2011

A novel bioactive glass-enhanced orthodontic bonding resin: A shear bond strength study

Cole Johnson
Virginia Commonwealth University

School of Dentistry
Virginia Commonwealth University

This is to certify that the thesis prepared by Cole R. Johnson, D.M.D., entitled A Novel Bioactive Glass-Enhanced Orthodontic Bonding Resin: A shear bond strength study has been approved by his committee as satisfactory completion of the thesis requirement for the degree of Master of Science in Dentistry.

Dr. Eser Tüfekçi, Thesis Director, VCU School of Dentistry

Dr. Steven J. Lindauer, Committee Member, VCU School of Dentistry

Dr. John Mitchell, Committee Member, OHSU School of Dentistry

Dr. Bhavna Shroff, Graduate Program Director, Department of Orthodontics,
VCU School of Dentistry

Dr. Laurie Carter, Director of Advanced Dental Education, VCU School of Dentistry

Dr. F. Douglas Boudinot, Dean of the School of Graduate Studies, VCU

May 3, 2011
Date

A Novel Bioactive Glass-Enhanced Orthodontic Bonding Resin:
A shear bond strength study

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Dentistry at Virginia Commonwealth University.

By

Cole Robert Johnson
D.M.D., Oregon Health & Science University, 2009
B.S., Brigham University Idaho, 2005

Thesis Director: Eser Tüfekçi, D.D.S, M.S., Ph.D
Associate Professor, Department of Orthodontics

Virginia Commonwealth University
Richmond, Virginia

Acknowledgment

I would like to thank Dr. Eser Tüfekçi for her guidance during this research project and assistance in writing this thesis. I appreciate all the time and effort she put into editing my thesis drafts over the past several months. She has been and will be a lifelong friend and mentor. I would like to thank Dr. Al Best for analyzing the data and helping me throughout the process of completing this thesis. I would like to thank dental students Mina Abdolahi and Samuel Allen who assisted me throughout my entire research process with a multitude of tasks. I would like to thank Dr. Steven Lindauer and Dr. John Mitchell for their help on my thesis committee. I thank Dr. Bhavna Shroff for her encouragement and for being a fantastic program director. I am grateful to my co-residents and especially my classmates for their help and support with this and other projects and for making these past two years so enjoyable. We started the program as classmates and finished as lifelong friends and colleagues. I thank my parents and siblings for their love and sacrifice throughout my life. I attribute my interest in such diverse topics to their energetic enthusiasm for all praiseworthy endeavors, education being paramount among them. Most importantly, I would like to thank my sweet wife Daisha and my wonderful children. There is no way I could have done this without their loving support and understanding of the time that was so often spent away from them in order to complete this thesis. The funding for this project was provided by the Virginia Commonwealth University Department of Orthodontics.

Table of Contents

List of Tables

List of Figures

Abstract

A Novel Bioactive Glass-Enhanced Orthodontic Bonding Resin: A shear bond strength study

By Cole R. Johnson, D.D.S.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Dentistry at Virginia Commonwealth University.

Virginia Commonwealth University, 2011

Thesis Director: Eser Tüfekçi, D.D.S, M.S., Ph.D
Associate Professor, Department of Orthodontics

Enamel decalcification caused by poor oral hygiene is a significant problem in orthodontics. Bioactive glass-containing resins have been shown to release Ca^{2+} ions into surrounding solution. The purpose of this study was to determine the shear bond strength of four different compositions of orthodontic resin prepared with bioactive glass (N=20).

Premolars were bonded using one of four BAG-BOND compositions. Brackets were debonded and ARI scores were given. The mean shear bond strength was 7.23 ± 2.47 MPa (62 BAG-BOND), 8.25 ± 2.87 MPa (65 BAG-BOND), 8.78 ± 3.08 MPa (81BAG-BOND) and 5.80 ± 2.27 MPa (85 BAG-BOND). 65 and 81 BAG-BOND were significantly higher than 85 BAG-BOND. The 62 BAG-BOND group was not statistically significantly different from any other group. All groups exhibited a cohesive bond failure and were not statistically significant from each other. Three compositions of the novel orthodontic adhesive exhibited adequate bond strength for clinical applications.

Introduction

Bond Strength

Enamel bonding has been one of the most critical steps in orthodontic treatment since the inception of direct bonding. Orthodontic appliances may be attached by cementing bands or by bonding brackets directly to the enamel surface using a retentive base. The bonding of brackets is preferred over bands as it leaves more surface area of tooth exposed for improved oral hygiene and generally causes less patient discomfort. Direct bonding with resin adhesives has become the most popular method for orthodontic bonding.[1,2] Transferring the force from an engaged archwire to the tooth requires bond strength sufficient enough to overcome the load generated by the deflected wire. The importance of the biomechanical interface between bracket and bonding agent is illustrated in the increasing number of bonding materials being developed, bonding techniques designed to increase efficiency and decrease failures, and related papers appearing in orthodontic journals.[3]

One of the most important considerations for a good orthodontic adhesive is to have adequate bond strength to be able to withstand both occlusal and orthodontic forces. A bond strength value of 6-8 MPa has been reported to be optimal as within this range brackets remain attached to tooth surfaces throughout orthodontic treatment while allowing safe debonding and adhesive removal without causing damage to enamel.[4] A failure rate of 1-5% has been reported to be acceptable clinically.[5] While searching for an ideal orthodontic bonding agent, high bond strength must be balanced with the ability of the material to leave little or no residue on enamel upon removal. The bonding material would also ideally be inexpensive and easy to work with. Currently, most orthodontic cements available in the market already have these features;[1] however, finding a bonding agent that may also prevent white spot lesions is a popular prospect.

White Spot Lesions

In orthodontics, circumbracket enamel decalcification caused by poor oral hygiene is a significant problem. It has been reported that about half of orthodontic patients will develop white spot lesions or enamel demineralization due to the prolonged plaque accumulation around brackets.[6-8] Besides providing plaque retention sites on tooth surfaces that are otherwise less susceptible to caries development, fixed orthodontic appliances make conventional oral hygiene procedures more difficult.[9] Patient education and the use of fluoride in the form of paste, varnish or solution is the first approach to be taken to prevent demineralization. Fluoride, as a cariostatic agent, works both by acting as a bactericidal agent at high concentrations but mostly by shifting solution equilibrium to favor the formation of fluorohydroxyapatite.[10-12] Numerous studies have reported that fluoride regimens can reduce caries during orthodontic treatment with fixed appliances.[13] However, due to unpredictable compliance and difficulty in producing localized effect in the areas adjacent to brackets, preventive measures to administer fluoride by topical application or home rinse programs are limited. In order to eliminate the need for patient compliance, orthodontic bonding agents with an ability to release ions such as fluoride, calcium and phosphate have been developed.[14, 15]

Glass Ionomer Cements

Glass ionomer cements (GICs) were first introduced to the dental profession in the early 1970s.[16] The use of GICs does not require acid etch or saliva isolation and has the additional distinct advantage of releasing fluoride which may diminish the occurrence of white spot lesions.[14, 17-19] Since fluoride releasing GICs have potential to reduce demineralization and eliminate the need for patient compliance, they have been used in orthodontics as a luting agent for cementing the bands. Previous studies have shown that the amount of fluoride released is decreased to undetectable levels in a few days.[20,21] Nevertheless, GICs exhibit the ability to be recharged with the use of a topical fluoride agent or fluoride containing toothpaste which is thought to increase fluoride to adequate levels for caries prevention.[16] However, the ability of the material to be recharged has been shown to exhibit a wide range[20] and their subsequent anticariogenic effect is therefore questionable.[22] In addition, GICs are not appropriate for direct bracket bonding due to their relatively low bond strength.[23] Brackets bonded with GICs have been shown to exhibit higher bracket failures than those bonded with composite resin.[24, 25] Enamel surfaces prepared with either phosphoric or polyacrylic acid prior to bonding have been shown to have a bond strength range of 2.4-5.5 MPa[18, 19] which is lower than the optimal 6-8MPa range.

Resin Modified Glass Ionomer Cements

Since fluoride release from an orthodontic bonding agent would be beneficial in reducing demineralization adjacent to brackets, resin modified glass ionomer cements (RMGICs) have been developed for bracket bonding purposes in orthodontics. With the addition of resin mechanical properties of GICs were improved.[26] Studies on RMGIC bonding agents have shown that these adhesives are able to release fluoride while providing adequate bond strength to withstand orthodontic forces. Nevertheless, it should be noted that their bond strength values are substantially lower compared to those of conventional resins.[26, 27] In addition, the literature has shown controversial results concerning the anticariogenic effects of these materials.[4, 22]

Amorphous Calcium Phosphate Cements

Amorphous calcium phosphate (ACP) containing composite resins have also been shown to have a potential for remineralizing carious enamel lesions by favoring remineralization dynamics.[29-32] Skrtic et al [15] demonstrated that ACP-filled resin can release supersaturated levels of calcium and phosphate ions in proportions favorable for the formation of hydroxyapatite over an extended period of time. However, it has been previously reported that brackets bonded with an ACP-containing composite material fail at significantly lower forces than brackets bonded with conventional resin-based orthodontic bonding agent.[33, 34] It is thought that the low mechanical strength is due to the ACP distribution within the composite which causes instability of the ACP/resin interface caused by the lack of bonding of the filler phase and polymer matrix.[34]

Currently, there is no marketed bonding agent that provides a biomimetic approach to inhibit the formation of white spot lesions by releasing Ca^{2+} and PO_4^{3-} ions to prevent demineralization near the brackets. Incorporating bioactive glass (BAG) into a biocompatible resin may provide protection from incipient lesions by releasing Ca^{2+} and PO_4^{3-} ions to areas adjacent to brackets. Sol-gel bioactive glass is a three-dimensional cross-linked matrix made of hydrolyzed alkoxides of SiO_2, CaO and P_2O_5. The morphology of the gel surface layer is a key component in determining the bioactive response. The inherent high porosity of bioactive glasses derived from the sol-gel process is thought to contribute to high bioactivity of this material. In addition, because of their high biocompatibility, these glasses have extensively been investigated for use as implant materials in the human body to repair and replace diseased or damaged bone. Many variations on the original composition of the FDA approved Bioglass® now exist.[35] The "bioactivity," or underlying mechanisms that enable bioactive glasses to enhance bone/enamel remineralization scaffolding, is thought to occur in five stages:[36]

1) Ion exchange, in which cations such Ca^{2+} in the glass exchange with H^+ ions in the external solution.

2) Hydrolysis, in which Si-O-Si bridges are broken, forming Si-OH silanol groups wherein the glass network is disrupted.

3) Condensation of silanols, in which the disrupted glass network changes its morphology to form a gel-like surface layer, depleted in calcium ions.

4) Precipitation, in which an amorphous calcium phosphate layer is deposited on the gel.

5) Mineralization, in which the calcium phosphate layer gradually transforms into crystalline hydroxyapatite, that mimics the mineral phase naturally contained with vertebrate bones and enamel.

BAG has been shown to exhibit a biomimetic property when immersed in simulated body fluids (SBF) that leads to the formation of tooth-like hydroxyapatite that can even deposit on organic polymers. Under these conditions, the contents of BAG ionize and interact with each other and with the ions present in the surrounding solution. When this solution exceeds the supersaturation point, a precipitate is deposited on the bioactive glass surface, creating CaP nucleation sites for apatite crystal growth. Once nucleated, apatite spontaneously continues to grow under physiological conditions .[37, 38]

BAG has also been shown to produce a dense, uniform Ca-P layer on the surface of dentin, sealing the exposed tubules.[39] In addition, experimental RMGICs containing 30wt% BAG have been found to inhibit growth of cariogenic bacteria such as Streptococcus mutans in vitro.[37] BAG's ability to nucleate growth of apatite on the surface of a tooth and to bond chemically to tooth structure in addition to RMGICs biocompatibility may help to develop orthodontic cements that would remineralize enamel at the enamel-band/bracket interface or prevent demineralization in the first place.

Preliminary studies[40,41] conducted to investigate ion release from a BAG-RMGIC bonding agent at neutral (pH=7) and acidic (pH=4) levels of SBF showed that the addition of BAG resulted in significantly higher calcium and phosphate ion levels in SBF under acidic (cariogenic) conditions than the conventional cement control. It was furthermore shown that this "smart material" was able to release crucial ions under cariogenic/acidic conditions that could be potentially inhibiting enamel demineralization.

As part of a companion investigation[41] it has been demonstrated that calcium and phosphate ions are able to release from polymeric adhesives as well, and to also do so in a pH dependent manner. However, the addition of BAG into resin may influence the physical and mechanical characteristics of the resin. While potentially exhibiting an anticariogenic behavior, the resulting novel orthodontic bonding material must provide adequate mechanical and physical properties in order to be accepted as an orthodontic bonding agent. Therefore, the purpose of this study was to determine the bond strength of four different compositions of a novel orthodontic resin prepared with bioactive glass.

Materials and Methods

Preparation of BAG-BOND

Four compositions of BAG-containing orthodontic resin bonding agents (62 BAG-BOND, 65 BAG-BOND, 81 BAG-BOND, and 85 BAG-BOND) were developed in a laboratory at Oregon Health & Sciences University (Table 1). The BAG samples were made by mixing (SpeedMixer DAC, Flack Tek, Landrum, SC) two resin monomers, ethoxylated bisphenol A dimethacrylate (EOBPADMA) and BisGMA (both from Esstech Corp., Essington, PA) in a ratio of 2.5:1 (EOBPADMA to BisGMA). This ratio was used based on a pilot study that showed this ratio had the highest Knoop hardness and shear bond strength values. Additionally 0.4 wt% camphoroquinone (Polysciences, Warrington, PA) and 0.8 wt% ethyl 4-dimethylaminobenzoate (Research Chemicals Ltd., Heysham, Lancs.) were added to the resin as photoinitiators.

Table 1: BAG Composition by Molar %, Surface area and Monomer ratio

	mol% SiO_2	mol% CaO	mol% P_2O_5	mol% B_2O_3	mol% F	Surface Area of BAG (m^2/g)	BAG:Monomer ratio (by weight)
62BAG	62	31	4	1	3	75	29:50
65BAG	65	31	4	0	0	144	49:100
81BAG	81	11	4	0	4	320	37:100
85BAG	85	11	4	0	0	268	33:100

The BAGs were prepared at Oregon Health & Science University laboratories by the sol-gel method,[42] ball-milled, sieved, and micronized (Sturtevant, Hanover, MA). Average particle size ranged from 0.04 to 3.0 µm, as determined by laser particle size measurements (Beckman Coulter LS13 320, Brea, CA). The BET method[43] was used to measure the surface areas of each BAG batch. BAGs were added to the monomer mixture until the workability and viscosity of each product was similar to that of Transbond XT (3M Unitek, Monrovia, CA). The viscosity of each BAG-BOND formulation was measured using a DV-III Ultra rheometer (Brookfield Engineering, Middleboro, MA) and the workability of each group was evaluated by the same experienced orthodontist. The variation in BAG:monomer ratios exhibited by each BAG-BOND group were likely due to the differing surface area of each four BAG group.

Human premolars extracted for orthodontic reasons were collected and stored in Chloramine-T trioxide (5%) at approximately 25°C. Care was taken to include only healthy teeth with no apparent defects on the buccal surface. Before preparing the specimens, teeth were debrided and washed under tap water with a soft toothbrush and then randomly assigned into the following groups: Group 1 (62 BAG-BOND), Group 2 (65 BAG-BOND), Group 3 (81 BAG-BOND), Group 4 (85 BAG-BOND).

Prior to bonding, each tooth was embedded in phenolic rings (Buehler Ltd, Lake Bluff, IL) using dental stone, covering the root surface up to the cemento-enamel junction. Samples were stored in distilled water at 37°C for 24 hours to prevent dehydration of tooth structure and were removed from the storage medium only for a short time to complete bonding procedures.

Teeth were cleaned and polished with rubber prophylactic cups and a fluoride free pumice to eliminate contaminants and then rinsed thoroughly. Facial enamel surfaces were etched with 37% phosphoric acid gel (3M Unitek, Monrovia, CA) for 20 seconds, rinsed with water and air dried using an oil free air-water syringe per manufacturer's instructions. Adhesive primer (Moisture Insensitive Primer, 3M Unitek) was applied to the etched surface of the specimens and gently air dried. A small amount of the novel resin adhesive sufficient to cover the entire bracket base surface was applied to the brackets (Victory Series^{TM}, 3M Unitek) which were positioned in the center of the crown using standard clinical bonding procedures. Any excess material was removed with a sharp scaler, and the bracket was light-cured for 10 seconds on the mesial and the distal aspects of the teeth with an Orthlux LED curing light (3M Unitek). After bonding, the specimens were stored in deionized water at 37°C for 24h before mechanical testing. All of the procedures were carried out by the same clinician.

The samples mounted in phenolic rings were placed in an adjustable attachment jig and positioned at custom angles in order to provide parallelism between the bracket-tooth interface and the upper member of the Instron Universal Testing machine (Instron Corp., Canton, MA). Brackets were debonded in shear mode with a crosshead speed of 0.5 mm/min. The force to debond the brackets was recorded in pounds (lbs). The shear strength was calculated by dividing the force by the bracket base area (0.01813 in^2) and reported in megapascals (MPa).

Figure 1: Mounting jig used to provide parallelism between the bracket and the upper member of the Instron testing machine

Following debonding, bracket surfaces were examined under 10X magnification using a light stereomicroscope (Leica MS5, Singapore, Singapore) to determine the location of the bond failure, and an adhesive remnant index (ARI) score was recorded. Any adhesive that remained on the bracket after removal was scored according to the following scale:[20] 0 = no adhesive left on bracket, 1= less than 25% of adhesive left on the bracket, 2 = 25-50% of adhesive left on the bracket, 3 = 50-75% of adhesive resin left on the bracket, 4 = 75-100% adhesive left on bracket, 5 = 100% of adhesive left on bracket.

Bond strength data were analyzed for differences among groups using one-way analysis of variance (ANOVA). Tukey’s HSD multiple comparison was used to determine statistically significant differences between the groups. Chi-square analysis was used to analyze ARI data. The significance level was set at $p<0.05$.

Results

The summary of results showing the shear bond strength of the four groups is shown in Table 2. The 62 BAG-BOND group had a mean shear bond strength of 7.23 MPa ± 2.47 while the 65 BAG-BOND group had a mean of 8.25 MPa ± 2.87. The 81 BAG-BOND group had the highest mean shear bond strength of 8.78 MPa ± 3.08 and the 85 BAG-BOND group had the lowest shear bond strength of 5.80 MPa ± 2.27. One-way ANOVA showed a significant difference among groups. ($p<0.05$). Tukey's HSD multiple comparison indicated that the 85 BAG-BOND had a significantly lower shear bond strength compared with both 65 and 81 BAG-BOND groups but not 62 BAG-BOND. The 62 BAG-BOND group was not statistically different from any of the other groups ($p<0.05$). Overall, three of the groups resulted in mean shear bond strength values at adequte levels (6-8 MPa). However, 85 BAG-BOND had a range of values from 3.53 - 8.07 MPa indicating that this group may not be a good candidate for orthodontic bonding purposes.

Table 2: Shear Bond Strength (Megapascals) by Group

Group	Mean	SD	95% CI	
62 BAG-BOND	$7.23^{A,B}$	2.47	6.08	8.39
65 BAG-BOND	8.25^{A}	2.87	6.91	9.59
81 BAG-BOND	8.78^{A}	3.08	7.33	10.22
85 BAG-BOND	5.80^{B}	2.27	4.74	6.86

Means with the same superscripts are not significantly different from one another (p <0 .05)

The figure shows the shear bond strength along with the ARI scores for the four groups. It was noted that although the bond strengths showed a wide range of values, the ARI scores were distributed in a similar manner and there were no statistically significant differences in ARI between the four groups ($p<0.05$).

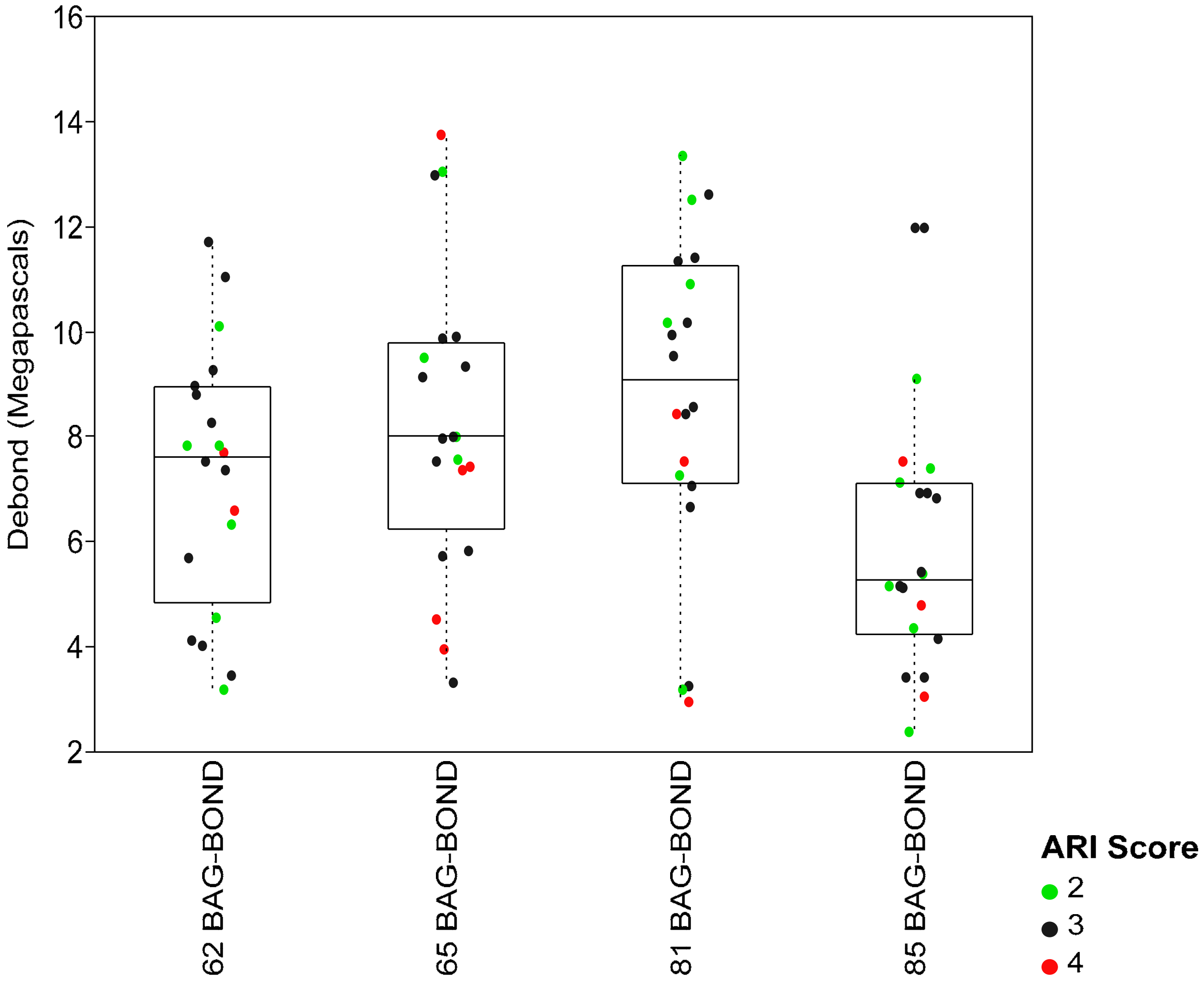

Figure 2: Shear Bond Strength (Megapascals) and ARI distribution by Group

The distribution of ARI scores among groups is provided in Table 3. None of the groups had ARI scores of 0, 1 or 5. In all groups, the predominant ARI score was 3 followed by 2 or 4. All four BAG-BOND groups exhibited a cohesive type of bond failure.

Table 3: ARI Score distribution by Group

	Adhesive Remnant Index					
Group	1	2	3	4	5	Total
62 BAG-BOND	0	6	12	2	0	20
65 BAG-BOND	0	4	11	5	0	20
81 BAG-BOND	0	6	11	3	0	20
85 BAG-BOND	0	7	10	3	0	20
Total	0	23	44	13	0	80
Total %	0	29	55	16	0	

Discussion

The bond strength of orthodontic adhesives should be at adequate levels to withstand the forces of mastication and the stress exerted by the archwires while allowing for bracket debonding without causing damage to the enamel surface.[45-47] According to Reynolds,[4] ideal bond forces for routine orthodontic treatment range between 5.9 and 7.8 MPa. The breaking strength of enamel is about 14 MPa.[44] Therefore, the maximum bond strength should be much lower than 14MPa to prevent damage to tooth structures during debonding procedures. The results of this study showed that the mean shear bond strength of three of the adhesives (BAG-BOND groups 62, 65 and 81) were well within the ideal range (6-8 MPa).[4] 85 BAG-BOND had a mean bond strength value of 5.8 ± 2.27 MPa. This may be attributed to the high proportion of SiO_2 (85mol%), a brittle compound within this composition. This group may not be suitable for clinical applications because the values ranged from well below acceptable levels (3.53 MPa) to adequate levels (8.07 MPa). Therefore, it may be concluded that the three compositions of novel BAG containing composite resin (62, 65 and 81) have potential to be a viable orthodontic bonding agent.

In addition to bond strength, the location of the bond failure is also important for considering a material as an orthodontic cement. Bond failures can occur either at the bracket-tooth interface (adhesive type) or within the adhesive itself (cohesive type).[49] In the literature, there has been controversy concerning which mode of failure is desirable during debonding procedures. Adhesive failure at the enamel-composite-resin interface is favored by some authors because less potential for enamel damage is anticipated during adhesive removal procedures due to the minimum amount of adhesive left on the tooth surface.[51] Martin and Garcia-Godoy[50] suggested that a weaker adhesive with a lower bond strength value might be preferable to increase failure or bracket debonding at the resin-enamel interface so that minimal clean-up effort would be needed and no damage to the enamel would occur. This is a controversial opinion as studies show enamel fracture and crazing may be seen during bracket debonding especially with ceramic brackets.[52]

Adhesive mode of failure at the bracket-adhesive interface or cohesive failure within the adhesive resin mainly on the enamel surface are also favored.[51, 52] Bennett et al[53] stated that this is important when a heavy filled resin is used to bond orthodontic attachments to the enamel because the micro porosities created by etching are filled with the resin and provide mechanical retention. In the current study, the dominant ARI score was 3 indicating a cohesive mode of failure where 50-75% of the adhesive remained on the bracket. Having equal amount of adhesive left on the tooth surface and bracket base may be desirable as it would decrease the potential to damage the enamel during debond procedures.[54] Because there were no ARI scores of either 0, 1 or 5 in this study it can be suggested that this novel BAG adhesive exhibits strictly cohesive failure. However, it should be kept in mind that the range of ARI scores within each group showed great parity among the score distribution. A larger sample size may be needed to determine clinical differences, if any, between the type of adhesive failure among groups.

While the universal testing machine is a suitable device capable of producing pure shear debonding forces *in vitro*, a clinician introduces a combination of shear, tensile, and torsional forces when performing debonding *in vivo*. In addition, the rate of loading for a universal testing machine is constant, whereas the rate of loading for *in vivo* debonding is not standardized or constant. Therefore, *in vitro* studies may not mimic the exact clinical situation. However, they provide a guide for the clinician in the selection of the bracket/adhesive choice for the clinical use.[54, 55]

In a companion study,[41] the same BAG-BOND batches were investigated for their chemical properties. Specifically, their potential for preventing demineralization through buffering capacity and the amount of Ca^{2+} and PO_4^{3-} ions released into a body simulated fluid solution (SBF) were investigated. In SBF4, a cariogenic environment at a pH of 4, 62 and 65 BAG-BOND exhibited significant buffering capacity at 1, 10 and 100 hrs ($p<0.05$). In SBF7, 62 BAG-BOND showed significant increases in pH at 10 and 100 hrs ($p<0.05$), while 65 BAG-BOND showed significant pH increases at 100hrs. However, 81 BAG-BOND and 85 BAG-BOND showed significant buffering capacity only at 100 hrs. The differences in SBF buffering capacity between BAG-BONDs are likely due to their differing amounts of calcium within their chemical compositions. 62 BAG-BOND and 65 BAG-BOND contain nearly 3 times more calcium than 81 BAG-BOND and 85 BAG-BOND. Therefore, 62 BAG-BOND and 65 BAG-BOND were able to absorb more H^+ ions into solution as calcium was released. Because the rate of enamel demineralization is inversely proportional to the pH of its environment[49] BAG-BONDs ability to buffer cariogenic environments may give them the potential for decrease the rate of enamel demineralization. Therefore, increasing the pH adjacent to the bracket-tooth interface, BAG-BONDs may prevent dissolution of enamel and keep surrounding environment above critical pH.[47, 48]

In the same study,[41] BAG-BOND groups also released significant amounts of Ca^{2+} ion into solution. In SBF solutions with a pH of 4 and 7, calcium concentration increased significantly ($p<0.05$) with the 62 and 65 BAG-BOND at 1,10 and 100 hrs. The 81 BAG-BOND elevated Ca^{2+} ion levels at 10 and 100 hrs, and 85 BAG-BOND at 100 hrs in both SBF solutions. With a significant release of calcium, BAG-BONDs could further decrease the critical pH of the surrounding enamel environment. A decrease in critical pH would require a greater reduction in pH from plaque before enamel dissolution takes place.[13] This would result in a decrease in risk for white spot lesions.

62 BAG-BOND, 65 BAG-BOND, 81 BAG-BOND and 85 BAG-BOND showed significant decreases ($p<0.05$) in phosphate concentration in SBF at a pH of 4 at 100 hrs only. In SBF7, significant decreases ($p<0.0001$) were shown with 62 BAG-BOND and 65 BAG-BOND at 100 hrs. The decreases in phosphate ion levels measured in SBF can likely be attributed to the incorporation of the ions onto the resin surface through precipitation of calcium phosphate and supersaturation of the solution immediately surrounding the BAG-BOND. The calcium phosphate (Ca-P) precipitate is the precursor for hydroxylapatite formation which is the main structural component of enamel.[49]

Although 62 BAG-BOND and 81 BAG-BOND contained fluoride no significant change in fluoride concentration was found in either solution with any of the BAG-BONDs at any time. This is possibly due to fluoride becoming incorporated into the polymer matrix during the process of polymerization of the BAG-BONDs rendering them unable to be released into solution. It is also possible that fluoride becomes incorporated in the Ca-P precipitate making it a precursor to highly insoluble fluoroapatite.

In summary, these BAG-BOND groups, especially the 62 and 65 BAG-BOND groups were shown to raise the pH of cariogenic environments which could result in a decreased amount of mineral loss from enamel. 62 and 65 BAG-BOND also exhibited the greatest ability to release Ca^{2+} and PO_4^{3-} ions into solution. The reservoir of calcium and phosphate within BAG-BOND may provide an ion source for precipitation of CaP onto the tooth surface, holding the potential for remineralization of enamel. The high buffering capacity of the 62 and 65 BAG-BOND groups is most likely due to by the higher concentration of CaO (see Table 1) than that of the 81 and 85 BAG-BOND groups. These two groups also showed bond strengths that were well within acceptable clinical ranges (6-8 MPa). The 85 BAG-BOND group showed the lowest bond strength which could possibly be explained by its high proportion of SiO_2 (85mol%). Perhaps the brittleness of SiO_2 ultimately contributed to the decrease in bond strength in the 85 BAG-BOND group. In addition, this group showed limited ion release. Therefore, 85 BAG-BOND may not be a good candidate for an orthodontic bonding agent.

The results of this *in vitro* study indicate that the novel bonding agent with 62 and 65 BAG compositions in its structure had adequate bond strength levels for clinical applications. In addition, 62 and 65 BAG showed the capacity for buffering acidic oral environments and releasing significant amounts of ions into the surrounding environment. Therefore, it may be concluded that 62 and 65 BAG-BOND show great promise as a novel orthodontic bonding agent with adequate bond strength and potential for preventing white spot lesions. Future *in vivo* studies would be needed to confirm the clinical bond failure of this material and to determine the ability of BAG-BOND for preventing demineralization in orthodontic patients with poor oral hygiene.

Conclusions

Results of this study suggest that 62 and 65 BAG-BOND may be considered as ideal orthodontic resins by providing a reservoir of crucial ions for the prevention of demineralization or for remineralization, and by exhibiting adequate bond strength for clinical applications.

List of References

1. Miyasaki M, Hirohata N, Takagaki K, Onose H, Moor BK. Influence of self-etching primer drying time on enamel bond strength of resin composites. J Dent. 1999;27:203-7.

2. Buonocore MG, Matsui A, Gwinett AJ. Penetration of resin dental materials into enamel surfaces with reference to bonding. Arch Oral Biol. 1968;13:61-70.

3. Eliades T, Brantley WA. The inappropriateness of conventional orthodontic bond strength protocols. Eur J Orthod. 2000;22:13-23.

4. Reynolds IR. A review of direct orthodontic bonding. Br J Orthod. 1975;2:171–8.

5. Bishara SE, Fehr DE. Ceramic Brackets: Something old, something new, a review. Semin Orthod. 1997;3:228-32.

6. Gorelick L, Geiger AM, Gwinnett AJ. Incidence of white spot formation after bonding and banding. Am J Orthod. 1982;81:93-8.

7. Giulio AB, Matteo Z, Serena IP, Silvia M, Luigi C. In vitro evaluation of casein phosphopeptide-amorphous calcium phosphate (CPP-ACP) effect on stripped enamel surfaces. A SEM investigation. J Dent. 2009;37:228-32.

8. Tufekci E, Dixon JS, Gunsolley JC, Lindauer SJ. Prevalence of white spot lesions during orthodontic treatment with fixed appliances. Angle Orthod. 2011;81:206-10.

9. Øgaard B, Rølla G, Arends J. Orthodontic appliances and enamel demineralization. Am J Orthod Dentofacial Orthop. 1988;94:68-73.

10. O'Reilly MM, Featherstone JDB. Demineralization and remineralization around orthodontic appliances: an in vivo study. Am J Orthod Dentofacial Orthop. 1987;92:33-40.

11. Kanemura N, Sano H, Tagami J. Tensile bond strength to and SEM evaluation of ground and intact enamel surfaces. J Dent. 1999;27:523-30.

12. Dunn WJ, Soderholm KJ-M. Comparison of shear and flexural bond strength tests versus failure modes of dentin bonding systems. Am J Dent. 2001;14:297-303.

13. Øgaard B, Rølla G, Arends J, ten Cate JM. Orthodontic appliances and enamel demineralization. Part 2. Prevention and treatment of lesions. Am J Orthod Dentofacial Orthop. 1988;94:123-8.

14. Tuncer C, Tuncer BB, Ulusoy C. Effect of fluoride-releasing light-cured resin on shear bond strength of orthodontic brackets. Am J Ortho Dentofacial Orthop. 2009; 135:14.e1-14.e6.

15. Skrtic D, Antonucci JM, Eanes ED, Eichmiller FC, Schumacher GE. Physicochemical evaluation of bioactive polymeric composites based on hybrid amorphous calcium phosphates. J Biomed Mater Res. 2000;53(4):381-91.

16. Wilson AD, Kent BE. A new translucent cement for dentistry. The glass ionomer cement. Br Dent J. 1972;132:133-5.

17. Bishara SE, Gordan WV, Von Wald L, Jakobsen JR. Shear bond strength of composite, glass ionomer, and acidic primer adhesive systems. Am J Orthod Dentofacial Orthop. 1999;115:24-8.

18. Bishara SE, VonWald L, Laffoon JF, Warren JJ. Effect of a self-etch primer/adhesive on the shear bond strength of orthodontic brackets. Am J Orthod Dentofacial Orthop. 2001;119:62-4.

19. Tang AT, Björkman L, Adamczak E, Andlin-Sobocki A, Ekstrand J. In vitro shear bond strength of orthodontic bondings without liquid resin. Acta Odontol Scand. 2000;58:44-8.

20. Attar N, Korkmaz Y, Kilical Y, Saglam-Aydinatay B, Ozge Bicer C. Bond strength of orthodontic brackets bonded to enamel with a self-etching primer after bleaching and desensitizer application. Korean J Orthod. 2010; 40:342-8.

21. Basdra EK, Huber H, Komposch G. Fluoride released from orthodontic bonding agents alters the enamel surface and inhibits enamel demineralization in vitro. Am J Orthod Dentofacial Orthop. 1996;109:466-72.

22. Gaworski M, Weinstein M, Borislow AJ, Braitman LE. Decalcification and bond failure: A comparison of a glass ionomer and a composite resin bonding system in vivo. Am J Orthod Dentofacial Orthop. 1999;116:518-21.

23. Cook PA, Luther F, Youngson CC. An in vitro study of the bond strength of light-cured glass ionomer cement in the bonding of orthodontic brackets. Eur J Orthod. 1996;18:199-204.

24. Pashley DH, Tay FR. Aggressiveness of contemporary self-etching adhesives, part II: etching effects on unground enamel. Dent Mater. 2001;17:430-44.

25. Craig RG. Restorative dental materials. St. Louis, MO: Mosby Year Book; 1997: p. 256.

26. Coups-Smith KS, Rossouw PE, Titley KC. Glass ionomer cements as luting agents for orthodontic brackets. Angle Orthod. 2003;73: 436-44.

27. Shammaa I, Ngan P, Kim H, Kao E, Gladwin M, Gunel, Brown C. Comparison of bracket debonding force between two conventional resin adhesive and resin-reinforced glass ionomer cement: An in vitro and in vivo study. Angle Orthod. 1999; 69:463-9.

28. Papagiannoulis L, Kakaboura A, Eliades G. In vivo vs in vitro anticariogenic behavior of glass-ionomer and resin composite restorative materials. Dent Mater. 2002;18:561-9.

29. McCourt JW, Cooley RL, Barnwell S. Bond strength of light-cure fluoride-releasing base-liners as orthodontic bracket adhesives. Am J Orthod Dentofacial Orthop. 1991;100:47-52.

30. Meehan PM, Foley TF, Mamandras AH. A comparison of the shear bond strengths of two glass ionomer cements. Am J Orthod Dentofacial Orthop. 1999;115:125-32.

31. Lippitz SJ, Staley RN, Jakobsen JR. In vitro 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. 1998;113:402-7.

32. Fricker JP. A new self-curing resin-modified glass ionomer cement for the direct bonding of orthodontic brackets in vivo. Am J Orthod Dentofacial Orthop. 1998;113:384-6.

33. Rogelio J, Scougall V, Seigo Y, Noriyuki K, Kohji Y. Shear bond strength of orthodontic brackets bonded with different self-etching adhesives. Am J Orthod Dentofacial Orthop. 2009;131:425-30.

34. Antonucci JM, Skritic D. Fine-tuning of polymeric resins and their interfaces with amorphous calcium phosphate. A strategy for designing effective remineralizing dental composites. Polymers. 2010; 2:378-92.

35. Kokubo T. Bioactive glass ceramics: properties and applications. Biomater. 1991;12:155-63.

36. Kokubo T, Kushitani H, Sakka T, Kitsugi T, Yamamuro T. Solutions able to reproduce *in vivo* surface-structure changes in bioactive glass-ceramic. J Biomed Mat Res. 1990;24:721–7.

37. Eliades G. General aspects of biomaterial surface alterations following exposure to biologic fluids. In: Eliades G, Eliades T, Vavuranakis M (eds). Dental Biomaterials in vivo: Aging and related phenomena. Chicago, IL: Quintessence. 2003;1-23.

38. Forsback AP, Areva S, Salonen JI. Mineralization of dentin induced by treatment with bioactive glass S53P4 in vitro. Acta Odontol Scand. 2004;62:14-20.

39. Yli-Urpo H, Narhi T, Soderling E. Antimicrobial effects of glass ionomer cements containing bioactive glass (S53P4) on oral micro-organisms in vitro. Acta Odontol Scand. 2003;61:241-6.

40. Crowe J, Davis HB, Mitchell JC. Ion release from a novel bioactive orthodontic bonding agent. J Dent Res 2008:87:B (Special Issue): Abstract #121.

41. Brown ML, Davis HB, Tufekci E, Crow JJ, Cowell DA, Mitchell JC. Ion release from a novel orthodontic resin bonding agent for the prevention of white spot lesions: An in-vitro study. Angle Orthod. *In press.*

42. Mitchell JC. Aging of bioactive glass bone-grafting materials. In: Eliades G, Eliades T, Brantley WA, Watts DC (eds). Dental Biomaterials in vivo: Aging and related phenomena. Chicago, IL: Quintessence. 2003; 263-76.

43. Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. J Am Chem Soc. 1938;60:309-19.

44. Keizer S, Ten Cate JM, Arends J. Direct bonding of orthodontic brackets. Am J Orthod Dentofacial Orthop. 1976;69: 318–27.

45. Lopez JI. Retentive shear strengths of various bonding attachment bases. Am J Orthod Dentofacial Orthop. 1980;77: 669–78.

46. Yli-Urpo H, Vallittu PK, Närh TO. Release of silica, calcium, phosphorus, and fluoride from glass ionomer cement containing bioactive glass. J Biomater. 2004;19: 5-20.

47. Buonocore MG. Principles of adhesive retention and adhesive restorative materials. J Am Dent Assoc. 1963;67: 382–91.

48. Retief DH. Failure at the dental adhesive-etched enamel interface. J Oral Rehabil. 1974;1:265–84.

49. Littlewood SJ, Mitchell L, Greenwood DC, Bubb NL, Wood DJ. Investigation of a hydrophilic primer for orthodontic bonding: an in vitro study. J Orthod. 2000;27:181–6.

50. Martin S, Garcia-Godoy F. Shear bond strength of orthodontic brackets cemented with a zinc oxide-polyvinyl cement. Am J Orthod Dentofacial Orthop. 1994;106:615–20.

51. Bishara SE, Von Wald L, Laffoon JF. Effect of altering the type of enamel conditioner on the shear bond strength of a resin-reinforced glass ionomer adhesive. Am J Orthod Dentofacial Orthop. 2000;118:288–94.

52. Britton JC, McInnes P, Weinberg R, Ledoux WR, Retief DH. Shear bond strength of ceramic orthodontic brackets to enamel. Am J Orthod Dentofacial Orthop. 1990;98:348–53.

53. Bennett CG, Shen C, Waldron JH. The effects of debonding on the enamel surface. J Clin Orthod. 1984;18:330-4.

54. Greenlaw R, Way DG, Khadry AG. An in vitro evaluation of a light-cured resin bonding systems. Am J Orthod Dentofacial Orthop. 1989;96:214–20.

55. Pickett KL, Sadowsky PL, Jacobson A, Lacefield W. Orthodontic in vivo bond strength: comparison with in vitro results. Angle Orthod. 2001;71:141–8.

Vitae

Dr. Cole R. Johnson was born in Salem, Oregon on January 15, 1981. He was raised in Oregon and has also lived in the Dominican Republic following graduation from high school and throughout college. He attended the Brigham Young University - Idaho on a track scholarship prior to graduating with a Bachelor of Science degree in Biochemistry in 2005. He attended dental school at the Oregon Health & Sciences University in Portland, OR where he graduated with High Honors and Distinction in 2009. He was granted admission to the graduate orthodontic program at the Virginia Commonwealth University Department of Orthodontics in 2009 and received a Certificate in Orthodontics as well as a Master of Science in Dentistry degree in 2011. Dr. Cole R. Johnson will enter the private practice of orthodontics in Salem, OR.