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Effect of Light-Cure Initiation Time on Polymerization and Orthodontic Bond Strength with a Resin-Modified Glass-Ionomer

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EFFECT OF LIGHT-CURE INITIATION TIME ON POLYMERIZATION
AND ORTHODONTIC BOND STRENGTH WITH A
RESIN-MODIFIED GLASS-IONOMER

by

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ABSTRACT
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Introduction: The polymerization and acid-base reactions in resin-modified glass-ionomers (RMGI) are thought to compete with and inhibit one another. The objective of this study was to examine the effect of visible light-cure (VLC) delay on the polymerization efficiency and orthodontic bond strength of a dual-cured RMGI.

Methods: An RMGI light-cured immediately, 2.5, 5, or 10 minutes after mixing comprised the experimental groups. Isothermal and dynamic temperature scan differential scanning calorimetry (DSC) analysis of the RMGI was performed to determine extents of VLC polymerization and acid-base reaction exotherms. Human premolars ($n = 18$/group) were bonded with the RMGI. Shear bond strength and adhesive remnant index (ARI) scores were determined.

Results: DSC results showed the 10 minute delay RMGI group experienced significantly ($P < 0.05$) lower VLC polymerization compared to the other groups. Acid-base reaction exotherms were undetected in all groups except the 10 minute delay group. No significant differences ($P > 0.05$) were noted among the groups for mean shear bond strength. A chi-square test showed no significant difference ($P = 0.428$) in ARI scores between groups.

Conclusions: Delay in light-curing may reduce polymerization efficiency and alter the structure of the RMGI, but orthodontic shear bond strength does not appear to be compromised.

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INTRODUCTION

Glass-ionomers (GI) were invented in the late 1960s and first introduced into dentistry in 1972.[1] GIs set via an acid-base reaction between polymers of polyacrylic acid and fluoroaluminosilicate bases.[2] The setting reaction begins when hydrogen ions from the polyacrylic acid attack and decompose the silica glass particles, releasing F^-, Ca^{2+}, and Al^{3+} ions. A rapid reaction in which the Ca^{2+} ions interact with the polyacrylic acid chains occurs, followed by a slower reaction between the chains and Al^{3+}, with the end result being a structure of cross-linked polyacrylic acid units. A silica hydrogel layer also forms around the glass particles. GIs are advantageous in that they are capable of chemically bonding to tooth structure and can release fluoride over a period of time. Disadvantages of GIs include moisture sensitivity and low initial strength. Resin-modified glass-ionomers (RMGI) were developed to overcome the disadvantages of conventional GIs by adding polymerizable components similar to those found in composite resins. Dental composite resins consist of an organic matrix usually composed of dimethacrylates such as bisGMA, urethane dimethacrylate (UDMA), and/or triethylene glycol dimethacrylate (TEGDMA) as well as inorganic filler such as quartz or silica glasses. When exposed to visible light, a photoinitiator such as camphorquinone reacts with an amine reducing agent to generate free radicals, causing the dimethacrylate monomers to form a chain reaction, creating polymers of the resin.

Although simplistically RMGIs may be viewed as a combination of traditional GIs and composite resins, they are complex materials since the acid-base and polymerizable components must coexist within one formulation. To achieve this, RMGIs

typically contain 2-hydroxyethyl methacrylate (HEMA) to act as a solvent and photopolymerizable monomer, allowing the aqueous and organic phases to become miscible. RMGIs also contain calcium flouroaluminosilicate glasses, just as the typical GIs do, which are the source for cross-linking ions for the acid-base process and to act as filler for the resin phase. Additional components include photoinitiators, polyacrylic acid (which may or may not have the HEMA grafted onto it), and water. The setting reaction of an RMGI is complicated due to the interacting process of chemical cure through acid-base reactions with the cross-linking, polymerization reaction due to visible light-curing (VLC). The photopolymerization reaction will be affected by the polarity of the acid-base nature, and the acid-base process will be inhibited by the presence of organic matter, as well as through the reduced diffusion of reactants through the cross-linked network.[3-5] In this system, the resin photopolymerization reaction occurs at a much faster pace than the acid-base reaction, but it relies entirely on the availability of monomer and its mobility/diffusion, which is affected by the amount of material already cross-linked in the matrix network by the acid-base reaction. It is thus acceptable to assume that, since one reaction affects the extent and speed of the other, if the initiation time of the photopolymerization reaction were modified, it would alter the balance of acid-base versus photopolymerization of the material. This would result in a product that might physically perform differently based on the extents of reactions that took place. For example, if light-curing were delayed, the RMGI would set more due to the acid-base reaction, less photopolymerization would take place, and the material may possess physical properties closer to that of a GI. On the other hand, if photopolymerization

occurred early on, the acid-base reaction would be diminished, resulting in a material with physical properties more similar to a composite resin.

Some studies have evaluated the properties of RMGIs with or without light-curing. Light-curing has been shown to affect diametral tensile strength,[6] water uptake,[7] wear rates,[8] fluoride release,[9] erosion, and compressive strength.[10] Two studies have examined whether delayed light exposure has an effect on orthodontic bond strength using an RMGI.[11,12] The data of the one study[11] appears to be also presented in the other.[12] Nevertheless, using bovine mandibular incisors, they examined tensile and shear bond strength using an RMGI (Fuji Ortho LC; GC America Inc., Alsip, Ill) that was light-cured 5, 10, 20, and 40 minutes after mixing the powder/liquid. Although the mean bond strength decreased approximately 20% with time from the 5 to 40 minute delay groups, there was no statistically significant difference between any time interval groups. However, light-cure delays of 20 and 40 minutes, and perhaps 10 minutes for a quadrant, are impractical clinically. Additionally, a recent report using thermal analysis to examine a restorative RMGI (Fuji II LC; GC America Inc.) showed a decrease in light-cure reaction exotherm would be expected to occur even within the working time of the material.[13] Therefore, utilizing more clinically relevant light-cure delay times, the objective of this study was to examine the effect of light-cure delay on the polymerization efficiency and orthodontic bond strength of a capsulized RMGI. The hypothesis of the research was that delay in an orthodontic RMGI light-activation (1) allows for greater acid-base reaction, (2) reduces resin polymerization extent, (3) results in a RMGI of a different structure, and (4) this different structure will affect the physical properties of the material and decrease the bond strength when used to bond brackets to enamel.

LITERATURE REVIEW

Glass-Ionomers

In 1972. Wilson and Kent[1] completed a study in which they investigated and introduced a new translucent dental cement called the glass-ionomer. They described this cement as being based on the hardening reaction between aluminosilicate glass powders and aqueous solutions of polymers and copolymers of acrylic acid. Their intent was for the cement to be used for cavity linings and filling anterior teeth and erosive cavities. The GI cement would replace the older cements such as zinc oxide eugenol, silicate, zinc phosphate, and silico-phosphate cements due to their disadvantages including damage to the pulp and weak bond characteristics. The use of silicates as a cement has been around since the 1960s, however use of silica with polyacrylic acid, forming a glass-ionomer, was first introduced by these authors. The use of a finely crushed mixture of alumina and silica along with polyacrylic acid allows the cement to exhibit comparable compressive strength and better tensile strength, along with greater resistance to acid erosion, adhesion and less irritant to the dental pulp compared to other cements.

Wilson and Nicholson[2] published a book on different types of acid-base cements, their histories, chemistry, uses, and structures. They detailed the different types and theories associated with acid-base reactions, as well as providing information on water as a component of the reaction, strengths of acids and bases, acid-base classifications, and the formation of different acid-base reactions. They report that an acid such as polyacrylic acid and a base like aluminosilicate undergo an acid-base reaction to form a glass-ionomer.

Fajen et al.[14] studied three different glass-ionomers and compared their bond strengths with a composite resin. Each glass-ionomer was also tested under different enamel preparations of pumice, pumice and 45% polyacrylic acid, and pumice with 1.23% acidulated phosphate fluoride gel. The composite resin was used with a 37% phosphoric acid enamel etch. Thirty extracted maxillary first premolars were used for each GI, 10 per each surface preparation group. Ten teeth were used for the composite resin. A universal testing machine was used and tensile bond strength was determined. Results indicated that the Ketac-Cem GI had the greatest bond strength, followed by Fuji I and then Precise. The pumice and polyacrylic acid combination of enamel preparation resulted in the highest bond strengths, but results were not significant. However, the composite resin exhibited almost a 3-fold increase in bond strength over the strongest GI.

Resin-Modified Glass-Ionomers: Setting Reaction and Properties

Nicholson and Anstice[4] completed a review of the physical chemistry of light-curable glass-ionomers. They list the components of an RMGI which include: a polyacrylic acid, HEMA, bisGMA, water, and silica glass. They undergo two separate but competing reactions. Upon light-activation, the material undergoes a photochemical cross-linking reaction rapidly, concurrently with the acid-base reaction which occurs much slower. The hydrophobic organic matter of the photochemical reaction will be affected by the polar nature of the acid-base medium, and as the acid-base reaction proceeds, the polyacrylic acid becomes more neutralized, so more hydrophobic organic species become less soluble in the aqueous phase.

In another review, Nicholson and Anstice[5] detailed the development of modified glass-ionomer cements in dentistry. They described the RMGIs as hybrids of self-curing glass-ionomers and composite resins, with the addition of HEMA to act as a co-solvent and photopolymerizable monomer. They also contain calcium flouroaluminosilicate glass to act as the source for crosslinking ions for the acid-base reaction and as filler for the resin phase. Further, they described the setting reactions for RMGIs and how the acid-base and photopolymerization phases can affect one another. They hypothesized that the photochemical reaction will be affected by the polarity of the acid-base medium of the polyacrylic acid, and in return, the acid-base process will be inhibited by the presence of the organic components, as well as the reduction of diffusion coefficients of the reactants through the crosslinked network. Therefore, they concluded that the presence of polar polyacrylic acid will alter the rate of the photopolymerization reaction, and the presence of non-polar photopolymerizable molecules will reduce the rate of the acid-base reaction. They showed this by adding either HEMA (a photopolymerizable monomer) or methanol to an unmodified glass-ionomer and compared it to just water. They found that the setting time for the methanol or HEMA was slower and the material had a weaker compressive strength than the reaction was completed with just water added.

Andrzejewska et al.[15] studied the effect of a polyacid aqueous solution on photocuring of polymerizable components of a resin-modified glass-ionomer cement using a DSC operated under argon gas or air and isothermal conditions. HEMA and TEGDMA were the two monomers used to test the effect the polyacid had on polymerization. Polymerization reactions were initiated with UV-initiator, DMPA, and

by a two-component visible light initiating system based on CQ. They found that the main effect of adding polyacrylic acid to HEMA polymerization with DMPA caused an earlier onset of autoacceleration. For polymerization of HEMA initiated with camphorquinone (CQ), the addition of polyacrylic acid strongly accelerated the polymerization and increased the conversion of double bond formation. This was displayed by the kinetic curves that showed the dependence of polymerization rate expressed as a fraction of double bonds reacted per second and the degree of conversion of double bonds on the irradiation time. Therefore polymerization exothermic values are directly related to the degree of conversion of double bonds. TEGDMA photopolymerization was not influenced by the addition of polyacrylic acid.

Young[3] investigated polymerization and polyacid neutralization kinetics of a resin-modified glass-ionomer. Fuji II LC and Fuji IX (a conventional GI) were mixed, and after 1 minute, placed into a ring in the FTIR spectrometer and sealed on the surface with an acetate sheet. After 3 minutes, the RMGI was exposed to light for 20 seconds. After 30-60 minutes, the specimens were submerged in water. Fuji II LC showed changes in the spectra due to 90% conversion of the monomer to polymer within 1 minute after light exposure. Both Fuji IX and Fuji II LC showed two mechanisms associated with polyacid neutralization. The initial rate of absorbance change were inversely proportional to the square root of time, something commonly observed for diffusion controlled processes and suggests that acid neutralization processes may be diffusion controlled. Also concluded was the theory that prior to polymerization, the replacement of water by monomer might also slow the acid-base reaction by reducing acid ionization. Further, once the monomer is polymerized, a reduction in the rate at

which ions and molecules can diffuse through the organic matter to the glass interface occurs, reducing the rate of acid neutralization.

Jevnikar et al.[7] studied water penetration into a RMGI prepared differently over time. Fuji II LC capsules were mixed and placed into quartz tubes, then covered with mylar matrix at the ends. Half of the samples were exposed to light for 120 seconds, the other half were allowed to chemically set in the dark. After 1 hour from mixing, samples were removed from the tubes and stored at 37°C in distilled water. Eight samples were prepared with each setting mode and imaged with MRI technology at different times. Results indicated after 24 hours that water diffused 1 mm into the chemical-cured material, and considerably less in the light-cured samples. After 96 hours, the water reached the center of all chemically cured samples. For the light-cured samples, the water was still within a well-defined ring of the cylinder cross section with the plane of the image. After 192 hours, water reached the center of the cylinders of both groups of samples. For the light-cured samples, water penetration seemed to be uniform. However, for the chemical cured samples large pores of water were detected, indicating a non-homogenous distribution of water. Conclusions were that light-cured samples withstand water penetration better than its chemical cured counterpart. This would suggest that both setting reactions contribute to the final structure of the cement.

Yoda et al.[9] investigated the effect of different curing methods and storage conditions on fluoride ion release from a RMGI. Two materials were compared, a chemical cure only RMGI, and a dual cured RMGI. Both materials were mixed and place into vinyl molds and covered. One of two methods was used to cure the material, light-cure mode or by chemical cure mode (no light). Samples were then placed into

demineralizing solution. Fluoride ions were measured for both groups over a period of 90 days. A burst of fluoride release was seen after one day of storage for both groups. Constant fluoride release was seen from each group after 30 days. Total fluoride release from the chemical cure only RMGI was more than seven times greater than that of the dual cured RMGI.

Hegarty and Pearson[10] studied the erosion and compressive strength of a RMGI when light-activated versus allowing to it set chemically in the absence of light. Two different resin-modified glass-ionomers were tested and compared against two conventional glass-ionomers. All samples were mixed and placed into molds with some of the light-activated materials polymerized with light, while others were kept in the dark. All samples were placed in an incubator for 1 hour, and then stored in water under dark conditions. Erosion and compressive strength tests were then completed 1 and 24 hours after mixing. Results showed that RMGIs showed greater erosion than the conventional GIs. For compressive strength tests, the RMGIs were significantly stronger than the GIs at 1 and 24 hours and when light polymerization occurred.

Eliades and Palaghias[16] investigated several in vitro properties of 3 visible light-cured glass-ionomers. They studied the compressive strength, diametral tensile strength, shear bond strength, and Vickers hardness of each light-cured GI, with or without HEMA. Total transmittance and diffuse reflectance measurements at 468 nm were also taken. Results showed that the extent of acid-base glass-ionomer reaction was significantly delayed when the specimens were light-cured immediately after mixing. The light-cured GI without HEMA provided significantly lower compressive strength, diametral tensile strength, and Vickers hardness than the samples with HEMA. Samples

containing HEMA had higher shear strength at the liner/composite interface than the dentin/liner interface. Significant correlations were detected between the optical properties of the liners and the top-bottom hardness differences as an indicator of the extent of conversion, as well as between the maximum marginal gap at the dentin/liner interface and the bond strength with dentin and composite.

de Gee et al.[8] investigated the structural integrity of a RMGI after various light-curing conditions consisting of omitting or delaying light-initiation. Two conventional glass-ionomers and three RMGI cements were studied. One sample of each resin was light-cured 2 minutes after mixing, another sample was light-cured 60 minutes after mixing, while a third sample was not light-cured. The integrity of the samples was evaluated by three-body wear experiments, conducted 8 hours, 1 week, and 4 months after hardening. Results showed that after 1 hour, the structural integrity (wear rate) of two of the three RMGIs improved significantly, while the other (Vitremer) significantly decreased, which declined further when light was omitted. The conclusion was that the RMGIs benefited from a chemical integration and increased structural integrity required an acid-base reaction before the HEMA photopolymerizes.

Berzins et al.[13] studied how the dual yet independent reactions of a RMGI can compete with and inhibit each other, resulting in a different structured material dependent on the predominant reaction. An RMGI was investigated using DSC with an alteration in initiation of visible light-cure. Three groups consisted of light-cure initiation times of immediate, 5, and 10 minutes post mixing. A fourth group, dark cure, was evaluated without visible light-cure. They found that as time allowed for the acid-base reaction to occur (longer delay in visible light-cure), the polymerization visible light-cure

polymerization enthalpy exotherm significantly decreased. A significant increase in decomposition endotherm enthalpy was also noted with an increase in time delay. These suggest that as an RMGI is allowed to set without light-cure, the predominant product is composed due to the acid-base reaction and this reaction competes with and inhibits the production of material through visible light-cure, resulting in a product more similar to a glass-ionomer than a composite resin.

Coutinho et al.[17] investigated to what extent the self-adhesiveness of resin-modified glass-ionomers can be attributed to its chemical bonding capacity. Three RMGIs were mixed and applied on the mid-coronal dentin from freshly extracted teeth. Respective conditioners were utilized with the RMGI. Three teeth per experimental group were investigated after one month storage in 0.5% chloramine. Transmission electron microscopy, atomic force microscopy, and field-emission scanning electron microscopy were used to study diamond-knife sectioned interface samples. X-ray photoelectron spectroscopy was also used to characterize the chemical interaction of polyalkenoic-acid copolymers in each RMGI with hydroxyapatite and dentin. Data showed that the RMGIs interacted with dentin following two distinct patterns. Fujibond LC and other RMGIs without conditioner clearly demineralized dentin, but could not withdraw hydroxyapatite from dentinal collagen. Hydroxyapatite that remained attached to collagen fibrils formed receptors for primary chemical bonding with the polyalkenoic acids incorporated into the RMGI. Further, it was found that some RMGIs without conditioner clearly demineralized dentin and created shallow hybrid layers enhancing micro-mechanical retention. This showed that with some RMGIs, a self-adhesiveness can be attributed to ionic bonding of hydroxyapatite that remained attached to exposed

collagen fibrils, as well as micro-mechanical interlocking by formation of hybrid layers of dentin.

Li et al.[6] studied the diametral tensile strength, fracture strength, and Vickers microhardness of three different RMGIs, one GI, and one composite resin under different conditions. Eight specimens were used for each condition and material. The three groups were: specimens kept in deionized water at 37°C for 10 min, 1 day, and 28 days after being light-cured for 60 seconds, specimens light-cured for 60 seconds and implanted into muscles of rats, and specimens of RMGI light-cured at 0, 5, 10, 20, 40 and 60 seconds and kept in deionized water at 37°C for 24 hours, specimens of 2 RMGIs mixed and kept in 100% humidity at 37°C for 3, 6, 10, 60 and 180 minutes before light-curing for 60 seconds, and control specimens of composite resin which were cured and left in water, and a GI control kept in 100% humidity at 37°C for 1 hour after mixing, then placed in water at 37°C for 23 hours and 28 days. Diametral tensile tests showed that RMGIs were stronger than the conventional GI. This was also the case for fracture strength and microhardness testing. The strengths of the GI increased with time. The tensile strength of a light-cured RMGI was 50% greater than the same RMGI without light-cure. Also, the tensile strength decreased significantly after a 10-min delay in light-cure. These results indicate that light-curing and when it takes place can affect the properties of a RMGI.

Resin-Modified Glass-Ionomer Bond Strength Studies

Komori et al.[11] determined tensile and shear orthodontic bond strength of a RMGI in comparison with a light-cured resin cement (LCR) subjected to various time intervals

of light initiation from the onset of mixing. Again, 240 extracted bovine mandibular

incisors were used for this study. The RMGI groups were prepared with a 10%

polyacrylic acid conditioner, while the LCR groups were prepared with 35% phosphoric

acid. Four time intervals for light-curing after onset of mixing the cement were used: 5,

10, 20 and 40 minute delays. Comparisons of tensile and shear bond strengths between

the LCR and RMGI groups found no differences were noted by the timing of light-

curing, whereas the bond strength of the LCR decreased as time intervals increased,

showing a 20% decrease in bond strength between the 5 and 40 minute time delay.

Ando et al.[12] similarly studied tensile bond strengths of a light-cured resin-

reinforced glass-ionomer cement subjected to various time intervals of light-cure, and

evaluated the durability of the material through thermocycling. They also made

comparisons of the RMGI with a light-cured composite resin. Two-hundred-forty

extracted bovine teeth were used for this study with time intervals from light-curing of 5,

10, 20 and 40 minutes after mixing the cement. Thermocycling was completed 2000

times at temperatures between 5°C and 55°C. The LCR group was prepared with 35%

phosphoric acid while the RMGI group was prepared with 10% polyacrylic acid. Results

showed that bond strengths were unaffected due to the thermocycling process and

differences in time intervals with the RMGI. However, the LCR showed significant

differences with regards to the time intervals only. Bracket failure in the RMGI group

occurred primarily at the bracket/adhesive interface, with the LCR exhibiting bond failure

at the tooth/adhesive interface.

De Munck et al.[18] evaluated the bonding effectiveness of a resin-modified glass-

ionomer adhesive to dentin after four years of water storage. A RMGI was bonded

without pretreatment of dentin, with a polyalkenoic acid conditioner, and with a 37%
phosphoric etch. Twenty-seven human third molars were used and the occlusal third of
the crown was sectioned off to expose dentin for bonding. Nine teeth were allocated to
each group, in which 3 were tested for tensile bond strength after 24 hours in water, 3
were stored in water that contained 0.5% chloramine for 4 years, and then tested for
tensile bond strength while the last 3 were sectioned in half 24 hours after bonding and
then stored in water for 4 years. Results indicated an increase in tensile bond strength for
all three groups over the 4 year period. After 24 hours and 4 years, the lowest tensile
bond strength occurred when dentin was not pretreated. The highest tensile bond strength
was found to be when the polyalkenoic acid pretreatment was used. Their theory was
that when phosphoric acid was used to pretreat the dentin, more of a micromechanical
bond occurs, versus when the polyalkenoic acid conditioner is used, a smear layer
remains and bonding primarily occurs via a chemical bond, which is more characteristic
of a glass-ionomer than a composite resin. Indirectly it can then be assumed that the
more a RMGI resembles a glass-ionomer, more of a chemical bond occurs and thus the
greater the bond strength.

Komori et al.[19] also completed a study in which they tested tensile and shear bond
strength between 2 different RMGIs and one composite resin after being left at room
temperature for 24 hours or after thermocycling. They also studied 3 different techniques
for preparation of enamel for bonding under scanning electron microscopy: progressive
polishing plus 10% polyacrylic acid, progressive polishing plus 37% phosphoric acid,
and progressive polishing only. Eighty-four teeth were divided into 12 groups: shear test
at 24 hours after storage at room temperature, shear test after thermocycling, tensile test

at 24 hours after storage at room temperature, and tensile test after thermocycling, for each RMGI or composite resin. Results showed that the enamel treated with polishing and polyacrylic acid produced a smooth surface without a prism-like etching pattern, while the enamel prepared with polishing and 37% phosphoric acid produced a distinct prism-like etching pattern. Bond strengths with the composite resin were the highest, followed by Fuji Ortho then Ketac-Cem. Thermocycling did not seem to alter the bond strength significantly within materials.

Bishara et al.[20] studied how different enamel conditioner concentrations can affect the shear bond strength of an RMGI. They used 46 freshly extracted human bicuspid molars, separated into two groups. The first group had enamel conditioned with 10% polyacrylic acid, while the second group was conditioned with 20% polyacrylic acid. Teeth were bonded and tested for shear bond strength. They found that the shear bond strength was significantly greater in the group conditioned with the 20% polyacrylic acid compared with the 10% polyacrylic acid. The 10% polyacrylic acid group had a mean shear bond strength of 0.4MPa, while the 20% polyacrylic acid group had a mean shear strength of 3.3 MPa. Also, the adhesive remnant index for the 20% polyacrylic acid group showed more of a cohesive failure, while the 10% polyacrylic group had predominantly an adhesive failure at the tooth/adhesive interface. Further, scanning electron microscopy tests revealed a relatively smoother enamel texture in the 10% polyacrylic group compared to that of the 20% polyacrylic group. It was concluded that the shear bond strength of an RMGI can be enhanced 8-fold when the enamel is conditioned with a 20% polyacrylic acid conditioner in comparison with a 10% polyacrylic acid conditioner.

Cacciafesta et al.[21] evaluated shear bond strength when using three different enamel conditioners: 10% polyacrylic acid, 37% phosphoric acid, and a self-etching primer. One-hundred eighty bovine permanent mandibular incisors were divided into 3 groups of 4, consisting of the 3 different conditioners plus a group with no conditioner. The groups were further divided based on surface bonding condition: dry, wet with water, and wet with saliva. All teeth were stored for 24 hours, and then debonded with a universal testing machine with shear bond strengths recorded. Results showed that the bond strengths of a RMGI bonded with the self-etching primer were significantly higher than those achieved with all other enamel conditioners, under both dry and wet conditions, except when the RMGI was used with 37% phosphoric acid under dry conditions. This showed that the self-etching primer was not affected by saliva or water contamination. Also, groups etched with 37% phosphoric acid showed higher bond strengths than those achieved after 10% polyacrylic acid conditioning, except when comparing the groups exposed to water. Bond failures with the 10% polyacrylic acid occurred mostly at the enamel/adhesive interface, while the 37% phosphoric acid samples had bond failure predominantly at the bracket/adhesive interface.

Godoy-Bezerra et al.[22] evaluated the shear bond strength of a RMGI variably exposed to saliva and different enamel surface preparations. One-hundred twenty-five freshly extracted bovine mandibular incisors were divided into 5 groups: RMGI etched with 10% polyacrylic acid followed by exposure to saliva, RMGI etched with 37% phosphoric acid followed by exposure to saliva, RMGI exposed to saliva with no etching, RMGI etched with 10% polyacrylic acid without exposure to saliva, and a control group consisting of Transbond XT etched with 37% phosphoric acid and not exposed to saliva.

All groups were thermocycled and tested for shear bond strength on a universal testing machine, after which ARI scores were recorded. Results showed the composite resin and RMGI group etched with phosphoric acid yielded the greatest shear bond strength, while no differences were noted between the other 3 RMGI groups. This shows that whether or not saliva is present, a 10% polyacrylic acid does not improve bond strength. The groups which had enamel preparation showed more than 50% of the material adhered to the tooth, while the one group which had no enamel preparation had bond failures at the enamel/adhesive interface.

Bishara et al.[23] completed another study comparing an RMGI and a composite resin and modes of debonding. Seventy-five extracted human molars were divided into five groups (material/etchant/surface condition): Transbond (a composite resin)/phosphoric acid/dried, RMGI/no etch/wet with water, RMGI/polyacrylic acid/wet with water, RMGI/no etch/wet with saliva, and RMGI/polyacrylic acid/wet with saliva. Teeth were bonded, thermocycled for 2000 cycles, then debonded and modes of debond were recorded. Results showed no statistical differences for shear bond strengths between groups that were etched, whether RMGI, composite resin, wet with saliva or water. However, unetched groups had significantly lower shear bond strengths, lowering the bond strength by a third to a half, compared to the etched RMGI groups. ARI scores indicated there was a significant difference in location of bond failure, with the etched groups predominantly debonding at the bracket/adhesive interface, whereas the unetched groups debonded at the enamel/adhesive interface. Conclusions were that the use of a RMGI with a polyacrylic acid conditioned surface with water or saliva present provides a similar bond strength to a traditional composite resin. However, past studies indicated

that shear bond strengths with a polyacrylic acid conditioned enamel surface were

reduced by 75% compared to surfaces etched with 37% phosphoric acid, due to the

roughness of the enamel created by the amount of enamel conditioning.

Literature Specifically Related to Thesis Methodology or Results

Next, several articles related to the methodology or interpretation of results will

be reviewed.

Moore et al.[24] studied the temperature variation at archwire sites adjacent to

maxillary incisors and premolars and its correlation with ambient temperature. Twenty

male dental students were used in this study in which a removable retainer with full

palatal coverage was worn continuously for 24 hours. Several thermocouples were

placed on the retainer to record intra-oral and ambient temperatures. Temperatures were

recorded every 5 seconds. The overall median ambient temperature recorded was

21.3°C. Total group median oral temperature was 34.9°C, nearly 35°C. Temperatures in

the incisal area were lower than those at the premolar site. It was also found that the oral

temperature decreased when mouth-breathing or mouth-opening occurred for extended

periods of time. They further concluded that 37°C should not be considered to represent

mouth temperature, and instead a temperature of 35.5°C should be used.

Khalil and Atkins[25] studied 6 glass-ionomer cements using differential scanning

calorimetry. DSC was used to measure the amount of heat flow of the glass-ionomers

during isothermal setting reactions at 37°C and dynamic scan settings. A small sample of

freshly mixed GI was placed immediately in the DSC in which the setting reaction

producing an exothermic peak was measured for all GIs. Fuji II LC in the absence of

light showed two distinct peaks, attributed to acid-base neutralization and chemical polymerization. Fuji II was then light-cured for 20 seconds before DSC, and no heat flow was measured. When light-cured Fuji II was allowed to set without light, it exhibited a very slow reaction. All GIs fully set without light within 10-11 minutes. A dynamic scan for the Chelon-Silver GI showed there was no remaining reaction after the isothermal stage, with the only endothermic peak occurring at 170°C due to degradation of the material. A dynamic scan of the powder and liquid components of the GI was then completed. DSC showed that the powder component had no peak in the temperature range covered, while the liquid component had an endothermic peak at 158°C which can be attributed to the degradation temperature of the polymeric constituent in the liquid. Comparing this peak to the peak from the cement, one can conclude that cross-linking of the polymer with the glass powder increased its degradation temperature by 12°C. This shows that the glass particles provided the polymer with more heat stability. A peak at 95°C is attributed to evaporation of distilled water. This shows that through the use of isothermal and dynamic scan DSC, one can degrade a material and measure exothermic and endothermic peaks to determine glass-ionomer character and structure.

Wilkie[26] reviewed the Thermogravimetric Analysis/Fourier Transform Infrared Spectroscopy (TGA/FTIR) technique for studying polymer degradation and studied the degradation of poly(methyl methacrylate), butadiene-based graft polymers, styrene-based graft polymers, and determined how cross-linking enhances the thermal stability of polymers. For the degradation of poly(methyl methacrylate), in order to enhance the thermal stability of the polymer and prevent degradation, one must either prevent the initial degradation or capture the products of this degradation so they cannot further

undergo reactions. One way to accomplish this is through additives which interact with the polymer by coordination to the carbonyl oxygen to a Lewis acid, and subsequent transfer of an electron from the polymer chain to the metal ion, or through formation of a radical which can trap the degrading radicals before they undergo further degradation. The graft layer has little effect on the degradation of styrene-butadiene copolymers; however, a different graft on polystyrene does enhance the thermal stability of the polymer. However, an organic graft is less efficacious than an inorganic graft. Further, it seems that cross-linked polymers provide a more thermally stable polymer that a thermoplastic polymer. Conclusions drawn were that TGA/FTIR provides a very useful tool to determine the degradation products of a polymer and therefore the original structure of the material.

Emami and Söderholm[27] set out to determine the degree and rate of conversion of light-cured resins by modifying light-curing procedures and using different photo-initiator/co-initiator combinations. They prepared monomer mixtures of 50% bisGMA and 50% TEGDMA. Different photo-initiators were added to the mixtures, such as CQ or 1-phenyl-1,2-propanedione. Co-initiators, such as DABE, CEMA, and DMAEMA, were then added at lower concentrations to enhance the photo-initiator efficiency. A total of 6 different initiator/co-initiator combinations were prepared. These samples were analyzed with DSC and cured with 3 different lights/curing regimens: halogen light with an irradiance of 850 mW/cm^2, halogen light with low irradiance for the first 5 seconds then followed by halogen light with high irradiance, and an LED light at 450 mW/cm^2. Four thermogram peaks were recorded. The first peak represented the exotherm produced by the polymerization of resin plus the heat released from the curing unit. The

three following peaks were in response to triggering of the light-curing unit and represent the exothermic irradiance caused only by the light-curing unit. The isothermal heat of resin polymerization was then determined by subtracting the average heat value of the last three peaks from the first peak value. Results showed that the fastest conversions were obtained with standard curing, followed by the LED and soft-start curing. However, after 40 seconds of curing, the conventional curing and soft-start curing produced a higher conversion than LED. Conclusions drawn were that by using soft-start curing and an appropriate photo initiator/co-initiator combination; it is possible to achieve a higher conversion within a curing time of 40 seconds.

Tavas and Watts[28] studied the mechanical performance of a visible light-cured orthodontic bonding material and compared it to other commercial adhesives. Freshly extracted bicuspids were pumiced and etched with 37% phosphoric acid. Twelve to sixteen teeth were bonded for each group in which six different adhesive system combinations were tested with three chemically and visible light-cured materials. Specimens were kept in 37°C distilled water for 5 minutes or 24 hours. Different irradiation times were used and the shear bond strength was tested with a universal testing machine. Results indicated that bond strengths for both chemically and visible-light-cured materials increased from 5 minutes to 24 hours. The light-cured materials produced similar bond strengths to the two chemically cured adhesives. Brackets bonded with any of the three adhesives tested failed at force levels well above those forces required to produce torque or movement of teeth. However, to resist occlusal forces, an orthodontic bonding adhesive should produce bond strengths of 4 kg in 5 minutes and 6

kg in 24 hours. These values were barely reached for a few of the adhesive

combinations, while other combinations fell far short.

MATERIALS & METHODS

Fuji Ortho LC (universal shade capsules; GC America Inc.) was the RMGI investigated in this two component research consisting of (1) differential scanning calorimetry (DSC) analysis to investigate the extent of acid-base and/or photopolymerization reaction and (2) bond strength determination. Four experimental groups were established via the RMGI being light-cured immediately (0), 2.5, 5, and 10 minutes after mixing. The material was prepared following the manufacturer's instructions using a mechanical mixer for 10 seconds (ProMix, Dentsply International, York, Penn) under dim light conditions to reduce ambient light-curing of the material. When prescribed, visible light polymerization was performed for 40 seconds using a light-curing unit (Optilux 501, Kerr, Danbury, Conn) with an irradiance of 600 mW/cm^2 as measured with a commercial radiometer (Model 100 Optilux Radiometer; Kerr).

DSC Analysis

Immediately after mixing, the RMGI was placed in a pre-weighed, 40 μl aluminum crucible and transferred to a DSC (Figure 1) (822e, Mettler-Toledo, Columbus, Ohio) synchronized in time with mixing. Five experimental protocols were initially tested to determine the effect of temperature on the acid-base reaction of the RMGI in the absence of light-curing (n = 5/group). Since the manufacturer recommends refrigerating the material to extend working time, three of the five RMGI groups were chilled in a refrigerator set at 5°C, with one group remaining at the chilled temperature for the DSC analysis, another group heated to 23°C (room temperature; RT), while the other group was heated to 35°C (oral temperature). This is analogous to leaving the chilled material

on a cooled glass slab (prior to bonding), leaving it exposed to room temperature, or placing it in the mouth (as in bonding), respectively. In this study, $35^{o}C$ has been designated as an average oral temperature noting differences arise due to location within the mouth and the mouth being open/closed.[24] The other two RMGI groups were kept at room temperature $(23^{o}C)$, with one group remaining at room temperature for the DSC analysis, while the remaining group was heated to $35^{o}C$ for the analysis. This represents a clinician using non-refrigerated material and similarly leaving it at room temperature or placing it in the mouth, respectively. Thus, these five groups may be designated by the initial temperature of the RMGI and the DSC analysis as: Chilled-$5^{o}C$, Chilled-$23^{o}C$, Chilled-$35^{o}C$, RT-$23^{o}C$, and RT-$35^{o}C$. For this DSC analysis, heat flow was monitored for 40 minutes at the indicated isothermal analysis temperature (5, 23, or $35^{o}C$). An exothermic peak, ascribed to the acid-base exothermic reaction,[13] was evaluated with the time at its summit noted. The peaks were not integrated to yield overall enthalpy because the varying profile of the peaks could lead to bias even with a standardized integration approach.

Figure 1. Mettler Toledo DSC used for measuring heat flow

DSC analysis was also conducted on the RMGI to determine the effect of delay of light-curing on polymerization efficiency. Experimental groups were established via the RMGI being light-cured immediately (0), 2.5, 5, and 10 minutes after mixing (n = 10/group). The RMGI capsules were refrigerated (5°C) prior to mixing. Immediately after mixing, the RMGI was placed in a pre-weighed crucible and transferred to the DSC synchronized in time with mixing. DSC measurements initially consisted of isothermal (35°C) heat flow evaluation for 25 minutes, to allow for measurement of polymerization and/or acid-base reaction exotherms. At the prescribed times, the RMGI was light-cured for 40 seconds. This produced an exotherm arising from the heat input of the light-curing unit and the polymerization reaction. Next, forward (@10°C/min) and reverse (@20°C/min) dynamic temperature scans were conducted between 35°C and 300°C. This dynamic scan degrades the material, producing an endotherm which serves as an indicator of glass-ionomer/resin material character[13,25] and its original structure.[26] The final thermal segment was a 15 minute, 35°C isothermal period with VLC initiated four times for the determination of mean enthalpy contributed from the VLC process. This energy was then subtracted from the initial VLC exotherm, resulting in an exotherm solely from the polymerization reactions.[27] The polymerization exotherm is directly related to degree of conversion.[15] DSC measurements were completed in a closed air environment, except during VLC, in which measurements were conducted with the light guide tip approximately 2 mm from the test material surface. One trained operator (JT) conducted all of the VLC DSC experiments. Additionally, as will be discussed later, an immediate group was also examined utilizing the same protocol except the RMGI capsule was warmed to 35°C prior to mixing (n = 5).

Bond Strength Determination

Bonding

With approval from the Institutional Review Board at Marquette University, freshly extracted human premolars were collected and stored in deionized water. The water was replaced frequently to limit bacterial proliferation, and the chosen teeth were free of fractures, caries, and restorations. All teeth were prepared by sectioning off the roots 2 mm below the CEJ utilizing a high-speed handpiece and tapered diamond bur, pumicing for 10 seconds with a rubber prophylactic cup and fluoride-free pumice (Whip-Mix Corp., Louisville, Ky), rinsing with water, and storing in deionized water at 35°C prior to bonding. The 72 teeth were randomly divided into 4 groups of 18 to constitute the aforementioned immediate (0), 2.5, 5, and 10 minute RMGI light-cure delay groups.

Every bracket was bonded one at a time using a direct bond technique and stainless steel brackets with a 0.022-inch slot, 0° tip, and 0° torque (Victory Series^{TM} Universal Bicuspid Twin; 3M Unitek, Monrovia, Calif). Before bonding, each tooth was rinsed with fresh deionized water, dried thoroughly with oil-free compressed air, and the buccal surface was scrubbed with 10% polyacrylic acid conditioner (GC Ortho Conditioner; GC America Inc.) for 20 seconds with a cotton tip applicator. The teeth were rinsed again and excess moisture was removed with a light flow of air for 1-2 seconds. Under dimmed light, the prepared RMGI was dispensed onto the bracket base which was immediately positioned onto the buccal aspect of the tooth, aligned to the center of the tooth, and seated with firm pressure. Visible light polymerization was initiated at the prescribed time after mixing (immediate (0), 2,5, 5, or 10 minutes) for 10 seconds at all sides of the bracket, angled at 45° from the enamel-bracket interface, for a

total of 40 seconds. Prior to light-curing, the teeth were kept under a box to prevent ambient light penetration.
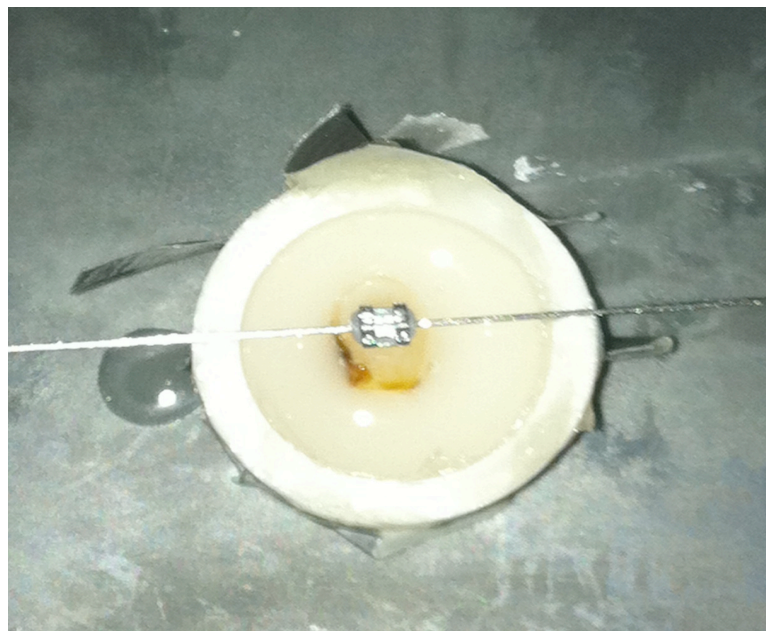
Mounting and Shear Bond Strength Testing

The bonded teeth were mounted in resin (Great Lakes Orthodontics, Tonawanda, N.Y.) up to the central groove of the tooth (Figure 2) and stored in fresh distilled water at 37°C for 24 hours. A universal testing machine (Instron Corp., Canton, Mass.) was used to debond the brackets from the teeth using a shear load applied to the bracket at a crosshead speed of 0.1 mm/min. Specimens were positioned such that the loading blade was directed parallel to the long axis of the tooth with contact made as close to the bracket/tooth interface as possible (Figure 3). Shear load forces to debond the bracket from the tooth were recorded and converted to MPa using a bracket base area of 10 mm^{2}.

Adhesive Remnant Index Classification

After debonding, the bracket base and tooth were analyzed under optical microscopy at 10X magnification using external illumination and given a score according to the adhesive remnant index (ARI). One of the four possible outcomes was recorded as follows: 0 = no adhesive left on tooth / all adhesive left on bracket, 1 = less than half of the adhesive left on tooth, 2 = more than half of the adhesive left on the tooth, and 3 = all of the adhesive left on the tooth

Figure 2. Bonded bicuspid being mounted in acrylic using a PVC cylinder

Figure 3. Mounted bicuspid in acrylic situated in the universal testing machine before debonding
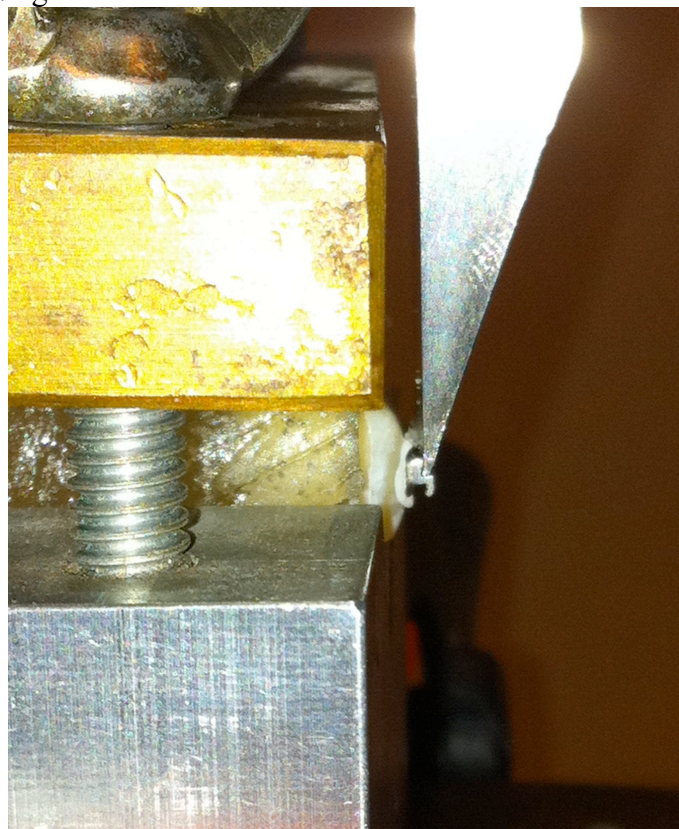
STATISTICAL ANALYSIS

Differences in DSC parameters and shear bond strength between the four groups were analyzed using a one-way analysis of variance (ANOVA) followed by a post-hoc Tukey test when indicated. A Weibull analysis was performed to determine bond strength reliability, Weibull modulus, characteristic strength, and probability of failure at 6.0 MPa. The latter value was selected following a recommendation that shear/peel bond strength should be approximately 6 kg at 24 hours (6 kg/10mm^2 = 6 MPa).[28] In addition, a chi-square test was used to compare the ARI scores between the groups. Significance for all statistical tests was set at $P < 0.05$ and the analysis was performed using SPSS Statistics 17.0 (SPSS Inc., Chicago, Ill).

RESULTS

The times of the maximum acid-base exotherm for the Chilled-5°C, Chilled-23°C,

Chilled-35°C, RT-23°C, and RT-35°C groups were 26.8±0.4, 24.4±1.8, 5.9±0.8,

23.0±1.7, and 5.4±0.4 minutes, respectively. Figure 4 displays a comparative

thermogram of these groups. For the light-cured RMGI, DSC exothermic and

endothermic values are listed in Table 1. Comparing the VLC polymerization

exothermic values, the 10 minute delay group had significantly (P <0.05) lower

polymerization efficiency compared to the other groups. The immediate, 2.5, and 5

minute delay groups were not significantly different from each other (P >0.05). No acid-

base exotherms were recorded in the immediate, 2.5, and 5 minute delay groups, while a

slight, but noticeable exothermic peak was observed around 5-7 minutes for the 10

minute delay group (Figure 5). The dynamic scan endotherm enthalpy values were not

significantly (P >0.05) different among the groups, but the temperature for the 10 minute

VLC delay endotherm peak was significantly (P <0.05) lower compared with the

immediate, 2.5, and 5 minute delay groups, which were not significantly different from

each other (P >0.05). Typical endotherms are presented in Figure 6.

Table 1. DSC Analysis Parameters

| Group	Light-activated Polymerization Exotherm (J/g)	Acid-Base Reaction Exotherm (J/g)	Dynamic Scan Endotherm (J/g)	Temperature of Endotherm Peak ($^{\circ}$C)
Immediate LC	22.7±5.4 AB	Not Detected	29.5±5.2 A	184±16 A
2.5 min delay LC	23.4±4.5 AB	Not Detected	25.9±6.7 A	186±15 A
5 min delay LC	21.0±5.9 B	Not Detected	21.9±3.8 A	170±4 AB
10 min delay LC	8.4±6.4 C	5.5±1.5	22.5±9.3 A	158±14 B
Immediate LC @ 35°C	30.3±7.6 AB	Not Detected	28.5±2.8 A	181±9 A

Within each parameter, different letters denote significant (P <0.05) differences exist.
LC = Light-cure

Fig 4. Isothermal DSC thermograms for the RMGI stored and analyzed at various temperatures
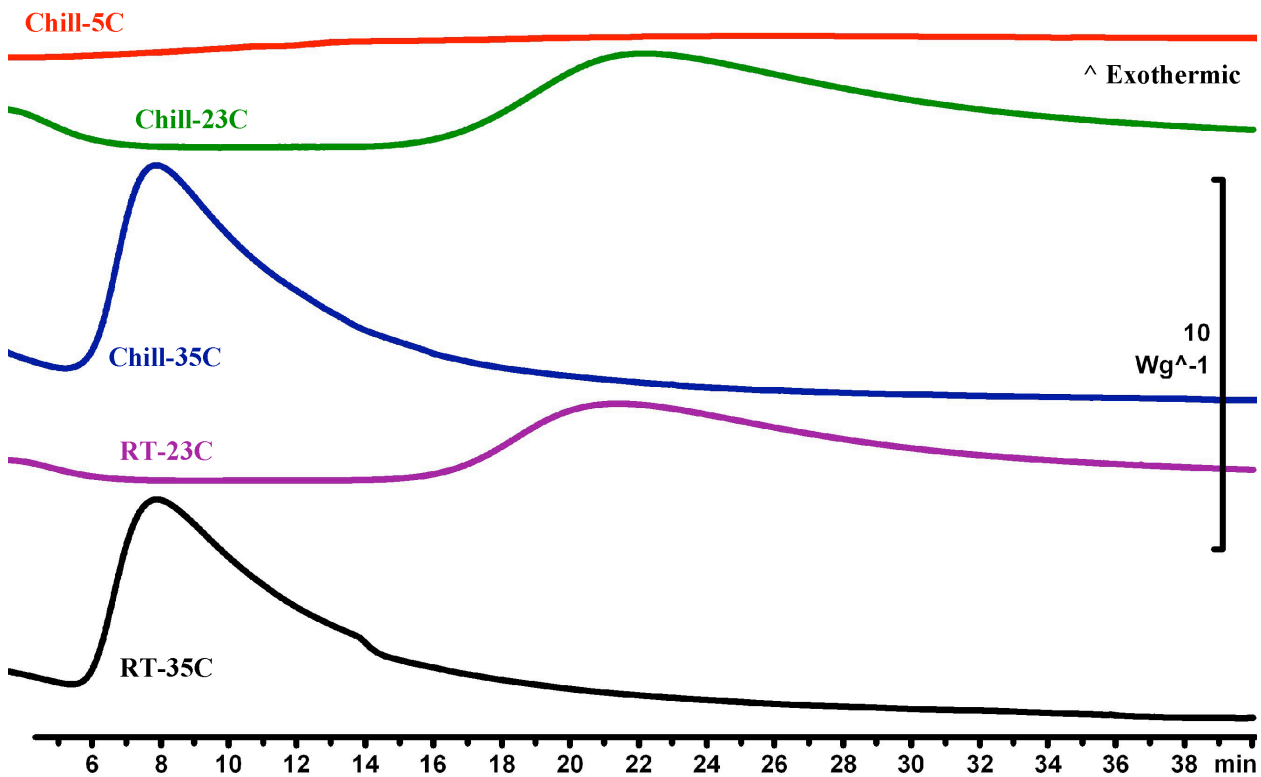
Fig 5. Comparison of light-cure polymerization exotherms
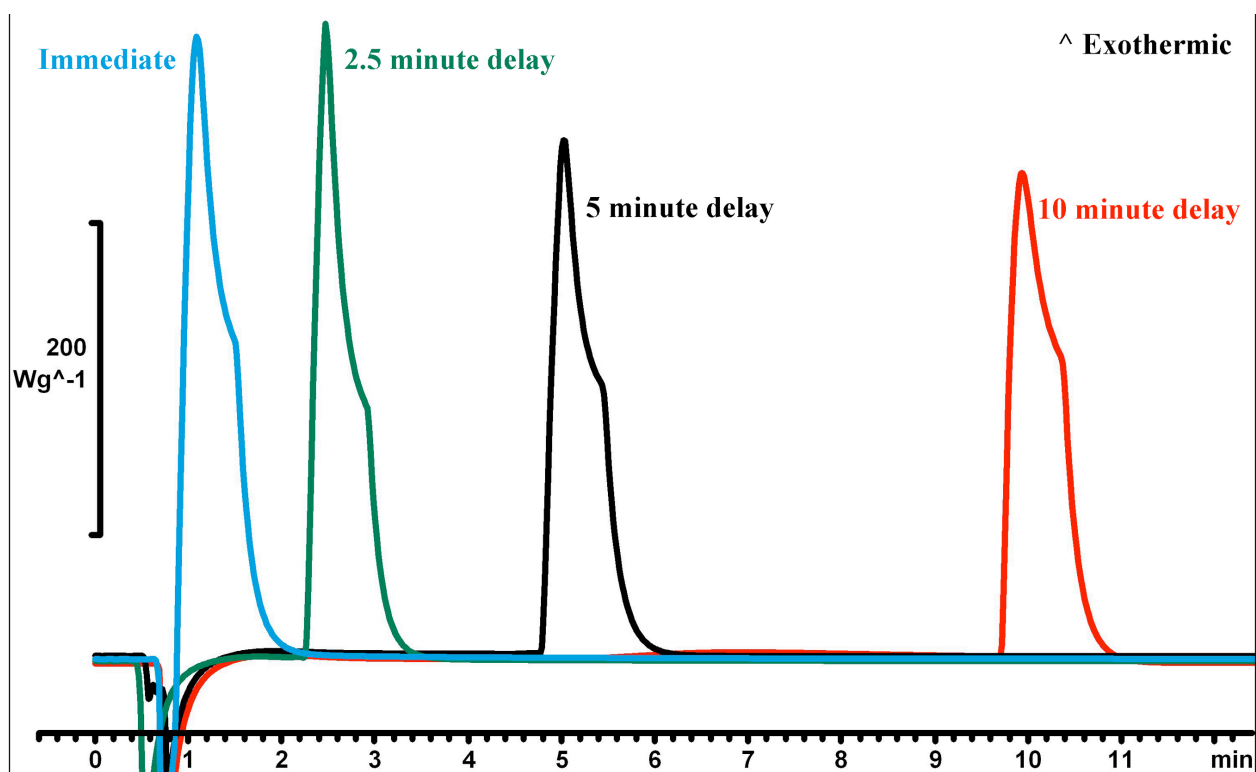
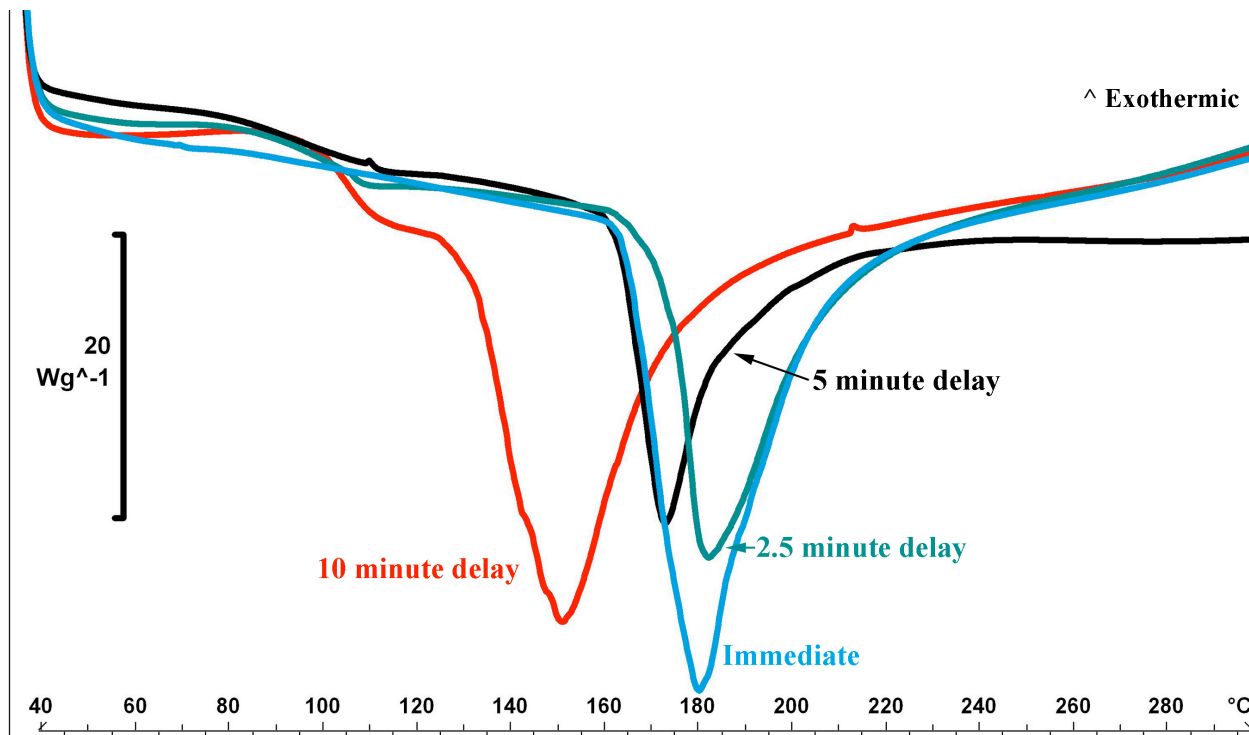**Fig 6**. Comparison of dynamic scan DSC endotherms

Table 2 displays the mean shear bond strength and Weibull analysis results. ANOVA indicated no significant ($P > 0.05$) difference in bond strength existed among the four VLC delay groups. The Weibull modulus was fairly similar between groups although the immediate group showed a greater value indicative of less variability in bond strength. Similarly, the immediate group presented with the lowest probability of failure at a bond strength of 6.0 MPa. This is further observed in Figure 7 which shows the probability of failure versus shear bond strength. ARI scores are listed in Table 3. A chi-square test found no significant difference ($P = 0.428$) between groups. An ARI score of 1 was found in at least 83% of the teeth for all groups, indicating a majority, but not all, of the adhesive remained on the bracket following debonding.

Table 2. Shear Bond Strength and Weibull Analysis Results

Group	Mean ± Standard Deviation (MPa)	Weibull Modulus (β)	Characteristic Strength (α; MPa)	Probability of Failure @ 6.0 MPa (%)
Immediate LC	14.3 ± 2.3	6.8	16.1	0.1
2.5 min delay LC	14.8 ± 3.2	4.9	16.0	0.7
5 min delay LC	12.8 ± 3.1	4.4	14.1	2.2
10 min delay LC	14.5 ± 2.7	5.5	15.6	0.4

One-way ANOVA indicated no significant ($P > 0.05$) differences exist for mean shear bond strength.

Fig 7. Probability of failure versus shear bond strength
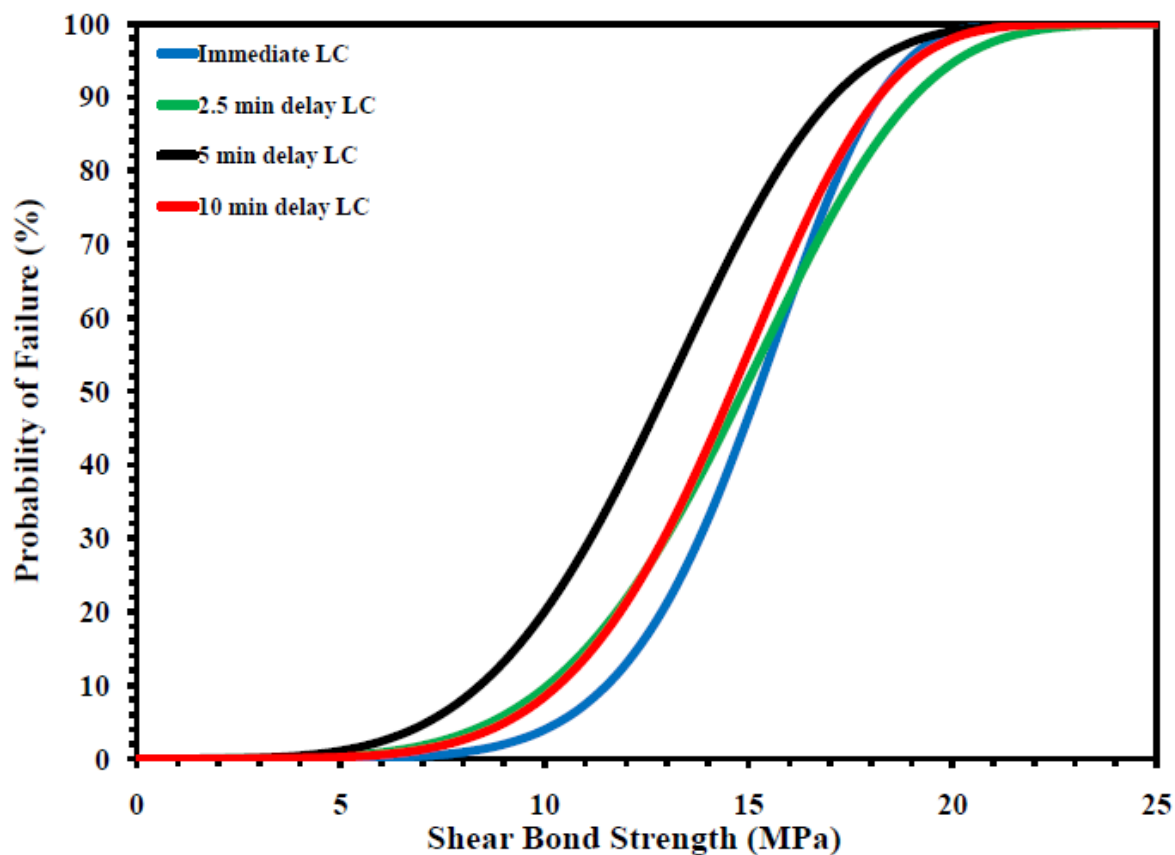
Table 3. Adhesive Remnant Index (ARI) Scores by Group

	ARI Scores*			
Group	**0**	**1**	**2**	**3**
Immediate LC	1	16	1	0
2.5 min delay LC	0	16	2	0
5 min delay LC	0	18	0	0
10 min delay LC	2	15	1	0

*A chi-square test showed no significant difference (P = 0.428) between groups

DISCUSSION

Nicholson and Anstice[4,5] hypothesized early on that the acid-base and VLC

polymerization reactions in RMGIs would compete with and inhibit each other.

Experimentally, Young[3] showed that after the VLC induced photopolymer cross-linked

network has formed, diffusion of acid-base reactants is reduced. Eliades and Palaghias[16]

also showed that the acid-base reaction rate is slower in VLC vs. dark-cured RMGIs.

Berzins et al.[13] tested the theory that there was a competition of reactions in RMGIs.

They discovered that as time was allowed for the acid-base reaction to occur, the VLC

polymerization exotherm significantly decreased. This is partially supported in the

present study. There were no significant differences in VLC polymerization exotherm

between the immediate, 2.5, and 5 minute VLC delay groups, but the 10 minute VLC

delay group had significantly lower polymerization conversion. The decrease in VLC

polymerization exotherm and the presence of acid-base exotherm in the 10 minute VLC

delay group would indicate the acid-base reaction inhibits the VLC polymerization. With

regard to the lack of difference noted between the immediate, 2.5, and 5 minute VLC

delay groups, it must be noted that refrigerated capsules (5°C) were used in these

experiments. Although the DSC sensor was set at 35°C, the immediate light-cure RMGI

was still more likely near its refrigerated temperature at the time of light-curing and this

would greatly impair diffusion of monomer reactants and thus polymerization efficiency.

The other delay groups had more time on the sensor, allowing it to equilibrate to the

increased temperature of the DSC sensor, thus allowing its monomer reactants greater

diffusion. To address this consideration, an immediate group was prepared with the

capsule heated to 35°C prior to mixing. As would be expected, the mean VLC

polymerization exotherm was increased and was significantly greater than the 5 minute

VLC delay group (Table 1). Thus, in general, it appears delay in light-curing of this

orthodontic RMGI allows more acid-base reaction to occur, limiting diffusion of

polymerizable components, and decreasing polymerization efficiency.

With regard to the rate of the acid-base reaction, the orthodontic RMGI reacts

more slowly than the restorative RMGI tested in a previous study.[13] The acid-base

exotherm peak was near the 3-4 minute mark for a restorative RMGI,[13] while it was near

5-7 minutes for the orthodontic RMGI, as viewed in the 10 minute delay group in Figure

5. The manufacturer must alter the components/composition of the RMGI to extend the

working/setting time to allow for multiple brackets to be placed as well as allow for

bracket position adjustment after placement but prior to light-curing. Of course,

refrigerating the material also contributes to this but on a fairly limited level as discussed

below. The dark cure DSC data further confirms the slower reaction in the orthodontic

RMGI (Figure 4). At a DSC analysis temperature of 35°C, the average acid-base

exotherm peak time was 5.4 and 5.9 minutes for when the capsule was stored in the

refrigerator or room temperature, respectively. The data presented above and in Figure 4

indicate the greatest determinant of the peak acid-base reaction time is not at what

temperature the capsule is stored, but rather what temperature the RMGI is exposed to

after mixing, i.e. a cooled glass slab, room temperature, or oral temperature. This is not

surprising since reactive components will have decreased diffusion rates at lower

temperatures, or alternatively worded, increasing temperature will increase chemical

reaction rates. Berzins et al.[13] found the exothermic peak of the acid-base reaction to be

decreased in time by 50% with an increase in temperature of $10^{\circ}C$ ($37^{\circ}C$ to $47^{\circ}C$). An increase from 23 to $35^{\circ}C$ in this study resulted in decreased times of approximately 75%. The curve profiles in Figure 4 provide further illustrative evidence of the effect of temperature on reaction rate. The RMGI exposed to $35^{\circ}C$ presented with sharper peaks, whereas exposure to $23^{\circ}C$ resulted in broadening of the peak, and finally very little exothermic activity was observed when the RMGI was exposed to $5^{\circ}C$. Once again, the diffusibility of the reactants at a given temperature will determine the reaction's rate and extent. It should be acknowledged that a myriad of possibilities exist as to the temperature profile, i.e. temperature over time, of the RMGI material during the bonding process. Using a refrigerated capsule as the manufacturer recommends, the RMGI used for the very first bracket to be situated on a tooth would quickly go from exposure to the refrigeration temperature to oral temperature, whereas the last bracket to be bonded with the RMGI would have more time exposed to room temperature or that of a cooled glass slab if used.

DSC analysis showed no differences ($P > 0.05$) with regard to the dynamic scan endotherm, which did not correlate with the study on a restorative RMGI[13] that showed a significant increase ($P < 0.05$) in values as VLC delay increased. However, endothermic peak temperatures did follow a similar trend observed previously[13] with the 10 minute delay group being significantly less than the other delay groups ($P < 0.05$). Since the dynamic scan endotherm is thought to be an indicator of GI/resin material character, with lower values more consistent with glass-ionomers, it appears allowing the acid-base reaction to occur resulted in a material more similar to a GI in structure.

The setting reaction competition in RMGIs is curious scientifically, but what effect does it have clinically in orthodontics? The bond strength determination component of this research was designed to discern this. As mentioned previously, two studies similar in design explored the effect of delayed light-curing on orthodontic bond strength.[11,12] However, at least two of their four delay groups are not practical clinically (20 and 40 minute delay groups). This study utilized more clinically relevant light-cure delay times to examine its effect on orthodontic bond strength. For instance, allowing 30-60 seconds per tooth for adhesive application, bracket seating, bracket positioning, and excess adhesive removal, bonding a quadrant before light-curing would take between 3 and 6 minutes, noting that the manufacturer's instructions mention placing all brackets in a quadrant or full arch prior to the light-curing step, although the latter is perhaps not common practice. Thus, the first bracket to be bonded would be delayed in light-curing by this amount. Of course, working time in addition to the amount of material available in a single capsule may limit the use to one capsule for every three teeth. Factoring in 40 seconds of light-curing per tooth, the third bracket bonded with the first capsule would experience a delay of 4.3 to 7.3 minutes before light-curing. Light-curing after dispensing only one capsule would reduce these delay times by 35-50%, alternatively consideration of a full arch would double the times. The experimental groups in the current study are among these clinically expected light-cure delay times. Results showed no significant difference in shear bond strength whether the RMGI was light-cured earlier or later within 10 minutes. The immediate light-cure group did show slightly favorable Weibull analysis results, but not noteworthy enough to provide a recommendation adopting this practice. Furthermore, this would result in an increase in the number of

capsules used to bond a case, although if it were deemed more reliable that would have to be weighed against the cost of rebonding a debonded bracket. Tavas and Watts[28] suggested that 6 kg (or 6 MPa in this study) of shear/peel bond strength is needed at 24 hours and the current data showed a consistent value greater than that for all groups, which confirms previous studies that RMGIs are reliable orthodontic bonding agents.

The fact that the 10 minute delay group showed significantly lower polymerization efficiency and a different structure via the DSC testing, but presented with similar bond strength to the other groups, appears contradictory. However, several possibilities exist to explain this. First, since RMGIs bond to tooth structure via both micromechanical interlocking and chemical bonding,[17] one might guess that a greater GI character in the RMGI may increase the chemical bond nature of the adhesive, increasing bond strength.[18] However, if this comes at the expense of a greater percentage of VLC polymerization, the resulting properties of the material may be more GI-like and lack bond strength.[14] It is possible these opposing effects combined to result in no difference in bond strength compared to the other groups.

Alternatively, it is possible the enamel preparation was not sufficient to discriminate between the RMGI groups with presumed varied physical properties. In this study, a 10% polyacrylic acid conditioner was applied for 20 seconds, following the manufacturer's instructions. Komori and Ishikawa[19] observed that conditioning enamel with 10% polyacrylic acid produced a smooth surface without evidence of enamel-prism etching patterns, while preparation with 37% phosphoric acid did. They suggested use of a 10% polyacrylic acid conditioner is insufficient for providing a mechanical bond of the adhesive. Bishara et al.[20] found using a 20% polyacrylic acid conditioner significantly (P

<0.05) increased the shear bond strength of an RMGI compared to a 10% polyacrylic acid conditioner. Cacciafesta et al.[21] observed a greater RMGI bond strength after using a 37% phosphoric acid etch than with 10% polyacrylic acid. Also, Godoy-Bezerra et al.[22] determined that enamel conditioning with 10% polyacrylic acid did not increase the shear bond strength of a RMGI. Based on these studies, one can hypothesize that the 10% polyacrylic acid conditioner provided little preparation of the enamel surface, resulting in an enamel-adhesive bond insufficient to differentiate between the bonding groups. Further investigation of the bonding properties of the RMGI groups could be conducted with increased preparation of the enamel surface to determine whether it was a factor.

ARI scores (Table 3) showed a majority of resin remained on the bracket and not on the tooth for all groups. This further suggests the amount of enamel etching was minimal in accordance with Bishara et al.[23] In their RMGI light-cure delay studies, Komori et al.[11] showed similar results that most of the resin remained on the bracket with no significant differences between groups ($P > 0.05$) whereas Ando et al.[12] found the resin remain mostly on the tooth following tensile bond strength testing.

It is of significance to mention that although the delay times of VLC were of clinical relevance in our study, the bonding protocol was completed under ideal conditions, such which may not be present in a clinical setting. For example, with a 10 minute delay in VLC, the bracket was placed onto the prepared tooth and left to set without ambient light penetration, moisture, or any disturbance in position. Whereas, in a clinical setting, after a bracket is seated and left for 10 minutes before VLC, some ambient light, moisture contamination and movement of the bracket could and may occur after initial positioning. The clinician would then proceed to reposition the bracket

before initiating VLC, after which a period of time has elapsed since the RMGI has been

mixed. It was concluded from this study that for a 10 minute delay of VLC, the RMGI

undergoes an acid-base reaction at approximately 5-7 minutes after mixing and the

bonding process has begun to the enamel. Therefore one can assume that any

repositioning of the bracket thereafter would break the initial bond of the bracket to the

tooth, and weaken the overall bond strength of the cement. This very common

occurrence in the clinical setting was not accounted for in our experimental protocol.

CONCLUSIONS

Within the confines of this in vitro study, it may be concluded that delay in light-curing an orthodontic RMGI does allow for greater acid-base reaction, thereby reducing the degree of conversion of the polymerizable components, and altering the structure of the material. However, the orthodontic bond strength of the material remains unaffected within clinically relevant delays in light-curing.

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