

**DIAMETRAL TENSILE STRENGTH, MICROHARDNESS, SURFACE
MODULUS, AND SURFACE MORPHOLOGY OF NOVEL, ANTIMICROBIAL
ORTHODONTIC ADHESIVES**

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ABSTRACT

Objective: Prior to the advent of bonded orthodontic appliances each tooth was fitted with a band made from stainless steel. Traditionally they were cemented to the tooth with a zinc phosphate cement. This acted more as a luting agent than adding to the actual adherence of the band to the tooth. In addition, often times the cement would wash out and upon the band removal white spot lesions and or carious lesions were present. The development of glass ionomer cements had a traumatic improvement over both the adhesion to the tooth and a diminishing of white spot lesions in part due to the release of fluoride.

Since the advent of the acid-etch technique and the bonding of orthodontic brackets directly to the enamel various bonding adhesives were developed. The first and most popular bonding resins were chemical curing bonding systems. The general class of self-adhesive and/or self-etching orthodontic adhesives are of several types, including resin-modified cements, such as resin-modified glass ionomer cements, that exhibit self-adhesive properties to enamel, as well as self-etching primers that combine the conditioning and priming agents into one acidic, polymerizable composition for application to the tooth surface, and do not require separate etching and rinsing steps. Not only do resin modified glass ionomers have the benefit of chemically bonding to a clean and un-etched enamel surface, but these self-adhesive cements also release significant and continuous levels of fluoride ion. Recently investigators have explored adding antimicrobial agents in addition to fluoride in orthodontic adhesives. One such approach has been the addition of ZnO powder, a known compound with anti-microbial properties, to an orthodontic resin modified glass ionomer adhesive. It should also be noted that zinc

ions and compounds have been shown to positively influence enamel remineralization and enhance apatite formation.

The objective of this research is to evaluate the effect of the addition of an antimicrobial agent, zinc oxide powder, on selected mechanical properties of a resin modified glass ionomer orthodontic adhesive.

Methods: A resin modified glass ionomer (Fuji Ortho LC), in its two-component, powder/liquid format were utilized in this study. Control specimens, according to manufacturer's directions for use, were prepared for both diametral tensile and microhardness testing with be prepared. Using the powder component provided in the marketed product; powder blends containing both 10 and 20 percent Zinc Oxide (by weight) will be added to the RMGI powder, and thoroughly mixed and blended to create a uniform powder blend.

The mechanical testing will be performed on 8-10 disc specimens, approximately 6.2 mm diameter by 3.1 mm in height, using a standardized mixing and molds for each material. The specimens will be tested using the Instron 5569 testing machine at a crosshead speed of 0.75 mm/minute for DTS until failure occurs. Data was recorded in Newton's (N) force. The microhardness testing was performed on 12 disc specimens, approximately 6.2 mm diameter by 3.1 mm in height, using a standardized mixing and molds for each material. A CSM microindentation testing device was used to measure the Vickers microhardness. The surface morphological evaluation of the specimens both control and experimental will be examined at 50 X magnification for comparison of surface characteristics and morphology.

One-way ANOVA for comparison of time- and material-specific mean Vickers microhardness values and post hoc pair-wise comparisons was employed to assess statistically significant differences in the mean values ($p < 0.05$).

Results: The diametral tensile strength test of all specimens including the modified control and experimental showed incremental decreases in the DTS as compared to the control mixed as per the manufacturer's specifications. The Vickers values illustrated minimal variation of Vickers microhardness for the control and experimental group. The surface morphological evaluation illustrated various differences between the control, modified control and the Zinc Oxide formulations.

Conclusions: Alterations in the liquid powder ration of the orthodontic resin modified glass ionomer adhesive resulted in a reduction of the DTS. The addition of both 10% and 20% zinc oxide powder also resulted in a significant reduction of the DTS as compared to the manufacturers mix proportions of liquid and powder. The Vickers microhardness did not illustrate a significant alteration in any of the specimens. The addition of both 10% and 20% zinc oxide powder to the mixture reduced the modulus and stiffness as compared to both of the control groups. Lastly, the morphology of the experimental samples with the zinc oxide showed a more irregular surface at the fracture site.

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TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	v
LIST OF FIGURES.....	viii
LIST OF TABLES.....	ix
CHAPTER	
1. INTRODUCTION	1
2. REVIEW OF THE LITERATURE	4
2.1 Conventional Acid-Base Cements	4
2.2 Resins/Composite Resins	10
2.3 Resin-modified, Glass Ionomer Cements	12
2.4 Polyacid-modified composite resins	16
2.5 Comparative <i>in-vitro/in-vivo</i> Properties of Orthodontic Adhesives & Cements.....	17
2.6 Anti-microbial/Anti-biofilm Modification of RMGI Orthodontic Adhesives.....	22
3. AIMS OF THE INVESTIGATION.....	22
4. MATERIALS AND METHODS.....	24
4.1 Laboratory Facilities	
4.2 Preparation of Formulations for Specimens	24
4.3 Mechanical Testing.....	25

4.4 DTS Data Analysis	26
4.5 CSM Micro-hardness Tester and Indentation Methodology.....	27
4.6 Statistical Analysis of Data	30
4.7 Surface Morphological Evaluation	31
5. RESULTS	32
5.1 Diametral Tensile Strength.....	32
5.2 Vickers Microhardness & Surface Modulus.....	35
5.3 Micromorphology of Control & Experimental Materials.....	38
6. DISCUSSION	41
7. CONCLUSIONS.....	45
BIBLIOGRAPHY.....	47

LIST OF FIGURES

Figure	Page
1. Photograph Illustrates Cylinders on the Instron.	26
2. CSM Micro-Hardness Tester	28
3. Typical Load-Depth Curve from CSM Microindentation Test	30
4. Bar Chart Depicting the Mean Stress to Failure	33
5. Mean Microhardness Values	36
6. Bar Chart Depicting the Mean Surface Modulus	37
7. Light Photomicrographs of Polished Surfaces of Control and Experimental Specimens	39
8. Size Determination for Zinc Oxide Particles	40
9. Surfaces of Fractured Specimens	40

LIST OF TABLES

Table	Page
1. Summary of Properties for Various Types/Classes of Orthodontic Adhesives/Cements	18
2. Mean Values (plus/minus standard deviations) for Force (Newtons)	33
3. P-Values for Mean DTS Values	34
4. Mean Values for Microhardness & Surface Modulus	35
5. P-Values for Possible Pair-Wise Comparisons Utilizing an Unpaired t-Test for Mean Surface Modulus Values	38

CHAPTER 1

INTRODUCTION

Fixed orthodontic devices are adhered- to natural tooth structure intraorally through the use of dental cements and resins. (Ewoldsen & Demke,2001) Ideally, orthodontic devices should minimally interfere with patient's comfort, appearance, function, and hygiene. Traditional powder-liquid cements, such as zinc phosphate, zinc polycarboxylate, and glass ionomer were and are still used, primarily for the attachment of orthodontic bands; where these cements were used as principal band cements until the early 1990s. (Gottlieb *et al*, 1996)

Yet the discovery of the ability to adhesively bond to enamel (Buonocore, 1955; Swift, 2002) and the subsequent development and the popularity of resin and resin-cement hybrid materials has increased dramatically in the last four to five decades; due in part to their improved physical properties and low solubility in oral fluids, as well as their essential role in bonding to acid-etched or conditioned enamel. Perhaps the most significant factor in the success of enamel bonding has been its reliability, with Swift (Swift, 2002) noting: "Enamel bonding has been widely and successfully used in dentistry for over 20 years." That view has apparently not changed almost a decade and one-half later. Non-resin containing cements may or may not bond chemically to enamel, as will be discussed later in this Introduction. Additionally, these conventional, acid-base cements have limited mechanical properties as they may be brittle and fracture cohesively, but if they do bond to tooth structure, their bond strengths are low (Ewoldsen & Demke, 2001). Alternatively, as described in more depth below, resin adhesives

penetrate micropores in etched enamel and also the mechanical retentive features in orthodontic devices, resulting in significantly higher bond strengths to both tooth structure and the bracket or device interface. Since modes of fracture at any adhesive-substrate interface can have both adhesive and cohesive behavior, the internal and cohesive strength properties of the adhesive material has a direct influence on the actual measured bond strength of the assembly. Because resins are more fracture resistant than non-resin cements, this property contributes to the stability and bond strength of an adhesively bonded orthodontic appliance.

Orthodontic adhesives provide an important clinical function in securing orthodontic appliances and devices to tooth structure. The discovery by Buonocore (Buonocore, 1955) concerning the ability to create a stable bond to enamel revolutionized restorative dentistry, but also the field of Orthodontics. The principle underlying this adhesive mechanism was the formation of micromechanical retentive pattern on the etched enamel surface due to the application of 35-40% phosphoric acid liquid or gel leading to selective etching and removal of calcium within the enamel prism structure (Goodman & Gwinnett, 1977) . This surface modification technique produces a roughened surface with a micromechanical retentive pattern as well as converting a low surface to one with significantly higher surface energy. This change in surface energy permits enhanced wetting of hydrophobic polymerizable resin materials that can penetrate this microscopic retentive pattern on the enamel surface, then curing to form a rigid adhesively bonded interface to enamel. Since the advent of the acid-etch technique by Buonocore (Buonocore, 1955) and the bonding of orthodontic brackets by Newman, (Newman, 1965) various bonding adhesives were developed. The first and most popular

bonding resins were chemical curing bonding systems. A major drawback of the self-cure adhesive systems is the inability to manipulate the setting time of the composite resin. (Joseph & Rossouw, 1990) Tavas and Watts (Tavas & Watts, 1979) initially, and later Read (Read, 1984), described the use of light-cured materials in vitro for orthodontic bonding. In the direct bonding technique, the material is cured under metal-based brackets by direct illumination from different sides and by trans-illumination because the tooth structure transmits visible light. Rapid polymerization occurs when visible light is applied, producing a “command set” that is of great advantage; such setting “on demand” results in a nearly unlimited working time, allowing more accurate bracket placement.

As noted by Ewoldsen and Demke (Ewoldsen & Demke, 2001), conventional hydrophobic resin-based materials however, do not bond well in the presence of moisture, and their attachment to surfaces is primarily mechanical. Alternatively, conventional glass ionomer cements are water-based and hydrophilic, therefore being able to display their chemical adhesive properties on moist tooth structure. Resin-modified glass ionomers, being a material that is a hybrid of glass ionomer and polymerizable resins, combine the advantages of cements and resins but also have certain disadvantages that will be considered below in a more depth concerning the discussion of various adhesive/cement types and chemistries. Variations in chemical differences and property limitations of today’s orthodontic cements, resins, and hybrid materials will now be considered below.

CHAPTER 2

REVIEW OF THE LITERATURE

2.1. Conventional Acid-Base Cements

Dental cements are composed of an acid component and an alkaline component that, when combined, result in a neutralization reaction leading to hardening or setting of the mixture. Cements set by a neutralization reaction. (Anusavice, 1996) Typically, the hardened cement's microstructure shows partially reacted glass particles (alkaline) suspended in a salt matrix formed when the acid component reacts with the alkaline glass. Cements are brittle, with relatively high compressive strength, low tensile strength, and relatively low fracture resistance. (Prosser *et al*, 1984) There are two basic cement types or formulas that have been utilized to lute, cement, and/or adhesively-bond orthodontic appliances: zinc phosphate and glass ionomer cement. Zinc-phosphate cement is the reaction product of zinc oxide and a phosphoric acid solution. When set, zinc-phosphate cement is dimensionally stable with relatively good physical properties, including low solubility in oral fluids. The cement components must be mixed properly to ensure that the acid-base reaction can proceed optimally, resulting in good physical characteristics and minimal effects on oral tissues. Mixing powder/liquid cement products is technique sensitive. Ideally, zinc-phosphate cement should be kept cool during mixing. Further control of setting is accomplished by slow incremental incorporation of the alkaline component during mixing. The greatest drawback to zinc-phosphate cement is that it does not bond to enamel and metals and therefore cannot be

used to attach brackets to teeth. Nevertheless, it has been used as a dental cement for the cementation of orthodontic bands for more than a century. (Kocadereli *et al*, 1995)

Polycarboxylate cement is a cement formed from the reaction product of zinc oxide and a polycarboxylic acid solution. (Friend, 1969) As a result, both zinc polycarboxylate cements and glass ionomer cements fall under the broader classification of polycarboxylate cements . Polycarboxylate cement was the first chemically adhesive dental cement. This class of cement is characterized by the formation of a chemical bond to tooth structure (i.e., between the cement and tooth structure), due to the ability of the carboxyl groups spaced along the polycarboxylic acid chain to chelate calcium ion in enamel and dentin. The actual mechanism of chemical bonding involves the chelation of carboxyl groups to divalent and trivalent cations results in an ionic bond to tooth surfaces and metal surface oxides.

As with zinc-phosphate cement, the mixing technique can be difficult and requires practice because incorporating zinc-oxide powder into the relatively viscous polycarboxylic acid liquid component is difficult. The resulting neutralization reaction between zinc oxide and polycarboxylic acid results in a mixed cement that is highly biocompatible, with little of any reaction to soft tissue or the dental pulp (not a major consideration in its use in orthodontics). (O'Brien, 2008) Despite polycarboxylate cement's chemical bonding to dental and orthodontic substrates; its relatively lower compressive strength, higher solubility, shorter working time than zinc phosphate cement, and relatively low fracture resistance has reduced and limited its clinical use as a luting cement. Polycarboxylate cements have been primarily used as luting cements for

cementation of orthodontic bands. (Valinoti, 1973) Unsuccessful attempts to use polycarboxylate cement to bond orthodontic brackets, but the low bond strength of these cements to enamel did not make this application clinically feasible. (Mizrahi & Smith, 1969)

Glass ionomer cements are utilized for cementation of orthodontics bands and have been attempted to be utilized for cementation of orthodontic brackets. (McComb, 1999) Glass ionomer cement (GIC) was introduced to the dental field in the 1970s by (Wilson & Kent 1972). The cement was composed of ion-leachable fluoroaluminosilicate glass in a solution of polyacrylic acid that sets through an acid-base reaction. The result was cement composed of ion-leachable fluoroaluminosilicate glass in a solution of polyacrylic acid called GIC. The first commercially available GIC in the US was called ASPA (alumino-silicate poly-acrylate). It was only indicated to restore cervical caries or abrasion lesions due to low mechanical properties. In addition, it was hydrolytically unstable in the oral environment. Since that time, GICs have undergone considerable research development. Improvements in several physical and mechanical properties have been sought in an attempt to expand the applications of GIC in restorative dentistry. GIC combines the advantages of translucency and fluoride release from silicate cement, and the advantages of biocompatibility and desirable adhesive properties from polycarboxylate cement. These materials have several benefits when used as a direct restorative material. These include fluoride release and uptake; chemical bonding to tooth structure, and expression of similar coefficients of thermal expansion to the tooth structure. The main disadvantage of GIC is in its low-value mechanical properties when

compared with other available restorative materials (Xie et al. 2000, Cattani-Lorente et al. 1994).

Conventional GICs are two component cements and are provided as a powder and a liquid (Barry et al. 1979). The powder consists of fluoroaluminosilicate glass particles, which are fused at high temperature and then crushed and powdered to small-size particles. The liquid is an aqueous solution of mainly polyacrylic acid in addition to other acids added to improve the handling and setting of the cement. Tartaric acid is added in the glass ionomer liquid to extend the working time, sharpen the final setting behavior, and to strengthen the cement (Crisp et al. 1975). Water is an essential component of the glass ionomer composition, and water is retained in the final set cement composition. The setting reaction of glass ionomer cements involves a liquid component employing various mixtures of carboxyl-containing acids (polyalkenoic acids) that are reacted with aluminosilicate glass. The aluminosilicate glass is fused in the presence of fluoride fluxes results in an alkaline composition that when ground into a powder component, releases fluoride ions when it is reacted with acids; and in the case of glass ionomers, polymer acids such as polyacrylic acid. (Nicholson, 1998) A hydrated, ion-rich matrix is formed as a result of this reaction that ultimately solidifies and forms the final set cement. An acid-base reaction occurs when the powder and liquid are mixed together. As the liquid attacks the glass particles, calcium and aluminum ions release, and metallic polyalkenoate salts start to form and begin to precipitate. Gelation occurs and then proceeds until the cement sets hard.

Glass ionomer cements (GICs), like polycarboxylate cements, capitalize on carboxyl chelation to the calcium component in enamel and dentin, as well as the cations found in most metals. (Fukuda *et al*, 2003) This chelation of calcium is the principal mechanism for the chemical bonding of glass ionomer to both enamel and dentin. Compared with polycarboxylate cements, GICs show higher bond strengths to enamel, dentin, and metals.^{4,5} (Saito S, *et al.*, 1999; McComb, 1999)

Glass ionomers also release fluoride. Fluoride is present and released from the reactive glass in the presence of water and polyacrylic does not participate in the formation of the structural matrix and so remains mobile to move within the water-containing glass ionomer matrix; and as such can be released from the set cement into the oral environment and adjacent tooth structure. (Sakaguchi & Powers, 2012a) The fluoride release, including its kinetic behavior, has been measured for GICs both during their setting reaction and after setting, (el Mallakh & Sarkar, 1990) This fluoride release process is sustained and occurs over a long period of time. The local environmental pH can also affect fluoride release from GICs and additional fluoride is released when GICs are exposed to acids. (Gandolfi *et al*, 2006) In-vitro, glass ionomers have demonstrated the ability to inhibit enamel demineralization and to also promote remineralization of adjacent enamel tooth structure. (Forss & Seppä, 1990) This effect has also been demonstrated in orthodontic model systems as well (Donly *et al*, 1995) One study has documented some degree of enamel demineralization inhibition/ remineralization that has been associated with a sustained low-level fluoride release from GICs. (Rezk-Lega *et al*, 1991) Nevertheless, these authors concluded: "However, these cements do not provide complete caries protection in sites where access is difficult." Furthermore, GICs

contain hydrogel phases, supporting the movement of calcium, strontium, and other ions that may be associated with the remineralization of enamel and dentin (Ewoldsen & demke, 2001). GIC hydrogel phases are thought to be responsible for the uptake and release of added environmental fluoride from topical gels, rinses, and dentifrices. (Forsten, 1998)

Mixing GICs, however, is technique sensitive, and the hydrogels desiccate and crack in dry environments. The development of encapsulated GICs eliminated most mixing variables. Low fracture resistance limits their orthodontic use primarily to band cementation; however, clinical use of GICs for bracket bonding has been reported. (White, 1986; Voss *et al*, 1993) GIC's inhibition of demineralization in adjacent enamel and its improved band retention are the chief reasons that it remains useful to orthodontists for cementing bands in caries-prone patients. (Fricker, 1989; Mizrahi, 1988; Stirrup, 1991; O'Reilly & Featherstone, 1987) GICs have been used for orthodontic bracket bonding, but bracket retention rates were poor compared with resin controls. Orthodontists generally agree that conventional GICs lack the physical properties necessary to retain brackets throughout treatment. (Millett & McCabe, 1996) Nevertheless, despite the low bracket-retention rates of GICs, the properties of chemical adhesion and moisture tolerance, thereby eliminating the need for acid etching and drying, are attractive features for an orthodontic adhesive.

2.2 Resins/Composite Resins

Composite resin orthodontic adhesives represent basic modifications of restorative composite resins, developed by Bowen in the early 1960's. (Bowen, 1963) These resin-based composites, developed in the early 1960s, provided materials with higher mechanical properties than acrylics and silicates, lower thermal coefficient of expansion, lower dimensional change on setting, and higher resistance to wear, thereby improving clinical performance. (Sakaguchi & Powers, 2012b) The basic composition consist of resin monomers and inert fillers. (Anusavice, 1996) Traditional composite resins are composed of a polymerizable monomer or prepolymer, a filler substance, and an initiator system that causes the material to polymerize and harden when desired. The inert, inorganic filler component is chemically linked to the resin matrix via a coupling agent, the most common of which are organic silicon compounds called silane coupling agents. The surface of the filler is treated with a coupling agent during the manufacture of the composite resin material. (Sakaguchi & Powers, 2012c) Polymerization can be either light activated, chemically activated, or dual cured with both light and chemical activation. (Platt, 2000) Early composites were chemically activated; the next generation were photo-activated composites initiated with ultraviolet (UV) wavelengths. These were later replaced by composites activated in the visible wavelengths. Chemically activated resin or composite resin materials require the mixing of two components to initiate the setting of the material. These chemically cured composites required the base paste to be mixed with catalyst paste, leading to problems with the incorrect mixing proportions, difficulties in mixing, and color stability issues related to the amine accelerator component. (Kinomoto *et al*, 1999) Light activated resin adhesives are always single-

component materials stored in opaque packages. Single-component resins are convenient because no mixing is required, thus eliminating technique variables. However, because resins harden solely through a polymerization reaction, they neither contain nor form hydrogels, and water is not a significant component. Although some resin adhesives release fluoride, the amount is quite low and most likely has no effect on caries. Certainly, without an acid-base reaction, the release of remineralization ions other than fluoride is unlikely unless the resin contains a soluble glass filler. Soluble fillers are subject to dissolution and ion release. However, without hydrogel formation, there is little fluoride recharge and movement of remineralization ions. (Itota *et al*, 2004)

Acid etching or other surface treatment is required before resin or resin-composite orthodontic adhesives are used, and polymerized. Resin adhesives attach to dry, etched enamel by a micro-mechanical bonding mechanism. Due to the fact that convention resin monomers used in composite resin materials contain few, if any, carboxyl groups or ion groups capable of chelation of calcium in enamel and dentin (i.e., a chemical bonding mechanism); and other cations in metal surfaces (Ewoldsen & Herwig, 1998); optimal adhesion with resins to enamel requires acid etching or other surface treatments and a dry operating field. (Platt, 2000; Cacciafesta *et al*, 1999) Resin polymerization with light activation is operator controlled, and resin adhesives acquire their optimal physical properties quickly. Generally resins are less brittle and more fracture-resistant than cements.

2.3 Resin-modified, Glass Ionomer Cements:

Hybrid glass ionomer cements have been developed that combine the desirable properties of composite resin bond strength and glass ionomer fluoride release. Traditional composite resins, as noted above, are composed of a polymerizable monomer or prepolymer, a filler substance, and an initiator system that causes the material to polymerize and harden when desired. (Vorhies *et al*, 1998) Also as was noted above, glass ionomer cements are formed by a polyalkenoic acid, a fluoroaluminosilicate glass powder, and water. The creation of hybrid glass ionomer cements results from modification or substitution of the liquid portion of the glass ionomer materials. (Vorhies, *et al*. 1998) Properties of hybrid glass ionomer cements appear to improve on some of the disadvantages of composite resins and traditional glass ionomer cements. The orthodontic use of GICs increased significantly with the development of the resin-modified glass ionomer cements (RMIGs or RMGICs). To create a longer working time yet quick setting time so that immediate finishing can take place, the concept of resin-modified glass ionomer (RMGI) was introduced in the late 1980s, initially as a photo-activated light-cured material with a background self-curing, glass ionomer reaction. The essential components are similar to those in conventional GIs in which an aqueous polycarboxylic acid undergoes an acid-base setting reaction with fluoroaluminosilicate glass. As a result, multiple curing mechanisms result for this class of cement. To this basic glass ionomer composition, hydrophilic/amphoteric, methacrylate components are added in limited amounts so a photo-initiated and/or redox (self-curing/chemical) curing reaction of the double bonds can also occur. Although commercial materials vary widely in composition, the essential components of true RMGIs are as follows: 1)

Polycarboxylic acid polymer—one formulation uses a polycarboxylic acid in which some pendant methacrylate groups are provided; 2) Fluoroaluminosilicate glass; 3) Water; 4) Hydrophilic methacrylate monomer; and 5) Free radical initiators. (Sakaguchi & Powers, 2012d)

The addition of 4% to 20% resin monomers to the GICs results in a cement that is initially hardened with the use of either light or chemical activators to polymerize the monomers. RMGICs are adhesive cements with improved physical properties and a more stable hydrogel matrix compared with conventional GICs. Delivery formats for RMGI's include conventional powder-liquid delivery that requires hand mixing, as well as capsulation of RMGIC powder and liquid components simplified mixing procedures with a triturator (Ewoldsen & Demke, 2001). Even paste-paste delivery modes are available for RMGI materials. Although a limited amount of resin monomer can be added to the polyalkenoic acid solution, polymerization of the resin monomers hastens the initial hardening of RMGICs without interfering significantly with the acid-base setting reaction, the fluoride release, or the chelation of carboxyl groups to metal and tooth surfaces. (Nicholson, 1998)

In addition to the chemical bonding of RMGICs, resin monomers penetrate surface irregularities to produce a micromechanical interlock (bond) after polymerization. In addition to the advantage of operator controlled setting, light-activated polymerization proceeds significantly faster than acid-base (cement forming) reactions, resulting in improved early physical properties, especially fracture resistance. Maturation hardening, sustained fluoride release/recharge, and caries inhibition are similar compared to both

conventional GICs and RMGICs. Also similar are the abilities of both GICs and RMGICs to chemically bond in the presence of moisture, thus eliminating the need to keep teeth dry during bonding (Silverman *et al.*, 1995). Properties of hybrid glass ionomer cements appear to improve on some of the disadvantages of composite resins and traditional glass ionomer cements. (Lippitz, 1998)

RMGIs have higher adhesive properties and, like conventional GICs, can absorb and release fluoride (Newman *et al.*, 2001). In a direct comparative study, the bond strength of hybrid resin ionomers was demonstrated to be greater than that of conventional glass ionomer cements, whereas the property of fluoride release lacking in resins is maintained. (Ashcraft *et al.*, 1997) With respect to a comparison of mechanical properties for conventional versus resin-modified glass ionomer cements; the resin-modified GICs (RM GICs) exhibited much higher flexural strength (FS) and diametral tensile strength (DTS), comparable compressive strength (CS), but often lower Knoop hardness and generally lower wear resistance, compared to the conventional GICs. (Xie *et al.*, 2000)

Although bonding to moist enamel is possible with RMGICs, conventional enamel etching can also be performed with RMGI orthodontic adhesives when a higher bond strength is needed. (Bishara *et al.*, 1998) When maximum bond strength is needed and if water or saliva contamination is expected or occurs, enamel surface treatment with 37 per cent phosphoric acid or 10 per cent polyacrylic acid can be done (Bishara *et al.*, 1998; Bishara *et al.*, 2000). Phosphoric acid at a concentration of 37 per cent is preferred

because etching with this concentration is shown to result in a comparable SBS to conventional orthodontic composites (Godoy-Bezerra *et al.*, 2006).

Resin modified glass ionomers have demonstrated the ability to release fluoride similar to that of conventional glass ionomer cements (Yi-chun *et al.*, 2008) All materials tested in this study, except for the Concise composite, exhibited the capability of fluoride release and re-uptake of fluoride ion after refluoridation treatments. The conventional GIC and the RMGICs had similar kinetics of fluoride release. However, the RMGICs showed greater fluoride release levels than the GIC both before and after topical fluoride treatment. Vitremer (3M/Espe) had initially the highest fluoride release, followed by Fuji Ortho LC (GC Dental) and Ketac-Cem (3M/Espe), whereas Fuji Ortho LC had a higher driving force for long-term fluoride release. Topical application of fluoride was demonstrated to recharge RMGICs and GIC followed by a short-term burst of fluoride release, but the rate declined rapidly. (Yi-chun *et al.*, 2000)

Similarly, a resin modified glass ionomer cement specially indicated for use as an orthodontic adhesive, Fuji Ortho LC (GC Dental), was evaluated for its ability to resist enamel demineralization in an in-vitro model utilizing cementation of orthodontic bands. (Vorhies *et al.*, 1998) The results of this in-vitro study demonstrated a similar ability of the resin-modified glass ionomer (Fuji Ortho LC/GC Dental) to reduce enamel demineralization adjacent to cemented metal orthodontic bands. Another in-vivo study also demonstrated the potential efficacy of RMGIs in reducing the severity of enamel demineralization adjacent to orthodontic brackets (Gordon & Featherstone, 2003) This study concluded: "The use of a glass ionomer cement" (Fuji Ortho LC - an RMGI),

"significantly reduced enamel mineral loss due to dental caries around orthodontic brackets in patients' mouths compared with composite resin during a 4-week period."

2.4 Polyacid-modified composite resins

Polyacid-modified composite resins, also known as *compomers*, were developed to bring the features of resin-modified glass ionomers, namely fluoride release and chemical bonding to tooth structure (carboxyl chelation), to a higher strength, single-component direct dental material that could also be utilized as an orthodontic adhesive or luting agent. (Eberhard *et al.*, 1997) Compomers, formally designated as "*polyacid modified composite resins*", are single-component systems consisting of aluminosilicate glass in the presence of carboxyl-modified resin monomers and light-activated conventional resin monomers. (Ewoldsen & Demke, 2001)

Although the alkaline glass and acidic carboxyl components are packaged in the same container, allegedly no acid-base setting reaction occurs because water is absent from the composition. However, after light-activation of the compomer, it is postulated that water sorbs into the compomer, allowing a delayed acid-base reaction that may release fluoride and other remineralizing ions from the aluminosilicate glass. (Small *et al.*, 1998) The relatively weak acid-base reaction does not result in increased physical properties of the compomer. The absence of distinct hydrogel matrix, as is present in both GICs and RMGICs, restricts ion uptake and release, including fluoride ion release and re-uptake; although fluoride recharging of compomers has been reported and can be explained by water sorption and diffusion dynamics. (Yip & Smales, 2000; Tate *et al.*,

2000; Abu-Bakr *et al.*, 2000; Millett *et al.*, 2000; Preston *et al.*, 1999a; Preston *et al.*, 1999b)

Compomers have been linked to possible reduced occurrence and severity of enamel demineralization and/or possible reduced caries risk due to elevated fluoride release from the aluminosilicate glass filler at low pH. (Chung *et al.*, 1998) Nevertheless, unlike glass ionomers and resin modified glass ionomer materials; acid etching or other surface treatment is required before compomer orthodontic adhesives are used and polymerized. (Glasspoole *et al.*, 2001) Additionally and similar to composite resin materials, bonding surfaces must be dry prior to placement of the compomer adhesive. (Tate *et al.*, 2000)

Early setting mechanical properties of compomers are superior to those of the RMGICs, but appear lower than those of the resin/composite resin adhesives. (Abu-Bakr *et al.*, 2000; Millett *et al.*, 1999) Carboxyl chelation with cations on enamel, dentin, and metallic surfaces has not been shown to occur with compomer adhesives. Physical properties are acquired quickly as compomers polymerize via photopolymerization, and their early setting strengths are superior to those of the RMGICs but inferior to those of the resin adhesives. (Abu-Bakr *et al.*, 2000; Millett *et al.*, 1999)

2.5 Comparative *in-vitro/in-vivo* Properties of Orthodontic Adhesives & Cements

Table 1 on the next page provides a summary of cement/adhesive chemistry, bonding conditions, fluoride release/recharge capacity, and curing mechanism for the

major types or classes of orthodontic cements/adhesives (adapted from Ewoldsen & Demke, 2001).

<i>Cements</i>	<i>Adhesion Mechanism</i>	<i>Acid etching Required</i>	<i>Tooth surface moisture conditions</i>	<i>Fluoride release/recharge</i>	<i>Light, Self, or Dual Curing Mode</i>
Zinc Phosphate	None	No	Dry	No	self-curing
Glass Ionomer	yes - chemical	No	Moist	Yes	self-curing
Resin Modified Glass Ionomer	yes - chemical/ mechanical	No/optional	Moist	Yes	self-curing light curing dual curing
Methacrylate-Based Polymers (Composite Resins)	yes - mechanical	Yes	Dry	No	self-cure light-cure
Polyacid Modified Composite Resins (Compomers)	yes - mechanical	Yes	Dry	Yes - but low	light-cure

Table 1. Summary of Properties for Various Types/Classes of Orthodontic Adhesives/Cements

2.6 Anti-microbial/Anti-biofilm Modification of RMGI Orthodontic Adhesives

As was noted above, not only do resin modified glass ionomers have the benefit of chemically bonding to a clean and un-etched enamel surface, but these self-adhesive cements also release significant and continuous levels of fluoride ion. Other composite resin-based orthodontic adhesives have incorporated fluoride-releasing compounds or fillers in their compositions, but the levels of fluoride release from these materials is significantly lower than that demonstrated by resin modified glass ionomer adhesives. Fluoride release from these materials may be beneficial in reducing and inhibiting enamel demineralization adjacent to the bonded bracket due to accumulation of biofilm and bacterial plaque. As has been documented in the references cited above, fluoride release may also reduce the potential for enamel demineralization and potentially enhance enamel remineralization. However, fluoride has limited and perhaps at best variable antimicrobial activity, limiting its ability to effectively reduce or eliminate bacterial plaque. (Randall *et al.*,2015) For example, when examining the antimicrobial behavior of fluoride in commercial toothpastes, this study indicated that the antimicrobial activity of commercial dentifrices against *S. mutans* may be exerted by components other than fluoride. Ingredients such as triclosan and sodium lauryl sulphate have larger antimicrobial effects than fluorides in this model. This finding suggests that other approaches to enhancing the antimicrobial activity of fluoride-releasing dental materials such as orthodontic adhesives should be explored and evaluated.

Recently investigators have explored adding antimicrobial agents in addition to fluoride in orthodontic adhesives. One such approach has been the addition of ZnO

powder, a known compound with anti-microbial properties, to an orthodontic resin modified glass ionomer adhesive, Fuji Ortho LC. (Jatania & Shivalinga, 2014) The resin modified glass ionomer orthodontic adhesive utilized in the above-mentioned study, Fuji Ortho LC, is composed of a polyalkenoic acid blended with a polymerizable monomer using free radical mechanisms. (Silverman *et al.*, 1995) This resin modified glass ionomer orthodontic adhesive utilizes both reactive methacrylates cured via free radical chemistry in addition to the aqueous, acid-base ionomer chemistry, resulting in three distinct reaction mechanisms, namely: an ionomer acid-base reaction, a self-initiated, chemical free radical polymerization, and a photo-polymerized (light cure) free radical polymerization to achieve a final set. This study (Jatania & Shivalinga, 2014) determined that addition of zinc oxide powder at levels of 10 and 20 percent in the powder component produced a set adhesive with demonstrated antimicrobial activity. The 20 percent zinc oxide material demonstrated a significantly higher level of antimicrobial activity than the 10 percent zinc oxide material. The authors did not evaluate the resulting effects of the addition of these levels of zinc oxide powder on the mechanical properties of this orthodontic adhesive, compared to the manufacture's formula. A thorough review of cited literature, thus far, has failed to demonstrate any published studies that examine the affect of additions of a zinc oxide component to an orthodontic adhesive.

While these researchers added zinc in the form of zinc oxide primarily for the antimicrobial activity of the zinc ion, it should also be noted that zinc ions and compounds have been shown to positively influence enamel remineralization and enhance apatite formation. (Mohammed *et al.*, 2014) This approach resulted in evidence

of antimicrobial activity, hence a potentially fruitful approach to integrating antimicrobial activity to an orthodontic adhesive. (Jatania & Shivalinga, 2014)

CHAPTER 3

AIMS OF THE INVESTIGATION

To date, there has not been a research report present in the publically available literature that explored the possible effects of such additions of zinc oxide powder to this RMGI orthodontic adhesive on its mechanical properties. Bonded orthodontic brackets and appliances must ultimately be removed (i.e., debonded) and any resinous residue completely removed from the enamel surface; the physical and mechanical properties of these polymeric materials are important to measure and correlate to such clinical performance properties. It is intuitively obvious that decreases in DTS could contribute to reduced bracket stability by early cohesive failure of the bonded bracket. (Zardiackas *et al.*, 1988)

Several prior studies have examined the diametral tensile strength (DTS) of orthodontic adhesives and cements.(Fonseca *et al.*,2010; Aguiar *et al.*,2013) These investigators measured the DTS of Fuji Ortho LC, an RMGI, and compared it directly to composite resin orthodontic adhesives and a conventional glass ionomer cement. They found that the mean value for the DTS of Fuji Ortho LC was between that of a composite resin orthodontic adhesive, and a convention glass ionomer cement. Critical to such an analysis would be the measurement of the change in tensile properties of the cement (Zardiackas *et al.*,1988), as well as measurement of surface properties of these modified cements such as Vickers microhardness and surface modulus as measured by micro indentation, therefore, are appropriate and useful measures of cement properties. While several researchers have explored the experimental microhardness values of several

orthodontic cements and adhesives (Vilchis *et al.*,2008; Uysal *et al.*, 2008); (Ramoglu *et al.*,2008) a search of the literature has failed to produce any studies that evaluated the microhardness and surface modulus (stiffness) of the orthodontic adhesive RMGI material, Fuji Ortho LC. Therefore it appears this study will be the first to determine those values for this class of orthodontic adhesive and this specific adhesive material. Light microscopy will be utilized to examine selected intact and fractured specimens of both the control and experimental systems. The same weight percent ratios (10 and 20 percent) of zinc oxide powder utilized in the Jatania & Shivalinga study (Jatania & Shivalinga, 2014) will be formulated and evaluated in this research evaluation. It is therefore the objective of this Masters thesis research project to evaluate the effect of addition of an antimicrobial agent, zinc oxide powder, on these selected mechanical properties and morphologic features of a resin modified glass ionomer orthodontic adhesive, Fuji Ortho LC.

CHAPTER 4

MATERIALS & METHODS

4.1 Laboratory Facilities

All laboratory procedures were performed in the Oral Biomaterials Research Laboratory, located on the second floor of the Dental School Building in Room 2L14, which is part of the Department of Restorative Dentistry, Temple University Maurice H. Kornberg School of Dentistry on the Temple University Health Sciences Center campus in Philadelphia, Pennsylvania.

4.2 Preparation of Formulations for Specimens:

A resin modified glass ionomer (Fuji Ortho LC, GC America, Chicago, Illinois), in its two-component, powder/liquid format were utilized in this study. Control specimens, according to manufacturer's directions for use, were prepared for both diametral tensile and microhardness testing. It was determined in preliminary experiments that in order to prepare the experimental formulations described below, that the manufacturer's recommended powder/liquid ratio of 4 drops to 4 standard scoops (2 double-scoops) required adjustment to 5 drops to 4 standard scoops (2 double-scoops), thus slightly increasing the amount of liquid in the mix. As such, two control systems were included in this study: A manufacturer's control (Control-Std), and a modified control (Control-Mod). Two experimental systems, with various proportions of zinc oxide powder added to this RMGI powder component, were utilized in this study for comparison to the control systems. Using the powder component provided in the marketed product; powder blends containing both 10 and 20 percent Zinc Oxide (by

weight) were be added to the RMGI powder, and thoroughly mixed and blended to create a uniform powder blend. These powder blends, constituting both 10 and 20 percent Zinc oxide in the manufacturer provided resin-modified glass ionomer powder, were used to prepare specimens for the mechanical and microhardness testing listed below, as well as the surface morphological examination of the cured cement surfaces.

4.3 Mechanical Testing:

Disc specimens, approximately 6.2 mm diameter by 3.1 mm in height, were made using a standardized mixing and molds for each material. After mixing and dispensing the material in a silicone mold, each specimen was covered by a mylar strip and glass slide and cured for four, 15 second exposures with a high intensity, LED curing light (The CURE Cordless TC-CL II, Spring Health Products, Inc; Serial # 10575 USA). All specials were stored in distilled water (DW) and stored at 37 degrees Celsius in a constant temperature oven until testing to simulate the oral environment. Eight (8) to ten (10) samples were evaluated for diametric tensile strength at a time interval of 1 day (1 D) after storage in distilled water at 37 degrees Celsius. The specimens were tested using the Instron 5569 testing machine at a crosshead speed of 0.75 mm/minute for DTS until failure occurs. Data was recorded in Newtons (N) force and analyzed as described on the section on data analysis below. Force data in Newtons was converted to stress values (force per unit area, MegaPascals, MPa) using the equation, $MPa = 2F / \pi dh$ (Aguiar *et al.*, 2013) where:

d: diameter (3.1 mm);

h: height (6.2 mm);

π : 3.1416.

Microscopic images (light photomicrographs) of the surfaces were taken after specimen failure at 24 hours and 1 month. Figure 1 illustrates the test assembly and configuration of the diametral tensile strength test, as well as the classical failure appearance of a specimen after ultimate failure due to tensile stresses perpendicular to the fracture plane and in alignment with the direction of the compressive load force vector.

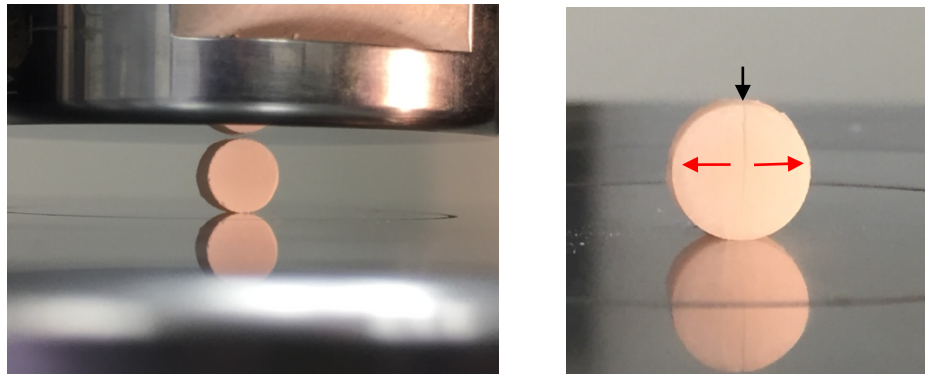


Figure 1. Photograph Illustrates Cylinders on the Instron. Specimens in position on the Instron load cell plate (left) applying force to specimen. Photograph (right) illustrates failed specimen with fracture line (arrow) diagonally and approximately 90 degrees perpendicular to both the load cell plate (black arrow) and the specimen fracture plane (red arrow).

4.4 DTS Data Analysis:

Data from Vickers (Hv) hardness and surface modulus (EIT) values were analyzed using standard descriptive statistics (mean, standard deviation). One-way ANOVA for material-specific mean values indicated statistically significant differences within each group's mean Vickers hardness and surface modulus values ($p < 0.05$). Pair-wise comparisons (unpaired T-test, $p < 0.05$) indicated statistically significant differences

in the mean values for both Vickers and Surface modulus comparing different pair-wise combinations of materials tested.

4.5 CSM Micro-hardness Tester and Indentation Methodology

Samples of the materials were prepared in a standard cylindrical mold approximately 5 mm in height and 11.0 mm in diameter and stored in distilled water (DW) at 37 degrees C prior to testing to determine Vickers microhardness and surface modulus in a CSM microindentation testing device. After mixing each group of specimens they were inserted into the test specimen cavity molds, each specimen was covered by a Mylar strip and glass slide and cured four times at 15 second exposures with a high intensity curing light (The CURE Cordless TC-CL II, Spring Health Products, Inc; Serial # 10575 USA). All specimens were stored in distilled water for one (1) day prior to testing and the specimen surfaces were sequentially finished and polished with aluminum oxide finishing discs from 400 to 1200 grit. All materials were tested by microindentation at 1 day incubation times. Microhardness and modulus values were collected via a 2 x 3 microindentation matrices on the exposed surfaces of the specimens A CSM Instruments hardness tester (Figure 1), with a fine load range of 0.01 to 10 N, was used in this study for the microhardness and surface modulus analysis. The microhardness tester sat on a Vibraplane Model 9100/9200 vibration isolation table (Kinetic Systems Inc., Boston, MA, USA) to eliminate slight environmental tremors which might interfere with the indentation tests.

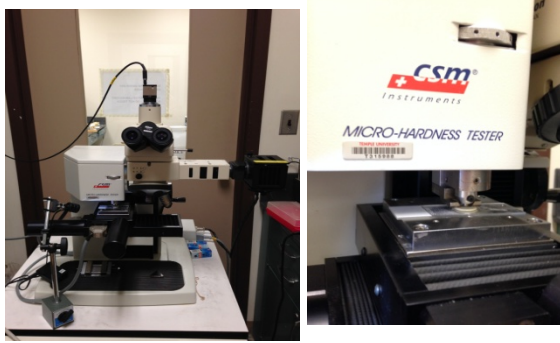


Figure 2. CSM Micro-hardness Tester

Using this micro-indentation system, a diamond Vickers indenter (tip radius 50 nm) was forced into the specimen with an increasing load for a known duration. Depth adjustment was performed using a contact load detection of 0.01 N. During testing, the cement specimen was loaded at 1 N min^{-1} and unloaded at 1 N min^{-1} . After reaching a maximum load of 0.4 N, with a five (5) second dwell time, the load was reduced to complete relaxation. The position of the indenter relative to the specimen surface was monitored continuously with a differential capacitive sensor with a $100 \mu\text{m}$ range. At the start of the experiment, a 2×3 matrix of indentations were recorded on each of two specimens by moving the sample $150 \mu\text{m}$ between indentations for a total of 12 indentations per material specimen. The data acquisition was automatic with real-time display of applied force and indentation depth. Vickers hardness was automatically calculated by proprietary software provided with the CSM Microindenter and processed by a Dell desktop computer, calculating the Vickers hardness from the force versus depth indentation curves. Indentation hardness (Vickers, HV) was calculated from the indentation curve with load plotted against depth. The following parameters were used:

elastic modulus of the indenter (1141 GPa), Poisson's ratio of the indenter (0.07), and Poisson's ratio of the sample (0.30). Earlier technology required the visual measurement of permanent plastic indentations, but this methodology measured total (including elastic) deformation. The depth resolution of the indentation was 0.3 nm, with a maximum indenter range of 200 μm . Indentation depth was measured using a Vickers (V-D44) indenter as described by Oliver and Pharr (Oliver & Pharr 1992). The sample specimen was moved to a previously defined position and the indenter located to within 100 μm . The final approach by the measurement head of the indenter was made, and following contact, indentation depth recorded continuously at 10 Hz.

In addition to Vickers (Hv) microhardness, the surface stiffness or modulus can also be determined using the method of Oliver and Pharr. (Oliver & Pharr 1992) This approach, which is numerically calculated by software interfaced with the CSM surface microindentation device, permits the calculation of the initial slope of the de-loading curve (see Figure 3 below), that provides a measure of the surface stiffness or modulus in conventional stress (force/unit area) units such as Mega Pascals (MPa) or Giga Pascals (GPa).

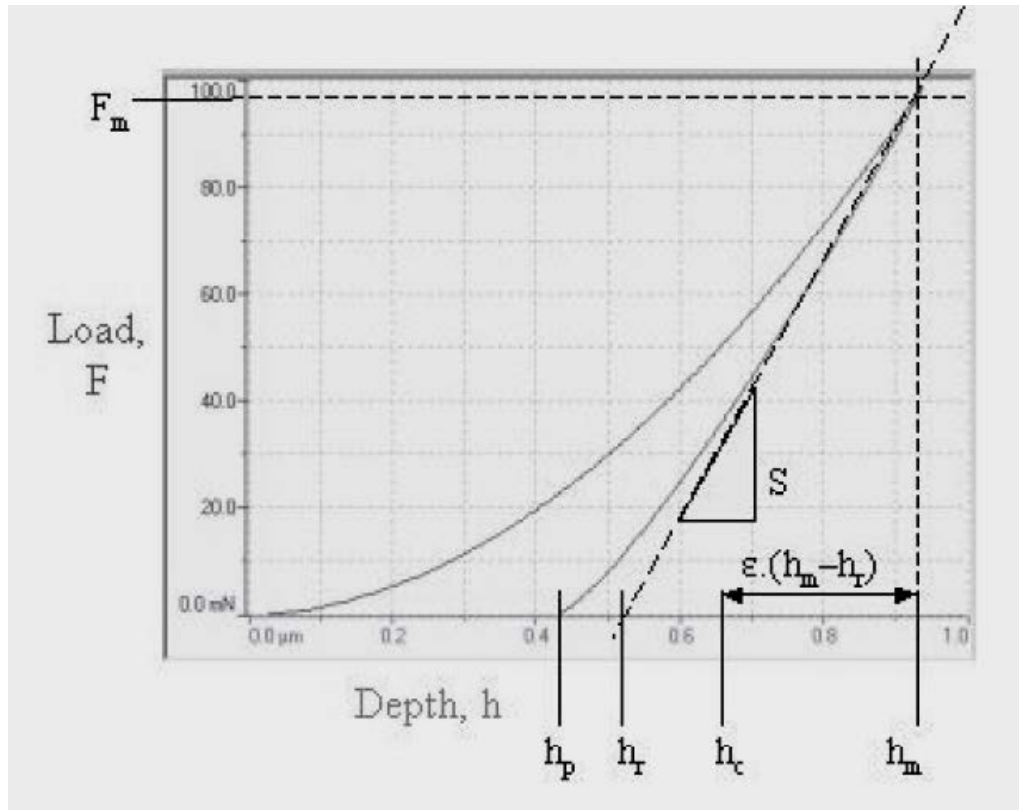


Figure 3: Typical Load-Depth Curve from CSM Microindentation Test

Demonstrates the calculation of the initial slope of the unloading curve to determine surface modulus (stiffness). (Source: CSM Instruments. Advanced Mechanical Surface Testing. Applications Bulletin. "Overview of Mechanical Testing Standards", Number 18, September 2002.)

4.6 Data Analysis

Data analysis was carried out by tabulating the Vickers (Hv) hardness and surface modulus (EIT) values. One-way ANOVA for material-specific mean values indicated statistically significant differences within each group's mean Vickers hardness values ($p \leq 0.05$). Pair-wise comparisons (unpaired T-test, $p \leq 0.05$) indicated statistically significant differences in the mean values for both Vickers and Surface modulus comparing different pair-wise combinations of materials tested.

4.7 Surface Morphological Evaluation

Specimens of the control-modified and the experimental RMGI orthodontic adhesive containing 10 and 20 percent zinc oxide were examined at 50 X magnification (light microscopy) for comparison of surface characteristics and morphology. All specimens (prior to testing for microindentation) were utilized for light microscopy. As noted above in the methodology on microindentation, specimens were stored in distilled water for one (1) day, sequentially finished and polished with aluminum oxide finishing discs from 400 to 1200 grit prior to examination by light microscopy. Internal surfaces of the fractured specimens of each tested system were also examined for micro-morphology using a similar methodology. Appropriate calibrated measurements of unique morphologic features of the ZnO crystals were measured at the greatest dimension within the particle.

CHAPTER 5

RESULTS

5.1 Diametral Tensile Strength

The results of the diametral tensile strength test (mean values plus/minus standard deviations) are listed below in Table 2. Mean force values to ultimate failure are expressed as Newtons and the stress (force/area) to ultimate failure is expressed as MegaPascals (MPa). Comparing the values for the control and experimental systems tested, the following results indicate the following: The modified control material (Control-Mod; 25% increase in the liquid component) demonstrated an approximate 30% reduction as compared to the control standard (Control-Std). The 10% ZnO powder system, which also utilized the increased liquid-powder ratio as the modified control system (Control-Mod), demonstrated an approximate 61% reduction as compared to the standard control (Control-Std); and a 44% reduction as compared to the modified control (Control-Mod). The 20% ZnO powder system, which also utilized the increased liquid-powder ratio as the modified control system (Control-Mod), demonstrated an approximate 64% reduction as compared to the standard control (Control-Std); and a 48% reduction as compared to the modified control (Control-Mod).

	Control (Std)	Control (Mod)	10% ZnO Powder	20% ZnO Powder
Force (Newtons) ± S.D.	1020.4 ± 156.3	706.67 ± 130.8	395.3 ± 38	364.3 ± 46.7
DTS (MPa) ± S.D.	33.7 ± 5.2	23.3 ± 4.3	13.1 ± 1.3	12.0 ± 1.5

Table 2. Mean Values (plus/minus standard deviations) for Force (Newtons) & Stress (MPa)

Demonstrates the ultimate failure and diametral tensile strength (DTS), stress to ultimate failure, for the control and experimental systems.

The mean stress values in MegaPascals, MPa, (including standard deviation "error" bars) for each of the test systems is graphically depicted in Figure 4 below:

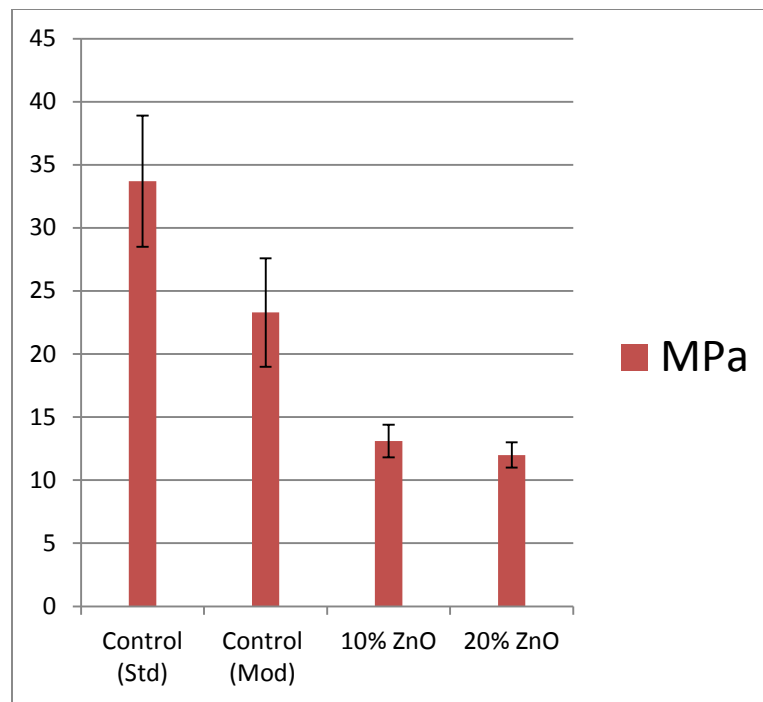


Figure 4. Bar Chart Depicting the Mean Stress to Failure

The values in MegaPascals (MPa) for the diametral tensile stress test applied to the control and experimental group specimens.

Statistical analysis of the diametral tensile strength (DTS) data indicated significant differences in the calculated mean values between the systems tested. A one-way Analysis of Variance (ANOVA) based on the single variable of material type, comparing the four systems tested as listed in Table 2, indicated a highly significant statistical difference between the systems tested (p value = $1.35E-14$). Based on the indication that statistically-significant differences existed within and between the mean values of the entire group; a post-hoc, pair-wise statistical test was applied. Pair-wise analysis (unpaired t-Test) of the mean values of the tested systems, listing the calculated p values for these pair-wise comparisons, are found in Table 3 below:

	Control (Std)	Control (Mod)	10% ZnO Powder	20% ZnO Powder
Control (Std)	-----	P = 0.00029 (S)	P= 1E-06 (S)	P=7.4E-07 (S)
Control (Mod)	P = 0.00029 (S)	-----	P=7.4E-05 (S)	P=2.3E-05 (S)
10% ZnO Powder	P= 1E-06 (S)	P=7.4E-05 (S)	-----	P=0.14 (NS)
20% ZnO Powder	P=7.4E-07 (S)	P=2.3E-05 (S)	P=0.14 (NS)	-----

Table 3. P-Values for Mean DTS Values

Possible pair-wise comparisons utilizing an unpaired t-Test for comparison of mean DTS values. NS = Not statistically significant ($p > 0.05$); S = Statistical Significant ($p \leq 0.05$)

As can be seen in Table 3, there appear to be significant difference in the mean strength values between the various control and experimental systems. The mean force and stress values for the standard control (Control-Std) were significantly higher than the modified control group (Control-Mod) and both zinc oxide powder-modified

experimental groups (10% ZnO & 20% ZnO powders). Likewise, the mean force and stress values of the modified control group (Control-Mod) were also significantly higher than both zinc oxide powder-modified experimental groups.

5.2 Vickers Microhardness & Surface Modulus

The results of the microindentation testing, Vickers microhardness and surface modulus (mean values plus/minus standard deviations), are listed below in Table 4. Mean microhardness values expressed as Vickers hardness values and the surface modulus (stiffness) are expressed as stress values (force/area) and expressed as GigaPascals (GPa).

	Control (Std)	Control (Mod)	10% ZnO Powder	20% ZnO Powder
Microhardness (Vickers) \pm S.D.	61.24 \pm 16.3	72.2 \pm 14.4	64.03 \pm 29.3	63.38 \pm 29.1
Surface Modulus (GPa) \pm S.D.	11.9 \pm 1.7	13.1 \pm 1.8	13.6 \pm 3.8	16.2 \pm 3.8

Table 4. Mean Values for Microhardness & Surface Modulus (plus/minus standard deviations) for microhardness (Vickers) and surface modulus (stiffness) for the control and experimental systems.

The mean microhardness values in Vickers units (including standard deviation "error" bars) for each of the test systems is graphically depicted in Figure 5 below:

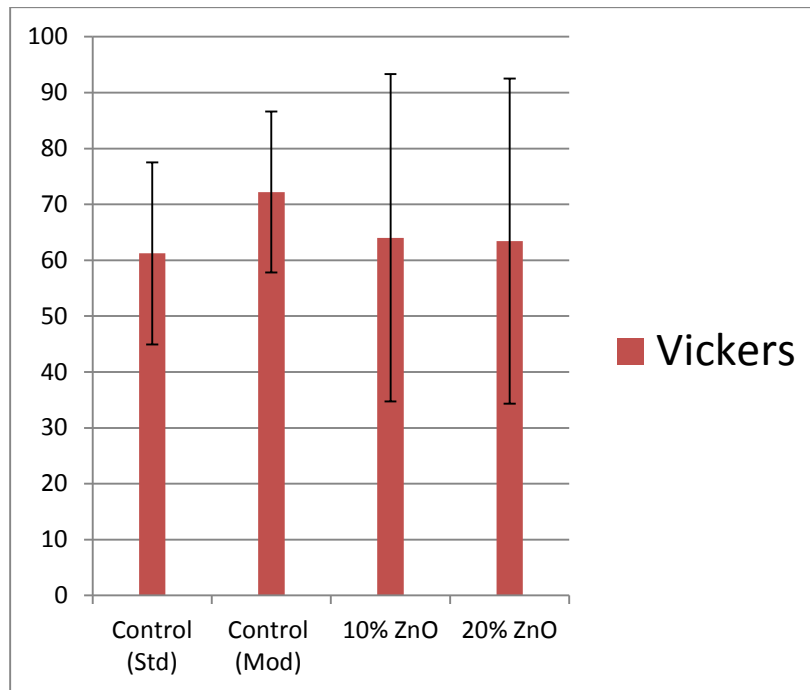


Figure 5. Mean Microhardness Values

Values illustrate the Vickers units (Hv) for the control and experimental group specimens.

Comparing the Vickers values for the control and experimental systems tested, Figure illustrates two points: There appears to be little variation in mean Vickers microhardness values for the control and experimental groups. In fact, this observation is supported by the Analysis of Variance (ANOVA) statistical analysis, which yielded a p value of $P = 0.34$; thus indicating an apparent lack of statistical significant within and between with the mean values for the systems evaluated. Although the standard deviations for the groups were extremely high (they actually expanded with experimental ZnO groups), the narrow range of mean values in contrast to the large range of

microhardness values suggests and supports a lack of significant differences between the mean values of the groups.

The surface modulus values are also listed in Table 4 and depicted in Figure 6 below:

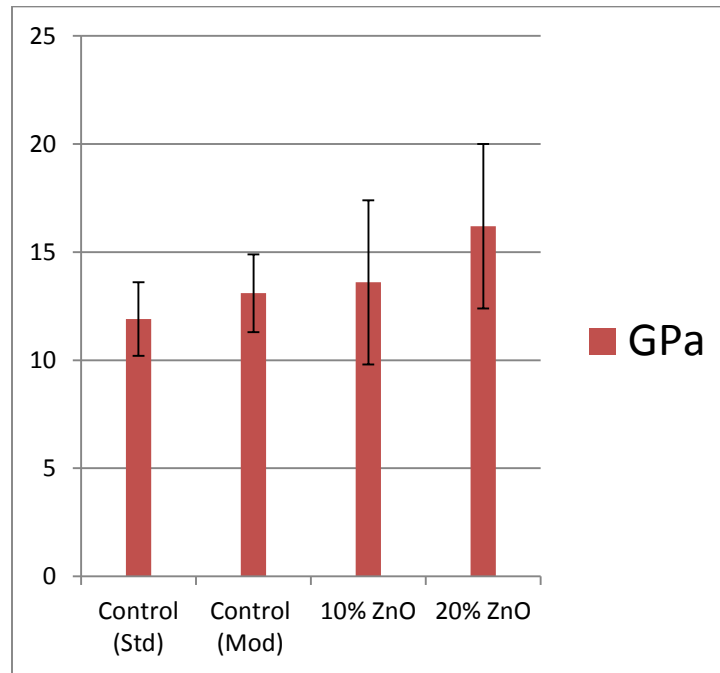


Figure 6. Bar Chart Depicting the Mean Surface Modulus
The values are in GigaPascals (GPa) units for the control and experimental group specimens.

The post-hoc, pair-wise statistical analysis values (significance p value ≤ 0.05) utilizing an unpaired t-Test are listed below in Table 5:

	Control (Std)	Control (Mod)	10% ZnO Powder	20% ZnO Powder
Control (Std)	-----	P = 0.07 (NS)	P= 0.08 (NS)	P=4.8E-05 (S)
Control (Mod)	P = 0.07 (NS)	-----	P=0.56 (NS)	P=0.001 (S)
10% ZnO Powder	P= 0.08 (NS)	P=0.56 (NS)	-----	P=0.02 (S)
20% ZnO Powder	P=4.8E-05 (S)	P=0.001 (S)	P=0.02 (S)	-----

Table 5. P-Values for Possible Pair-Wise Comparisons Utilizing an Unpaired t-Test for Mean Surface Modulus Values.

NS = Not statistically significant ($p > 0.05$); S = Statistical Significant ($p \leq 0.05$)

As can be seen in Table 5, there appear to be significant differences in the mean surface modulus values between the various control and experimental systems. There did not appear to be statistically-significant differences between the values for the standard control (Control-Std) and the modified control group (Control-Mod), and not between either control system and the 10% ZnO system. There appear to be significant differences in the mean values comparing the 10% ZnO and 20% ZnO powders groups, as well as comparisons between the mean values for both controls with the 20% ZnO powder group.

5.3 Micromorphology of Control & Experimental Materials

Light microscopy of the polished surfaces of the modified control specimen, 10% zinc oxide powder, and 20 % zinc oxide are depicted in Figures 6 & 7. Light microscopy of the fractured surfaces of the modified control specimen, 10% zinc oxide powder, and 20 % zinc oxide are depicted in Figures 7.

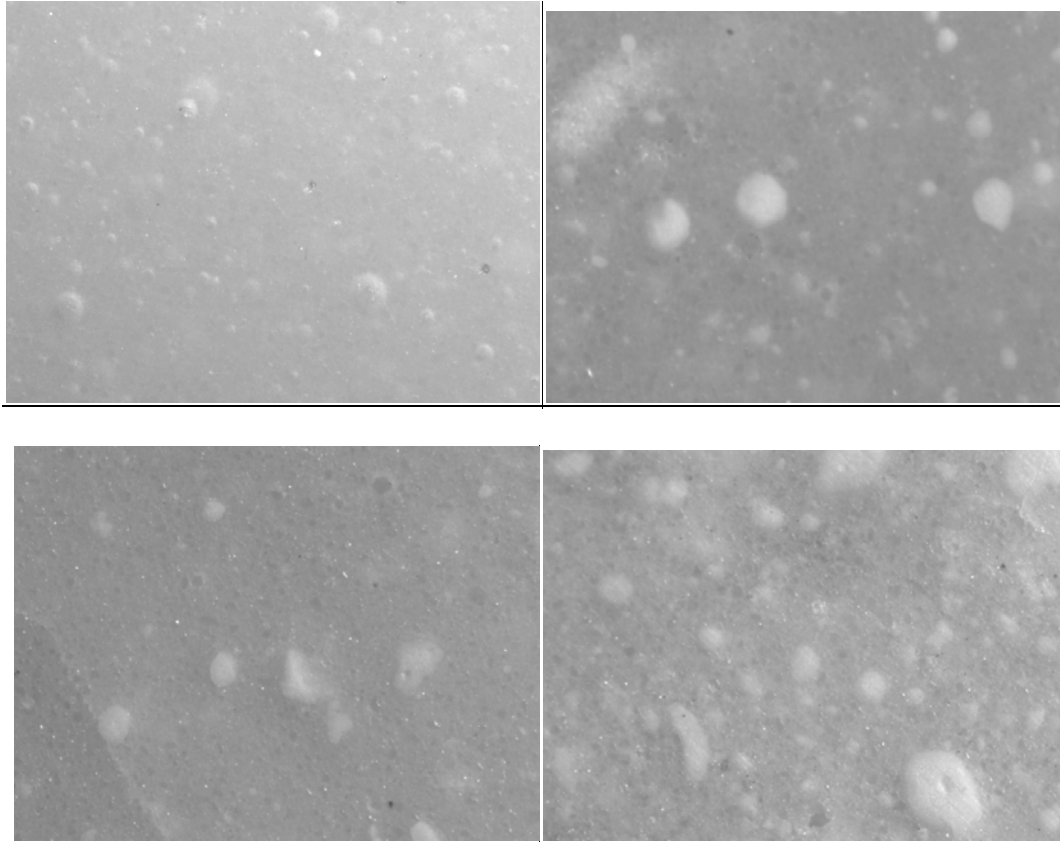


Figure 7. Light Photomicrographs of Polished Surfaces of Control and Experimental Specimens.

Upper left – ZnO particles shown in the modified control specimen; Upper right and lower left - ZnO particles shown in the 10% Zinc Oxide Formulation; Lower Right – ZnO particles shown in the 20% Zinc Oxide Formulation.

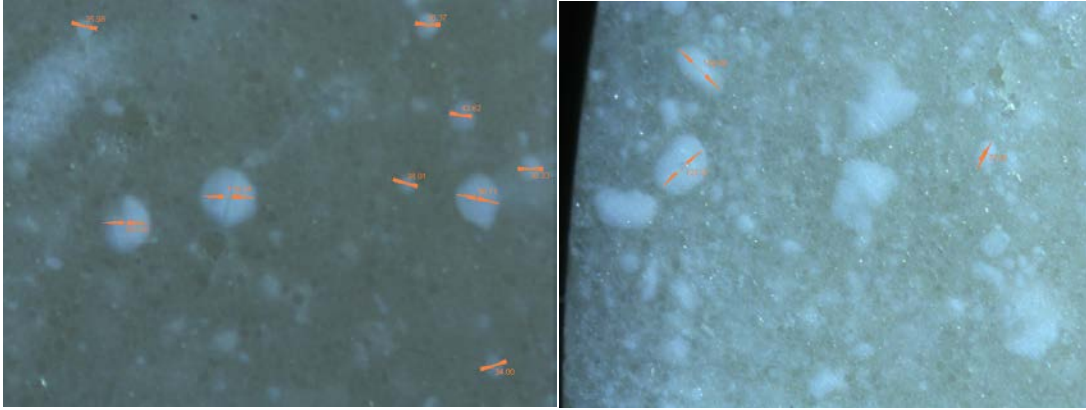


Figure 8. Size Determination for Zinc Oxide Particles

Specimen with 20% zinc oxide powder formulation specimens. ZnO Particle sizes varied from approximately 30 to 150 microns in diameter.

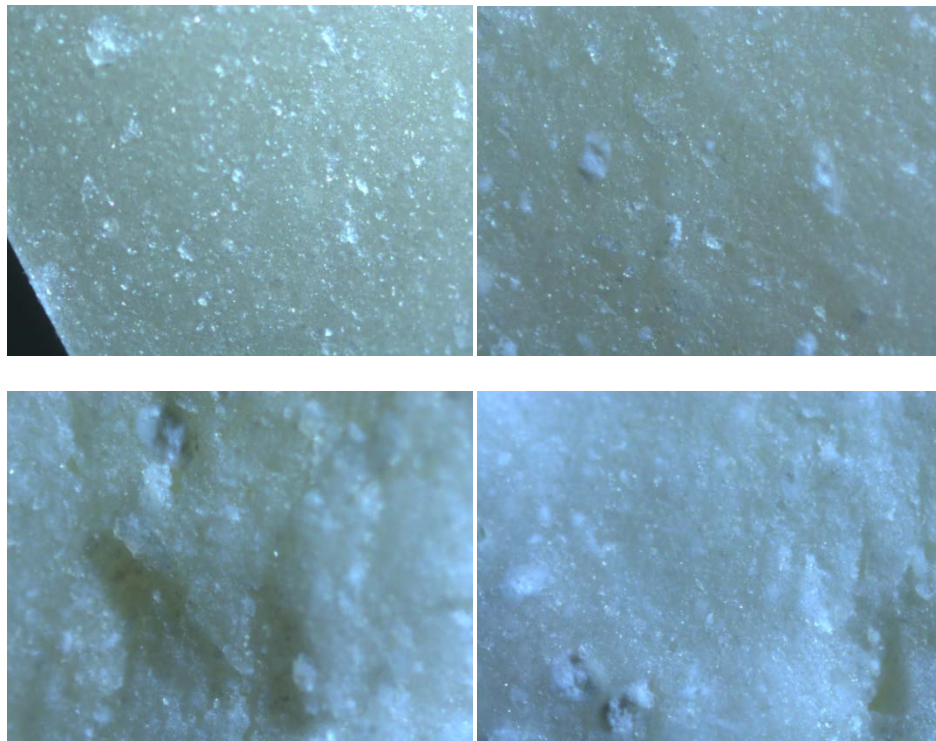


Figure 9. Surfaces of Fractured Specimens

Upper left - modified control specimen; Upper Right - 10% zinc oxide powder group specimen; Lower left and right - 20% zinc oxide powder group.

CHAPTER 6

DISCUSSION

Bonded orthodontic appliances, including cemented bands and bonded brackets, undergo the important function of withstanding physical stresses during the placement of forces in order to achieve the controlled movement of teeth in the process of orthodontic treatment. As such, orthodontic cements and adhesives must display sufficient internal strength and integrity to withstand these forces while maintaining a stable and sufficient bond to tooth structure. Likewise, while such cements and adhesives should display sufficient hardness and surface rigidity to resist washout and undo plastic strain upon application of forces to the appliance, these adhesives should not be so hard or rigid to present ease of surface removal from enamel upon debanding or bracket debonding. In addition to these physical and mechanical properties, the problem of plaque and biofilm facilitated enamel demineralization adjacent to the cemented interface, has emphasized the use of fluoride-containing and -releasing cements and adhesives. As noted in the Background chapter of this thesis, the resin modified glass ionomer can achieve the necessary minimum physical and mechanical properties, while providing an exceptionally high level of fluoride release to the adjacent enamel. Nevertheless, as noted in the Background chapter of this thesis, fluoride release can reduce but does not eliminate the risk of enamel demineralization. In addition, the limitations of fluoride as an antimicrobial have stimulated the exploration of additional additives to orthodontic adhesives to further suppress biofilm formation. Zinc and zinc oxide compounds have been known to possess antimicrobial activity. The addition of zinc oxide powder to an RMGI orthodontic adhesive has demonstrated *in-vitro*, as was noted above, antimicrobial

activity. This thesis, apparently for the first time, explored the effects of such an addition on the mechanical properties and morphology of an RMGI orthodontic adhesive, Fuji Ortho LC.

In order to obtain a workable consistency of the mixed material containing both 10 and 20 percent zinc oxide powder, the amount of liquid component in the mix had to be increased by approximately 25% by volume. Therefore, it became necessary to examine this effect on the diametral tensile strength (DTS), Vickers microhardness, and surface modulus. With respect to DTS, the mean values for DTS reduced significantly by increasing the liquid/powder ratio. This 30% decrease, however, was not inconsistent with other findings in the literature. Other researchers (Fonseca *et al*, 2010) also found that diametral tensile strength decreased significantly with increasing liquid/powder (L/P) ratios.

The additions of zinc oxide powder had an even greater impact on the diametral tensile strength. With both additions of 10 and 20 percent zinc oxide powder to the powder component, even greater reductions of approximately 40 and 60 percent were seen in the DTS. Clearly, these powder additions may have weakened the internal structure of the cement, thus reducing the internal cohesive structure of the cement to tensile stresses. Such effects could have a clinical impact, resulting in premature cohesive cement/adhesive failure, leading to appliance or bracket loss.

The effect of an increased liquid/powder ratio (L/P) and the additions of the two levels of zinc oxide powder to the powder component did not appear to have any significant effect on the mean values of Vickers (Hv) microhardness for any of the systems tested in this study. That said, it was quite apparent that the addition of zinc

oxide powder to the RMGI formulas significantly increased the standard deviations of the populations of Vickers hardness measurements for both the experimental systems. Such a result suggests that there is a greater variability in measured microhardness on these surfaces.

The effects of zinc oxide powder addition to the RMGI on the surface modulus (the stiffness of the surface measured by microindentation), nevertheless, were more pronounced than that seen with Vickers microhardness. Here significant changes were seen, especially with comparisons of the 20% zinc oxide powder group to both the standard control (Control-Std) and the modified control group (Control-Mod) . Thus this finding suggests that the zinc oxide powder increased the stiffness of the surface. Such an effect may product a more rigid assembly of the cement at both enamel and appliance/bracket interfaces, but the clinical consequence of this behavior requires more investigation.

The micromorphologic analysis of the control (modified control) and experimental cements (see Figures 6 & 7) clearly demonstrated the presence and apparent morphology of the zinc oxide particles. The relative number and density of the zinc oxide particles, as expected, appears to increase significantly from 10 to 20 percent in the respective specimens. Additionally, the size distribution of the particles (Figure 7) varies considerably, ranging from approximately sizes on the order of 20-30 microns to as large as 150 microns or more. There may also be evidence of some degree of particle agglomeration or aggregation of particles into larger masses; however further analysis is necessary to confirm this possibility.

The microscopy of the fractured surfaces (Figure 8) suggests that the increasing addition of zinc oxide particles alters the morphology of the fracture plane, with apparent greater surface irregularity and surface confirmation, especially in the 20% zinc oxide specimens.

CHAPTER 7

CONCLUSIONS

The conclusions of this study are as follows:

- 1) Alterations in the liquid/powder ratio of an orthodontic resin modified glass ionomer adhesive (Fuji Ortho LC) caused a significant reduction in diametral tensile strength and possibly surface modulus/stiffness, as compared to the cement utilizing the manufacturer's recommended liquid/powder ratio.
- 2) The addition of both 10% and 20% zinc oxide powder to the powder component of this adhesive orthodontic material caused a significant reduction in the diametral tensile strength of these modified materials as compared to both the standard and modified control formulations.
- 3) Neither alteration of the liquid/powder ratio nor addition of 10% and 20% zinc oxide powder to the powder component altered significantly the Vickers microhardness of the control or experimental materials.
- 4) The addition of 10% and 20% zinc oxide powder to the powder component altered significantly (reduced) the surface modulus/stiffness of these experimental resin modified glass ionomer formulations, as compared to both control groups.
- 5) The morphologic appearance of surfaces of the zinc oxide powder-containing groups clearly demonstrated the presence of the zinc oxide particles and a broad range of particle sizes in the set/cured materials.
- 6) The morphology of the fracture plane with the addition of zinc oxide powder/particles appeared altered and more irregular compared to the control without zinc oxide.

BIBLIOGRAPHY

- Abu-Bakr N, Han L, Okamoto A, Iwaku M. Changes in the mechanical properties and surface texture of compomer immersed in various media. *J Prosthet Dent* 2000;84:444-52. 23.
- Aguiar DA, Ritter DE, Rocha R, Locks A, Borgatto AF. Evaluation of mechanical properties of five cements for orthodontic band cementation. *Braz Ora Res.* 2013 Mar-Apr;27(2):136-41.
- Anusavice KJ. Dental cements for restoration and pulp protection. In: *Phillips science of dental materials*. 10th ed. Philadelphia: WB Saunders; 1996a. p. 526.
- Anusavice KJ. Restorative resins. In: *Phillips science of dental materials*. 10th ed. Philadelphia: WB Saunders; 1996b. p. 273.
- Ashcraft DB, Staley RN, Jakobsen JR. Fluoride release and shear bond strengths of three light cured glass ionomer cements. *Am J Orthod Dentofacial Orthod*, 111 (1997), pp. 260–265.
- Barry TI, Clinton DJ, & Wilson AD. (1979). The structure of a GIC and its relationship to the setting process. *Journal of Dental Research*, 58(3), 1072-9.
- Bishara SE, Olsen ME, Damon P, Jakobsen JR. *Evaluation of a new light-cured orthodontic bonding adhesive. American Journal of Orthodontics and Dentofacial Orthopedics* 1998;114:80-87.
- Bishara SE, VonWald L, Laffoon JF, Jakobsen JR. . *Effect of altering the type of enamel conditioner on the shear bond strength of a resin-reinforced glass ionomer adhesive. American Journal of Orthodontics and Dentofacial Orthopedics* 2000;118:288-294.
- Bowen RL. Properties of a silica-reinforced polymer for dental restorations. *J Am Dent Assoc* 1963;66:57–64.
- Buonocore MG. A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res.* 1955;34:849–53.
- Cacciafesta V, Bosch C, Melsen B. Clinical comparison between a resin-reinforced self-cured glass ionomer cement and a composite resin for direct bonding of orthodontic brackets. Part 2: Bonding on dry enamel and on enamel soaked with saliva. *Clin Orthod Res* 1999;2:186-93.
- Cattani-Lorente MA, Godin C, & Meyer JM. (1994) Mechanical behavior of GICs affected by long-term storage in water. *Dental Materials*, 10(1), 37-44.

- Chung CK , Millett DT, Creanor SL, Gilmour W H, Foye RH. Fluoride release and cariostatic ability of a compomer and a resin-modified glass ionomer cement used for orthodontic bonding. *J Dent.*1998Jul-Aug;26(5-6):533-8.
- Crisp S, Ferner AJ, Lewis BG, & Wilson AD. (1975) Properties of improved GIC formulations. *Journal of Dentistry*, 3(3), 125-30.
- Donly KJ, Istre S, Istre T. In vitro enamel remineralization at orthodontic band margins cemented with glass ionomer cement. *Am J Orthod Dentofacial Orthop.* 1995 May;107(5):461-4.
- Eberhard H , Hirschfelder U, Sindel J. Compomers--a new bracket bonding generation in orthodontics? *J Orofac Orthop.* 1997Feb;58(1):62-9).
- el Mallakh BF , Sarkar NK. Fluoride release from glass-ionomer cements in de-ionized water and artificial saliva. *Dent Mater.* 1990 Apr;6(2):118-22.
- Ewoldsen N, Demke RS. *Am J Orthod Dentofacial Orthop* 2001;120:45-8.
- Ewoldsen N, Herwig L. Decay-inhibiting restorative materials: past and present. *Compend Contin Educ Dent* 1998;19:981-4, 986, 988.
- Fonseca RB, Branco CA, Quagliatto PS, Gonçalves Lde S, Soares CJ, Carlo HL, Correr-Sobrinho L. Influence of powder/liquid ratio on the radiodensity and diametral tensile strength of glass ionomer cements.*J Appl Oral Sci.* 2010 Dec;18(6):577-84.
- Forss H , Seppä L Prevention of enamel demineralization adjacent to glass ionomer filling materials. *Scand J Dent Res.* 1990 Apr;98(2):173-8.
- Forsten L. Fluoride release and uptake by glass-ionomers and related materials and its clinical effect. *Biomaterials.* 1998Mar;19(6):503-8.
- Fricker JP. A 12-month clinical study comparing four glass ionomer cements for the cementation of orthodontic molar bands. *Aust Orthod J* 1989;11:10-13. 9.
- Friend LA. Handling properties of a zinc polycarboxylate cement. An investigation. *Br Dent J.* 1969 Oct 21;127(8):359-64.
- Fukuda R, Yoshida Y, Nakayama Y, Okazaki M, Inoue S, Sano H, Shintani H, Snauwaert J, Van Meerbeek B. Bonding efficacy of polyalkenoic acids to hydroxyapatite, enamel and dentin. *Biomaterials* 2003;24:1861-7.
- Gandolfi MG, Chersoni S, Acquaviva GL, Piana G, Prati C, Mongiorgi R. Fluoride release and absorption at different pH from glass-ionomer cements May 2006 Volume 22, Issue 5, Pages 441-449.

- Glasspoole EA , Erickson RL, Davidson CL. Effect of enamel pretreatments on bond strength of compomer. *Dent Mater.* 2001Sep;17(5):402-8.
- Godoy-Bezerra J, Vieira S, Oliveria JHG, Lara F.. *Shear bond strength of resin-modified glass ionomer cement with saliva present and different enamel pretreatments. Angle Orthodontist* 2006;76:470-474.
- Goodman BD, Gwinnett AJ. A comparison of laser-and acid-etched human enamel using scanning electron microscopy. *Arch Oral Biol.* 1977;22(3):215-20.
- Gorton J, Featherstone JD. In vivo inhibition of demineralization around orthodontic brackets. *Am J Orthod Dentofacial Orthop.* 2003 Jan;123(1):10-4.
- Gottlieb EL, Nelson AH, and Vogels III DS. 1996. JCO study of orthodontic diagnosis and treatment procedures. Part 1. Results and trends. *J Clin Orthod* 1996. 30:615–629.
- Itota T , Carrick TE, Yoshiyama M, McCabe JF. Fluoride release and recharge in giomer, compomer and resin composite. *Dent Mater.* 2004Nov;20(9):789-95.
- Jatania A, Shivalinga BM. An in vitro study to evaluate the effects of addition of zinc oxide to an orthodontic bonding agent. *Eur J Dent* 2014;8:112-7.
- Joseph VP, Rossouw E. The shear bond strengths of stainless steel and ceramic brackets used with chemically and light-activated composite resins. *Am J Orthod Dentofacial Orthop.* 1990;97:121–5.
- Kinomoto Y, Torii M, Takeshige F, Ebisu S. Comparison of polymerization contraction stresses between self-and light-curing composites. *J Dent* 1999;27:383–9.
- Kocadereli I, Ciger S. Retention of orthodontic bands with three different cements. *J Clin Pediatr Dent* 1995;19:127-30.
- Lippitz SJ, Staley RN, Jakobsen JR. An in vitro comparative study of 24 hour and 30 day shear bond strengths of three resin-glass ionomer cements used to bond orthodontic brackets. *Am J Orthod Dentofacial Orthop*, 113 (1998), pp. 620–624.
- McComb D. Luting in orthodontic practice. In: Davidson CL, Mjör Ivar A, editors. *Advances in glass ionomer cements.* Chicago: Quintessence Publishing Co; 1999.
- Millett DT, Cattnach D, McFadzean R, Pattison J, McColl J. Laboratory evaluation of a compomer and a resin-modified glass ionomer cement for orthodontic bonding. *Angle Orthod* 1999; 69:58-63).

- Millett DT, McCabe J. Orthodontic bonding with glass-ionomer cement: a review. *Eur J Orthod* 1996;18:385-99.
- Millett DT, McCluskey LA, McAuley F, Creanor SL, Newell J, Love J. A comparative clinical trial of a compomer and a resin adhesive for orthodontic bonding. *Angle Orthod* 2000;70: 233-40. 24.
- Mizrahi E, Smith DC. Direct cementation of orthodontic brackets to dental enamel. An investigation using a zinc polycarboxylate cement. *Br Dent J.* 1969 Oct 21;127(8):371-5.
- Mizrahi E. Glass ionomer cements in orthodontics. *Am J Orthod Dentofacial Orthop* 1988;93:505-7. 10.
- Mohammed NR , Mneimne M , Hill RG , Al-Jawad M , Lynch RJ , Anderson P . Physical chemical effects of zinc on in vitro enamel demineralization. *J Dent.* 2014 Sep;42(9):1096-104.
- Newman GV, Newman RA, Sengupta AK. Comparative assessment of light-cured resin-modified glass ionomer and composite resin adhesives: in vitro study of a new adhesive system. *American Journal of Orthodontics and Dentofacial Orthopedics* 2001;119:256-262.
- Newman GV. Epoxy adhesives for orthodontic attachments: Progress report. *Am J Orthod.* 1965;51:901–12. [PubMed: 5214895]
- Nicholson JW. Chemistry of glass-ionomer cements: a review. *Biomaterials* 1998;19:485-94.
- O'Reilly MM, Featherstone JDB. Demineralization and remineralization around orthodontic appliances: an in vivo study. *Am J Orthod Dentofacial Orthop* 1987;92:33-40.
- O'Brien WJ. Dental Cements. In: *Dental Materials and Their Selection.* Quintessence Publishing Co, Inc., Hanover park, Illinois. 2008, P 145.
- Oliver WC & Pharr GM. (1992). An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research*, 7, 1564–1583.
- Platt JA. Resin-based luting cements. *Compend Contin Educ Dent* 2000;21:740-2, 744.
- Preston AJ, Higham SM, Agalamanyi EA, Mair LH. Fluoride recharge of aesthetic dental materials. *J Oral Rehabil* 1999;26:936-40. 25.

- Prosser HJ, Powis DR, Brant P, Wilson AD. Characterization of glass-ionomer cements. The physical properties of current materials. *J Dent* 1984;12:231-40.
- Ramoglu SI, Usumez S, Buyukyilmaz T. Accelerated aging effects on surface hardness and roughness of lingual retainer adhesives. *Angle Orthod.* 2008 Jan;78(1):140-4.
- Randall, J., Seow, W. and Walsh, L. (2015), Antibacterial activity of fluoride compounds and herbal toothpastes on *Streptococcus mutans*: an *in vitro* study. *Aust Dent J*, 60: 368–374.
- Read MJ. The bonding of orthodontic attachments using a visible light cured adhesive. *Br J Orthod.* 1984 Jan;11(1):16-20.
- Rezk-Lega F, Ogaard B, Arends J. An *in vivo* study on the merits of two glass ionomers for the cementation of orthodontic bands. *Am J Orthod Dentofacial Orthop.* 1991 Feb;99(2):162-7.
- Saito S, Tosaki S, Hirota K. Characteristics of glass ionomer cements. In: Davidson CL, Mjör Ivar A, editors. *Advances in glass ionomer cements*. Chicago: Quintessence Publishing Co; 1999.
- Sakaguchi RL & Powers JM. *Craig's Restorative Dental Materials*, 13th edition. Chapter 9: Restorative Materials - Composites & Polymers. p 188, Elsevier Mosby, 2012a.
- Sakaguchi RL & Powers JM. *Craig's Restorative Dental Materials*, 13th edition. Chapter 9: Restorative Materials - Composites & Polymers. p 162, Elsevier Mosby, 2012b.
- Sakaguchi RL & Powers JM. *Craig's Restorative Dental Materials*, 13th edition. Chapter 9: Restorative Materials - Composites & Polymers. p 169, Elsevier Mosby, 2012c.
- Sakaguchi RL & Powers JM. *Craig's Restorative Dental Materials*, 13th edition. Chapter 9: Restorative Materials - Composites & Polymers. p 184, Elsevier Mosby, 2012d.
- Silverman E, Cohen M, Demke RS, Silverman M. A new light-cured glass ionomer cement that bonds brackets to teeth without etching in the presence of saliva. *Am J Orthod Dentofacial Orthop.* 1995 Sep;108(3):231-6.
- Small ICB, Watson TF, Chadwick AV, Sidhu SK. Water sorption in resin-modified glass ionomer cements: an *in vitro* comparison with other materials. *Biomaterials* 1998;19:545-50.

- Stirrup DR. A comparative clinical trial of a glass-ionomer and a zinc-phosphate cement for securing orthodontic bands. *Br J Orthod* 1991;18:15-20. 11.
- Swift EJ. Dentin/enamel adhesives: review of the literature *Pediatr Dent*. 2002;24:456-461.
- Tate WH, You C, Powers JM. Bond strength of compomers to human enamel. *Oper Dent* 2000;25:283-91.
- Tavas MA, Watts DC. Bonding of orthodontic brackets by transillumination of a light activated composite: An *in vitro* study. *Br J Orthod*. 1979;6:207-8.
- Uysal T , Basciftci FA, Sener Y, Botsali MS, Demir A. Conventional and high intensity halogen light effects on water sorption and microhardness of orthodontic adhesives. *Angle Orthod*. 2008 Jan;78(1):134-9.
- Valinoti JR. Bonding and cementing. *J Clin Orthod*. 1973 Feb;7(2):106-10.
- Vilchis RJ , Hotta Y, Yamamoto K. Examination of six orthodontic adhesives with electron microscopy, hardness tester and energy dispersive X-ray microanalyzer. *Angle Orthod*. 2008 Jul;78(4):655-61.
- Vorhies AB, Donly KJ, Staley RN, Wefel JS. Enamel demineralization adjacent to orthodontic brackets bonded with hybrid glass ionomer cements: An in vitro study *American Journal of Orthodontics and Dentofacial Orthopedics*, Volume 114, Issue 6, December 1998, Pages 668-674.
- Voss A, Hickel R, Molkner S. In vivo bonding of orthodontic brackets with glass-ionomer cement. *Angle Orthod* 1993;63:149-53.
- White LW. Glass ionomer cement. *J Clin Orthod* 1986;20: 387-91.
- Wilson AD & Kent BE. (1972) A new translucent cement for dentistry. The glass ionomer cement. *British Dental Journal*, 132(4),133-5.
- Xie D, Brantley WA, Culbertson BM, & Wang G. (2000) Mechanical properties and microstructures of GICs. *Dental Materials*, 16(2), 129-38.
- Yi-chun L, Yu-lin L, Wei-tze C, Shyh-yuan L. Kinetics of fluoride release from and reuptake by orthodontic cements. *American Journal of Orthodontics and Dentofacial Orthopedics*, Volume 133, Issue 3, March 2008, Pages 427-434.
- Yip HK, Smales RJ. Fluoride release from a polyacid-modified resin composite and three resin-modified glass-ionomer materials. *Quintessence Int* 2000;31:261-6. 21.

Zardiackas LD, Caldwell DJ, Caughman WF, Lentz DL, Comer RW. Tensile fatigue of resin cements to etched metal and enamel. Dent Mater. 1988 Jun;4(3):163-8.