27
3.2 Methods ........................................................................................... 29
  3.2.1 Sample Size Calculation .............................................................. 29
  3.2.2 Sample Preparation .................................................................... 30
    3.2.2.1 Ceramic Material ................................................................. 30
    3.2.2.2 Ceramic Resin Composites .................................................... 42
3.2.2.3  Resin Cement........................................................................................................47
3.2.3  Surface Treatment..................................................................................................48
3.2.4  Cementation Protocol............................................................................................50
3.2.5  Storage Media .......................................................................................................51
3.2.6  Determination of Interfacial $K_{IC}$ ....................................................................52
3.2.7  Scanning Electron Microscopy .............................................................................55
3.2.8  Statistical Analysis ................................................................................................56

Chapter 4: Results.........................................................................................................57

4.1  SEM Analysis ............................................................................................................61
    4.1.1  Lava Ultimate.....................................................................................................61
        4.1.1.1  Sandblasting...............................................................................................61
        4.1.1.2  Surface Silicatisation Sample ..................................................................63
    4.1.2  Enamic ...............................................................................................................66
    4.1.3  IPS e.max Press..................................................................................................68
    4.1.4  RelyX Ultimate Cement ..................................................................................71

Chapter 5: Discussion....................................................................................................73

Chapter 6: Conclusion....................................................................................................82

References......................................................................................................................83
List of Tables

Table 1: Experimental Materials.................................................................................................................................................. 23
Table 2: Composition of ceramic part ......................................................................................................................................... 25
Table 3: Composition of RelyX Ultimate...................................................................................................................................... 28
Table 4: Mechanical properties of tested materials ................................................................................................................ 28
Table 5: Experimental Design ......................................................................................................................................................... 30
Table 6: Sprueing guidelines (Ivoclar-Vivadent, Liechtenstein)................................................................................................. 34
Table 7: Preheating parameters (Ivoclar-Vivadent, Liechtenstein).............................................................................................. 36
Table 8: Press parameters for IPS e.max Press (Ivoclar-Vivadent, Liechtenstein)................................................................. 39
Table 9: Results of $K_{IC}$ tests (Mean ± SD) in MPa$m^{1/2}$ ......................................................................................................... 57
Table 10: Scheffé Multiple Comparisons .................................................................................................................................. 59
Table 11: Means for groups in homogeneous subsets – 24 h ................................................................................................. 59
Table 12: Means for groups in homogeneous subsets – 60 d ................................................................................................. 60
List of Figures

Figure 1: Sandblasting (3M ESPE internal data, 2013) ................................................................. 11
Figure 2: Silicatisation (3M ESPE internal data, 2013) ................................................................. 13
Figure 3: Silane chemical structure (3M ESPE internal data, 2013) .............................................. 15
Figure 4: Silanization (3M ESPE internal data, 2013) ................................................................. 15
Figure 6: TEGDMA molecule (Vita-Zahnfabrik internal data, 2013) .............................................. 25
Figure 5: UDMA molecule (Vita-Zahnfabrik internal data, 2013) .............................................. 25
Figure 5: PVS mold ......................................................................................................................... 31
Figure 6: Wax prism ....................................................................................................................... 31
Figure 7: IPS investment ring system (200g) ................................................................................... 32
Figure 8: Wire and positioning wax .............................................................................................. 32
Figure 9: Wax prisms sprued to the base part of the investment ring ........................................... 33
Figure 10: All wax prisms sprued to the base part of the investment rings ................................. 33
Figure 11: Investment rings ready to be invested ......................................................................... 35
Figure 12: Investment rings invested and setting ......................................................................... 35
Figure 13: Investment rings without the silicone ring and ring base and gauge .......................... 36
Figure 14: Investment rings placed in the preheating furnace ..................................................... 37
Figure 15: IPS Alox Plunger being coated with coated with the separator ................................. 37
Figure 16: IPS e.max Press high opacity (OH) ingots ................................................................. 38
Figure 17: Investment rings cooling off after pressing ................................................................. 40
Figure 18: Divesting of pressed triangular prisms ....................................................................... 40
Figure 19: Pressed triangular prisms ......................................................................................... 41
Figure 20: IPS e.max sample ready for surface treatment and bonding ....................................... 42
Figure 21: Enamic (left) and Lava Ultimate (right) CAD/CAM blocks .............................. 42
Figure 22: Resin composite block mounted to the metal slab using sticky wax .................. 43
Figure 23: Low speed Isomet saw .................................................................................. 43
Figure 24: Cutting of Lava Ultimate block using the diamond-wafering blade ................. 44
Figure 25: Enamic sample mounted into the custom jig on top of wheel grinder ............... 44
Figure 26: Cutting of NTP specimen in two halves.......................................................... 45
Figure 27: Cutting steps of Lava Ultimate NTP specimen ............................................... 46
Figure 28: Cutting steps of Enamic NTP specimen ......................................................... 46
Figure 29: Resin cement being dispensed into the plastic mold ....................................... 47
Figure 30: Micro-etcher .................................................................................................... 48
Figure 31: Rocatec Junior blasting module ...................................................................... 49
Figure 32: Acid-etching of Enamic NTP specimen ......................................................... 49
Figure 33: Specimen mounted into the custom jig ......................................................... 50
Figure 35: Bonding of NTP specimen ............................................................................. 51
Figure 34: Cementation procedure ................................................................................. 51
Figure 36: NTP specimen holder .................................................................................... 52
Figure 37: Crack initiation ............................................................................................... 53
Figure 38: NTP specimen holder in mounting with spacer .............................................. 53
Figure 39: NTP specimen loaded for testing .................................................................... 54
Figure 40: SEM samples .................................................................................................. 56
Figure 41: Box plots of the effect of time and surface treatment on interfacial $K_{IC}$ .......... 58
Figure 42: SEM image – Sandblasting (D) / Lava Ultimate ............................................. 61
Figure 43: SEM image – Fractured-surface (D) / Lava Ultimate ....................................... 62
Figure 44: SEM image – Fractured-surface (24h, D) / Lava Ultimate .......................... 62
Figure 45: SEM image – Fractured-surface (60d, D) / Lava Ultimate .......................... 63
Figure 46: SEM image – Silicatisation (S) / Lava Ultimate ........................................ 64
Figure 47: SEM image – Fractured-surface (S) / Lava Ultimate ................................. 64
Figure 48: SEM image – Fractured-surface (24h, S) / Lava Ultimate .......................... 65
Figure 49: SEM image – Fractured-surface (60d, S) / Lava Ultimate .......................... 65
Figure 50: SEM image – Acid-etched / Enamic ................................................................. 66
Figure 51: SEM image – Fractured-surface / Enamic ..................................................... 67
Figure 52: SEM image – Fractured-surface (24h) / Enamic .......................................... 67
Figure 53: SEM image – Fractured-surface (60d) / Enamic .......................................... 68
Figure 54: SEM image – Acid-etched / IPS e.max ......................................................... 69
Figure 55: SEM image – Fractured-surface / IPS e.max ................................................. 69
Figure 56: SEM image – Fractured-surface (24h) / IPS e.max ....................................... 70
Figure 57: SEM image – Fractured-surface (60d) / IPS e.max ....................................... 70
Figure 58: SEM image – Fractured-surface / RelyX resin cement ................................. 71
Figure 59: SEM image – Fractured-surface (24h) / RelyX resin cement ....................... 72
Figure 60: SEM image – Fractured-surface (60d) / RelyX resin cement ....................... 72
Figure 61: Cohesive failure of Lava Ultimate specimen .............................................. 76
Figure 62: Adhesive failure of Enamic specimen ......................................................... 79
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Dedication

To my precious family: Georges, Amal, Jean and Sirine. I thank you for your continuous support and encouragement throughout this journey. You never stopped believing in me and always helped me reach my dreams.

To my future wife: Nadia. I thank you for being always there for me through thick and thin. Distance has kept us away but our love and friendship have always kept us together. I love you.
Chapter 1: Introduction

1.1 Computer-Aided Design / Computer-Aided Manufacturing

Computer-aided design / computer-aided manufacturing (CAD/CAM) is a technology that has been increasing in popularity with its numerous applications in dentistry. The research and development of CAD/CAM systems started in the 1970s and has evolved significantly since. Among the many researchers and developers, three pioneers in particular contributed remarkably to the advancement of CAD/CAM technology.

1.1.1 History

In the 1970s, Dr. Francois Duret of France was the first to use an intra-oral optical impression of an abutment tooth to then design and mill a crown using a numerically controlled milling machine. He is the developer of the Sopha system that was later commercialized\(^1\). Dr. Werner Mörmann of Switzerland was the main developer of the first commercially available CAD/CAM system (in 1985) that was capable of scanning, designing and milling an inlay restoration from a ceramic block using chair-side compact machinery\(^2\). The system was named CEREC, an acronym for Chairside Economical Restoration of Esthetic Ceramics. Lastly, Dr. Matts Andersson of Sweden developed the Procera system (in 1983), capable of milling high-precision crowns\(^3\). Also, he was the first to extend the application of CAD/CAM technology to composite veneer restorations.
With today’s technology and research, CAD/CAM systems have extended their application in dentistry to include designing and manufacturing inlays, onlays, veneers, crowns, fixed partial dentures and implant abutments\(^4\). It is certainly an appealing solution, providing several advantages, impacting all parties involved: the restorative dentist, the dental laboratory and the patient.

### 1.1.2 Advantages of CAD/CAM Technology

Conventional dental laboratory technologies are labor-intensive, time-consuming, potentially costly and require skilled laboratory technicians for the technique-sensitive procedures involved\(^4\). In contrast, the application of CAD/CAM technology is potentially more effective and provides several advantages. The intra-oral scanning has the potential to be faster and easier than conventional impression, with the advantage of allowing selective re-scanning of only certain areas rather than retaking full impressions\(^4\). The complete process of designing and manufacturing of the restoration is done digitally, which eliminates casts, wax-ups, investing, casting and firing. As a result, savings in time and labor provide financial benefits for the patient by reducing the cost of the restoration\(^5\). Moreover, the quality of CAD/CAM blocks is more consistent than that of conventional powder build-up and baked porcelain products since they have considerably less internal defects\(^6\). Also, the software-based designing process ensures proper thickness of the restoration depending on the material used, providing added quality control. Lastly, the processing data can be saved and stored digitally, eliminating the need for physical space to store multiple casts that could degrade or be damaged over time\(^5\).
1.1.3 Disadvantaged of CAD/CAM Technology

CAD/CAM systems also have disadvantages. The initial cost of all the necessary equipment and software is quite high. In order to be cost-effective and a lucrative investment, the restorative dentist needs to process a considerable volume of restorations using the technology. Moreover, the learning curve for the practitioner could be difficult, requiring several hands-on learning sessions prior to in-office use\textsuperscript{4, 6}.

Depending on the restoration, the scanning of the finish lines could require the same type of soft-tissue management as conventional impression, including retraction, moisture control and hemostasis\textsuperscript{5}. Therefore, the speed at which the digital impression is taken is dependent on the type of restoration and the experience of the operator\textsuperscript{6}.

1.2 Dental Biomaterials

Dental biomaterials are defined as synthetic products used for restoring compromised teeth or replacing missing teeth\textsuperscript{5}. Innovative dental biomaterials with improved properties are being continuously developed and introduced to practitioners. The advanced CAD/CAM technology led to the development and introduction of new dental biomaterials that have different properties and are indicated for various applications\textsuperscript{6}. 
1.2.1 Dental Ceramics

Ceramics are defined as heat resistant, non-metallic, inorganic, crystalline solid structures that contain metallic and non-metallic elements linked by ionic and/or covalent bonds. The traditional ceramics consist of three basic components: clay (Al₂O₃·2SiO₂·2H₂O) — acting as plasticizer, silica (SiO₂) — acting as a refractory component, and feldspars (MO·Al₂O₃·4SiO₂) — acting as the matrix. The mix of these components forms a pasty material that can be easily shaped and fired to create a ceramic object⁷.

In contrast, a glass is defined as a non-metallic, inorganic solid in which its composing elements are heated to fusion and then cooled to a rigid solid without crystallization. When different ceramic components are embedded into a glassy matrix, the material is termed porcelain, or glass-ceramic⁷,⁸.

It is important to mention that the term “dental ceramics” is not clearly defined and it is used vaguely in the dental literature. The terms ceramics and glass-ceramics will be used in this thesis.

1.2.1.1 History

The history of dental ceramics started with the first all-ceramic crown reported by Charles H. Land in 1886 and known as the porcelain jacket crown. He described a method for fabricating the porcelain jacket crown using a platinum foil matrix on which high-fusing feldspathic porcelain was fired⁹. Later, in 1965, McLean and Hughes developed a porcelain jacket crown
with an inner core of aluminous porcelain containing (40 – 50) % alumina crystals (Al₂O₃) to block the propagation of cracks, which improved its strength significantly¹⁰. However, the use of such restorations was limited by significant clinical failure due to their brittleness, low tensile strength and wear resistance, in addition to inadequate marginal accuracy⁷.

Another development in the 1950s led to the creation of the castable Dicor (Dentsply International) crown system. Glass was strengthened with various forms of mica. Dicor was composed of 55 % tetrasilic fluormica crystals precipitated in 45 % glass matrix⁹. The processing method was based on the lost-wax technique with the transformation of the casting through heat to form tetrasilic fluormica crystals within the glass matrix, resulting into an increase of the strength and toughness of the glass-ceramic. The processing difficulties and high incidence of fracture due to low flexural strength were factors that led to the abandonment of this system.

Today, several types of ceramics with different properties are available and indicated for specific applications. One clinically relevant classification of all-ceramic systems is based on the ability to be etched and bonded⁸.

1.2.1.2 The Etched and Bonded Ceramics

The etched and bonded ceramics are glass-ceramics with an amorphous matrix derived from the natural mineral feldspar reinforced with silica and/or various other fillers to improve mechanical properties. Due to their high mechanical properties, they have the advantage of offering the most
conservative of the tooth-colored indirect restorative option and have minimal demands for retention and resistance form in tooth preparation\textsuperscript{11}. These ceramics are etched with hydrofluoric acid and bonded using resin cements.

Feldspathic porcelain contains a variety of oxide components including silica (SiO\textsubscript{2}), alumina (Al\textsubscript{2}O\textsubscript{3}), potash (K\textsubscript{2}O), soda (Na\textsubscript{2}O) and certain additives. It contains a glass matrix with silica, its main oxide component, acting as filler\textsuperscript{12}.

Leucite-reinforced glass ceramic contains up to 45 vol\% of leucite (KAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{6}) crystals. The presence of leucite strengthens the feldspathic porcelain because the greater expansion of leucite generates compressive stresses in the glassy phase during cooling\textsuperscript{8}. These stresses increase the resistance to crack propagation by acting as crack deflectors. The high leucite content increases the coefficient of thermal expansion, and flexural (104 MPa) and compressive strength\textsuperscript{13}. Leucite-reinforced glass ceramic restorations are fabricated using different methods: sintering, heat-pressing or CAD/CAM\textsuperscript{8}.

Lithium disilicate-reinforced glass ceramic contains about 65 vol\% of lithium disilicate (Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}) crystals. The material is heat-pressed at around 920 °C, producing a microstructure of highly interlocked prismatic lithium disilicate crystals (5.2 µm in length and 0.8 µm in diameter) dispersed in a glassy matrix (Ivoclar-Vivadent internal data, 2005). Similar to leucite-reinforced glass ceramic, the thermal expansion mismatch between the lithium disilicate crystals and the glassy matrix contribute to the enhanced mechanical properties\textsuperscript{14}. Lithium disilicate-reinforced
glass ceramic has the advantage of a significantly increased flexural strength (around 300 MPa) and fracture toughness (2.9 MPa · m$^{1/2}$) and can be fabricated by press-heating or CAD/CAM.

1.2.1.3 The Non-etched Ceramics

The non-etched ceramics have the advantage of high strength but poor esthetics when compared to the previous materials. Due to the lack of a silica-based glass matrix in their composition, they cannot be etched to provide a micro-retentive surface. Therefore, other methods, such as sandblasting, are available to create such surface. A luting agent is used to cement non-etched ceramic restorations.

Alumina-reinforced ceramics contains 68 vol% alumina particles, 27 vol% glass and 5 vol% porosity. They are fabricated using the slip-casting technique which consists of condensing a porcelain slip, aqueous slurry containing 90% alumina particles between 0.5 µm and 3.5 µm in size, on a porous refractory die. Through capillary action, the water is absorbed from the slip by the porosity of the refractory die. The process involves drying followed by multiple firings at specific temperatures of the porous alumina coping, which is thereafter infiltrated with a lanthanum-containing glass. The result consists of a microstructure of two interpenetrating networks, one formed by the crystalline infrastructure and the other being the glass phase. A densely sintered alumina-reinforced ceramic restoration has a flexural strength of around 600 MPa.
Zirconia-reinforced ceramics are polycrystalline without a glassy phase. The stable form of zirconia is monoclinic at room temperature, then during sintering, changes its crystallinity to tetragonal and cubic crystalline\(^5\). Pure zirconia has a monoclinic structure at room temperature which is stable up to 1170°C. Between this temperature and 2370°C, tetragonal zirconia is formed, while cubic zirconia is formed at temperatures above 2370°C. The cooling of cubic or tetragonal normally results in reverse transformation associated with increase in volume which results in the shattering of the solid structure\(^6\).

Different oxides, such as yttrium oxide (Y\(_2\)O\(_3\)), calcium oxide (CaO) or magnesium oxide (MgO), can be added to zirconia to stabilize it in its tetragonal phase at room temperature, thus avoiding the volume increase due to the tetragonal to monoclinic phase (t→m) transformation\(^7\). The addition of varying amounts of stabilizers allows the formation of partially stabilized zirconia which result in ceramics with exceptional properties such as high flexural strength and fracture toughness, high hardness, excellent chemical resistance and good ionic conductivity\(^6\).

In dental applications, the most common method of stabilizing the tetragonal phase and maintaining zirconia in a metastable condition at room temperature is by adding a small amount of yttria (3 mol\%). It creates a multiphase structure consisting of tetragonal and cubic zirconia in majority with monoclinic precipitated in small amounts\(^8\).

A property unique to yttrium-stabilized polycrystalline tetragonal zirconia is that of phase transformation. It is defined as stress-induced phase transformation (t→m) accompanied by a volumetric expansion of approximately 4 % adjacent to the crack, creating compressive stress.
that shields the crack tip from the applied stress, stopping it from propagating and thus enhances the fracture toughness of the material\textsuperscript{19}.

### 1.2.2 Ceramic Resin Composites

Indirect resin composite blocks have been recently introduced for CAD/CAM application as an alternative to ceramics. They present the advantage of being cost-effective, easier to process and to repair when compared to ceramics blocks\textsuperscript{20}. Their mechanical and physical properties are improved when compared to direct resin composite materials by minimizing the effect of polymerization shrinking by industrial polymerization under standardized high pressure and temperature, therefore showing reduced deficiencies and increased degree of conversion\textsuperscript{21}. Moreover, they provide a simple and efficient way for creating functional and anatomical shapes in large defects. Most importantly, clinical indications for indirect composite restorations are based on the evaluation of the remaining tooth structure, intraoral conditions, and cost\textsuperscript{22}.

The successful function and longevity of these indirect ceramic and resin composite restorations depends greatly on their bonding to tooth structure. Two adhesive interfaces are involved: the one between dentin/enamel and the adhesive resin cement layer, and the one between the ceramic resin composite and the adhesive resin cement layer\textsuperscript{21}.

A durable and resilient adhesive bond could offer a predictable and clinically successful restoration. It could provide adequate retention, prevent microleakage leading to secondary
caries and sensitivity, enhance marginal adaptation and could increase fracture resistance of the restored tooth\textsuperscript{23, 24}.

In the adhesive assembly, failure occurs at the weakest link, either adhesively at either one of the two interfaces, or cohesively within the adhesive cement. Therefore, with the introduction of new materials, the adhesive resin bond and its components have to be constantly improved and adapted to remain compatible.

1.3 Bonding to Dental Materials

In the scientific dental literature, protocols of resin-bonding to silica-based ceramics are well documented. However, very limited information is available about the surface treatment and bonding properties/behavior between resin composite blocks and adhesive resin cements\textsuperscript{25}. Several studies have reported on the effect of surface conditioning using different methods, such as air-particle abrasion using different size and type particles, hydrofluoric acid etching, and priming using a silane coupling agent\textsuperscript{25}.

Bonding of resin composite to silica-based materials is achieved effectively through priming by the application of silane coupling agents. Silanes are used to promote adhesion to ceramic restorations and mediate repair with resin composites\textsuperscript{26}. However, for non-silica based materials, such as resin composite blocks, the application of silane only is not sufficient for a predictable bonding with resin composite cements.
To solve this problem, different surface treatments have been introduced to promote better interaction between dissimilar inorganic and organic materials. Surface conditioning of dental materials consists of a treatment of the surface resulting into an increase in surface roughness / energy and creation of micropores for infiltration of silane and resin cements.

1.3.1 Conditioning

1.3.1.1 Sandblasting

One of the most common methods of conditioning polymeric materials is the use of airborne-particle abrasion. It has the main objective of cleaning the surface prior to bonding and increasing the surface area\textsuperscript{27}. Alumina particles of varying sizes (50 – 120 µm) are blasted onto the surface under air pressure (around 380 kPa) for around 10 – 15 s from a perpendicular short distance (10 – 15 mm) from the surface\textsuperscript{28}. The parameters of the sandblasting procedure should be carefully set according to the manufacturer’s recommendations to avoid damaging the surface.

![Sandblasting Diagram](image)

**Figure 1: Sandblasting** (3M ESPE internal data, 2013)
and embedding alumina particles into the surface, which may negatively impact the bond strength. It has been reported that a higher blasting pressure and higher amount of embedded alumina could lead, after silanization, to the formation of Al-O-Si bonds which are unstable and weaker compared to Si-O-Si bonds\textsuperscript{29}.

1.3.1.2 Surface Silicatisation

The Rocatec system (3M ESPE, Seefeld, Germany) was introduced in Germany in 1989. It consists of a tribochemical method for silicatising surfaces. Tribochemistry involves creating chemical bonds by applying mechanical energy (3M ESPE internal data, 2005). This supply of energy may take the form of grinding or sandblasting. There is no application of heat or light which would normally be the case with chemical reactions. For this reason, the Rocatec system may also be referred to as cold silicatisation because the mechanical energy is transferred to the substrate in the form of kinetic energy and the silicatisation takes place macroscopically without any change in temperature (3M ESPE internal data, 2005).

The tribochemical coating of the microblasted surface with silica-modified aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) is accomplished using either 110 µm or 30 µm blast grit. The aluminum oxide sand particles of different grits are coated with a thin layer of silicon dioxide (SiO\textsubscript{2})\textsuperscript{30}. With substrates that are highly susceptible to abrasion, such as resin blocks, the use of the 30 µm silica-modified aluminum oxide (Rocatec Soft, 3M ESPE) is indicated\textsuperscript{26}. 
Silicatisation of the blasted surface takes place when the grains hit the surfaces creating transfer of impulses and energy. The affected surfaces of the substrate and grit in the atomic and molecular ranges are excited to such extent that a so-called “triboplasma” forms\textsuperscript{31, 32}.

The SiO\textsubscript{2} is impregnated into the surface up to a depth of 15 µm and at the same time is fused to the surface in islands. The high level of required energy is created by the acceleration of the grains to velocity of up to 1000 km/h due to the geometry of the blast nozzle and a blast pressure of at least 2.8 bar (0.28 MPa) (3M ESPE internal data, 2005).

![Figure 2: Silicatisation (3M ESPE internal data, 2013)](image)

### 1.3.1.3 Acid Etching

Hydrofluoric acid reacts with the silica matrix of silica-based ceramics leading to the creation of a porous structure on the ceramic surface\textsuperscript{29}. The first reaction leads to the formation of volatile silicon tetrafluoride,

\[
4 \text{ HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2 \text{H}_2\text{O}
\]

Hydrofluoric Acid \quad Silica Matrix \quad Silicon Tetrafluoride \quad Water
The hydrofluoric acid reacts further with the formed silicon tetrafluoride to form hexafluorosilicate, a soluble complex ion,

\[
2 \text{HF} + \text{SiF}_4 \rightarrow \left[\text{SiF}_6\right]^{2-} + 2 \text{H}^+
\]

Hydrofluoric Acid  Silicon Tetrafluoride  Hexafluorosilicate  Hydrogen ions

The hydrogen ions react with the hexafluorosilicate to form fluorosilic acid that can be rinsed off,

\[
\left[\text{SiF}_6\right]^{2-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{SiF}_6
\]

Hexafluorosilicate  Hydrogen ions  Fluorosilic acid

By dissolving and removing the glassy matrix that contains silica, the ceramic surface becomes porous, creating a micro-retentive surface. The surface topography left after etching depends on the ceramic microstructure and composition, the type and concentration of the acid, and the duration of acid etching.

1.3.2 Priming

The coated surface is primed, using silane, in order to create a chemical bond with the resin. The silane coupling agent used in dentistry is 3-methacryloxypropyltrimethoxysilane, which has three hydrolysable methoxy groups attached to the silicon atom (Figure 3).

The bifunctional hydrophobic silane monomer has one backbone end containing a non-hydrolysable methacrylate group with a vinylic carbon-carbon double bond (\(-\text{CH}═\text{CH}_2\)), while
the other end consists of relatively fast hydrolysable alkoxy groups (-O-CH₃). Once activated by hydrolysis, the alkoxy groups form hydrophilic labile silanol groups (≡Si-OH)²⁸.

![Silane chemical structure](image)

**Figure 3: Silane chemical structure** (3M ESPE internal data, 2013)

During the silane application onto the substrate surface, the free hydrophilic labile silanol groups form hydrogen bonding with the hydroxyl groups (-OH) of the silica substrate surface. Through condensation, the silanol groups link with HO-(substrate) present on the surface to form –Si-O-(substrate)- linkages. Moreover, the silanol groups react with each other to form hydrophobic siloxane bonds –Si-O-Si–²⁸. On the other end, the reactive functional groups of the resin composite (C=C) react with the organofunctional groups of the silane coupling agent creating a linkage between resin composite and substrate surface⁷, 2³, ²⁸.

![Silanization](image)

**Figure 4: Silanization** (3M ESPE internal data, 2013)
1.4 Testing of Adhesion

Dental biomaterials and adhesive interfaces have been tested in the laboratory using different methodologies in order to predict their clinical performance. This section presents an overview and a critique of the commonly used bond strength tests used in dental research.

1.4.1 Bond Strength Testing

Bond strength testing has been traditionally accomplished by loading a test specimen to failure in either shear or tension. Furthermore, the test specimen dimension/bonding area classifies the bond strength test as being micro- or macro-. As a result, bond strength testing has several variations, namely: macro-shear bond strength (SBS), macro-tensile bond strength (TBS), micro-shear bond strength ($\mu$SBS) and micro-tensile bond strength ($\mu$TBS). The International Organization for Standardization (ISO) technical specification ISO/TS 11405 describes in great details the characteristics and preparations involved in the bonding procedures. However, the details regarding the bonding area, testing assemblies and loading conditions are vague. Consequently, the protocols of the different bond strength experimental research vary greatly among studies. As a consequence, the ability to compare results from different studies is quite difficult. SBS technique has the advantage of being an easy and fast testing method, requiring no further specimen processing post-bonding procedure. It is a convenient method, easy to perform, requiring minimal equipment and specimen preparation. In contrast, TBS is less popular because of the more time-consuming methodology and laborious sample preparation involved.
Multiple limitations and flaws are incorporated in the SBS technique. Several variables of influence related to the specimen design and to test mechanics have been identified\textsuperscript{35}. The *bonding area* is variable among studies and has a direct influence on the bond strength. The larger the bonding area, the lower is the bond strength of the specimen because of a higher probability of a critical size flaw being present in the larger bonding area. Furthermore, the type of loading and test design has a great impact on the SBS results recorded \textsuperscript{35}. Most importantly, it has been shown that the shear stress distribution is not uniform and not entirely concentrated at the interface, which greatly questions the validity of such test\textsuperscript{37}.

The validity of SBS method was further questioned during investigation of resin-ceramic bonding\textsuperscript{38}. By keeping the geometric design and adhesive interface identical, the results of SBS testing differed upon the modification of the specimen configuration. In other words, the modification of one of the parameters that are inherent to the SBS testing method resulted in an evident effect on the outcome.

To further demonstrate the wide variety of experimental protocols among the studies, in a recent survey of 100 SBS and TBS studies published between 2007 and 2009, the authors found no consensus of the parameters discussed previously\textsuperscript{35}.

In 1994, Sano et al. developed the µTBS. It differs from the TBS with the tested bonding area being much smaller, about 1 mm$^2$ or less\textsuperscript{39}. The test result is calculated by dividing the tensile load at failure by the cross-sectional area of the bonded interface. Similarly, any change in the
testing variables, such as the specimen shape, bond area and gripping device specification, could result in different outcomes, making the comparison between studies of little value. In a survey of 90 published papers of µTBS studies, only 10% described in detail the experimental protocol\textsuperscript{40}.

µTBS testing has numerous advantages, making it more versatile. It has a more uniform stress distribution at the adhesive interface and it minimizes the influence of interfacial defects\textsuperscript{39}. It has fewer cohesive failures and the bond strengths are higher than those measured from macro-bond strength testing due to the lower probability of defects present in the substrate at the bond interface. Moreover, accelerated environmental aging by storage in water is available due to the short diffusional distance. Also, scanning electron microscopy (SEM) fractography can be readily performed to evaluate the mode of failure\textsuperscript{40}.

Some of its limitations include more laborious and technically demanding specimen preparation, with considerable amount of pre-testing failure\textsuperscript{36}. Specimens are more difficult to fabricate with consistent geometry and surface finish without the use of special equipment and specimens could be easily damaged and dehydrated\textsuperscript{41}.

In conclusion, bond strength test (BST) does no quantify an inherent material property of the bond between two materials. The results obtained from a BST are dependent inherently on the parameters of the test itself. As a result, the validity of a BST is highly questionable because “no amount of standardization will overcome inconsistency problems if a test is fundamentally flawed”\textsuperscript{42}.

18
1.4.2 Fracture Mechanics

As an alternative to BST, a fracture mechanics approach has been suggested to measure an intrinsic adhesive property\(^{40}\). More specifically, an interfacial fracture mechanics approach studying the failure of a bond interface by initiation and crack propagation, such as fracture toughness test, would be a more appropriate test method for assessing adhesion\(^{43}\).

During the loading of an adhesive joint, the adhesive and bonded substrata are deformed by the applied forces, disrupting the adhesive bonds at the interface and resulting in the creation of new surfaces. Fracture/failure occurs when the applied forces create enough energy to exceed the work of adhesion by breaking the interfacial bonds, which depends only on the number and type of bonds disrupted at the interface. Fracture mechanics measures the energy needed to create new fracture surfaces in a controlled environment. Thus, it measures intrinsic adhesive properties, independent of joint geometry\(^{44}\).

Fracture toughness is defined as the resistance of a brittle material to crack propagation from existing defects/flaws under an applied force\(^8\). In 1964, George Rankine Irwin defined a parameter representing the stress field around a sharp crack in a linear-elastic material. This parameter was named the stress intensity factor \(K\) and is independent of the material. He stated that fracture occurs when the value of \(K\) exceeded a critical value \(K_c\). The latter is a measure of an inherent material property\(^{44}\).
Three different load conditions can be applied to the test specimen. Mode-I represents tensile forces, mode-II represents shear forces and mode-III represents torsional forces. Therefore, $K_{IC}$ represents the critical intensity facture value for crack growth in a brittle material during tensile loading/mode-I failure\textsuperscript{44}.

Several test configurations are available to evaluate fracture toughness. A widely used test approach has been the chevron-notched short rod (CNSR) test, introduced by Baker in 1979\textsuperscript{8}. It consists of cutting a chevron notch inside a cylindrical specimen. The specimen preparation could be technically challenging and time-consuming, especially when testing brittle materials.

Ruse et al. in 1996 introduced a novel approach for evaluating fracture toughness and interfacial fracture toughness using a notchless triangular prism (NTP) specimen that, when placed in the specimen holder, reproduces the configuration of the standardized CNSR test. This method overcomes the difficulties of the CNSR and has been recognized as a valid alternative\textsuperscript{44,45}.

It consists of NTP specimen of dimensions (6x6x6x12 mm or (4x4x4x8) mm fitted in a custom holder to mount the specimen into a holder while a nominated bar is used to create a standardized space between the specimen holder halves. A defect, of approximately 100 μm, is introduced at the level of the adhesive interface, under magnification, to facilitate crack initiation. The assembly is then tested under tensile mode in a universal testing machine at a cross speed of 0.1 mm/min (Instron model 4301, Instron Canada, Inc.) until fracture or crack arrest.
The value for $K_{IC}$ is calculated using the standard formula:

$$K_{IC} = \frac{P_{\text{max}}}{DW^{1/2}} Y_{\text{min}}^*$$

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$^{45}$.

### 1.5 Clinical Significance

With the increasing popularity of CAD/CAM technology, specific bonding protocols for the different CAD/CAM restorations have been developed for various luting systems. The long term clinical survival of these restorations depends on the CAD/CAM system, the type of restoration, the selected material and the luting agent$^{46}$. When it comes to ceramic restorations, the clinical success is heavily dependent on the cementation procedure$^{47}$. Laboratory tests under standardized testing conditions provide crucial information before clinical use and/or testing of new materials$^{25}$.
Chapter 2: Research Protocol

2.1 Specific Aims

The goal of this study was to apply fracture mechanics methodology to assess the effect of surface preconditioning on the short and long term adherence between a widely used adhesive resin luting cement (RelyX Ultimate, 3M ESPE) and recently introduced CAD/CAM materials: two ceramic resin composites (Lava Ultimate – 3M ESPE and Enamic – Vita-Zahnfabrik) and a ceramic (IPS e.max Press – Ivoclar-Vivadent, Liechtenstein).

2.2 Research Hypotheses

H01: There is no significant difference in interfacial $K_{IC}$ between bonded Lava Ultimate preconditioned by sandblasting and bonded Lava Ultimate preconditioned by silicatisation.

H02: There is no significant difference in interfacial $K_{IC}$ between bonded Lava Ultimate, Enamic and IPS e.max.

H03: Water storage at 37 °C for 60 days does not affect the interfacial $K_{IC}$ of the adhesive interfaces tested.

H04: There is no difference in interfacial crack propagation path between bonded Lava Ultimate, Enamic and IPS e.max.

H05: Water storage at 37 °C for 60 days does not affect the $K_{IC}$ of the adhesive resin cement.
Chapter 3: Materials and Methods

3.1 Materials

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

Table 1: Experimental Materials

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Material Description</th>
<th>Lot Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic resin composites</td>
<td>Lava Ultimate (3M ESPE)</td>
<td>LOT 510200</td>
</tr>
<tr>
<td></td>
<td>Enamic (Vita-Zahnfabrik)</td>
<td>LOT 540433</td>
</tr>
<tr>
<td>Glass-ceramic</td>
<td>IPS e.max Press (Ivoclar-Vivadent, Liechtenstein)</td>
<td>LOT P36594</td>
</tr>
<tr>
<td>Silane coupling agent</td>
<td>Scotchbond Universal Adhesive (3M ESPE)</td>
<td>LOT 475514</td>
</tr>
<tr>
<td>Adhesive resin cement</td>
<td>RelyX Ultimate (3M ESPE)</td>
<td>LOT 156882</td>
</tr>
<tr>
<td>Acid</td>
<td>5% HF acid (IPS ceramic etching gel; Ivoclar-Vivadent, Liechtenstein)</td>
<td>LOT S07435</td>
</tr>
<tr>
<td>Air abrasion particles</td>
<td>27 micron Al₂O₃ (3M ESPE)</td>
<td>LOT 28482</td>
</tr>
<tr>
<td></td>
<td>30 micron silica-modified Al₂O₃ (3M ESPE)</td>
<td>LOT 450384</td>
</tr>
</tbody>
</table>

3.1.1 Lava Ultimate

The material is composed of a resin matrix reinforced with silica and zirconia fillers. It contains silica nanomers of 20 nm diameter and zirconia nanomers of (4 – 11) nm diameters. The engineered nanoparticles are treated with a silane coupling agent using a proprietary method. The
silane coupling agent bonds chemically to the nanoparticles surface and also bonds chemically to the resin matrix during the manufacturing of the blocks. To allow incorporation of higher proportion of the fillers into the resin matrix, zirconia-silica nanoclusters are incorporated by aggregation of the same engineered nanoparticles. The average nanoclusters size is (0.6 – 10) µm.

As a result, the material is formulated using both nanomers and nanocluster fillers (80 wt%) embedded into a resin matrix (20 wt%). Processing involves multiple hours in a special heat treatment process. The addition of nanomer particles to formulations containing nanoclusters reduces the interstitial spacing of the filler particles leading to the high filler content (3M ESPE internal data, 2013).

3.1.2 Enamic

The structure of Enamic is a double interpenetrating network that consists of a controlled porosity-sintered ceramic matrix, the pores of which are filled with a polymer material. The ceramic network accounts for 75 vol% (86 wt%). The composition of the ceramic corresponds to that of a fine-structure feldspar ceramic enriched with aluminum oxide (Table 2).
### Table 2: Composition of ceramic part

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide</td>
<td>SiO₂</td>
<td>58 – 63 %</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>Al₂O₃</td>
<td>20 – 23 %</td>
</tr>
<tr>
<td>Sodium oxide</td>
<td>Na₂O</td>
<td>9 – 11 %</td>
</tr>
<tr>
<td>Potassium oxide</td>
<td>K₂O</td>
<td>4 – 6 %</td>
</tr>
<tr>
<td>Boron trioxide</td>
<td>B₂O₃</td>
<td>0.5 – 2 %</td>
</tr>
<tr>
<td>Zirconium dioxide</td>
<td>ZrO₂</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>CaO</td>
<td>&lt; 1 %</td>
</tr>
</tbody>
</table>

The polymer component is composed of urethane dimethacrylate (UDMA, Figure 5) and triethyleneglycol dimethacrylate (TEGDMA, Figure 6).

**Figure 5: UDMA molecule** (Vita-Zahnfabrik internal data, 2013)

**Figure 6: TEGDMA molecule** (Vita-Zahnfabrik internal data, 2013)
### 3.1.3 IPS e.max

The microstructure of the pressable lithium disilicate (Li$_2$Si$_2$O$_5$) material consists of approximately 70 vol% of needle-like lithium disilicate crystals that are crystallized in a glassy matrix. These crystals measure approximately 3 µm to 6 µm in length.

The IPS e.max Press ingots are composed mainly of quartz, lithium dioxide, phosphor oxide, alumina, and potassium oxide. The mix of these oxides produces a glass melt. Once the proper viscosity is achieved, the glass melt is poured into a separable steel mould of the proper shape and left to cool to room temperature to produce glass ingots. This process minimizes the presence of internal defects/flaws within the material. The glass ingots are then nucleated and crystallized in one heat treatment to produce the final ingots. The process consists of a controlled nucleation process where lithium meta-silicate crystals are completely dissolved (after precipitation) and the lithium disilicate is crystallized. The ingots are then pressed at approximately 920 °C for (5 – 15) minutes to obtain the restoration (Ivoclar-Vivadent internal data, 2013).

### 3.1.4 IPS Ceramic Etching Gel

The etching gel contains 4.5 % hydrofluoric acid (HF). It is indicated for preconditioning of the bonding surfaces of etchable glass ceramics to increase micro-retention.
3.1.5 Scotchbond Universal Adhesive

The adhesive is composed of methacryloxydecyl phosphate (MDP) monomer, methacrylate-modified polyalkenoic acid copolymer, 2-hydroxyethyl methacrylate (HEMA), silane, dimethacrylate resins, filler, ethanol, water and inhibitors. The first four components contain active functional groups and are intended to provide chemical bonding to hard tooth tissues and any restorative material.

3.1.6 RelyX Ultimate

RelyX Ultimate is a dual-cure resin cement indicated for adhesive cementation of glass-ceramic, composite and metal restorations. It contains mixture of dimethacrylates and proprietary components (Table 3). While the RelyX Ultimate is marked as “adhesive resin cement”, the fact that it has to be used in conjunction with adhesive systems suggests that it is not an adhesive resin cement but just a resin cement. The proportion of inorganic fillers is about 43 % by volume, with an average filler particle size is about 13 µm. The mixing ratio, based on the volume, is 1 part paste: 1 part catalyst. It has a working time from start of mixing of 2 minutes and 30 s, with a setting time after start of mixing of 6 minutes.
### Table 3: Composition of RelyX Ultimate

<table>
<thead>
<tr>
<th>Base Paste</th>
<th>Catalyst Paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methacrylate monomers</td>
<td>Methacrylate monomers</td>
</tr>
<tr>
<td>Radiopaque, silanated fillers</td>
<td>Radiopaque alkaline (basic) fillers</td>
</tr>
<tr>
<td>Initiator components</td>
<td>Initiator components</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>Stabilizers</td>
</tr>
<tr>
<td>Rheological additives</td>
<td>Pigments</td>
</tr>
<tr>
<td></td>
<td>Rheological additives</td>
</tr>
<tr>
<td></td>
<td>Fluorescence dye</td>
</tr>
<tr>
<td></td>
<td>Dual-cure activator for single bond universal adhesive</td>
</tr>
</tbody>
</table>

Mechanical properties of the different materials are summarized in Table 4.

### Table 4: Mechanical properties of tested materials

<table>
<thead>
<tr>
<th></th>
<th>Lava Ultimate</th>
<th>Enamic</th>
<th>IPS e.max Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural Strength (MPa)</td>
<td>204</td>
<td>150 – 160</td>
<td>400</td>
</tr>
<tr>
<td>Fracture Toughness (MPa · m^{0.5})</td>
<td>2.02</td>
<td>1.5</td>
<td>2.75</td>
</tr>
<tr>
<td>Modulus of Elasticity (GPa)</td>
<td>12.77</td>
<td>30</td>
<td>95</td>
</tr>
</tbody>
</table>
3.2 Methods

3.2.1 Sample Size Calculation

A power analysis was used to calculate the sample size \( n \) needed for K\textsubscript{IC} test with \( \alpha = 0.05 \), power of 80\% and a standardized difference (\( \Delta \)) of 1.1.

Lehr’s basic formula was used to obtain \( n \) value:

\[
n = \frac{16}{\Delta^2}
\]

Where

\[
\Delta = \frac{\delta}{\sigma}
\]

Where \( \delta \) is the target difference and \( \sigma \) is the standard deviation. In order to be able to detect a difference of 20\% between the groups, the calculated sample size was 13 and 15 samples per group were made.
The experimental design is summarized in Table 5.

### Table 5: Experimental Design

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Treatment</th>
<th>Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>24 hours</td>
</tr>
<tr>
<td>Lava Ultimate</td>
<td>A) Sandblasting with 27 µm Al₂O₃ + adhesive</td>
<td>n = 15</td>
</tr>
<tr>
<td></td>
<td>B) Silicatisation using 30 µm silica-modified Al₂O₃ +</td>
<td>n = 15</td>
</tr>
<tr>
<td></td>
<td>adhesive</td>
<td></td>
</tr>
<tr>
<td>Enamic</td>
<td>HF acid-etching + adhesive</td>
<td>n = 15</td>
</tr>
<tr>
<td>IPS e.max Press</td>
<td>HF acid-etching + adhesive</td>
<td>n = 15</td>
</tr>
<tr>
<td>RelyX Ultimate</td>
<td></td>
<td>n = 10</td>
</tr>
</tbody>
</table>

#### 3.2.2 Sample Preparation

#### 3.2.2.1 Ceramic Material

The fabrication process started with the preparation of thirty (6x6x6x13) mm wax prisms using a mold. The mold (Figure 7) was made using a (6x6x6x13) mm plexiglass prism impressed using medium body polyvinylsiloxane (PVS) impression material (Aquasil, Dentsply, York, PA). The length of the wax prisms were between 13 mm and 14 mm so that after pressing, cutting and bonding the length was larger than 12 mm. After setting of the PVS material, the plexiglass prism was retrieved leaving a space into which the melted dipping wax was poured.
Figure 5: PVS mold

Figure 6: Wax prism
The wax prims (Figure 8) were pressed at the Ivoclar-Vivadent research facility (Amherst, NY). The process started by sprueing four wax prisms using wire and positioning wax (Figure 10) (ABF-wax, Metalor, Canada). The IPS investment ring system (200g) (Figure 11) was used following the manufacturer guidelines summarized in Table 6.
Figure 9: Wax prisms sprued to the base part of the investment ring

Figure 10: All wax prisms sprued to the base part of the investment rings
Table 6: Sprueing guidelines (Ivoclar-Vivadent, Liechtenstein)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring base</td>
<td>200 g</td>
</tr>
<tr>
<td>Diameter of wax wire</td>
<td>2.5 – 3 mm</td>
</tr>
<tr>
<td>Length of the wax wire</td>
<td>min. 3 mm, max. 8 mm</td>
</tr>
<tr>
<td>Length of the wax wire including waxed-up object</td>
<td>max. (15 to 16) mm</td>
</tr>
<tr>
<td>Sprue angle at the waxed-up object</td>
<td>Axial</td>
</tr>
<tr>
<td>Sprue angle to the ring base</td>
<td>45° to 60°</td>
</tr>
<tr>
<td>Distance between the objects</td>
<td>min. 3 mm</td>
</tr>
<tr>
<td>Distance to silicone ring</td>
<td>min. 10 mm</td>
</tr>
</tbody>
</table>

Investing (Figures 13 and 14) was carried out using IPS PressVEST Speed, phosphate-bonded investment material. Following the manufacturer instructions, 200 g of IPS PressVEST Speed investment powder was mixed with 32 mL of IPS PressVEST Speed investment liquid (water and colloidal silica) and 22 mL of distilled water. The mixing time is 2.5 minutes under vacuum at approximately 350 rpm using Amann Girrbach Ivoclar vacuum mixer (Ivoclar-Vivadent, Liechtenstein).
Figure 11: Investment rings ready to be invested

Figure 12: Investment rings invested and setting
After 45 minutes setting time, the investment rings were prepared for preheating by removing the ring gauge and ring base and carefully pushing the investing ring out of the IPS Silicone Ring (Figures 15 and 16). The preheating parameters instructed by the manufacturer (Table 7) were followed.

![Figure 13: Investment rings without the silicone ring and ring base and gauge](image)

**Table 7: Preheating parameters (Ivoclar-Vivadent, Liechtenstein)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preheating furnace temperature upon placing the investment ring</td>
<td>850°C (1562°F)</td>
</tr>
<tr>
<td>Position of the investment ring in the preheating furnace</td>
<td>Towards the rear wall, tipped with the opening facing down</td>
</tr>
<tr>
<td>Final temperature upon preheating the investment ring</td>
<td>850°C (1562°F)</td>
</tr>
<tr>
<td>Holding time at the final temperature</td>
<td>200 g investment ring – min. 60 minutes</td>
</tr>
</tbody>
</table>
The investment rings were removed from the pre-heating furnace (Jelenko Accu-Therm III 6000) immediately after completion of the preheating cycle. A cold IPS e.max Press ingot (Figure 17) was then placed into the hot investment ring followed by the cold IPS Alox Plunger which has

**Figure 15:** IPS Alox Plunger being coated with coated with the separator

**Figure 14:** Investment rings placed in the preheating furnace
been coated with IPS Alox Plunger Separator (Figure 18). The complete investment ring assembly was then placed in the center of the hot press furnace.

Programat EP 5000 press furnace was used and the press and firing parameters set for the 200 g IPS Investment ring system using a high opacity (HO) IPS e.max Press ingot (parameters summarized in Table 8).
Table 8: Press parameters for IPS e.max Press (Ivoclar-Vivadent, Liechtenstein)

<table>
<thead>
<tr>
<th>Press Furnace</th>
<th>Programat EP 5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPS e.max Press ingots</td>
<td>High opacity</td>
</tr>
<tr>
<td>IPS investment ring system</td>
<td>200 g</td>
</tr>
<tr>
<td>Stand-by temperature (°C / °F)</td>
<td>700 / 1292</td>
</tr>
<tr>
<td>Temperature increase (°C / °F / minute)</td>
<td>60 / 108</td>
</tr>
<tr>
<td>Holding temperature (°C / °F)</td>
<td>925 / 1697</td>
</tr>
<tr>
<td>Holding time (minutes)</td>
<td>25</td>
</tr>
<tr>
<td>Vacuum on (°C / °F)</td>
<td>500 / 932</td>
</tr>
<tr>
<td>Vacuum off (°C / °F)</td>
<td>925 / 1697</td>
</tr>
<tr>
<td>Program / software version</td>
<td>11-20 / 2.9</td>
</tr>
</tbody>
</table>

The investment ring was removed from the press furnace using the investment tongs immediately after completion of the pressing, to be then placed on a cooling grid to cool in a place protected from draft (Figure 19).
After cooling to room temperature for 60 minutes, the divesting of the investment ring was carried by using a microblaster (Comco Inc.) with polishing glass beads (80 μm) at 200 kPa pressure (Figure 20).

Figure 17: Investment rings cooling off after pressing

Figure 18: Divesting of pressed triangular prisms
The prisms (Figure 21) were then cut at the sprue base using a high speed electric hand piece (NSK Ti-Max Z95L, Nakanishi International) with a diamond burr (Brasseler 850 medium, Brasseler, USA), under continuous water irrigation. Each triangular prism was then mounted in a holding jig (UBC Dentistry, Vancouver BC, Canada) to be cut into two halves using a diamond-wafering blade (UKAM, Valencia, CA, USA) mounted on a low speed Isomet saw (Buehler, Lake Bluff, IL, USA), under constant water irrigation.

Corresponding halves were marked to facilitate their alignment during the bonding procedure (Figure 22).
3.2.2.2 Ceramic Resin Composites

The preparation started by cutting each block (Figure 23) into six blocks for Lava Ultimate and four blocks for Enamic, of roughly equal size.
This process was completed by adhering each block to a metal slab using sticky wax, to permit retention and cutting on a low speed Isomet saw using a diamond-wafering blade under constant water irrigation (Figures 24 – 26).

Figure 22: Resin composite block mounted to the metal slab using sticky wax

Figure 23: Low speed Isomet saw
Each sample was then mounted into a custom jig (Figure 27) (UBC Dentistry, Vancouver BC, Canada). Through constant rotation of the sample onto a series of abrasive disks of different grit (240, 400 and 600) mounted onto a Buehler Metaserv wheel grinder under constant water
irrigation, equilateral triangular prisms of (6x6x6x13) mm were produced.

Each triangular prism was then mounted on a holding jig to be cut into two halves following the procedure described for IPS e.max Press (Figure 28). Following the bonding procedure, the length of each specimen was at least 12 mm. The slight increase in length of the bonded specimen has no bearing on the results\textsuperscript{48}.

![Figure 26: Cutting of NTP specimen in two halves](image)

To produce the surface roughness matching the specifications of the Sirona CAD/CAM milling unit, the adhesive surface of all prisms was ground using a 600 grit SiC abrasive disks mounted on the sample assembly described previously. Each two halves of one sample were marked on one of their surfaces to ensure proper alignment during cementation (Figures 29 and 30).
Figure 27: Cutting steps of Lava Ultimate NTP specimen

Figure 28: Cutting steps of Enamic NTP specimen
3.2.2.3 Resin Cement

Twenty samples of (4x4x4x8) mm triangular prisms were prepared using a teflon mold (UBC Dentistry, Vancouver BC, Canada). The process was completed by first placing a mylar film to block one end of the jig followed by the injection of the resin cement into the space and placement of a mylar film on the other end (Figure 31). Each end was then light cured (Litex 680A Curing Unit, DenAmerica, USA) for 60 s prior to removal of the sample from the plastic mold. Finally, each surface of the triangular prism was light cured for an additional 60 s and allowed a total setting time of 6 minutes prior to storage in water at 37 °C.

Figure 29: Resin cement being dispensed into the plastic mold
3.2.3 Surface Treatment

Lava Ultimate samples were divided into two groups. The adhesive surface of the first group was sandblasted with 27 μm alumina oxide particles using a micro-etcher (MicroEtcher II, Danville, USA) at 200 kPa pressure (Figure 32).

The second group received a surface treatment of silicatisation using 30 μm silica-modified alumina oxide (Rocatec Soft, 3M ESPS) using a Rocatec Junior blasting module (3M ESPS) at 200 kPa pressure (Figure 33).

The surface was blasted at right angle from a distance of 15 mm for 13 s, which resulted into a matte bonding surface recommended by the manufacture. The surface was then cleaned from any particle residue using an oil-free and moisture-free air jet prior to cementation.
According to the manufacturer recommendations, Enamic samples were acid etched for 60 s and IPS e.max Press samples for 20 s, using 4.5 % hydrofluoric acid (Figure 34). The etched surface was then cleaned using a water jet and dried using an oil-free and moisture-free air jet prior to cementation.
3.2.4 Cementation Protocol

The cementation procedure was carried out using a custom jig (UBC Dentistry, Vancouver BC, Canada) holding securely each half of the prism by an adjustable lid fastened by screws (Figure 35). The design of the jig allowed the two halves, through a sliding motion, to be brought in contact with the adhesive surfaces properly aligned.

Once both halves of one sample are securely placed in each half of the jig and properly aligned, the cementation procedure started with the application of the adhesive layer of Scotchbond Universal using a micro-brush. The adhesive layer was left on the surface to react for 60 s for e.max Press and 20 s for Enamic and Lava Ultimate, according to the manufacturers’ recommendation. An oil-free air jet was then used for a period of 5 s to evaporate the solvent.
RelyX Ultimate cement was applied on both adhesive surfaces from the automix syringe and the two halves were then brought in contact. To ensure a standardized continuous pressure during the setting period of the cement, a weight of 25 g was placed on top of the assembly (Figure 34).

![Figure 35: Cementation procedure]

All margins were light cured for 20 s followed by additional curing for 60 s after removal of the bonded specimen from the holder.

### 3.2.5 Storage Media

All bonded specimen were stored in water at 37 °C prior to 24 h or 60 d testing.
3.2.6 Determination of Interfacial $K_{IC}$

The NTP specimen $K_{IC}$ fracture toughness test was used to determine the interfacial $K_{IC}$ for all test specimens. Each bonded NTP specimen was fitted into a custom holder reproducing a configuration similar to the CNSR test. The holder consists of two symmetrical parts incorporating each a loading collar at one end and a triangular prismatic groove at the other forming the base into which the NTP specimen is placed. The specimen is secured in place by two symmetrical half-disks fastened with screws (Figure 37).

![Figure 36: NTP specimen holder](image)

The specimen was first placed into one half of the holder with the bonded interface positioned visibly near the edge. Under magnification, a sharp razor blade was used to create a $\sim 0.1$ mm deep crack initiation point along one of the edges of the NTP specimen (Figure 38). The second half of the holder was then fitted on the other end of the specimen.
To ensure a standardized space between the two halves of the holder, a custom mounting jig was used on which the holder assembly was placed. A 200 µm thick spacer was used to keep the two specimen holder halves apart by replicating the space produced by the cutting blade in the CNSR specimen (Figure 39).

Figure 37: Crack initiation

Figure 38: NTP specimen holder in mounting with spacer
Prior to testing, a visual inspection under magnification was carried out to ensure the proper position of the NTP specimen into the holder with the crack initiation point visible within the bonded interface contained within the space separating the two halves of the holder assembly.

The test assembly was then placed in the custom designed grips connected to a computer-controlled Instron 4301 universal testing machine, with a 1 kN Instron load cell (Figure 40). The assembly was loaded in tension at a crosshead speed of 0.1 mm/min until crack propagation or crack failure. The load and displacement were monitored and recorded constantly.

The maximum load recorded before crack arrest or complete failure was used to calculate the interface $K_{IC}$ using the following equation:

$$K_{IC} = \frac{P_{max}}{DW^{1/2}} Y_{min}^{*}$$
$P_{\text{max}}$ represents maximum load recorded during testing, $D$ represents specimen diameter, $W$ represents specimen length and $Y_{\text{min}}^*$ represents the dimensionless stress intensity factor coefficient with a value of 28 for the NTP test\textsuperscript{45}.

### 3.2.7 Scanning Electron Microscopy

In order to determine the mode of failure, the features of fractured surfaces need to be examined under magnification. Scanning electron microscope (SEM) was used to perform the fractographic analysis. It uses a focused beam of electrons whose wavelength is much lower than light which allows for the resolution of an image of a surface to be at the nanoscale level. The captured SEM images of the fractured surfaces allows then for material structural analysis and characterization of fracture paths.

Moreover, in order to evaluate the effect of the different surface treatments for each group, a random surface treated sample was selected from each group for SEM observation. Following $K_{\text{IC}}$ testing, selected samples closest to the mean of each group were also selected for SEM observation. The specimen halves were labeled and gold coated (Figure 41) with an Edwards S150A sputter coater (Edwards Vacuum, Crawley, UK). The specimens were then observed under a scanning electron microscope (Cambridge Stereoscan 260, Cambridge Instruments, England). For each sample, photomicrographs were taken at various magnifications.
3.2.8 Statistical Analysis

The $K_{IC}$ results were analyzed using a two-way ANOVA followed by Scheffé multiple means comparisons. The statistical analysis was conducted at $\alpha=0.05$, using SPSS (SPSS for Windows, version 12.0; Chicago, IL).
Chapter 4: Results

The mean and standard deviation interfacial \( K_{\text{IC}} \) for all groups at the two time intervals, along with the results of the statistical analysis are presented in Table 9; the results are also presented as box plots in Figure 42.

Levene test was performed prior to ANOVA to confirm uniformity of variance of the obtained data.

Table 9: Results of \( K_{\text{IC}} \) tests (Mean ± SD) in MPa•m\(^{1/2}\)

<table>
<thead>
<tr>
<th>Material / Surface Preparation</th>
<th>( K_{\text{IC}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 hours</td>
</tr>
<tr>
<td>Lava Ultimate machined and sandblasted using 27 ( \mu ) m ( \text{Al}_2\text{O}_3 ) – (LUME)</td>
<td>1.63 ± 0.29(^{aA})</td>
</tr>
<tr>
<td>Lava Ultimate machined and silicatized using 30 ( \mu ) m silica-modified ( \text{Al}_2\text{O}_3 ) – (LUR)</td>
<td>1.74 ± 0.31(^{aA})</td>
</tr>
<tr>
<td>Enamic machined and HF acid etched – (EHF)</td>
<td>1.16 ± 0.19(^{bA})</td>
</tr>
<tr>
<td>IPS e.max Press machined and HF acid etched – (EMHF)</td>
<td>0.97 ± 0.11(^{bA})</td>
</tr>
<tr>
<td>RelyX Ultimate cement – (RXU)</td>
<td>1.71 ± 0.29(^{aA})</td>
</tr>
</tbody>
</table>
Figure 41: Box plots of the effect of time and surface treatment on interfacial $K_{IC}$
Table 10: Scheffé Multiple Comparisons

<table>
<thead>
<tr>
<th>(I) Group</th>
<th>(J) Group</th>
<th>Mean Difference (I-J)</th>
<th>Std. Error</th>
<th>Sig.</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lower Bound</td>
</tr>
<tr>
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<td>EMHF</td>
<td>.1511*</td>
<td>.04651</td>
<td>.045</td>
<td>.0020</td>
</tr>
<tr>
<td></td>
<td>LUME</td>
<td>.3743*</td>
<td>.05590</td>
<td>.000</td>
<td>.1951</td>
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<tr>
<td></td>
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<td>.0735</td>
<td>.05159</td>
<td>.731</td>
<td>-.0919</td>
</tr>
<tr>
<td></td>
<td>RXU</td>
<td>.2035*</td>
<td>.05159</td>
<td>.008</td>
<td>.0381</td>
</tr>
<tr>
<td>EMHF</td>
<td>EHF</td>
<td>-.1511*</td>
<td>.04651</td>
<td>.045</td>
<td>-.3002</td>
</tr>
<tr>
<td>LUME</td>
<td>EHF</td>
<td>.2232*</td>
<td>.05661</td>
<td>.008</td>
<td>.0417</td>
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<tr>
<td></td>
<td>RXU</td>
<td>-.0776</td>
<td>.05236</td>
<td>.700</td>
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<tr>
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<tr>
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<td>.000</td>
<td>-.4959</td>
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<td>.06085</td>
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<td>-.3659</td>
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* The mean difference is significant at the .05 level.

Table 11: Means for groups in homogeneous subsets – 24 h

<table>
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<th>Group</th>
<th>Subset</th>
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<th>2</th>
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</thead>
<tbody>
<tr>
<td>EMHF</td>
<td></td>
<td>.97</td>
<td></td>
</tr>
<tr>
<td>EHF</td>
<td></td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>LUME</td>
<td></td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>RXU</td>
<td></td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>LUR</td>
<td></td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>Sig.</td>
<td></td>
<td>.53</td>
<td>.90</td>
</tr>
</tbody>
</table>

59
At 24 h, the results showed no significant difference in interfacial $K_{IC}$ between the Lava Ultimate groups and the cement, while the Enamic and IPS e.max showed significantly lower interfacial $K_{IC}$ value compared with the Lava Ultimate groups and the cement.

At 60 d, the results showed lower interfacial $K_{IC}$ for Lava Ultimate sandblasted group compared to Lava Ultimate silicatized group. Both Lava Ultimate groups and IPS e.max showed no significant difference in interfacial $K_{IC}$ when compared to the cement. Enamic showed significantly higher interfacial $K_{IC}$ value compared to the cement.

The results showed that time had a significant effect on the interfacial $K_{IC}$ with the exception of Enamic that showed no significant difference interfacial $K_{IC}$ between 24 h and 60 d.

The results of this study led to the rejection of all null hypotheses with the exception of that regarding Enamic, for which storage in water at 37 °C for 60 d did not affect the interfacial $K_{IC}$.  

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**Table 12: Means for groups in homogeneous subsets – 60 d**

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>LUME</td>
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<tr>
<td>RXU</td>
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<td>LUR</td>
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<td>EHF</td>
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<tr>
<td>Sig.</td>
<td>.06</td>
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</tbody>
</table>

---

60
4.1 SEM Analysis

4.1.1 Lava Ultimate

4.1.1.1 Sandblasting

SEM image of Lava Ultimate preconditioned with sandblasting is displayed in Figure 42. It shows a rough microretentive surface with exposed particle fillers. The fractured surface of the tested specimen shows that the fracture initiated from the induced defect (Figure 43). SEM images of fractured surfaces at 24 h and 60 d (Figures 45 and 46, respectively) show surfaces covered with a resin cement layer, indicative of cohesive failure in the cement.

![Filler particle](image)

Figure 42: SEM image – Sandblasting (D) / Lava Ultimate
Figure 43: SEM image – Fractured-surface (D) / Lava Ultimate

Figure 44: SEM image – Fractured-surface (24h, D) / Lava Ultimate
4.1.1.2 Surface Silicatisation Sample

SEM image of Lava Ultimate preconditioned with surface silicatisation is displayed in Figure 46. It shows a rough microretentive surface with exposed particle fillers, in addition to a silica coating of the surface. The fractured surface of the tested specimen shows that the fracture initiated from the induced defect (Figure 47). SEM images of fractured surfaces at 24 h and 60 d (Figures 48 and 49, respectively) show surfaces covered with a resin cement layer, indicative of cohesive failure in the cement.
Figure 46: SEM image – Silicatisation (S) / Lava Ultimate

Figure 47: SEM image – Fractured-surface (S) / Lava Ultimate
Figure 48: SEM image – Fractured-surface (24h, S) / Lava Ultimate

Figure 49: SEM image – Fractured-surface (60d, S) / Lava Ultimate
4.1.2 Enamic

SEM image of Enamic preconditioned with acid etching is displayed in Figure 50. It shows the polymer network exposed, providing a microretentive surface. Moreover, ceramic particles are present in some of the porosities. The fractured surface of the tested specimen shows that the fracture initiated from the induced defect (Figure 51). SEM images of fractured surfaces at 24 h and 60 d (Figures 52 and 53, respectively) show surfaces covered with the adhesive layer, indicative of cohesive failure in the adhesive layer, rather than in the cement.

![SEM image – Acid-etched / Enamic](image)

Figure 50: SEM image – Acid-etched / Enamic
Figure 51: SEM image – Fractured-surface / Enamic

Figure 52: SEM image – Fractured-surface (24h) / Enamic
4.1.3 IPS e.max Press

SEM image of IPS e.max Press preconditioned with acid etching is displayed in Figure 54. It shows the lithium disilicate crystals exposed, providing a microretentive surface. The fractured surface of the tested specimen shows that the fracture initiated from the induced defect (Figure 55). SEM images of fractured surfaces at 24 h and 60 d (Figures 56 and 57, respectively) show surfaces covered with the adhesive layer, indicative of cohesive failure in the adhesive layer, rather than in the cement.
Porosity

Glass-ceramic crystal

Figure 54: SEM image – Acid-etched / IPS e.max

Crack initiation

Adhesive layer

Figure 55: SEM image – Fractured-surface / IPS e.max
Figure 56: SEM image – Fractured-surface (24h) / IPS e.max

Figure 57: SEM image – Fractured-surface (60d) / IPS e.max
4.1.4 RelyX Ultimate Cement

SEM image of RelyX Ultimate cement is displayed in Figure 58 with the fractured surface of the tested specimen showing that the fracture initiated from the induced defect. SEM images of fractured surfaces at 24 h and 60 d (Figures 59 and 60) display the surface characteristics/features of the cement, to which the tested materials are compared to in order to determine the mode of failure.

Figure 58: SEM image – Fractured-surface / RelyX resin cement
Figure 59: SEM image – Fractured-surface (24h) / RelyX resin cement

Figure 60: SEM image – Fractured-surface (60d) / RelyX resin cement
Chapter 5: Discussion

The dental industry is always in search for new innovative biomaterials with the intention to offer improved products. The new so-called “hybrid ceramic” and “resin nanoceramic” have been introduced to the market with the idea of combining the positive aspects of both composites and ceramics with advantageous properties to the patients\(^{25}\). The manufacturers claim that these materials, integrating both ceramic and polymer materials, provide less brittleness, excellent machinability and edge stability\(^{25}\).

3M ESPE has introduced a new CAD/CAM material, a resin-based nanocomposite block named Lava Ultimate (3M, ESPE, Bad Seefeld, Germany). It consists of a highly cured resin matrix in which nanoceramic particles are embedded. In the technical product profile, the manufacture categorizes the material as a “Resin Nano Ceramic”. It is neither a ceramic nor a composite but rather a mix of both.

Another innovative CAD/CAD material is Vita Enamic (VITA Zahnfabrik, Bad Säckingen, Germany), referred to as a “hybrid ceramic”. It has been defined in the literature as “a material consisting of a ceramic substructure infiltrated with a composite material”\(^{32}\). It consists of a ceramic component of aluminum oxide-enriched, fine-structure feldspar matrix (86 wt\%) infused by a polymer component of urethane dimethacrylate and triethyleneglycol dimethacrylate (14 wt\%).
As discussed previously, both materials are being referred to as ceramic resin composites in this thesis. In the literature, scientific evidence on the bonding behavior and surface treatment of indirect composite is very limited\textsuperscript{49}, and almost non-existent for the new ceramic resin composites. A recent literature review found no in vitro studies referring to the new ceramic resin composites and no information regarding recommendation for surface treatment, resin cement or artificial aging methods\textsuperscript{25}. Similarly, no information regarding the new ceramic resin composite was found during our review of the literature up to the date of publication of this thesis. Considering some similarities in the composition with the new ceramic resin composite, a brief literature review of the bonding protocols and surface treatment procedure of indirect composite restorations will be pertinent in providing some valuable information.

It is important to consider that fracture mechanics was not used to assess the bond strength, with almost all of the earlier studies using bond strength tests such as $\mu$TBS and SBS\textsuperscript{25}. Therefore, a direct comparison with the new materials cannot be made and information reported in these studies provides only a background for discussion.

The bonding mechanisms between two composite materials involve three possible mechanisms being the chemical bonding to the resin matrix, chemical bonding to the exposed filler particles, and micromechanical retention caused by the penetration of the resin cement into the microcracks present in the resin matrix\textsuperscript{50}.

The chemical bonding is based on the principle of improving adhesion between resin and SiO$_2$ filler by using a silane coupling agent, surface silicatisation by silica coating, and infiltration of
resin monomers into composites. As discussed previously, silane is a bifunctional molecule that bonds to the exposed silica fillers in the composite, increasing the bond strength by improving the wettability of the treated surface. The positive effect of silane application as chemical treatment has been reported in numerous studies evaluating the effect of silane as a surface treatment of indirect composite restorations. Furthermore, in review of the literature of resin bond to indirect composite, silane treatment yielded increased bond strength in most studies and is considered as an essential factor.

Surface silicatisation has been initially introduced and devised primarily to enhance the bonding of dental resin to metal substrates. The effect of silica coating using the tribochemical procedure and silane conditioning have been proven to be effective by improving the bond strength of resin to metal alloys. When it comes to surface silicatisation of indirect resin composite, few studies have been reported in the literature. One study investigated the effect of two abrasive systems on resin bonding to laboratory-processed indirect resin composite restorations and found higher bond strength with sandblasting with 30 µm silica-modified Al₂O₃ compared to 50 µm Al₂O₃. The effect of surface silicatisation as a surface treatment for the new ceramic resin materials has not been reported in the literature.

Of the three materials tested in this study, the composition of Lava Ultimate resembles the most the composition of the resin composite cement used, both having a resin matrix in which particulate fillers are embedded. Therefore, the chemical and mechanical bonding mechanisms discussed previously between two composite materials may be applicable in this case. The SEM analysis showed a micro-retentive surface allowing the penetration of the resin cement into the
microcracks of the resin matrix, providing mechanical bonding. Moreover, the sandblasting exposed more of the SiO\textsubscript{2} fillers, creating a more chemically compatible surface to bond with the silane layer. It allows more of the silane molecules to react with the silica particles exposed on surface, providing chemical bonding.

Figure 61: Cohesive failure of Lava Ultimate specimen

The surface silicatisation did not significantly enhance the chemical bond with the silane layer when comparing the 24 h interfacial K\textsubscript{IC} values to the sandblasted group. This finding may be
related to the fact the material itself contains already a high volume of silica particles that are readily available to react with the silane layer. More importantly, the bonded interface has not yet been challenged by water diffusion during this short water storage.

Water storage for 60 d had a negative effect on the interfacial $K_{IC}$ for both Lava Ultimate groups, concurrently with the adhesive resin cement. It has been reported that immersion of resin composite in water may cause a degradation of the matrix-filler interface\textsuperscript{57}. It has been hypothesized that this slow diffusion causes the polymer network to swell and consequently producing a plasticizing effect and softening of the polymer resin matrix, which reduces the frictional forces between the polymer chains\textsuperscript{58}. This plasticizing effect may explains the deterioration of the resin cement and the decrease of the interfacial $K_{IC}$ after 60 d obtained in both groups.

Interestingly, the group that was treated with surface silicatisation showed a significantly higher 60 d interfacial $K_{IC}$ when compared to the sandblasted group. This finding may be related to the fact that the chemical bond between the surface and the silane layer was more difficult to disrupt considering the larger number of bonds between the silane coupling agent and the silicatised surface.

The SEM images of the fractured adhesive interface of both Lava Ultimate groups showed surface features similar to the cement suggesting a cohesive failure within the cement layer. The statistical analysis showed no significant difference of $K_{IC}$ values between Lava Ultimate and
RelyX Ultimate cement. Therefore, it confirmed the nature of failure mode being cohesive within the cement layer.

Enamic is characterized by a ceramic substructure infiltrated by a polymer network. The surface treatment recommended is hydrofluoric acid etching that dissolves and removes the silica-based glassy matrix, leaving a very porous surface formed mainly by the polymer network. It provides good micromechanical retention. As for the chemical bonding, the adhesive layer containing the silane infiltrates the porous surface reacting with the glassy matrix. It could be possible that HEMA and MDP present in the adhesive improve the wetting of the polymer network ensuring a good micromechanical retention.

The SEM images of the fractured adhesive interface displayed similar features of the polymer network with the microporosities impregnated with the adhesive layer, suggesting a cohesive failure occurring within the adhesive layer rather than in the cement (compare with SEM of cement fractured surface, Figure 60). The statistical analysis of the 24 h results showed significant difference of interfacial $K_{IC}$ values between Enamic and RelyX Ultimate cement, with Enamic having a lower interfacial $K_{IC}$ value. These results indicated that the failure did not occur cohesively within the cement layer but rather within the adhesive layer, being the weakest link.

This obtained result may relate to the fact that the higher viscosity RelyX Ultimate resin cement did not displace the adhesive layer and did not penetrate into the microporosities to provide micromechanical retention, leaving only the adhesive layer in that area. Therefore, the crack propagated within the adhesive layer leaving the surface microporosities of one half of the prism
impregnated with some adhesive, while the other surface was left covered by the cement layer. To better illustrate the failure mode, a schematic representation is included with the corresponding SEM of an Enamic tested specimen (Figure 63).

![Schematic representation and SEM images of the fractured surfaces](image)

**Figure 62: Adhesive failure of Enamic specimen**

Interestingly, the statistical analysis of the collected data of the Enamic specimens showed no significant difference in the interfacial $K_{IC}$ values between the 24 h and 60 d test groups. The SEM images of the fractured surfaces showed similar features when comparing the
non-aged to the aged specimens, indicating the same mode of failure. No significant
deterioration of the adhesive bond occurred after the 60 d period of water storage. This finding
may be related to the fact that bonding to the Enamic substrate is mainly dependent on the
micromechanical retention provided by the adhesive layer infiltrating deep into the
microporosities, thus delaying the effect of hydrolysis due to water sorption.

IPS e.max is a lithium-disilicate reinforced glass ceramic that has been successfully
introduced in dentistry. Its microstructure consists of many small interlocking and randomly
oriented plate-like lithium-disilicate (Li$_2$Si$_2$O$_5$) crystals dispersed in a glassy matrix, which
results in significant improvement of its mechanical properties when compared to other
feldspathic and reinforced glass ceramics$^{14}$.

The bonding surfaces of e.max specimens were coated with an adhesive layer containing
silane following the acid-etching treatment of the surface. The hydrofluoric acid reacted with the
silica matrix of the ceramic leading to the creation of a porous microretentive structure on the
ceramic surface$^{29}$. The chemical reaction occurred through a condensation reaction between the
silanol group (Si-OH) of the hydrolyzed silane and the ceramic to create a siloxane bond (Si-O-
Si) with water as a by-product$^{23}$. Therefore, the quality of the ceramic surface and the application
of silane both affect the quality of the chemical bond.

The 24 h interfacial $K_{IC}$ of IPS e.max was significantly lower when compared to the $K_{IC}$ of the
cement. The SEM images of the fractured surface showed features dissimilar to the cement
suggesting a surface on which the adhesive layer seems to be still present. This may be indicative
of cohesive failure occurring within the adhesive layer rather than in the cement. This finding may be related to an inadequate surface silanization of the ceramic by the adhesive that contains the silane coupling agent along with several other primers (HEMA, MDP).
Chapter 6: Conclusion

Restorative dentistry involves placement of restorations made from different biomaterials. The longevity of resin ceramic composite and ceramic restorations depends on the ability of the resin cement to adhere properly to the tooth structure and the restoration. Therefore, it is crucial to select the appropriate resin cement and follow a predictable bonding protocol.

In this study, using a fracture mechanics approach, the effect of surface preconditioning and storage on the bonding interface between an adhesive resin cement and two resin ceramic materials and a lithium disilicate ceramic material was assessed.

The results showed that for Lava Ultimate, surface silicatisation seems to be a more effective surface treatment compared to only sandblasting. Therefore, surface treatment of Lava Ultimate restoration using the Rocatec soft (30 µm silica-modified alumina oxide particles) is recommended.

For Enamic and IPS e.max, the application of silane coupling agent and adhesive contained in one solution does not seem to be effective. The individual application of silane coupling agent followed by the application of adhesive is recommended.

Finally, storage in 37 °C water for 60 d led to lower fracture toughness of the adhesive resin cement and to lower interfacial fracture toughness of the adhesive interfaces investigated, with the exception of the one involving Enamic, the double penetrating network composite material.
References