



Evaluation of mechanical and adhesion properties of glass ionomer cement incorporating nano-sized hydroxyapatite particles

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Abstract

Glass ionomer cement is a widely used luting agent for indirect restorations but presents inferior mechanical properties compared to resin cement due to its low elastic modulus. This study evaluated the mechanical and adhesion properties of glass ionomer luting cements reinforced with nano-sized hydroxyapatite particles (HA). The nano-sized HA particles were synthesized using the co-precipitation technique and the resulting precipitate was characterized using X-ray diffraction analysis (XRD), field emission scanning electron (FESEM) and transmission electron microscopy (TEM). HA particles were incorporated into the glass powder (FUJI I, GC) and the luting agent was manipulated in a liquid to powder ratio of 3:1 into 6% by weight after determining the best ratio. The flexural strength of the luting agent and shear bond strength of dentin were analyzed and compared to other luting agents namely, (a) glass ionomer (FUJI I), (b) resin-modified glass ionomer (RelyX Luting Plus) and (c) adhesive resin cement (RelyX U200). Failure types after debonding from dentin were evaluated under SEM. Flexural strength and bond strength data were analyzed using one-way ANOVA and Tukey's tests ($\alpha = 0.001$). Addition of 6 w % HA particles in the range of 80–150 nm enhanced the flexural strength (30.97 ± 5.9 versus 11.65 ± 5.63) and shear bond strength (0.97 ± 0.41 versus 0.39 ± 0.16) of a conventional glass ionomer luting agent significantly compared to the non-reinforced ones when manipulated at a liquid to powder ratio of 3:1 ($P < 0.001$). While conventional glass ionomer, HA-reinforced glass ionomer and resin-modified glass ionomer specimens showed exclusively mixed type of failures, adhesive resin cement showed cohesive failures within the resin cement. Increased mechanical and adhesion potential of the experimental glass ionomer luting agent after incorporation of HA particles could expand the scope of application of this cement.

Keywords Adhesion · Cement · Glass ionomer · Hydroxyapatite · Mechanical properties

Introduction

The correct cementation of indirect restorations to teeth using luting agents forms the basis of successful restorative dentistry. Such restorations include metal, metal–ceramic and ceramic restorations, provisionals, veneers for anterior teeth, orthodontic appliances and pins and root posts used for retention of restorations. The primary function of a luting agent is to fill the void at the restoration–tooth interface and mechanically lock the restoration in place to prevent its dislodgement during mastication.

An ideal luting agent must meet the basic mechanical, biological and handling prerequisites such as biocompatibility, sufficient working time, flowability, compressive strength, minimal microleakage, low solubility in oral fluids, adhesiveness, esthetics, low cost and ease of removal in case of excess material [1]. No single luting agent is capable of

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meeting all the stringent requirements, which is why, there is a plethora of luting agents currently available, ranging from water-based to contemporary adhesive resin cements.

Glass ionomer cements (GIC) were invented in the late 1960s [2, 3]. GICs bond well to enamel and to some extent to dentin and at the same time release fluoride [3]. Initially used as a restorative material, GICs further evolved into luting agents, liners, bases, fissure sealants and is also used as filling materials in the atraumatic restorative treatment (ART) technique [4]. The major concern with this cement is its sensitivity to early moisture contamination and desiccation which compromises the integrity of the material [2, 3]. It is also prone to elastic deformation in areas of high masticatory stress due to its lower modulus of elasticity compared to resin-based luting agents [5]. Various modifications of GICs have been studied so far by addition of fibers, hydroxyapatite, amalgam, proline and zirconia [6].

Hydroxyapatite (HA) ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a calcium phosphate bioceramic that is composed of calcium and phosphorus in the ratio of 1.67:1. It is the main mineral component of the enamel and contributes to more than 60% of the composition of dentin by weight [7]. In addition, HA comprises the inorganic matrix of human bone in the form of phosphocalcic hydroxyapatite. HA with a nanoporous structure has been proven to enhance cell adhesion, proliferation and differentiation required for tissue functions [8]. Since HA has excellent biocompatibility and similarity in crystal structure to that of apatite in human dental and skeletal systems, a number of studies have been carried out to study the effect of addition of HA powder to dental restorative materials. Incorporation of HA particles have led to a significant improvement in mechanical properties such as compressive, diametral tensile strength and shear bond strength of GICs [9, 10]. HA granules exposed on the surface of GIC could facilitate a bioactive reaction involving the formation of carboxylate groups in the polyacid [11]. Therefore, the incorporation of HA into the GICs may not only improve the biocompatibility of GICs in contact with hard tissues but also enhance its mechanical properties.

The refinement of the technique of bonding of biomaterials to teeth has driven the development of several bonding agents [12]. In this century, the production of materials with nanostructures has gained much attention for adsorption, catalytic, biomaterials and optical applications. The addition of such nano-sized HA particles to GIC used for luting purposes has not been reported in the literature and requires investigation. Therefore, the aim of this study was to analyze the effect of incorporation of nano-sized HA particles in glass ionomer luting agents on their flexural strength and shear bond strength to the tooth and compare it with other commercially available other luting agents such as conventional GIC, resin-modified GIC and adhesive resin. The

hypothesis tested was that incorporation of HA particles to GIC would increase both flexural and bond strength.

Materials and methods

Synthesis of nano-sized hydroxyapatite

Analytical grade calcium hydroxide ($\text{Ca}(\text{OH})_2$) (MERCK Chemicals, Darmstadt, Germany), orthophosphoric acid (H_3PO_4) (Qualigens Fine Chemicals, Mumbai, India), methanol ($\text{CH}_3(\text{OH})$) (SDFCL, Mumbai, India) and ammonia solution (NH_3) (SDFCL) were used for synthesizing nano-sized hydroxyapatite (HA) particles. All the reagents were used without any further purification. The synthesized HA particles were then added to commercial glass ionomer powder (Fuji 1, GC, Tokyo, Japan) and the resulting mixture was used for cement preparation.

Calcination of nano-sized hydroxyapatite

Nano-sized HA particles were prepared by the co-precipitation method of synthesis [13]. Briefly, 1 M of calcium hydroxide was dissolved in 150 ml of methanol. A solution of 0.6 M orthophosphoric acid in methanol was added dropwise to the calcium hydroxide solution under vigorous stirring at room temperature. pH of the resultant solution was adjusted to 11 using the ammonia solution. The precipitate obtained after the reaction was aged at room temperature over a period of 24 h under continuous stirring. This HA precipitate was then filtered and washed continuously with distilled water to remove unwanted ions and impurities. The resulting precipitate was dried in an oven at 80 °C for 24 h. The powder was ground using mortar and pestle initially and then ball milled over a period of 24 h to achieve uniformity in the particle size of the precipitate. The precipitate was calcined in a conventional furnace in air atmospheric pressure at 900 °C for 4 h. The calcinations were performed stepwise with intermittent ball milling to avoid lump formation.

Characterization of hydroxyapatite particles

X-ray powder diffraction (XRD) studies of nano-sized HA were carried out using an X-ray diffractometer (Model D8 Advance by Bruker GmbH, Karlsruhe, Germany) with $\text{CuK}\alpha$ radiation ($\lambda = 1.54\text{\AA}$). The scan was performed in the 2θ range 20°–80° at intervals of 0.03° with the count time of 0.6 s. Sample identification was performed by comparing the diffraction patterns with the joint committee on powder diffraction standards (JCPDS) data. The XRD analysis was carried out at different stages of the synthesis to evaluate the resulting precipitate [14].

The surface morphology of the prepared nano-sized HA powder was observed using the field emission scanning electron microscopy (FESEM) (Model No. S4800, Hitachi, Tokyo, Japan) operated at 10 kV and with transmission electron microscopy (TEM) (Model No. CM200, Philips, Amsterdam, Netherlands) operated at 20–200 kV.

Determination of liquid/powder ratio

The synthesized nano-sized HA particles were incorporated into the glass powder of the commercially available GIC (Fuji 1, GC) in five different proportions by weight (1%, 2%, 4%, 6%, 8%) and was manipulated at three varying liquid: powder ratios (3:1, 4:1, 5:1) to test for the best possible flexural strength ($N = 150$, $n = 10$ per group).

Flexural strength test

To prepare the specimens for flexural strength measurements ($N = 60$, $n = 15$ per group), polyvinylsiloxane putty (Flexceed, GC) molds ($25 \times 2 \times 2 \text{ mm}^3$) were fabricated. GIC (Fuji 1, GC), resin-modified GIC (RelyX Luting Plus 3 M ESPE, St. Paul, USA) and adhesive resin luting agents (RelyX U200, 3M ESPE), were manipulated as per the manufacturer's instructions. Based on the favorable results obtained from the pilot study, HA-modified GIC was manipulated after adding 6 w% of nano-sized HA particles to the glass powder and mixing at a liquid:powder ratio of 3:1.

The specimens were tested for flexural strength 24 h after preparation, using the three-point bending test with 20 mm span at a crosshead speed of 0.5 mm/min (Model Instron UTM 5582, Instron, Massachusetts, USA) according to ISO 9917-2:1996 [15].

Shear bond strength test

Freshly extracted non-carious maxillary premolars ($N = 60$, $n = 15$ per group) were cleaned off any soft tissues, blood and stored in distilled water. The teeth were randomly divided into four groups comprising 15 teeth each. The crown portions of the teeth were sectioned at the cemento-enamel junction and mounted in acrylic blocks such that the bonding surface rested flat above the level of acrylic. The bonding surfaces of the teeth were cleaned and polished using a wet silicon carbide paper (No. 400). Luting agents were applied using a cylindrical silicone split mold (height: 2 mm; diameter: 4 mm) as described previously [16]. With the silicon mold set on the dentin surface, each material was syringe loaded into the mold and left to set for 24 h. The specimens were retrieved by separating the silicone molds exerting minimal stress. The specimens were then mounted on the jig of a universal testing machine (Model Instron UTM 5582) and shear stress was applied at a crosshead speed of 0.5 mm/

min until failure occurred. The shear bond strength was calculated by dividing the load at failure by the bonding area.

Failure analysis

After the shear bond test, failure analysis was performed at the cement–tooth interface and SEM images ($\times 500$) were made from randomly selected specimens. Failure types were classified as follows: adhesive: adhesive failure at the tooth–cement interface with no cement remnants left on the substrate, mixed: $< 1/3$ cement left adhered on the substrate, cohesive: cohesive failure within the cement.

Statistical analysis

The data obtained from flexural strength test and shear bond test were statistically analyzed using the software package (IBM SPSS Software V.23, Chicago, IL, USA). Kolmogorov–Smirnov and Shapiro–Wilk tests were used to test normal distribution of the data. One-way ANOVA and the Tukey's post hoc tests were used to identify the significant differences between the groups. P values less than 0.001 were considered to be statistically significant in all tests.

Results

Characterization results

The XRD pattern of the synthesized nano-sized HA particles showed characteristic peaks confirming the formation of HA compared with that of HA (JCPDS 00-009-0432). Few peaks corresponding to calcium oxide were also found in the analysis which could be the result of calcination cycles performed on the precipitate (Fig. 1). The crystal system of the HA synthesized was hexagonal bearing the space group of P63/m and space group number of 176. The average crystalline size was found to be more than 60 nm using the Scherrer's formula:

$$t = K\lambda/B\cos\theta,$$

where t was the average crystallite size (nm); K was the shape factor ($K = 0.9$); λ was the wavelength of the X-rays ($\lambda = 1.54056 \text{ \AA}$ for $\text{CuK}\alpha$ radiations); B was the full width at half maximum (radian) and θ was the Bragg's diffraction angle ($^\circ$) [14].

The FESEM images of nano-sized HA showed particle size in the range of 80–150 nm that were hexagonal in shape and were clumped together forming agglomerates (Fig. 2a). TEM images of nano-sized HA demonstrated particles with diverse size in hexagonal shapes (Fig. 2b).

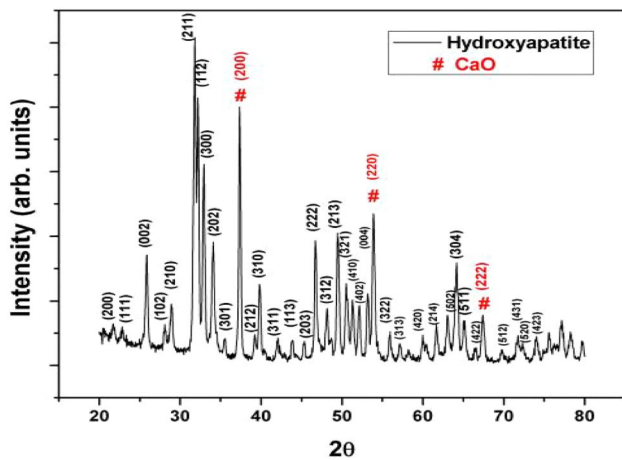


Fig. 1 X-ray diffraction analysis of the synthesized nano-sized hydroxyapatite particles showing characteristic peaks confirming the formation of hydroxyapatite

Fig. 2 a Field emission scanning electron microscopy image of synthesized nano-sized hydroxyapatite showing particle size in the range of 80–150 nm, hexagonal in shape forming agglomerates, **b** transmission electron microscopy image indicating particles with diverse size in hexagonal shapes

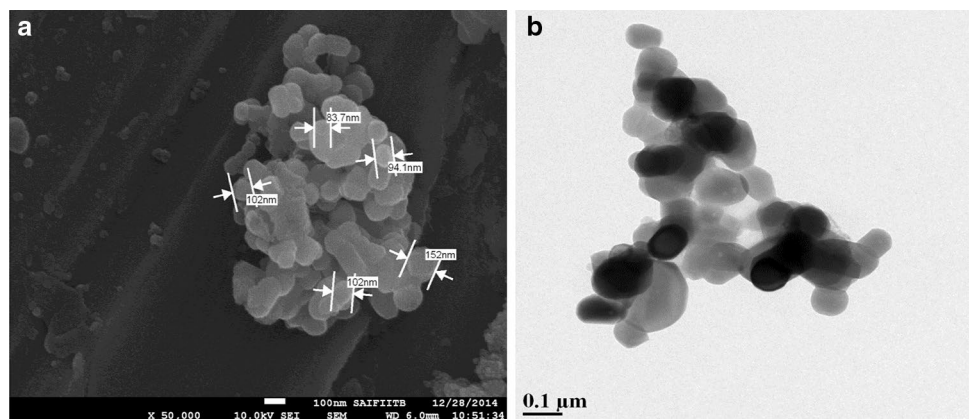


Table 1 Mean flexural strength and standard deviations of nano-sized hydroxyapatite (HA)-incorporated glass ionomer cement (GIC) prepared at different weight percent showing significantly higher values with 6 w% HA addition at 3:1 mixing ratio (ANOVA, Tukey’s test)

Experimental groups	Powder: liquid mixing ratio (<i>n</i> = 10 per group)	Mean flexural strength ± standard deviations (MPa)	ANOVA <i>F</i>	<i>P</i> value
GIC + 1 w% HA	3:1	11.59 ± 1.34	145.19	0.000**
	4:1	8.95 ± 0.43		
	5:1	6.86 ± 2.21		
GIC + 2 w% HA	3:1	11.61 ± 0.45		
	4:1	11.53 ± 2.69		
	5:1	13.21 ± 1.33		
GIC + 4 w% HA	3:1	11.91 ± 4.78		
	4:1	10.37 ± 0.44		
	5:1	10.01 ± 1.46		
GIC + 6 w% HA	3:1	34.16 ± 1.17		
	4:1	21.38 ± 1.23		
	5:1	11.35 ± 2.14		
GIC + 8 w% HA	3:1	11.88 ± 0.26		
	4:1	10.23 ± 0.53		
	5:1	6.55 ± 0.29		

***P* < 0.001

Liquid/powder ratio results

The mean values for flexural strength data at different combinations of liquid to powder ratios and different weight proportions are displayed in the Table 1. The cement formed by incorporating nano-sized HA particles at 6 w% into the powder of GIC, manipulated at a ratio of 3:1 showed significantly higher (*P* ≤ 0.001) strength compared to those of other combinations (Table 1). Hence, 6 w% of HA and a liquid: powder ratio of 3:1 were used in the future experiments for adding nano-sized HA particles to the commercially available GIC.

Flexural strength test results

Mean flexural strength values of GIC with and without HA, resin-modified GIC, adhesive resin are presented

Table 2 Mean flexural strength and standard deviations of the luting cements tested

Luting agent (<i>n</i> = 15 per group)	Mean flexural strength \pm standard devia- tions (MPa)	ANOVA <i>F</i>	<i>P</i> value
GIC	11.65 \pm 5.63 ^a	179.9	<0.001
RMGIC	41.07 \pm 11.5 ^b		
AR	66.70 \pm 5.26 ^c		
GIC-6 w% HA	30.97 \pm 5.9 ^d		

Different superscript letters in one column indicate significant differences between materials (ANOVA, Tukey's test)

GIC glass ionomer cement, RMGIC resin-modified glass ionomer cement, AR adhesive resin cement, GIC-6 w% HA GIC with 6 weight % hydroxyapatite

Table 3 Mean shear bond strength and standard deviations of the luting cements tested

Luting agent (<i>n</i> = 15 per group)	Shear bond strength \pm standard devia- tions (MPa)	ANOVA <i>F</i>	<i>P</i> value
GIC	0.39 \pm 0.16 ^a	251.57	<0.001
RMGIC	0.59 \pm 0.39 ^{a,b}		
AR	3.59 \pm 0.42 ^c		
GIC-6 w% HA	0.97 \pm 0.41 ^d		

See Table 2 for group abbreviations. Different superscript letters in one column indicate significant differences between materials (ANOVA, Tukey's test)

in Table 2. Mean flexural strength of adhesive resin was significantly higher (66.7 \pm 5.26 MPa) than those of other groups ($P < 0.001$), while GIC showed the lowest results (11.65 \pm 5.63 MPa). Incorporating nano-sized HA particles to the GIC improved the flexural strength of GIC significantly (30.97 \pm 5.9 MPa) compared to non-reinforced group (11.65 \pm 5.63 MPa) ($P < 0.010$). Resin-modified GIC (41.07 \pm 11.5 MPa) showed significantly higher results

compared to that of HA-modified GIC (30.97 \pm 5.9 MPa) ($P < 0.01$).

Shear bond strength results and failure types

Shear bond strength of adhesive resin was significantly higher (3.59 \pm 0.42 MPa) compared to that of GIC (0.39 \pm 0.16 MPa) ($P < 0.001$). Incorporating nano-sized HA particles to the GIC improved the shear bond strength (0.97 \pm 0.41 MPa) significantly ($P < 0.001$) (Table 3).

While conventional GIC, HA-reinforced GIC and RMGIC specimens showed exclusively mixed type of failures, adhesive resin cement showed cohesive failures within the resin cement. In SEM images, GIC showed multiple crack line formations, while such cracks were less visible in RMGIC and in GIC with 6 w% HA. No crack lines were evident in AR which failed exclusively within the cement itself (Figs. 3a–d).

Discussion

GICs are commonly used for cementation of cast alloy and porcelain fused to metal restorations. The clinical advantages exhibited by this cement include physicochemical bonding to tooth structure, good biocompatibility, long-term fluoride release and low coefficient of thermal expansion [2, 3]. Many modifications to the parent GIC have been reported in the literature, to reinforce the conventional GICs [6]. Some of these methods include the use of dispersed phases such as alumina, titanium oxide and zirconium oxide in the glass powder, addition of alumina fibers or other fibers such as glass fibers, silica fibers and carbon fibers to increase flexural strength, glasses reinforced with metals: mixing with amalgam powder, referred to as “Miracle Mix”, cermet ionomer, produced by sintering metal and glass powder, which resulted in a strong bond between them, conventional GI with a high viscosity to be used in ART technique and

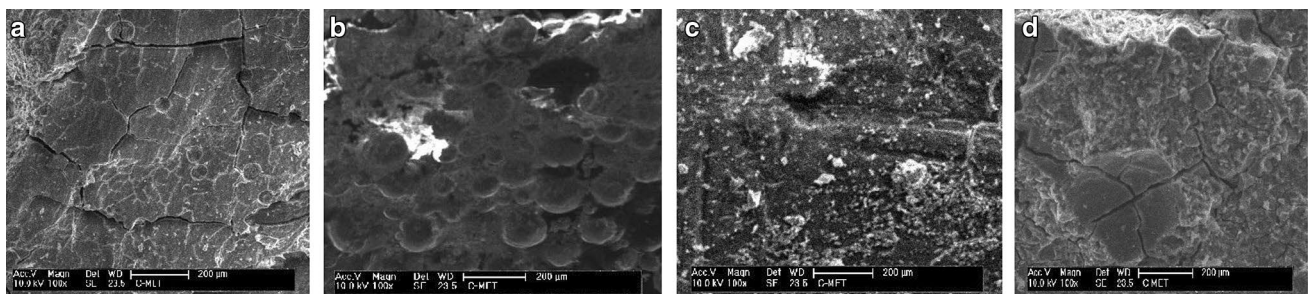


Fig. 3 a–d Scanning electron microscope images from a GIC, b RMGIC, c AR, d GIC-6 w% HA–tooth interfaces. Note that in GIC multiple crack line formations were visible, while such cracks were

less visible in RMGIC and in GIC with 6 w% HA. No crack lines were evident in AR which failed exclusively within the cement itself

resin-reinforced glass ionomers and amino acid-modified glass ionomers [6, 17].

To improve the mechanical properties of conventional GICs, RMGI luting agents have been introduced. These contain hydrophilic monomers and polymers such as hydroxyethylmethacrylate (HEMA). RMGIs have been reported to have higher flexural strength compared to conventional GICs [6]. However, the greatest disadvantage of resin ionomers is increased water absorption, plasticity and hygroscopic expansion due to the presence of poly-HEMA. Initially, water absorption reduces the stress during polymerization shrinkage but continuous water absorption creates a harmful effect. As these cements display significant dimensional changes, they are not applicable while luting full ceramic restorations [18]. On the other hand, dual-polymerized self-adhesive resin cements (AR) do not require pretreatment of the tooth surface and offer several advantages like high compressive and tensile strengths, low solubility and good esthetic qualities [19]. These materials are usually expensive and technique sensitive. Moreover, they are difficult to clean once set and do not have long shelf lives.

GICs therefore still remain the luting agents of choice for metal and porcelain fused to metal restorations. However, some of the major drawbacks encountered with the conventional GICs include high solubility, lack of modulus of elasticity and toughness [2, 3]. HA was first incorporated in restorative GICs by Nicholson et al. [20] in the year 1993. Then, Lucas studied the effect of incorporating commercially available HA granules in GICs and concluded that addition of HA maintains long-term bond strength to dentin [21]. In a study by Lee et al. [22], addition of nano-sized HA to GIC reported a better bond strength to dentin when compared to micro-sized HA. In fact, HA increases the crystallinity of the set matrix that makes the set cement more stable and improve its bond strength to the tooth structure [23]. No reports have been documented so far, studying the effect of nano-sized HA on the mechanical and adhesive performance of GICs. The present study was undertaken to reinforce GIC by incorporating indigenously synthesized nano-sized HA into the glass powder and to evaluate its flexural strength and shear bond strength in comparison to other commonly used luting agents. Numerous techniques have been reported so far for the synthesis of nano-sized HA, namely, dry methods, wet methods, high temperature processes, using biogenic sources for synthesis and combination of procedures [24]. The co-precipitation technique requires simple armamentarium being cost effective and hence, this technique was chosen for synthesizing nano-sized HA. The HA precipitate was repeatedly washed to ensure complete removal of impurities and unreacted reagents. The degree of purity of HA has been reported to be directly proportional to its biocompatible behavior [12]. To ensure purity, the resulting precipitate in this study was processed meticulously. The

calcinations were performed stepwise with intermittent ball milling to avoid lump formation. Characteristic peaks of HA showed the absence of other phases, confirming the phase formed to be that of apatite. The FESEM images indicated HA particles in roughly spheroidal shape with size in the range of 80–150 nm. Previous studies have reported the addition of HA particles of about 10 μm diameter to conventional GIC to improve its performance and strength [25]. In the present study, addition of indigenously synthesized HA particles with diameter in the range of 100–150 nm showed enhanced strength. Based on favorable results obtained from a pilot study, HA-modified GIC luting agent was manipulated by adding 6 w% nano-sized HA to glass powder and mixing the same in a liquid: powder ratio of 3:1.

An assessment of the flexural strength is important to understand the mechanical strength of luting agents. The test was performed in accordance to the recommendations outlined in ISO 9917-2:1996. The flexural strength obtained was the highest for adhesive resin luting agent and the lowest for conventional GIC. On the other hand, flexural strength of RMGIC and HA-modified GIC showed a slight difference which was statistically significant. The highest values obtained for the AR are in accordance with the studies reported in the literature [19]. The fillers present in the resin matrix make the cement more resistant to forces and decreases solubility. The flexural strengths shown by GIC and RMGIC were less than that of adhesive resin [1, 17, 19]. Of significance is the finding that the HA-modified GIC showed higher flexural strength when compared to conventional GIC, which could be due to reinforcement of the cement matrix with the HA particles and the chemical reactivity of the HA crystals with the acid molecules of the luting agent [26]. Similarly, Barandehfard et al. [10] reported that addition of synthesized nano-HA and fluoroapatite crystals led to improved compressive strength and diametral tensile strength of GICs.

In the present study, shear bond strength of the experimental luting agent was also evaluated. Kim et al. [16] tested the shear bond strength of RMGIC using a Teflon split tube to prepare cylindrical specimens of luting agent bonded to tooth. A similar technique was used in the present study, wherein, the cylindrical plastic split mold was utilized. Adhesive resin luting agent showed the highest shear bond strength while the lowest was observed with GIC. Adhesive resin bonds to the tooth enamel via micromechanical interlocking of resin to HA crystals and acid-etched enamel prisms. The bonding phenomenon becomes complex in dentin, wherein, it occurs by formation of a hybrid layer. The shear bond strength of GIC to the tooth is also typically low owing to its low flexural strength and compressive strength. These results are in agreement with the studies reported previously [27–30]. The shear bond strength of HA-modified GIC, however, showed greater bond strength compared to

non-reinforced one and RMGIC luting agent. The reaction mechanism between HA and GIC may be similar to that of adhesion of GIC to enamel and dentin, as the interaction of apatite found in the tooth structure with the polyacrylic acid produces polyacrylate ions. Evidence of the chemical bonding taking place between the carboxyl group of the polyacid with calcium from natural tooth structure or from synthetic HA was shown through electron spectroscopy for chemical analysis (ESCA) [31]. On the basis of adsorption and infrared spectroscopic studies performed, during adsorption, polyacrylate penetrates the surface of HA, displacing and replacing surface phosphate. Calcium ions are displaced from HA along with phosphate as a part of a complex series of ionic exchanges. As a consequence, an “intermediate layer” of calcium and aluminum phosphates and polyacrylates would form at the interface between the cement and HA. This layer is very resistant to acid and is difficult to break, resulting in stronger bonds between the organic and inorganic network of the set cement [26]. Therefore, the incorporation of HA into GIC may improve its bonding characteristics to the tooth surface.

The results of the study clearly show that while adhesive resin cements have the highest flexural strength and shear bond strengths, the experimental luting agent studied here showed significantly improved properties compared to conventional GIC. The addition of nano-sized HA to GIC has a beneficial effect by virtue of bonding taking place between the carboxyl group of the polyacid with calcium from natural tooth structure or from synthetic HA. However, further research should be carried out to investigate the potential applications of HA-incorporated GIC luting agent. Studies regarding incorporating different grades and concentrations of HA, effect of HA on other physical and optical properties of GICs along with microleakage studies are planned for future investigations.

Conclusions

The results of this study indicated that the addition of 6 w% hydroxyapatite particles of 80–150 nm enhanced the flexural strength and shear bond strength of conventional glass ionomer luting agent when manipulated at a liquid to powder ratio of 3:1. This promising novel glass ionomer luting agent requires further investigation for its application in restorative dentistry.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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