

Effect of Incorporation of Nano-Hydroxyapatite and Nano-Zinc Oxide in Resin Modified Glass Ionomer Cement on Metal Bracket Debonding

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Abstract

Background and Aim: Use of fluoride releasing materials to decrease the risk of demineralization around orthodontic brackets would be reasonable as an adhesive for bracket bonding only if they provide acceptable shear bond strength (SBS). The aim of this study was to evaluate the SBS of resin-modified glass ionomer cements (RMGICs) modified by nano-zinc oxide (NZnO) and nano-hydroxyapatite (NHA) in comparison with composite resins.

Materials and Methods: In this experimental study, 80 extracted human premolars were used. The teeth were randomly divided into 4 groups as follows: Group 1: Transbond XT as a control group, Group 2: RMGIC (Fuji II LC), Group 3: RMGIC with 5% NHA and Group 4: RMGIC with 2% NZnO. After etching the enamel, brackets were bonded. The SBS was measured for each group. The percentage of adhesive remnants on the enamel surface was quantified using the adhesive remnant index (ARI). The data were analyzed using one-way ANOVA and the Kruskal Wallis test.

Results: According to the results of ANOVA, no significant difference was found in the SBS of groups ($p=0.075$). The mean shear bond strength in groups 1 to 4 was 15.43 ± 4.61 , 14.95 ± 4.34 , 17.97 ± 3.65 and 17.08 ± 3.59 , respectively. According to the Kruskal-Wallis test, there was no significant difference in ARI score among the groups ($p=0.413$).

Conclusion: The amount of SBS was similar among all groups and addition of NZnO and NHA particles had no negative effect on SBS of RMGIC. Less than half the adhesive remained on the enamel surface after bond failure in all groups.

Key Words: Resin modified glass ionomer cement, Nanohydroxyapatite, Nano-zinc oxide, Shear bond strength

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Introduction

Nowadays, Composite resins are commonly used by orthodontists because they allow easy manipulation and reduce the time of bracket placement [1]. One of the most important shortcomings of composite resins is their lack of fluoride release; thus, they cannot impede enamel demineralization around brackets [2].

Glass Ionomer Cements (GICs) were first introduced by Wilson and Kenton in 1972 for anterior tooth restorations [3]. In addition to biocompatibility with the enamel and dentin, they have cariostatic effect and they promote remineralization by releasing fluoride [4]. Some in vitro and in vivo studies have reported that GICs have weak clinical bond strength; thus they are not

recommended for routine clinical orthodontic bracket bonding [5]. In an attempt to improve bond strength, RMGICs were developed [4]. RMGICs are composed of glass-ionomer (fluoroaluminosilicate glasses and polyacrylic acid) and composite resins (photo or chemical initiators and methacrylate monomers) [6]. The incorporation of resin improved bond strength to the enamel surface [4]. They also have less technical sensitivity and better physical and mechanical properties than conventional GICs [7] but the amount of released fluoride is similar to that of conventional GICs [8]. Different techniques have been introduced to improve the properties of RMGIs. Addition of zinc oxide (ZnO) particles to RMGIs is among these techniques [9]. ZnO has been used for several years in dentistry due to its biocompatibility and antimicrobial effect [10].

Zinc serves as an activator of enzymes. It can be toxic to microorganism at low concentrations and can inhibit plaque accumulation at high concentrations. Addition of ZnO particles to RMGICs increases their antimicrobial efficacy with no negative effect on their SBS [9].

By decreasing the particle size of ZnO to nanometer, the antimicrobial effect of composite resins, which contain this particle increases significantly [11]. In addition to increased antimicrobial activity, NZnO particles improve physical properties and flexural strength of GICs, because these particles bond to polyacrylic liquid of GICs [12]. Hydroxyapatite is a type of calcium phosphate, which is the main mineral component of the enamel; it also constitutes more than 60% of dentine by weight. In addition, hydroxyl apatite constitutes the inorganic matrix of human bone. The ability of hydroxyapatite to integrate with bone structure can help the bond between bone and implant [13]. As hydroxyapatite particles and inorganic ions infiltrate into the demineralized surface they impede the movement of calcium released from the enamel surface; therefore, resistance to demineralization is intensified [14]. GICs have been found to interact with hydroxyapatite via the carboxylate groups in the polyacid. Therefore, the incorporation of HA into GICs may not only improve the biocompatibility of GICs but also have the potential of enhancing their mechanical properties. In addition, it has the ability to

increase the bond strength to tooth structure due to its similar composition and structure to enamel and dentin [15]. One of the most important characteristics of bonding agents used in orthodontics is their SBS. Adding nano particles to RMGICs will be acceptable only if they do not have a negative effect on SBS; thus, evaluation of SBS of cements, which contain these nano particles is very important. The aim of this study was to evaluate the SBS of RMGICs modified by NHA and NZnO to metal brackets in comparison with composite resin.

Materials and Methods

In this experimental study, 80 sound premolar teeth without cracks, restorations or decalcifications were collected. The teeth were cleaned from calculus and tissue debris and then buccal surfaces of all teeth were polished using a rubber cup operated at low speed and pumice powder for 10 seconds. After extraction, all teeth were stored in distilled water at room temperature for about 3 months. The teeth were randomly divided into 4 groups of 20. All the samples were blindly prepared as follows in two consecutive days by the same operators specifically trained for this purpose. The composition of materials used in this study is shown in Table 1.

The teeth were randomly divided into 4 groups as follows:

Group 1: Transbond XT (TBXT) (3M ESPE, St. Paul, MN, USA)

Group 2: Fuji II LC (RMGIC) (GC Corp. Tokyo, Japan)

Group 3: Fuji II LC (RMGIC) (GC Corp. Tokyo, Japan) containing %5 NHA

Group 4: Fuji II LC (RMGIC) (GC Corp. Tokyo, Japan) containing %2 NZnO. In this study, NZnO particles with grain size of 20-40 nm and purity of more than 99.7% and NHA particles with grain size of 50 nm and purity of 90% obtained from Nanoshel were added to RMGIC.

After weighing of nanoparticles by a digital scale (Iran taraz, Tehran, Iran), particles were mixed with RMGIC powder by means of mortar and pestle. In group 1, after cleaning, the buccal surfaces of the teeth were etched with 37% phosphoric acid (Ultra-etch, Ultradent, South Jordan, USA) for 30 seconds, washed for 10 seconds and dried with gentle flow of air.

Table 1. Materials used in this study

Material	Manufacturer	Composition
Fuji II LC	GC Corporation Tokyo, Japan	Powder: Fluoro-alumino-silicate glass Liquid: Polyacrylic acid, 2-hydroxyethyl methacrylate (HEMA), dimethacrylate, camphorquinone, water
Transbond XT	3M Unitek Orthodontic Products, Monrovia, CA, USA	Adhesive paste: Silica, BIS-GMA, Silane, Ndimethyl benzocaine, hexa-fluoro-phosphate
Metal Bracket	TSNPT company Tehran, Iran LOT BN:BRFA910522	Edgewise/Standard/Metal/Hook 3/QltH/.018
*Nano zinc oxide	NanoshelPvt Ltd. Delhi, India	Zinc oxide Nano particles Grain size: 20-40 nm Purity: 99.7+ % Lead(pb) (%) ≤ 0.037 Manganese (Mn) (%) ≤ 0.0001 Copper (Cu) (%) ≤ 0.0002
*Nano Hydroxyapatite	Nano sized, Rod like Hydroxyapatite particles(NHA) final product from NanoSHEL corporation(Batch No:20090627) Delhi, India	Ca ₅ (OH) (PO ₄) ₃ Grain size: 50 nm Purity: 99%

* Both formulations of RMGIC plus 2%NZnO and RMGIC plus 5%NHA were prepared at Shahed University of Medical Sciences, Faculty of Dental Science. Registration number 76918 for RMGIC +2%NZnO and 75084 for RMGIC+5%NHA

A thin layer of TBXTPrimer (3M ESPE, St. Paul, MN, USA) was applied on the buccal surfaces by an applicator and then cured for 10 seconds using a LED light curing unit (L.E. Demetron, SDS Kerr, Orange, USA) with a wavelength of 470nm and light intensity of 1100mW/cm². Composite resin (Transbond XT, 3M Unitek, Monrovia, Calif) was then applied on the base of brackets and brackets were placed at the center of the buccal surfaces using a bracket positioned. Excess adhesive was removed and finally the bonding material was cured for 40 seconds (10 seconds from each side).

In group 2, after cleaning, the buccal surfaces of the teeth were etched with 37% phosphoric acid for 30 seconds, washed for 10 seconds and dried with gentle flow of air. According to the manufacturer's instructions, 1 scoop of powder was mixed with 2 drops of liquid, with 3.2 to 1 ratio. The powder was divided into 2 parts and each part was mixed with liquid by a plastic spatula for 10 seconds. RMGIC was then applied on the base of brackets and brackets were placed at the center of the buccal surfaces using a bracket positioner.

Excess adhesive was removed and finally the bonding agent was cured for 40 seconds (10 seconds from each side). Next, 5% NHA powder and 2% NZnO powder were added to the RMGIC powder in groups 3 and 4, respectively. Brackets were placed at the center of the buccal surfaces as in group 2. The specimens were mounted and incubated at 37°C in distilled water bath for 24 hours [16]. For assessment of the SBS, a chisel-shaped rod with 0.5 mm thickness was attached to the head of the Instron universal testing machine (Zwick-Roell, Ulm, Germany) and shear force was applied at a crosshead speed of 1mm/min as close to the bracket-tooth interface as possible in incisal-cervical direction. The load at failure was recorded using the testXpert V11.0- software (Zwick-Roell, Ulm, Germany) and reported in megapascals (Mpa).

Following debonding, each tooth was examined under a stereomicroscope (Carton Optical Industries, Bangkok, Thailand) at $\times 10$ magnification. The percentage of adhesive remained on the enamel surface was quantified according to the values of the adhesive remnant index (ARI) previously described by Artun and Bergland [17] as follows:

0: No adhesive remained on the enamel surface.

1: Less than 50% of adhesive remained on the enamel.

2: More than 50% of adhesive was left on the enamel.

3: The entire adhesive remained on the tooth structure.

In this study, data were analyzed using SPSS Software (version 20) (Microsoft, IL, USA). In all groups, SBS was analyzed using one-way ANOVA. The Kruskal-Wallis test was used to compare the ARI score among the 4 groups. $p < 0.05$ was considered statistically significant.

Results

The bond strength values (in MPa) and standard deviations (SD) are shown in Table 2. The results of one-way ANOVA showed that there was no significant difference in SBS among the 4 groups ($p = 0.075$). Furthermore, addition of NHA and NZnO particles to RMGICs had no negative effect on SBS of RMGICs compared to composite resins.

Distribution of the modes of failure (ARI scores) is shown in Table 3. The Kruskal-Wallis test showed that there was no significant difference in ARI scores among the 4 groups ($p = 0.413$).

In all groups, ARI type 1 had the highest frequency (less than 50% of adhesive remained on the enamel surface).

Discussion

In spite of the advances made in the field of

Table 2. Shear bond strength and standard deviation values

Material	N	Minimum	Maximum	Mean \pm Std. deviation
Transbond XT	20	7/41	22/96	15/43 \pm 4/61
RMGI	20	8/19	22/75	14/95 \pm 4/34
NHA 5%	20	11/10	23/96	17/97 \pm 3/65
NZnO 2%	20	11/01	25/12	17/08 \pm 3/59

Table 3. Distribution of ARI scores

ARI scores				
	0	1	2	3
Material				
Transbond XT	1	12	5	2
RMGI	0	14	5	1
5% NHA	0	12	5	3
2% NZnO	0	10	5	5

orthodontics, a basic issue has not yet been completely resolved, that is, the increasing risk of WSLs. The most efficient clinical approach described in the literature to minimize the risk of occurrence of these lesions has been bracket bonding with GICs. However, orthodontists are still reluctant to use this cement particularly due to technique sensitivity and concerns regarding the SBS [4].

Mitral introduced RMGIC as a hybrid material in 1991 [18]. RMGICs have been developed to combine the desirable properties (such as high SBS) of composite resins and fluoride release potential of GICs. The manufacturer's instruction for RMGICs is to use 10% polyacrylic acid as enamel conditioner and light curing for 40 seconds. Because of high rate of bond failure compared with composite resins, some authors have proposed different bonding protocols to increase the SBS, such as etching with 37% phosphoric acid or increasing the duration of light curing. Maruo et al. indicated that SBS of RMGICs was enhanced by the use of 37% phosphoric acid in comparison with 10% polyacrylic acid; but increasing the light curing duration had no significant effect on SBS [19].

Previous studies indicated that RMGICs exhibited SBS values similar to those of composite resin when phosphoric acid was used for etching [16]. In the current study, we used 37% phosphoric acid and there was no difference in SBS between RMGIC and composite resin similar to the findings of previous studies. In contrast, in absence of etching, the SBS achieved with RMGIC was significantly lower than that of conventional composite resin [20]. Khurushi et al. assessed the effect of pre-conditioning with phosphoric acid on SBS of three different RMGICs and concluded that the effect of acid pre-conditioning on SBS was material-dependent and only SBS of Fuji II LC increased due to etching.

Safaralizadeh and Rezvani showed that adding 2% NZnO to RMGIC significantly increased the fluoride releasing potential and improved the cariostatic effect of RMGICs. Malekhoseini and Rezvani also observed that adding 2% NZnO not only increased flexural strength and flexural elastic modulus of RMGICs but also inhibited the growth of *Streptococcus mutans* [21].

According to the results of the current study, adding 2% NZnO had no negative effect on SBS of RMGICs. Jatania and Shivalinga observed that as the concentration of ZnO in RMGIC increased, antimicrobial effect was enhanced but the SBS decreased [22]. This finding is not in agreement with our results. Three reasons can be proposed for this controversy:

- 1-ZnO nanoparticles which have superior properties compared to ZnO particles [11,12] were not used in their study;
- 2-In the two groups containing zinc oxide, larger than normal amount of RMGIC liquid was used, which might have weakened the material and
- 3-The blade used in their study applied the force closer to the tie wing rather than the base [23].

Klocke and Kahl-Nieke demonstrated that variations in the direction of debonding force significantly influence the SBS measurement. Changes in the direction of the shearing force as small as 15° can decrease the bond strength values by 27.4% [24].

Mohammadi Basir et al. observed that incorporating 5% NHA into RMGIC did not decrease the compressive strength and enhancement occurred with addition of 5wt% NHA [25]. Seyedtaba'i and Nurisari reported that RMGIC plus 5% NHA had no negative effect while adding 10% NHA significantly lowered the SBS. Therefore, we used 5wt% NHA to evaluate its effect on SBS to metal brackets. According to the results of the current study, adding 5% NHA had no negative effect on SBS of RMGICs. Researchers have also shown that incorporating NHA into GICs increases the demineralization resistance more effectively than HA [14, 15]. This may be related to the smaller particle size of NHA, which enhances its deposition into micro-pores in demineralized enamel. In addition, high solubility of NHA leads to efficient release of calcium and phosphate ions, which fill the demineralized micro-pores [26].

The ARI score for the debonded interfaces of composite resin was mainly 1 (60% of specimens) in our study; therefore, most failures occurred at the composite/ enamel interface. A disagreement exists in this regard among different studies; some studies reported the highest frequency of failures at the composite/enamel interface with the greatest composite remnants on the base of brackets

[16]; while others reported the highest frequency of failures at the composite/bracket interface with the greatest amount of composite remnant on the enamel surface [4,20]. Our results also showed that the score for the debonded interfaces of RMGICs and RMGIC plus 5% NHA was mainly 1 (70% and 60% of specimens, respectively); thus, in these two groups the highest frequency of bond failures occurred at the adhesive/enamel interface. For RMGIC plus 2% NZnO, ARI score in 50% of specimens was 1, and it was 2 and 3 for the remainder, which indicated bond failure at the adhesive/enamel and adhesive/bracket interface. Controversy also exists among different studies in this respect; some studies reported bond failure at the adhesive/enamel interface [16,20] while others reported failure at the adhesive/bracket interface [14,15].

The following reasons may explain this variation in results:

1. Different methods for ARI analysis (evaluation of enamel surface versus base of bracket)
2. Different location of force exertion or different angulations of blade during SBS testing
3. Different methods of enamel surface conditioning before bonding
4. variable types of adhesives and brackets used [24]. Profit introduced the adhesive/bracket interface to be the favorable region for bracket debonding because the risk of enamel damage would be minimal if bracket debonding occurs at this interface. Furthermore, in case of accidental bracket debonding, RMGIC remnants on the conditioned tooth surface would continue to release fluoride [19]. However, this method of debonding has the disadvantage of requiring more chairside time for adhesive remnant removal after bracket debonding. In our study, adding 2% NZnO or 5% NHA to RMGIC had no significant effect on SBS.

Most clinical studies are time consuming and costly; thus, it is recommended to evaluate material characteristics under *in vitro* conditions to obtain an overall estimate before conducting *in vivo* studies. Due to the presence of significant differences between oral and clinical conditions, we cannot fully generalize the results of *in vitro* studies to the clinical setting.

Therefore, future studies are required to evaluate

the properties of RMGICs containing 2% NZnO and 5% NHA in the clinical setting.

Conclusion

1. In this study, the amount of SBS was similar among all groups.
 2. RMGICs can be as effective as composite resins for bonding of metal brackets to enamel surfaces.
 3. Adding 2% NZnO and 5% NHA particles to RMGICs had no negative effect on their SBS in comparison with composite resin.
- In all groups, less than half of the adhesive remained on the enamel surface after bond failure.

References

1. Bishara SE, Olsen ME, Damon P, Jakobsen JR. Evaluation of a new light-cured orthodontic bonding adhesive. *Am J Orthod Dentofacial Orthop*. 1998 Jul;114(1):80-7.
2. Ogaard B, Rølla G, Arends J. Orthodontic appliances and enamel demineralization. Part 1. Lesion development. *Am J Orthod Dentofacial Orthop*. 1988 Jul;94(1):68-73.
3. Wilson AD, Kent BE. A new translucent cement for dentistry. The glass ionomer cement. *Br Dent J*. 1972 Feb 15;132(4):133-5.
4. Pereira TB, Jansen WC, Pithon MM, Souki BQ, Tanaka OM, Oliveira DD. Effects of enamel deproteinization on bracket bonding with conventional and resin-modified glass ionomer cements. *Eur J Orthod*. 2013 Aug;35(4):442-6.
5. Hitmi L, Muller C, Mujajic M, Attal JP. An 18-month clinical study of bond failures with resin-modified glass ionomer cement in orthodontic practice. *Am J Orthod Dentofacial Orthop* 2001 Oct;120(4):406-15.
6. Cardoso MV, Delmé KI, Mine A, Neves Ade A, Coutinho E, De Moor RJ, et al. Towards a better understanding of the adhesion mechanism of resin-modified glass-ionomers by bonding to differently prepared dentin. *J Dent* 2010 Nov; 38 (11):921-9.
7. Mount GJ, Patel C, Makinson OF. Resin modified glass ionomers: strength, cure depth and translucency. *Aust Dent J*. 2002 Oct; 47(4):339-43.
8. McCabe JF. Resin modified glass ionomers. *Biomater*. 1998 Mar;19(6):521-7.
9. Spencer CG, Campbell PM, Buschang PH, Cai J Honeyman AL. Antimicrobial effects of zinc oxide

- in an orthodontic bonding agent. *Angle Orthod* 2009 Mar;79(2):317-22.
10. Phan TN, Buckner T, Sheng J, Baldeck JD, Marquis RE. Physiologic action of zinc related to inhibition of acid and alkali production by oral streptococci in suspensions and biofilms. *Oral Microbiol Immunol*. 2004 Feb;19(1):31-8.
 11. Adams LK, Lyon DY, McIntosh A, Alvarez PJ. Comparative toxicity of nanoscale TiO₂, SiO₂ and ZnO suspensions. *Water Sci Technol*. 2006;54(11-12):327-34.
 12. Jones N, Ray B, Ranjit KT, Manna AC. Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. *FEMS Microbiol Lett*. 2008 Feb; 279(1):71-6.
 13. Le Geros RZ. Calcium phosphates in demineralization and remineralization processes. *J Clin Dent*. 1999 Jan; 10(2):65-73.
 14. Lee JJ, Lee YK, Choi BJ, Lee JH, Choi HJ, Son HK, et al. Physical properties of resin reinforced glass ionomer cement modified with micro and Nano hydroxyapatite. *J Nanosci-Nanotechnol* 2010 Aug;10(8):5270-6.
 15. Moshaverinia A, Ansari S, Moshaverinia M, Roohpour N, Darr JA, Rehman I. Effects of incorporation of hydroxyapatite and fluoroapatite Nano-bioceramics into conventional glass ionomer cements (GIC). *Acta Biomater*. 2008 Mar;4(2):432-40.
 16. Cheng HY, Chen CH, Li CL, Tsai HH, Chou TH, Wang WN. Bond strength of orthodontic light-cured resin-modified glass ionomer cement. *Eur J Orthod*. 2011 Apr;33(2):180-4.
 17. Artun J, Bergland S. Clinical trials with crystal growth conditioning as an alternative to acid-etch enamel pretreatment. *Am J Orthod* 1984 Apr; 85(4):333-40.
 18. Uysal T, Amasyali M, Koyuturk A E, Sagdic D. Efficiency of amorphous calcium phosphate – containing orthodontic composite and resin modified glass ionomer on demineralization evaluated by a new laser fluorescence device. *Eur J Dent*. 2009 Apr;3(2):127-134.
 19. Seyedtabaie E, Nurisari M. Evaluation of shear bond strength of resin reinforced glass ionomer cement modified by Nano-hydroxyapatite on ceramic bracket debonding using full-dimension wire. *Ann Res&Rev in Biol*. 2014 Feb; 4(10): 1578-1586.
 20. Khoroushi M, Hosseini-Shirazi M, Soleimani H. Effect of acid pre-conditioning and/or delayed light irradiation on enamel bond strength of three resin-modified glass ionomers. *Dent Res J (Isfahan)*. 2013 May-Jun;10(3):328-36.
 21. Jatania A, Shivalinga B M. An in vitro study to evaluate the effects of addition of zinc oxide to an orthodontic bonding agent. *Eur J Dent*. 2014 Jan-Mar ;8(1):112-7.
 22. Hu W, Fu M, Sun Z. Shear bond strength of glass ionomer cement for orthodontic bracket bonding. *Zhonghua Kou Qiang Yi Xue Za Zhi*. 2000 May; 35(3):227-9.
 23. Klocke A, Kahl-Nieke B. Effect of debonding force direction on orthodontic shear bond strength. *Am J Orthod Dentofacial Orthop*. 2006 Feb; 129(2):261-5.
 24. Mohammadi Basir M, Ataei M, Rezvani MB, Golkar Taft P. Effect of incorporation of various amounts of nano-sized Hydroxyapatite on the mechanical properties of a resin modified glass ionomer. *J Dent Sch*. 2013 Winter; 30(4):216-223.
 25. Huang M, Feng J, Wang J, Zhang X, Li Y, Yan Y. Synthesis and characterization of nano-HA/PA66 composites. *J Mater Sci Mater Med*. 2003 Jul;14(7):655-60.
 26. Proffit WR, Fields HW, Sarver DM, Ackerman JL. *Contemporary Orthodontics*. 5th ed. Canada: Mosby. Elsevier; 2013.