EFFECT OF SURFACE CONDITIONING AND STORAGE TIME ON THE BOND STRENGTH OF ORTHODONTIC BRACKETS TO LITHIUM DISILICATE CERAMIC

by

Jonathan Paxon

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Abstract

The effect of different surface conditioning procedures on bracket bond strength to lithium disilicate ceramic were investigated after 30 min, 24 h and 6 months of water storage. Brackets were bonded to 300 IPS e.max samples (Ivoclar Vivadent). Five surface conditioning procedures were tested: 15 seconds 37% H$_3$PO$_4$; 20 seconds 9.5% hydrofluoric acid (HF); 60 seconds 9.5% HF; 60 seconds 9.5% HF plus a low-viscosity enamel bonding agent; 20 seconds non-thermal plasma (NTP) only. All samples were further treated with a silane coupling agent prior to bonding with an orthodontic resin cement and were stored in distilled water at 37°C for 30 minutes, 24 hours and 6 months before testing the shear bond strength. Results showed that bond strengths increased from 30 minutes to 24 hours and then decreased at 6 months. At 30 minutes and 24 hours, HF etching for 60 seconds followed by enamel bonding agent exhibited significantly higher bond strength than all other groups. At 6 months, all groups etched with HF exhibited similar bond strengths that were significantly greater than both H$_3$PO$_4$ and NTP surface conditioning. Etching with HF resulted in increased adhesive residue on the sample surface after debonding compared to treatment with NTP or H$_3$PO$_4$. The results suggest that surface treatment with 20 to 60 second 9.5% HF etching times yields stable bond strengths, as the bond strengths did not significantly reduce after 6 months.
Preface

This research project was designed by Dr. Jonathan Paxon under the supervision of Dr. Ricardo M. Carvalho and the guidance of Drs. N. Dorin Ruse and Benjamin Pliska. The data was collected and analyzed by Dr. Jonathan Paxon who prepared the manuscript with advice from Drs. Ricardo M. Carvalho, N. Dorin Ruse and Benjamin Pliska. The orthodontic brackets used in this study were donated by American Orthodontics. No ethics approval was needed or obtained for this study.
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List of Abbreviations

HF       Hydrofluoric acid
PA       Phosphoric acid
NTP      Non-thermal plasma
ARI      Adhesive remnant index
SEM      Scanning electron microscopy
SBS      Shear bond strength
EBA      Enamel bonding agent
Monobond Plus     MBP
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Dedication

For my loving wife and children . . .

Thanks for all of your support and encouragement throughout my studies.
Chapter 1: Introduction

Good long-term bracket bond strength is highly sought after in orthodontics. Poor bond strength and the resultant bond failures results in increased chair time and treatment cost for the orthodontist and increased visits and treatment time for the patient. The bracket bond must be able to withstand multiple forces, including those exerted by archwires and mastication, all within the moist oral environment, which is subject to rapid changes in temperature and pH(1). Prior to the advent of suitable orthodontic bracket adhesives, orthodontists were forced to band every tooth; a procedure that resulted in poor esthetics during treatment, required extensive time, caused patient discomfort, increased risk of decalcification and lead to poor periodontal health(2).

Adult orthodontics is becoming increasingly popular and has introduced additional complexities to bonding orthodontic attachments. The dentition is often restored with composites, alloys and ceramics in the form of fillings, veneers and crowns resulting in markedly different bonding requirements. While bands remain an option for these restored teeth, for the reasons discussed above, it is often advantageous to bond attachments. As with traditional bonding to enamel, the bond must be able to withstand challenges of the oral environment while being easily debonded and cleaned up without causing damage to the substrate. Demand for esthetics has increased significantly and ceramic-based materials are the most common option for restoring large crown losses in both anterior and posterior teeth. Because of this, it has become increasingly frequent that orthodontists face the challenge of bonding brackets and other accessories to ceramic instead of enamel.
1.1 Bonding to traditional ceramics

Traditional dental ceramics are silica-based and are composed of feldspar (KAlSi$_3$O$_8$), quartz (SiO$_2$) or kaolin (Al$_2$O$_3$•2SiO$_2$•2H$_2$O)(2,3). Bonding to traditional feldspathic ceramics has been well-studied and various bond enhancing methods have been evaluated including sandblasting (4-12), etching with hydrofluoric acid (HF) and phosphoric acid (4-6,11,13-22) and laser preconditioning (11,23,24). No clear consensus on the ideal bonding system exists, but a recent systematic review has shown that there are multiple bonding methods that are acceptable(25). The most commonly employed method is a 60 second HF etch followed by treatment with a bifunctional silane.

1.1.1 Ceramic surface conditioning

There are two primary goals of surface conditioning: to remove surface contaminants and increase surface area of the substrate(26,27). Removal of surface contaminants increases the free surface energy of the substrate to be bonded ($\gamma_{SV}$) relative to the surface liquid interface ($\gamma_{SL}$) and the liquid ($\gamma_{LV}$) resulting in a decreased contact angle ($\theta$) and increased surface wetting by the adhesive (Figure 1.1)
Increases in surface area can be accomplished through a variety of means including HF etching, sandblasting, and lasers, with the goal of creating a larger bonding surface and micromechanical retention for the adhesive. HF etching of the silica-based ceramic surface increases both the free surface energy, through eliminating surface contaminants, and the surface area, through removing a portion of the glass component (28). HF first reacts with silica to form silane tetrafluoride, which then further reacts with HF to produce hydrofluorosilicic acid, which can then be rinsed away with an air/water spray.

\[
\text{SiO}_2(\text{s}) + 4\text{HF}(\text{aq}) \rightarrow \text{SiF}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})
\]

\[
4\text{SiF}_4(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + 2\text{HF}(\text{aq}) \rightarrow 3\text{H}_2\text{SiF}_6(\text{aq}) + \text{H}_2\text{SiO}_3(\text{aq})
\]

*Figure 1.1 Surface wetting and contact angle*

*Figure 1.2 Ceramic surface etching reaction between silica and hydrofluoric acid*
1.1.2 Ceramic surface priming

Procedures for adhesive application following surface conditioning often include priming with a silane-coupling agent, with the purpose of altering the chemical makeup of silica-based ceramic surface. Alkene groups are bonded covalently to the inorganic surface resulting in a surface that is compatible with the organic adhesive (28). Silane is available in a two-bottle system that needs to undergo hydrolysis prior to application or a low concentration pre-hydrolysed and pre-activated solution that is ready-to-apply. Two bottle systems come in the general form of $Y-(CH_2)_m-Si-(OR)_3$. $Y$ is a methacrylate group, which is capable of polymerizing with the adhesive, and OR is an alkoxy group. Hydrolyzation at low pH results in the formation of the activated silanol $Y-(CH_2)_m-Si-(OH)_3$. The activated silanol then undergoes a condensation reaction with the surface (substrate)-OH groups to form (substrate)-O-Si-(CH$_2$)$_m$-Y. An example of a pre-activated silane-coupling agent is Monobond Plus (Ivoclar Vivadent, Schaan, Liechenstein). This product contains a low concentration of the silane-coupling agent 3-trimethoxysilylpropyl methacrylate. Coating the silica-based surface with this agent results in a layer in the form of (Substrate)-O-Si-(CH$_3$)$_3$-O-C-C(CH$_3$)=CH$_2$, which is capable of polymerizing with the adhesive resulting in a chemical bond between the adhesive and the silica-based substrate.

1.1.3 Adhesive application

Following surface conditioning and priming, an orthodontic composite resin adhesive paste may be applied. However, this is frequently preceded by application of an enamel bonding agent (EBA). These bonding agents possess lower viscosity than the adhesive paste, theoretically allowing for increased surface wetting, allowing for a more intimate interaction
with the surface. Multiple forms of EBA materials for orthodontics exist; some without filler, as in Transbond XT Primer (3M Unitek, St Paul, Minnesota), and others with a low filler content, as in OrthoSolo (Kerr Corporation, Orange, California).

1.2 Bracket bond strength and methods of testing

1.2.1 Ideal bracket bond strength

The bracket bond needs to withstand the forces applied by orthodontic mechanics and by mastication, all within the relatively harsh oral environment, for the duration of orthodontic treatment. Reynolds proposed that a clinically acceptable bond strength is 6 to 8 MPa and this is the value that is commonly cited in the literature(29). However, this recommended bond strength is hypothetical and untested. It fails to take into consideration the complexity of the forces arising in the oral environment, the effects of bond aging and does not specify a margin of safety(30).

A high bond strength value does not preclude bond failure. For example, sandblasting, followed by HF etching and silane-coupling, has been shown to result in bracket bond strengths to feldspathic porcelain above 14 MPa(31), well above the recommended values suggested by Reynolds. However, Zachrisson(32) showed that the clinical incidence of debonds using this method was 8.9%. This rate of bracket bond failure with porcelain is comparable to the overall rate of bracket bond failure to enamel reported by Zachrisson to be 11%(33).
Additionally, care must be taken to ensure that bond strength is not so high that damage to the porcelain occurs when debonding, although it is unclear at what bond strength porcelain damage becomes likely. Risk of porcelain damage is largely mitigated if the bond undergoes adhesive failure(34), which has been shown to occur if bond strength is less than 13 MPa(35). An example of this can be found in a comparison of bonding studies by Kitayama(36) and Schmage(37) who both used a similar methodology of brackets bonded to porcelain with HF etching, silane treatment and a chemically-cured resin-cement. Kitayama observed a relatively high mean shear bond strength of 32.5 ± 8.9 MPa, resulting in damage of all porcelain samples upon debonding whereas Schmage observed a much lower mean bond strength of 12.2 ± 3.4 MPa and found the risk of damage to porcelain to be significantly less. It is therefore important to balance the clinical benefit of increased bond strength with the increased risk for porcelain damage.

1.2.2 Bracket bond strength testing

Several in vitro bond strength testing methods exist using various loading modes, including shear, tension and torsion(38). While in vitro studies are appealing due to their simplicity, the results are not representative of true clinical mechanical/stress challenges(39-41). An orthodontic bracket in an intraoral setting is subject to 6 loading components, comprised of 3 forces (F_x, F_y, F_z) and 3 moments (M_x, M_y, M_z)(42). Testing methods generally attempt to apply a force or moment along a single axis but actual results of the test are less simplistic. Knox(43) used finite element stress analysis to show that the forces at the bond interface are inhomogeneous, exhibiting marked variation in both magnitude and direction. For example, shear bracket bond strength testing results in a more complex pattern of force vectors, including
shear forces at the middle of the bracket and compression and tension in the gingival and coronal aspects, respectively. Similar force vector distribution patterns exist for tension and torsion testing.

In addition, studies using different bond strength testing methods and even different equipment cannot be easily compared. Tension and shear bond strength tests utilize forces that are orthogonal to each other while the torsional test utilizes a moment. Moments and forces cannot be directly compared and, while the units are the same for tension and shear bond strengths, loading patterns at the adhesive interface are very different, generating very different results for the same bonding protocol. Also, shear bond strength tests alone are highly dependent on several parameters, including crosshead speed (typically 0.5 mm/min) and crosshead design.

Despite the limitations of shear bond strength testing as a true representation of bond strength, it remains a clinically relevant methodology to compare bonding protocols by providing important information regarding instances of clinical bracket debonding(42).

1.2.3 Storage time

The effects of intraoral aging should be considered when evaluating bond strength, as the bracket bond must remain clinically acceptable throughout the entire course of orthodontic treatment, frequently lasting 2-3 years. Polymerization and aging in the intraoral environment is a dynamic process, including continued polymerization and crosslinking, hydrolytic degradation of the bonding polymers and effects of the oral biofilm(30,44). The complexity of intraoral aging demonstrates the need for bond strength evaluations beyond a single time point.
Oesterle and Shellhart along with Choo and Ireland examined the effects of water aging on orthodontic bracket bond strength to enamel\(^{(45,46)}\). The two studies yielded similar results in the short-term, with Oesterle showing that bond strength increased significantly from 30 minutes to 24 hours, while Choo and Ireland found that bond strength increased from 1 hour to 1 week. This initial increase in bond strength, exhibited in both studies, was posited to be due to continued polymerization of the adhesive polymer matrix. This is supported by Helvatjoglou-Antoniadi et al who found that microhardness of light-cured and chemically-cured composites increased from 10 minutes to 4 weeks followed by stabilization or decrease at 12 months\(^{(47)}\).

The results of long-term storage in water varied between the two studies, with Oesterle showing a significant decrease in bond strength from 24 hours to 12 and 24 months, while Choo and Ireland did not observe a decrease from 1 week to 12 months. The smaller sample size of the latter study may account for why a significant difference was not observed. Regardless, in both studies, the bond strength remained high (12.44 MPa at 24 months), suggesting that orthodontic composite resin paste adhesives are capable of yielding relatively stable bracket/enamel bonds, suitable for the full length of orthodontic treatment.

While these results illustrate the relatively stable bond to enamel, there are currently no studies that extend beyond 2 weeks of storage evaluating orthodontic bracket bond strength to dental ceramics.
1.2.4 Types of bond failure: adhesive versus cohesive

Bond failure can occur as an adhesive failure on the ceramic surface, cohesive failure within the adhesive cement, or mixed, involving both adhesive and cohesive failure. Artun developed the adhesive remnant index (ARI) as a four-point scale (48), which was later modified by Bishara to a five-point scale (49) as a way to qualify the type of bracket bond failure and, more importantly, the amount of material that remained on the surface of the tooth upon bracket debonding. This has been regarded as a useful tool when combined with the actual bond strength data to better interpret bracket bond findings regarding the benefits of high versus low bond strength and the need for post-debonding procedures to clean the bonded surface. While this index was developed for bonding to enamel, it can and has been used to qualify bracket debonds to other substrates (13,50,51). The modified ARI scores are 1, all adhesive remaining on the ceramic surface; 2, >90% of the adhesive remaining; 3, >10% but <90% of the adhesive remaining; 4, <10% of the adhesive remaining; 5, none of the adhesive remaining.

1.3 Hazards of hydrofluoric acid etching and alternatives

1.3.1 Hazards of hydrofluoric acid

The dangers associated with the intraoral use of HF have been known for some time and were outlined for the first time in a dental journal by Moore (52). Hazards include soft-tissue burns and both soft and hard-tissue necrosis. In addition to the harmful biological effects, etching with HF is a destructive process through its chemical reaction with silica and will necessitate refinishing (6). Also, given the high bond strengths obtained through HF etching,
bond failure is often cohesive within the ceramic, resulting in a greater risk for permanent damage to the ceramic surface(8).

Despite the risks of HF, it continues to be used due to its consistently positive performance in laboratory studies and clinical applications. A recent review concluded that the best protocol for bonding orthodontic brackets to dental ceramic was to etch with 9.6% HF for 1 minute, rinse for 30 seconds, air-dry, followed by application of silane(25).

1.3.2 Phosphoric acid conditioning

Several authors have suggested the use of phosphoric acid (PA) as an alternative to HF etching in an attempt to promote adhesive failure due to expected lower bond strengths and therefore decrease the risk to the ceramic surface(11,13,21,53-55). Application of PA to the ceramic surface is non-destructive and has been shown to simplify, although not eliminate, the process of residual bond cleanup(6). Despite the adequate bond strength and tendency towards adhesive failure that was obtained in these in vitro studies, it is unknown if ceramic surface conditioning with PA will be sufficient for the long-term stresses encountered in the oral environment. Many studies fail to accurately report the length of storage time while others employ thermocycling and storage times as long as 2 weeks(11). However, given the long term decrease in bond strength shown by Oesterle(45), it would be prudent to employ longer term storage times in order to accurately assess the usefulness of PA as a surface conditioner.
1.3.3 Non-thermal plasma conditioning

1.3.3.1 Enamel and dentin

Surface conditioning with non-thermal plasma (NTP) has been proposed as an alternative method for surface conditioning in the intraoral environment. Chen (56) demonstrated that application of a neutral argon non-thermal argon plasma brush could be used to significantly increase the surface wettability of both enamel and composite. Application of NTP did not result in any changes to the surface roughness when applied for less than 30 seconds. Lehmann (57) treated polished and etched enamel and dentin with NTP and found that contact angles for both water and ethylene glycol were significantly reduced to the point that NTP application following etching resulted in contact angles that were often too low to measure. This marked increase in surface wetting was proposed to be due to a reduction in carbon compounds on the surface through oxidation, leading to an increase in surface energy. Additionally, surface temperature of the NTP treated enamel was found to reach a relatively safe maximum of 32.6 °C, although caution must be applied to this value as the experiment was performed at room temperature and the oral environment would be warmer. This is in stark contrast with laser conditioning techniques which clearly show fine surface cracks likely associated with the high heat employed in the process (11).

Teixeira (58) was the first to analyze the effects of NTP conditioning on bond strength and found that NTP treatment of etched and unetched enamel resulted in higher bond strengths than etching alone. However, the storage period was only two days without thermocycling, leaving the stability of the bond in question.
As with PA conditioning, NTP does not result in significant changes to surface roughness, therefore its usefulness in creating a bond with adequate long-term strength is questionable. Arora found that the shear bond strength of orthodontic brackets to NTP treated PA etched enamel decreased from an initial value of 17.5 MPa to 11.9 MPa following 1 month of water storage(59). This decrease in bond strength was posited to be due to increased water sorption at the bond interface due to increased hydrophilicity imparted by the application of non-thermal plasma (NTP) to condition the enamel prior to bonding. While still clinically acceptable, it is unknown if the decrease in bond strength will continue significantly over time.

1.3.3.2 Dental ceramics

NTP application to zirconia has been shown to result in both surface modification and cleaning(60,61). The addition of oxygen in the plasma mixture results in the formation of peroxide radicals and the incorporation of oxygen-containing functional groups into the NTP treated upper layer. Hydrocarbon breakdown also occurs resulting in a clean surface with increased oxygen and decreased carbon content and a resultant high surface energy surface exhibiting increased wetting. Valverde et al demonstrated through microtensile bond strength testing that NTP application increased bond strength of zirconia to cured composite disks (61). However, Lopes et al showed that while the increase in surface energy is significant, it is also transient, lasting only a few hours, suggesting that bonding procedures should be carried out immediately following NTP application(62).
Lanza reports similar findings in a preliminary abstract with application of NTP to lithium disilicate ceramic(63). Application of NTP following HF etching resulted in higher bond strengths at 24 hours and 3 months compared with HF etching alone. Application of NTP alone resulted in bond strengths similar to unconditioned lithium disilicate that were prone to rapid bond degradation with storage time. These results suggest that HF etching to increase surface area is a necessary component of conditioning and that NTP application is merely an adjunctive procedure. This is in contrast to Arora’s results with enamel where NTP application following phosphoric acid etching resulted in decreased bond strength after 30 days relative to phosphoric acid etching alone. Arora’s hypothesis that increased hydrophilicity at the bond interface imparted by NTP application resulted in bond degradation via water sorption is either incorrect or does not apply to ceramics.

1.4 Are enamel bonding agents necessary?

1.4.1 Efficacy on enamel

Low viscosity enamel bonding agents (EBA) are used by many orthodontists following conditioning due to their improved surface wetting capability compared to orthodontic composite resin adhesive pastes. However, despite their widespread use, the benefits of their application remain contentious.

Multiple in vitro studies have found that application of a low-viscosity bonding agent fails to result in any change in bracket bond strength to both bovine teeth(64) and human premolars(65,66). In addition, a recent systematic review concluded that there is no benefit to
using EBAs when bonding metal brackets to enamel(67). While application of an EBA did not increase bond strength in any of the aforementioned studies, its application consistently resulted in increased adhesive residue, therefore requiring greater time following debonding to clean the enamel surface.

While in vitro studies imply that there is no benefit to using EBAs when bonding orthodontic brackets, clinical studies yield different results. Bazargani found that the incidence of bracket debonding was lower in younger patients (10-13 years old) when a bonding agent was applied (4.1%) versus those that were bonded without (12.1%)(68). No difference in debond frequency was seen in older patients (14-18 years old). In a similar study, Nandra found that orthodontic primer failed to reduce debond frequency(69), however, patients were not divided based on age and included several older patients. Also, the study was powered to detect a 5% difference between groups, while many clinicians may consider a smaller difference to be significant.

Given these findings, only limited conclusions can be drawn regarding the use of bonding agents when bonding brackets to enamel. While in vitro studies suggest that their use does not result in significant increases in bond strength, in vivo studies suggest that their application may reduce the incidence of bond failures, particularly in younger patients. Despite these limitations, their use continues to be part of standard bonding protocols employed by many clinicians.
1.4.2 Efficacy on ceramic

The impact of EBA application to a conditioned ceramic surface on orthodontic bracket bond strength or on the incidence of bracket debonding has not been studied. EBA application is inconsistent, with reported use in some bracket bonding methods (7,13) but not in others (8,24,70).

1.5 Bonding to lithium disilicate

Almost all orthodontic bracket bonding literature is based on silica-based feldspathic porcelain leaving the usefulness of the surface conditioning techniques with modern dental ceramics, such as Lithium Disilicate (LiDi), largely unknown. Lithium disilicate (LiDi) ceramics, such as Empress II and e.max (Ivoclar Vivadent)(71), possess large amounts of LiDi filler that greatly improves flexural strength. Empress II is an older version of LiDi ceramic and is no longer available but is significantly different from e.max, which includes higher quantities of LiDi (70 vol%) and is processed at a higher temperature. The result is a stronger ceramic with an esthetic glaze that is superior in both flexural strength and esthetics to the previous Empress II ceramics.

Turk found that multiple methods were suitable for bracket bonding to Empress II including sandblasting, HF etching and roughening with a bur followed by application of silane (51). Research by Abu Alhaija (12) and Karan (50) confirm these results and together suggest that traditional feldspatic bonding techniques, including HF etching and silane application, are suitable for bonding to Empress II.
As previously discussed, Lanza examined the effects of several different surface-conditioning techniques on the bond strength between e.maxCAD and a self-adhesive dual-cure resin cement(63). The results suggested that HF conditioning to increase surface area is a necessary component of conditioning and that NTP is merely an adjunctive step. Lanza also compared multiple experimental and commercially available silanes including Monobond Plus (Ivoclar Vivadent). In addition to a pre-activated silane-coupling agent, Monobond Plus contains methacrylated phosphoric acid ester making it suitable for bonding to multiple forms of dental ceramic including zirconia. Monobond Plus performed well, relative to other tested silane agents and is the manufacturer’s recommended bonding agent for e.max ceramics.

1.6 Study rationale

While limited research exists on bonding to the lesser filled, and no longer available, LiDi ceramic Empress II(50,51,72), no such studies exist for bonding to e.max ceramic. The manufacturer (Ivoclar, Vivadent) recommends an HF etching time of 20 seconds but no literature exists to support this value or to suggest that a 60 second etching time is not equally beneficial towards achieving a high bond strength. Clinically, it is difficult for the clinician to distinguish feldspathic and LiDi ceramics, therefore, it would be ideal if a single etching time could be utilized for both ceramic types.

The application of EBAs has been shown to be of limited clinical benefit when bonding orthodontic brackets to enamel(73), however, there has been no discussion in the literature regarding its application to ceramics when bonding orthodontic brackets.
Additionally, while Oesterle(45) has clearly shown the relationship between decreasing bracket bond strength to enamel with time, it remains unclear if a similar relationship exists with bracket bond strength to LiDi ceramic. While many support the use of PA conditioning over HF etching(11,13,21,53-55) for ceramic bonding, the long term efficacy remains in question. Alternative methods of surface conditioning, in an attempt to exclude HF from the oral cavity, such as NTP should also be considered and evaluated.

The purpose of this study was to evaluate various methods of bonding to e.maxCAD. HF etching time, suitability of PA and NTP conditioning and efficacy of EBAs were evaluated.

1.7 Research aims and null hypothesis

1.7.1 Research aims

1) To investigate the effects of different surface treatment protocols on the bond strength of brackets to a lithium disilicate ceramic

2) To investigate the effect of water storage periods on bond strength.

1.7.2 Null hypotheses

1) Ho: there are no differences in bracket SBS among the e.max surface treatment groups

2) Ho: there are no differences in bracket SBS among the storage periods
Chapter 2: Materials and methods

2.1 e.max ceramic sample preparation

Blocks of e.max CAD ceramic (Ivoclar Vivadent, Schaan, Liechenstein) were sectioned to obtain 300 samples approximately 1 mm thick and fired according to the manufacturer’s specifications. The ceramic chips were embedded in self-curing acrylic and previously used for a separate bonding study. Since the samples had already been used in a prior study, they were reconditioned for use through polishing the ceramic surface with 180, 400 and 600 SiC papers on a wet polishing wheel. This process is similar to sandblasting or roughening with a bur to remove the glaze prior to application of HF, which has been recommended by some authors(7).

2.2 Bracket area measurement

Bracket area was measured by tracing the outline of a bracket base on a high-resolution photo in AutoCAD (Autodesk Inc., San Rafael, California). The image was scaled using the bracket base length measured with digital calipers. This bracket base area was used for calculating the shear bond strength in MPa.

2.3 Sample size

A limited trial experiment was designed to determine sample size, consisting of only 3x groups: NTP conditioning for 20 seconds, 9.5% HF etching for 20 seconds and HF etching for 60 seconds. Seven samples were included per group but it was found that some of the ceramic chips lifted out of the embedding resin during shear bond strength testing. All samples that lifted either completely or partially out of the resin during bond strength testing were discarded. The
results from this trial are shown in Table 2.1. A power calculation determined that a sample size of 13 was required to show a 20% difference between the two HF etching times. Approximately 40% of the samples lifted from the embedding resin. In order to compensate for this sample loss, the sample size was increased to 20 samples per group.

<table>
<thead>
<tr>
<th>Conditioning method</th>
<th>Sample size</th>
<th>Debond Force (MPa)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5% HF 20 seconds</td>
<td>6</td>
<td>14.77</td>
<td>2.71</td>
</tr>
<tr>
<td>9.5% HF 60 seconds</td>
<td>4</td>
<td>15.58</td>
<td>1.87</td>
</tr>
<tr>
<td>NTP 20 seconds</td>
<td>4</td>
<td>17.81</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 2.1 Trial experiment results

2.4 Assignment to surface conditioning groups and bonding

2.4.1 Surface conditioning group assignment

In total, 300 samples were polished according to the method outlined above. The samples were randomly assigned to one of 5 groups (A, B, C, D and E). The groups were further randomly divided into 3 subgroups of 20 samples corresponding to each storage period (1: 30 minutes, 2: 24 hours, 3: 6 months).

2.4.2 Surface conditioning

Immediately prior to surface conditioning and bonding, each disc was rinsed with water and dried. Group A was conditioned with 37% phosphoric acid (Etch-37, Bisco, Schaumburg Illinois) for 15 seconds. Groups B to D were etched with 9.5% hydrofluoric acid (Porcelain Etchant, Bisco, Schaumburg Illinois); 20 seconds for group B and 60 seconds for groups C and D. Group E was treated with NTP for 20 seconds (Figure 2.1). Argon plasma application to the
ceramic surface was accomplished with a hand-held unit produced by Neoplas Control (Kinpen, Greifswald, Germany). Argon gas flow was maintained at 5 L min$^{-1}$ with oxygen as an additive gas. The ceramic was held at a distance of 5 mm from the NTP tip and moved slowly in a small circular pattern to condition the entire bonding region. After conditioning, and immediately prior to bonding, samples from groups A to D were rinsed with and air/water spray for 30 seconds and air-dried.

Figure 2.1 Non-thermal plasma conditioning of the ceramic surface
<table>
<thead>
<tr>
<th>Group</th>
<th>Conditioning method</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (1, 2, 3)</td>
<td>37% phosphoric acid (15 seconds)</td>
</tr>
<tr>
<td>B (1, 2, 3)</td>
<td>9.5% hydrofluoric acid (20 seconds)</td>
</tr>
<tr>
<td>C (1, 2, 3)</td>
<td>9.5% hydrofluoric acid (60 seconds)</td>
</tr>
<tr>
<td>D (1, 2, 3)</td>
<td>9.5% hydrofluoric acid (60 seconds) with EBA</td>
</tr>
<tr>
<td>E (1, 2, 3)</td>
<td>Non-thermal plasma (20 seconds)</td>
</tr>
</tbody>
</table>

Table 2.2 Surface preparation groups

2.4.3 Bracket bonding

Monobond Plus (Ivoclar Vivadent, Schaan, Liechenstein), the manufacture’s recommended bonding agent, was used to silanate the ceramic surface in all groups. This product contains 3-trimethoxysilylpropyl methacrylate and methacrylated phosphoric acid ester in an ethanol carrier(74). It was applied in a thin coat and air-dried after 60 seconds. Following silane application, a thin coat of Ortho Solo, (Kerr Corporation, Orange, California) an EBA was applied only to group D without curing. Ortho Solo is composed primarily of unspecified alkyl dimethacrylate resins and low amounts of various inorganic fillers with a Vf of 17-39%(75).

Standard metal twin lower incisor brackets were used for all samples (Mini Master, American Orthodontics, Sheboygan, Wisconsin). A composite resin bracket adhesive (Transbond XT, 3M Unitek, St Paul, Minnesota) was applied to the bracket base and pressed onto the ceramic surface with 500 g pressure.
Transbond XT adhesive paste is a composite material composed of various alkyl dimethacrylates with high inorganic filler content (Wf = 70-82%)(76). Excess adhesive was removed with a #5 explorer. Each sample was cured for 5 seconds from both the mesial and distal aspects of the bracket with a Bluephase Style curing light (Ivoclar Vivadent, Schaan, Liechenstein). Immediately prior to each bracket bonding the light intensity was confirmed to be greater than 1,100 mW/cm² with a Bluephase Meter.

2.5 Water storage and shear bond strength testing

2.5.1 Water storage

Immediately following bonding the brackets, all samples were placed in a bath of distilled water maintained at 37°C. Samples were stored for 30 minutes, 24 hours and 6 months for subgroups 1, 2 and 3 and were debonded immediately after removal from the bath after the designated storage time.

2.5.2 Shear bond strength testing

Shear bond strength testing was accomplished with a Bisco Shear Bond Tester (T-63010K, Shaumburg, Illinois) with a 0.5 mm min⁻¹ crosshead speed (Figure 2.2). It was found that the standard notched blade significantly deformed the bracket base; therefore, a custom straight blade was fabricated and used for all testing. Loading was always applied to the upper, incisal aspect of the bracket. The resultant force was measured in newton and converted to megapascals using the measured bracket base area. (AutoCAD Autodesk Inc., San Rafael, California).
Figure 2.2 Setup for shear bond strength testing
2.5.3 Fracture mode assessment

The fracture mode was assessed under a light microscope at 16X original magnification using a modified adhesive remnant index (ARI) to score the amount of adhesive adhering to the ceramic\(^{(49)}\). The ARI scores are presented in Table 2.1.

<table>
<thead>
<tr>
<th>ARI score</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>no composite remaining on the ceramic surface</td>
</tr>
<tr>
<td>4</td>
<td>less than 10% of composite remaining</td>
</tr>
<tr>
<td>3</td>
<td>more than 10% but less than 90% of the composite remaining</td>
</tr>
<tr>
<td>2</td>
<td>more than 90% of the composite remaining</td>
</tr>
<tr>
<td>1</td>
<td>all of the composite remaining on the ceramic</td>
</tr>
</tbody>
</table>

Table 2.3 Scoring system for the adhesive remnant index

2.5.4 Scanning electron microscopy

High-magnification images of the surface preparation groups and adhesive/ceramic interfaces were obtained with scanning electron microscopy (Hitachi S-3000N). Ceramic surface images were obtained for e.max ceramic that was not previously etched or bonded (C1), previously bonded e.max ceramic that was repurposed by polishing up to 600 grit as previously described (C2) and for each group that utilized a different surface conditioning technique (A, B, C and E). Images for the adhesive/ceramic interfaces were obtained by sectioning the bonded bracket and ceramic with a diamond cutting wheel followed by polishing with wet/dry sandpaper.
up to 2000 grit and finishing with 3 μm diamond paste on a felt pad. Magnifications of 1000X and 5000X were used for ceramic surface images while 800X and 8000X were used for the bracket/ceramic interface.

2.6 Statistics

The SBS values were analyzed with a two-way analysis of variance (ANOVA) and group comparison were made with the Tukey HSD test with the significant level set at α=0.05. The statistical analysis was performed with SigmaPlot software (Version 13, San Jose, California).
Chapter 3: Results

The results of bracket SBS testing are reported in Table 3.1, including the sample size, mean, standard deviation, minimum and maximum for all groups. Differences between groups were determined by two-way ANOVA and are reported in Table 3.2 with corresponding boxplots in Figure 3.1, Figure 3.2, Figure 3.3 and Figure 3.4. There was not a statistically significant interaction between surface conditioning and storage time (p=0.259). During SBS testing some ceramic samples lifted out of the embedding resin and were discarded from the results, resulting in uneven group size.

3.1 Bracket bond strength at 30 minutes and 24 hours

After 30 minutes of water storage, surface treatment with 9.5% HF for 60 seconds followed by the application of an EBA yielded the highest SBS (15.71 MPa) which was significantly greater than all other surface conditioning groups. At 24 hours, the SBS of all groups increased. This increase was significant for all groups except NTP conditioning. Surface treatment with 9.5% HF for 60 seconds and EBA continued to yield the highest SBS (19.12 MPa) and was significantly greater than all groups.

3.2 Bracket bond strength at 6 months

After 6 months of water storage, the general trend was for SBS to decrease from the 24-hour values. This decrease was significant for surface treatments with 9.5% HF for 60 seconds with EBA, PA and NTP. Surface treatment with 9.5% HF and EBA continued to yield the highest SBS (15.24 MPa) but was no longer significantly different from the other groups.
employing HF etching. All groups treated with 9.5% HF exhibited significantly greater SBS than surface treatment with PA (8.93 MPa). SBS following surface treatment with NTP was significantly less than when etched with 9.5% HF for 60 seconds but was comparable to etching with 9.5% HF for 20 seconds. There was no significant difference between PA and NTP conditioning.

At 6 months, the mean SBS of all groups was higher than the minimum clinical bond strength proposed by Reynolds of 6 – 8 MPa (8.93 – 15.24 MPa); however, groups treated with PA and NTP had multiple values lower than this range, with minimums of 3.89 and 3.15 MPa, respectively.

3.3 Adhesive residue index scores

ARI scores are reported in Table 3.3. There was a greater tendency for composite to remain on the ceramic surface for the HF etched groups at all time periods. At 6 months there was very little remaining composite for both the PA and NTP groups, suggestive of adhesive failure, while cohesive failure within the adhesive paste remained a prominent mode of bond failure for HF etched groups. No porcelain fractures were observed in any of the samples.

3.4 Scanning electron microscopy

3.4.1 Scanning electron microscopy: conditioned ceramic surface

Qualitative comparison of the SEM images in Figure 3.5 and Figure 3.6 show a relatively smooth surface of the unmodified e.max ceramic (C1) compared to the scratched surface of the
reused ceramic that was polished (C2). Surface treatments with PA and NTP (Figure 3.7 and Figure 3.10 respectively) are not qualitatively different from the polished ceramic. Conversely, drastic morphological change was clearly visible in all groups conditioned with HF and increased surface porosity was observed in groups C and D when compared with group B (Figure 3.9 and Figure 3.8 respectively), corresponding with increased length of the acid etch.

3.4.2 Scanning electron microscopy: bond/ceramic interfaces

No visible differences could be seen between any of the experimental groups at either 800X or 8000X magnification. The thin bonding agent layer employed in group D could not be clearly distinguished from the composite adhesive in the other groups.
<table>
<thead>
<tr>
<th>Group</th>
<th>Sample Size</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1: 30 min</td>
<td>10.47</td>
<td>2.80</td>
<td>6.20</td>
<td>15.79</td>
</tr>
<tr>
<td>(37% PA)</td>
<td>2: 24 hours</td>
<td>13.24</td>
<td>2.93</td>
<td>8.93</td>
<td>18.65</td>
</tr>
<tr>
<td></td>
<td>3: 6 months</td>
<td>8.93</td>
<td>3.36</td>
<td>3.89</td>
<td>18.28</td>
</tr>
<tr>
<td>B</td>
<td>1: 30 min</td>
<td>11.94</td>
<td>2.68</td>
<td>8.06</td>
<td>20.50</td>
</tr>
<tr>
<td>(20 seconds 9.5% HF)</td>
<td>2: 24 hours</td>
<td>15.14</td>
<td>4.08</td>
<td>7.82</td>
<td>23.33</td>
</tr>
<tr>
<td></td>
<td>3: 6 months</td>
<td>13.25</td>
<td>3.28</td>
<td>7.77</td>
<td>19.03</td>
</tr>
<tr>
<td>C</td>
<td>1: 30 min</td>
<td>12.42</td>
<td>3.02</td>
<td>9.02</td>
<td>20.46</td>
</tr>
<tr>
<td>(60 seconds 9.5% HF)</td>
<td>2: 24 hours</td>
<td>15.81</td>
<td>5.35</td>
<td>8.24</td>
<td>27.68</td>
</tr>
<tr>
<td></td>
<td>3: 6 months</td>
<td>14.92</td>
<td>3.41</td>
<td>8.43</td>
<td>20.00</td>
</tr>
<tr>
<td>D</td>
<td>1: 30 min</td>
<td>15.71</td>
<td>2.64</td>
<td>12.26</td>
<td>22.04</td>
</tr>
<tr>
<td>(60 seconds 9.5% HF + EBA)</td>
<td>2: 24 hours</td>
<td>19.12</td>
<td>3.27</td>
<td>12.82</td>
<td>25.41</td>
</tr>
<tr>
<td></td>
<td>3: 6 months</td>
<td>15.24</td>
<td>3.90</td>
<td>7.91</td>
<td>22.31</td>
</tr>
<tr>
<td>E</td>
<td>1: 30 min</td>
<td>11.62</td>
<td>2.10</td>
<td>7.77</td>
<td>14.86</td>
</tr>
<tr>
<td>(20 seconds NTP)</td>
<td>2: 24 hours</td>
<td>14.08</td>
<td>3.12</td>
<td>7.86</td>
<td>19.58</td>
</tr>
<tr>
<td></td>
<td>3: 6 months</td>
<td>11.32</td>
<td>4.66</td>
<td>3.15</td>
<td>21.11</td>
</tr>
</tbody>
</table>

Table 3.1 Descriptive statistics: means, standard deviations, minimums and maximums
<table>
<thead>
<tr>
<th>Surface Conditioning / Storage Time</th>
<th>30 minutes</th>
<th>24 hours</th>
<th>6 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) 37% PA</td>
<td>10.47 (2.80)</td>
<td>13.24 (2.93)</td>
<td>8.93 (3.36)</td>
</tr>
<tr>
<td>(B) 20 seconds 9.5% HF</td>
<td>11.94 (2.68)</td>
<td>15.14 (4.08)</td>
<td>13.25 (3.28)</td>
</tr>
<tr>
<td>(C) 60 seconds 9.5% HF</td>
<td>12.42 (3.02)</td>
<td>15.81 (5.35)</td>
<td>14.92 (3.41)</td>
</tr>
<tr>
<td>(D) 60 seconds 9.5% HF + EBA</td>
<td>15.71 (2.64)</td>
<td>19.12 (3.27)</td>
<td>15.24 (3.90)</td>
</tr>
<tr>
<td>(E) NTP</td>
<td>11.62 (2.10)</td>
<td>14.08 (3.12)</td>
<td>11.32 (4.66)</td>
</tr>
</tbody>
</table>

Table 3.2 Differences between groups by two-way ANOVA with Tukey HSD

Note: Mean values expressed in MPa. Different letters indicate a statistically significant difference (p<0.05). Upper case letters compare surface treatments within each column and lower case letters compare storage times within each row.
Figure 3.1 Boxplot showing differences between time periods within groups

Notes: * = p<0.05
Figure 3.2 Boxplot of shear bond strengths at 30 minutes

Notes: * = p<0.05
Figure 3.3 Boxplot of shear bond strengths at 24 hours

Notes: * = p<0.05
Figure 3.4 Boxplot of shear bond strengths at 6 months

Notes: * = p<0.05
<table>
<thead>
<tr>
<th>Group</th>
<th>Subgroup</th>
<th>Sample Size</th>
<th>1 (%)</th>
<th>2 (%)</th>
<th>3 (%)</th>
<th>4 (%)</th>
<th>5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 37% PA</td>
<td>1: 30 min</td>
<td>20</td>
<td>1 (5%)</td>
<td>1 (5%)</td>
<td>1 (5%)</td>
<td>6 (30%)</td>
<td>11 (55%)</td>
</tr>
<tr>
<td></td>
<td>2: 24 h</td>
<td>19</td>
<td>0 (0%)</td>
<td>3 (16%)</td>
<td>3 (16%)</td>
<td>8 (42%)</td>
<td>5 (26%)</td>
</tr>
<tr>
<td></td>
<td>3: 6 mo</td>
<td>19</td>
<td>0 (0%)</td>
<td>2 (11%)</td>
<td>1 (5%)</td>
<td>5 (26%)</td>
<td>11 (58%)</td>
</tr>
<tr>
<td>B 20 seconds 9.6%</td>
<td>1: 30 min</td>
<td>19</td>
<td>1 (5%)</td>
<td>5 (26%)</td>
<td>2 (11%)</td>
<td>6 (32%)</td>
<td>5 (26%)</td>
</tr>
<tr>
<td></td>
<td>2: 24 h</td>
<td>19</td>
<td>0 (0%)</td>
<td>5 (26%)</td>
<td>8 (42%)</td>
<td>4 (21%)</td>
<td>2 (11%)</td>
</tr>
<tr>
<td></td>
<td>3: 6 mo</td>
<td>19</td>
<td>2 (11%)</td>
<td>7 (37%)</td>
<td>3 (16%)</td>
<td>5 (26%)</td>
<td>2 (11%)</td>
</tr>
<tr>
<td>C 60 seconds 9.6%</td>
<td>1: 30 min</td>
<td>19</td>
<td>0 (0%)</td>
<td>5 (26%)</td>
<td>2 (11%)</td>
<td>8 (42%)</td>
<td>4 (21%)</td>
</tr>
<tr>
<td></td>
<td>2: 24 h</td>
<td>16</td>
<td>0 (0%)</td>
<td>4 (25%)</td>
<td>3 (19%)</td>
<td>3 (19%)</td>
<td>6 (38%)</td>
</tr>
<tr>
<td></td>
<td>3: 6 mo</td>
<td>20</td>
<td>0 (0%)</td>
<td>12 (60%)</td>
<td>2 (10%)</td>
<td>4 (20%)</td>
<td>2 (10%)</td>
</tr>
<tr>
<td>D 60 seconds 9.6%</td>
<td>1: 30 min</td>
<td>19</td>
<td>1 (5%)</td>
<td>6 (32%)</td>
<td>5 (26%)</td>
<td>6 (32%)</td>
<td>1 (5%)</td>
</tr>
<tr>
<td></td>
<td>2: 24 h</td>
<td>18</td>
<td>0 (0%)</td>
<td>5 (28%)</td>
<td>10 (56%)</td>
<td>2 (11%)</td>
<td>1 (6%)</td>
</tr>
<tr>
<td></td>
<td>3: 6 mo</td>
<td>18</td>
<td>0 (0%)</td>
<td>10 (56%)</td>
<td>4 (22%)</td>
<td>3 (17%)</td>
<td>1 (6%)</td>
</tr>
<tr>
<td>E 20 seconds NTP</td>
<td>1: 30 min</td>
<td>19</td>
<td>4 (21%)</td>
<td>1 (5%)</td>
<td>1 (5%)</td>
<td>8 (42%)</td>
<td>5 (26%)</td>
</tr>
<tr>
<td></td>
<td>2: 24 h</td>
<td>20</td>
<td>0 (0%)</td>
<td>1 (5%)</td>
<td>5 (25%)</td>
<td>8 (40%)</td>
<td>6 (30%)</td>
</tr>
<tr>
<td></td>
<td>3: 6 mo</td>
<td>19</td>
<td>0 (0%)</td>
<td>2 (11%)</td>
<td>2 (11%)</td>
<td>6 (32%)</td>
<td>9 (47%)</td>
</tr>
</tbody>
</table>

Table 3.3 Adhesive remnant index scores
Figure 3.5 e.max without surface modification (previously unbounded): (a) 1000X, (b) 5000X
Figure 3.6 Polished e.max: (a) 1000X, (b) 5000X
Figure 3.7 Polished e.max conditioned with PA for 15 seconds: (a) 1000X, (b) 5000X
Figure 3.8 Polished e.max etched with HF for 20 seconds: (a) 1000X, (b) 5000X
Figure 3.9 Polished e.max etched with HF for 60 seconds: (a) 1000X, (b) 5000X
Figure 3.10 Polished e.max conditioned with NTP for 20 seconds: (a) 1000X, (b) 5000X
Figure 3.11 Cross section of the ceramic (i) /adhesive (ii) interface after conditioning with PA for 15 seconds:

(a) 800X, (b) 8000X
Figure 3.12 Cross section of the ceramic (i) / adhesive (ii) interface after etching with HF for 20 seconds: (a) 800X, (b) 8000X
Figure 3.13 Cross section of the ceramic (i) /adhesive (ii) interface after etching with HF for 60 seconds: (a) 800X, (b) 8000X
Figure 3.14 Cross section of the ceramic (i)/adhesive (ii) interface after etching with HF for 60 seconds followed by the application of an EBA: (a) 800X, (b) 8000X
Figure 3.15 Cross section of the ceramic (i) /adhesive (ii) interface after conditioning with NTP for 20 seconds: (a) 800X, (b) 8000X
Chapter 4: Discussion

4.1 Comparison of surface conditioning techniques

All surface conditioning groups resulted, on average, in clinically acceptable SBS relative to Reynolds’ proposed minimum of 6 to 8 MPa at all time periods, however, etching with 9.5% HF for either 20 seconds or 60 seconds resulted in a trend towards higher SBS at all time periods compared with PA and NTP conditioning. The general trend for all groups was for SBS to increase from 30 minutes to 24 hours and then decrease at 6 months. These results are consistent with previous research which shows that bracket bond strength to enamel increases from 30 minutes to 24 hours(49) followed by a gradual decrease over 24 months(45).

The greater SBS observed with HF relative to PA and NTP conditioning at 6 months is assumed to be due to the increased surface area associated with HF etching. This increased surface area creates the opportunity for micromechanical retention that is not possible with non-destructive surface conditioning techniques.

SEM of HF treated ceramic surfaces shows increased surface area and potential for micromechanical retention obtained through HF etching relative to NTP and PA, which did not result in a significant alteration of the porcelain surface. Although apparent greater porosity is obtained through etching with HF for 60 seconds compared to 20 seconds, this did not result in a significant difference in SBS at any storage time. However, the 60 second etch was not detrimental to bond strength, lending preliminary evidence to suggest that adequate bond
strength will be obtained if clinicians are unaware of the type of ceramic and etch lithium disilicate for 60 seconds.

Despite the general trend towards increased SBS with HF, this study showed that at 30 minutes and 24 hours of water storage, similar SBS were obtained by conditioning with PA and NTP with all groups exhibiting clinically acceptable mean SBS (ca. > 8.0 MPa).

These findings are in agreement with previous bracket bond strength studies using feldspathic ceramics. Akhoundi(13), Bourke(53) and Larmour(54) found that there was no difference between HF etching and PA conditioning in bracket SBS and concluded that PA could be used as a replacement for HF when bonding to feldspathic ceramic. In contrast, Akova(11) found that HF etching yielded greater bond strength relative to PA, although the difference was relatively small and unlikely to be clinically significant. Although there was no direct comparison to HF, Nebbe(55) and Pannes(21) also found that PA also yielded adequate bond strengths to feldspathic porcelain. The longest storage time in the aforementioned studies was 48 hours, including thermocycling, and no comparisons between storage time in water and bracket bond strength were made. This study showed that bond strength tends to decrease from 24 hours to 6 months of water storage, although this decrease was variable amongst the groups. A significant reduction in SBS occurred with PA and NTP conditioning and HF etching followed by EBA application. The groups that were etched with HF for 20 seconds and 60 seconds without EBA did not undergo a significant decrease. The result of this decrease was that after 6 months of water storage, PA conditioning performed worse that all groups etched with HF.
suggesting that PA should not be considered as an alternative to HF etching for surface conditioning of lithium disilicate ceramic.

Similarly to PA, NTP, which also did not appear to increase surface porosity, exhibited a significant decrease in SBS at 6 months. SBS was significantly lower compared to most groups etched with HF but remained comparable to etching with HF for 20 seconds. These results are contrary to Lanza who found that e.max treatment with NTP alone performed poorly in comparison to HF etching for 20 seconds with a significantly lower mean bond strength at 24 hours and a significant reduction after just 90 days of water storage(63). Lanza’s study employed a self-adhesive dual-cured resin cement, which may have been responsible for the discrepancy.

The greater decrease in SBS for the PA and NTP groups relative to HF etching is assumed to be in part due to lack of micromechanical retention, as shown through SEM images. It was initially conjectured that NTP application could result in improved surface wetting relative to PA resulting in improved contact between the adhesive and the ceramic substrate and decreased porosity for water sorption and hydrolytic bond degradation, however, a significant difference between PA and NTP conditioning was not observed.

The results suggest that PA and NTP are not suitable alternatives for HF etching when higher bond strengths are desirable. Although the average SBS remained within the range of clinical acceptability as proposed by Reynolds, SBS as low as 3.89 MPa for PA and 3.15 MPa for NTP were observed, suggesting that some bond failures could be expected in a clinical
setting. Clinical use of PA or NTP would likely result in increased failures with extended treatment time. Moreover, NTP technology is currently not suited for use in a clinical setting as it is both bulky and relatively immobile, requiring cylinders of compressed argon and oxygen. Additionally, its range of usefulness is currently limited with questionable efficacy on enamel(59). Further studies examining different adhesives and substrates with longer storage times are required to adequately determine the clinical usefulness of NTP. As new portable and clinically-friendly NTP devices become available it is warranted to encourage continued studies on the topic. Other methods of surface conditioning that do not result in substantial increases in micromechanical retention, such as laser conditioning as proposed by Ahrari(24) and Akova(11), would benefit from similar long-term water storage studies to determine their suitability for orthodontic bracket bonding.

4.2 Water storage time and bracket shear bond strength

Increased bond strength is expected from the time of initial bonding to 24 hours and this was the observed trend, with significant increases in all groups except for NTP conditioning. This is consistent with Kao who found that there was a significant increase in bond strength of orthodontic brackets to feldspathic porcelain from <30 minutes to 24 hours, although, the exact time of testing in the <30 minute group was variable(77). In contrast, Nebbe found that bond strength to porcelain increased from 0 minutes to 10 minutes but that there was no further significant increase up to 72 hours(55).

Bracket bond strength to porcelain beyond 7 days has not been previously studied. Oesterle’s research showed that a significant decrease in bond strength to enamel occurred at 12
months. This study showed that the decrease in SBS to LiDi ceramic occurred earlier at 6 months, in all groups except for HF etching without EBA. It is likely that a similar trend is occurring in these experimental groups but that additional storage time would be necessary to show a significant decrease. The results imply that the rate of bond degradation is comparable to enamel or slightly faster but further studies would be required to draw an accurate comparison.

4.3 The effect of bonding agents on bracket bond strength

Surface conditioning with a 60 second HF etch followed by an enamel bonding agent yielded the highest SBS at all time periods and was significantly greater than all groups at 30 minutes and 24 hours. This result is in contrast with previous in vitro orthodontic bracket bonding studies which found that there is no benefit to their application to enamel(66,67). However, at 6 months, there was no longer a significant difference between any of the groups etched with HF, suggesting that while EBA may be beneficial in the short term, it has limited benefit for the maintenance of long-term bond strength.

The effect of EBA could have been masked by the use of Monobond Plus (MBP) in all groups. MBP is designed to serve the role of both silane coupling agent and bonding agent and may have masked the benefit of applying the Ortho Solo EBA at 6 months. Additionally, it is possible that orthodontic bracket composite resin adhesive pastes exhibit viscosities low enough to allow for adequate surface wetting on their own, making the use of an EBA unnecessary.

The results of this in vitro study or others do not rule out a clinical benefit to the application of EBAs on ceramics or enamel. In this study and the aforementioned research, the
general trend is for EBA application to result in increased SBS, suggesting that a relatively small, but potentially clinically significant, difference could exist. Also, in vitro studies are highly controlled and are unable to account for clinical variability. The increased hydrophilicity of EBAs relative to bracket composite resin adhesive pastes may account for the variabilities observed between clinical(68) and in vitro(67) studies. A clinical study on the incidence of bracket bond failure to ceramic would be required to better assess the usefulness of EBAs.

SEM images of the bonded cross section for the group with EBA application (Figure 3.14) did not appear any different from the other groups. As per the Ortho Solo instructions, the EBA was not cured prior to placing the bracket with the composite resin adhesive paste. It is possible that mixing of the EBA and the adhesive paste occurred under the pressure of bracket bonding and the EBA layer rendered too thin or even displaced so that it was not observed in the images. This mixing or displacement, in combination with the presence of inorganic filler in Ortho Solo, likely resulted in the similarity between the substrates as observed in the SEM images.

4.4 Adhesive residue index

There was a trend towards increased composite residue for samples bonded with HF etching. Adhesive failure in the NTP and PA conditioning groups left relatively little residual composite suggesting that adhesive removal would be the simplest and result in less damage to ceramic surface. Interestingly, no major fracture to the ceramic surface was observed in any of the samples after debonding despite mean SBS as high as 19.12 MPa and a high prevalence of cohesive resin failure observed in group D2. This is in contrast to previous work with
feldspathic ceramics showing that porcelain fracture increases with cohesive resin failure and bond strengths above 13 MPa(36,37). Because LiDi is reportedly stronger than feldspathic ceramic, it is possible that the LiDi ceramic was able to withstand the forces associated bracket debonding better than feldspathic ceramics.

4.5 Limitations of the current research

The surface of the unmodified e.max ceramic, that would likely be the surface encountered in a clinical situation, appeared much smoother compared with the scratched appearance of the polished surface used in this study for bonding. It is not known from this study how the surface conditioning methods would interact with the unmodified e.max surface. It was impractical for the purpose of this study to bond to unpolished e.max surfaces. As discussed previously, no attempt is made to compare absolute values of bond strengths to other studies due to the extensive range of variabilities in testing methods, bonding techniques and storage times. Rather, comparisons between bonding methods are made and remain valid within this study. External validity would need to be assessed through additional in vivo and in vitro studies to adequately assess the usefulness of the porcelain conditioning methods in a clinical setting.
Chapter 5: Conclusion

Multiple differences were observed between the surface conditioning techniques employed. The general trend was for SBS to increase from 30 minutes to 24 hours and then decrease from 24 hours to 6 months, however, the significance of these changes with time were variable depending on the method of surface conditioning employed. Notably, PA and NTP conditioning exhibited significant decreases in SBS from 24 hours to 6 months resulting in generally lower SBS relative to HF conditioning. Therefore, both null hypotheses were rejected.

1) Ho: there are no differences in bracket SBS among the e.max surface treatment groups
2) Ho: there are no differences in bracket SBS among the storage periods

In addition to rejection of the null hypotheses, the following conclusions can be made.

• All surface conditioning methods yielded, in average, clinically acceptable SBS after 30 minutes, 24 hours and 6 months of water storage at 37°C (Clinical acceptability: 6 to 8 MPa as proposed by Reynolds 1975)

• The general trend was for SBS to increase from 30 minutes to 24 hours, and then decrease at 6 months, but the increase was not significant for NTP conditioning and the decrease was not significant for groups etched with HF without application of EBA.

• At all water storage times, HF for 60 seconds + bonding agent exhibited the highest SBS. It was significantly greater than all groups at 30 minutes and 24 hours but at 6 months was comparable to other groups etched with HF.
• At 6 months, PA and NTP conditioning were similar in SBS and were generally lower than groups etched with HF.

• Etching with HF results in a trend towards increased adhesive residue compared to treatment with NTP or H₃PO₄
Works Cited


