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SYNTHESIS AND EVALUATION OF PROPERTIES OF AN EXPERIMENTAL NANO-SIZED HYDROXYAPATITE MODIFIED GLASS IONOMER LUTING AGENT.

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ABSTRACT

Objective: This paper describes the development and evaluation of an experimental luting agent formed by incorporating nanosized hydroxyapatite particles into glass ionomer luting cement and compares its properties to commonly used commercially available luting agents. **Method:** The nanosized hydroxyapatite was synthesized using co-precipitation technique and the resulting precipitate was characterized using X-Ray diffraction analysis, field emission scanning electron microscopy and transmission electron microscopy. The hydroxyapatite particles were incorporated into the glass powder(GC FUJI I, Japan) and the luting agent was manipulated in a liquid to powder ratio of 3:1 in proportion of 6% by weight. The flexural strength and shear bond strength to the tooth dentine were analyzed and compared with other commercially available luting agents which included Glass ionomer luting agent(GC FUJI I), Resin modified Glass ionomer luting agent (RelyX™ luting plus) and adhesive resin cement (RelyX™ U200). The fractured interface of the cement to the tooth dentine was evaluated under scanning electron microscope. **Results:** The results from this study demonstrated that the addition of 6 percent mass of HA of particle size in the range of 80-150 nm enhanced the flexural strength and shear bond strength of conventional glass ionomer luting agent when manipulated at a higher liquid to powder ratio of 3:1. **Significance:** Higher flexural and shear bond strengths of the experimental luting agent on comparison with those of the commercially available glass ionomer luting agent, confirms the beneficial role of HA in glass ionomer matrix and expands the scope of applications of glass ionomers.

KEYWORDS: Nano sized Hydroxyapatite, Glass Ionomer, Luting agent, Bond strength.

ABBREVIATIONS

HA- Hydroxyapatite
GIC- Glass Ionomer Cement
R- GIC – Resin modified Glass Ionomer Cement
XRD- X-Ray Diffraction
SEM- Scanning Electron Microscopy
FESEM- Field Emission Scanning Electron Microscopy
TEM- Transmission Electron Microscopy

INTRODUCTION

Cementation of indirect restorations to teeth by means of a luting agent is an important aspect of restorative treatment. 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.[1] Luting agents should meet basic mechanical, biological and handling requisites like compatibility with the tooth and the tissue, sufficient working time, good flow, high compressive strength, minimal microleakage, low solubility in oral fluids, adhesiveness, esthetics, low cost, ease of removal of any excess cement.[2] The choice of material used for the purpose of luting is solely the responsibility of the clinician. Since no single luting agent is capable of meeting all these stringent requirements, there is a plethora of luting agents currently available- ranging from water based agents to contemporary adhesive resin cements. This paper describes the development of an experimental luting agent formed by incorporating Hydroxyapatite(HA) into Glass ionomer cement(GIC)

and compares its properties to commercially available luting agents.

Glass ionomer cements(GIC) were invented in the late 1960s in the laboratory of the Government Chemists in Great Britain and were reported by Wilson and Kent in 1971.[3,4] This cement binds chemically to the dental enamel and to some extent to dentine and releases fluoride ions imparting an anticariogenic potential to the cement.[5-9] The major concern with this cement is its sensitivity to early moisture contamination and desiccation which compromises the integrity of the material.[3,4,6-23]

Various modifications of GIC have been documented with the objective of improving its clinical performance. Resin fillers have been incorporated into the glass to enhance the physical properties of the cement (low early strength and high water solubility). These resins are water soluble or polymerizable resins added to conventional glass ionomer cements in order to form hybrid cements.[2] In order to improve the antibacterial effect of the cement, chlorhexidine along with cetrimide has been incorporated in glass ionomer cements.[24] Various compositions of glass used for reinforcing the mechanical properties of the cement have also been described.[25,26]

Addition of HA to restorative GIC(Type II) has been reported in the past; and has been proved to influence the physical properties of GIC.[23,27-34] However, the effect of incorporating HA to glass ionomer luting agent has not been investigated in the literature. Hydroxyapatite (HA) is a calcium phosphate bioceramic with the molecular formula Ca_{10} $(PO_4)_6(OH)_2$ comprising of calcium and phosphorus in the ratio of 1.67:1. It is the main mineral component of the enamel of the tooth and comprises of more than 60% of the tooth dentine by weight.[23] In addition, HA also comprises the inorganic matrix of human bone in the form of phosphocalcic hydroxyapatite. Since HA has excellent biocompatibility and similarity in its composition and crystal structure to that of apatite in human dental and skeletal system, a number of studies have been carried out to study the effect of addition of HA powder to dental restorative materials such as GICs.[27-35] HA granules exposed on the surface of GIC facilitate a bioactive reaction involving carboxylate groups in the polyacid. Therefore, the incorporation of HA into the GICs may not only improve the biocompatibility of GICs but also enhance its mechanical properties.

This study describes the development of an experimental HA reinforced luting GIC, evaluates the flexural strength and shear bond strength of this combination to the dentine and compares it with conventional GIC and contemporary luting agents(resin modified GIC and adhesive resin luting agents).

MATERIALS AND METHODS

Analytical grade calcium hydroxide ($Ca(OH)_2$)(MERCK chemicals, Germany), orthophosphoric acid (H_3PO_4) (Qualigens Fine Chemicals, India), methanol ($CH_3(OH)$)(SDFCL, India) and ammonia solution (NH_3) (SDFCL, India) were used for synthesizing nano-sized hydroxyapatite. All the reagents were used without any further purification. The synthesized hydroxyapatite was then added to commercial glass ionomer powder (GC Fuji 1, Japan) and the resulting mixture was used for cement preparation. Commercially available GIC luting agent (GC Fuji 1, Japan), resin modified glass ionomer luting agent (RelyX™ luting plus cement, 3M ESPE) and resin adhesive agent (RelyX™ U200, 3M ESPE), were used for fabrication of samples of other groups included in the study.

Synthesis of Nano-sized Hydroxyapatite

Nano-sized HA was prepared by the co-precipitation method of synthesis.[36] Briefly, 1M of Calcium Hydroxide was dissolved in 150 ml of Methanol. A solution of 0.6M ortho-Phosphoric acid in Methanol was added drop-wise to the Calcium Hydroxide solution under vigorous stirring at room temperature. pH of the resultant solution was adjusted to 11 by means of ammonia solution. The precipitate obtained after the reaction, was aged at room temperature over a period of 24 hours under continuous stirring. This hydroxyapatite precipitate was then filtered and washed continuously with distilled water to remove unwanted ions and impurities. The resulting precipitate was dried in hot air oven at 80°C over duration of 24 hours. The powder was grounded using mortar and pestle initially and then ball milled over a period of 24 hours to achieve uniformity in the particle size of the precipitate. The precipitate was calcined in conventional box furnace in air atmospheric pressure at 900°C for 4 hours. The calcinations were done stepwise with intermittent ball milling so as to avoid lump formation.

Characterization of HA particles

X- Ray Diffraction Analysis (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM)

The X Ray powder diffraction (XRD) studies of nano-sized HA was carried out using a X-Ray diffractometer(Model D8 Advance by Bruker GmbH) with CuKα radiation(λ= 1.54Å). The scan was performed in the 2θ range 20-80^o at intervals of 0.03° with the count time of 0.6seconds. Sample identification was made by comparing the diffraction patterns with the JCPDS data. The XRD diffraction analysis of the nanosized hydroxyapatite was carried out at different stages of synthesis in order to evaluate the resulting precipitate. The surface morphology of the prepared nanosized HA powder was observed with FESEM microscope (Hitachi, Japan Model No S4800) operated at 10.0KV and with TEM microscope(Philips, Model No CM200) operated at 20-200KV.

Determination of Liquid/Powder (L/P) ratio and proportion of HA to be added to GIC by weight.

The synthesized nano-sized HA was incorporated into the glass powder of the commercially available GIC (GC Fuji 1, Japan). The nano-sized HA was added to GIC in 5 different proportions by weight (1%, 2%, 4%, 6%, 8%) and was manipulated at 3 varying L:P ratios(3:1, 4:1, 5:1) to test for the best possible flexural strength of the resulting HA modified GIC cement.

Fabrication of samples for testing of flexural strength

To prepare specimens for flexural strength measurements (n= 12 per group), polyvinylsiloxane putty(Flexceed, GC Corporation, Japan) molds of dimensions 25x2x2 mm were used in the study. GIC, resin modified GIC, adhesive resin luting agents were manipulated as per manufacturer's instructions. Based on favourable results obtained from a previous experiment, HA modified GIC was manipulated by adding 6% by weight of nano-sized HA to glass powder and mixing the same in L/P ratio of 3:1.The specimens were tested after 24 hours of preparation, for flexural strength using three point bending test with 20 mm span and at crosshead speed of 0.5mm/min (Model Instron UTM 5582) as outlined in ISO 9917-2:1996.[37]

Fabrication of samples for testing of shear bond strength to the tooth dentin

Freshly extracted non carious maxillary premolars (n= 15 per group) were cleaned off any soft tissues, blood and stored in distilled water. Teeth were randomly divided into four groups comprising of 15 samples each. The crown portions of the teeth were sectioned at the cemento-enamel junction. The crowns were sectioned vertically on the proximal aspect along the long axis of the tooth. The teeth were 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). To prepare the specimens for the shear bond strength measurement, a cylindrical silicone split mold (2 mm height, 4 mm diameter) was utilized. With the silicon mold set on the dentin surface, each material was syringe loaded into the mold and left to set for 24 hours. The specimens were retrieved by separating the silicone mold exerting minimal stress. The specimens thus obtained were mounted on a universal testing machine (Model Instron UTM 5582) and shear stress was applied at 0.5mm per minute crosshead speed and the load at which shear failure had occurred was recorded. The shear bond strength was calculated by dividing the fracture load over the area(πr^2; where r= 2 mm).[37]

Fractured Surface Analysis using Scanning Electron Microscopy(SEM)

Fractured specimens, one from each group was randomly selected and was analyzed with SEM to evaluate the type of failure that had taken place at the cement-tooth interface.

Statistical Analysis

The mean and standard deviation (SD) was calculated for each group studied for the comparison of flexural and shear bond strengths. Analysis was performed using Tukey's post hoc test.

RESULTS

X- Ray Diffraction Analysis (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM)

The XRD pattern of the synthesized nano-sized HA(Figure1) was compared with that of HA(JCPDS 00-009-0432). The XRD analysis of the nano-sized HA showed characteristic peaks of HA confirming the formation of hydroxyapatite. Few peaks corresponding to calcium oxide were also found in the analysis which could be the result of calcinations cycles performed on the precipitate. The crystal system of the hydroxyapatite 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 Scherrer's formula

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

wherein, t is the average crystallite size(nm); K is the shape factor (K= 0.9); λ is the wavelength of the X-Rays(λ=1.54056 Å for CuKα radiations); B is the full width at half maximum(radian) and θ is Bragg's diffraction angle(degree).[38] FESEM image of nano-sized hydroxyapatite is shown in Figure 2. The particles are hexagonal in shape which have clumped together to form an agglomerate. The particle size was distributed in the range of 80 nm- 150 nm. TEM image of nano-sized hydroxyapatite is shown in Figure 3. The HA sample consisted of particles having diverse sizes with hexagonal shape.

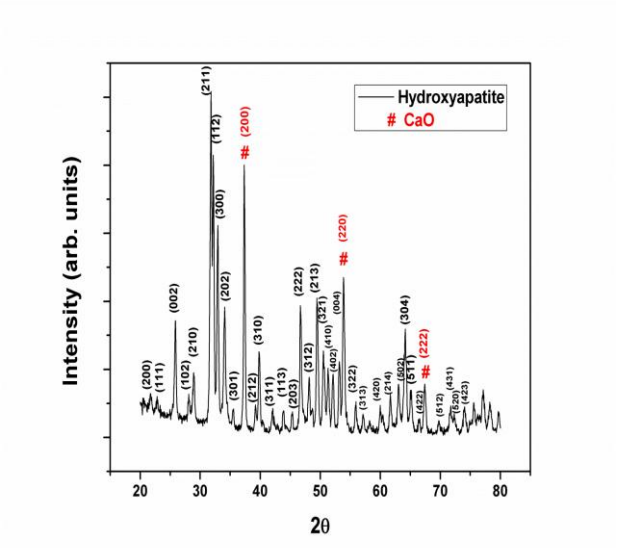

Figure 1- X Ray Diffraction analysis of the synthesized nanosized hydroxyapatite

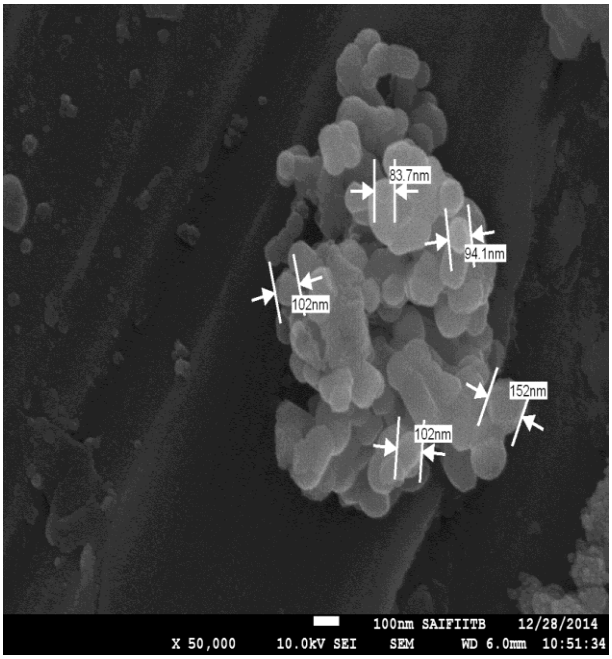

Figure 2- Field Emission Scanning Electron Microscope image of synthesized nanosized hydroxyapatite

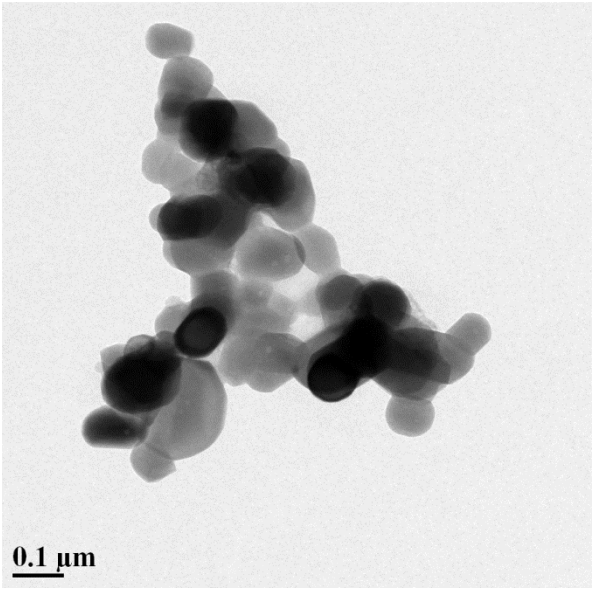

Figure 3- Transmission Electron Microscope image of synthesized nanosized hydroxyapatite.

Determination of liquid/powder ratio and proportion of HA to be added to GIC by weight

The average values of flexural strength of the samples prepared at different combinations of liquid to powder ratios and different weight proportions are displayed in the Table 1.

Table 1- Flexural strength of nanosized hydroxyapatite incorporated glass ionomer cements prepared with different combinations.

Sample	Liquid:Powder ratio	Flexural strength Average(MPa)
GIC+ 1% HA	3:1	11.59
	4:1	8.95
	5:1	6.86
GIC+ 2% HA	3:1	11.61
	4:1	11.53
	5:1	13.21
GIC+ 4%HA	3:1	11.91
	4:1	10.37
	5:1	10.01
GIC+ 6%HA	3:1	34.16
	4:1	21.38
	5:1	11.35
GIC+ 8%HA	3:1	11.88
	4:1	10.23
	5:1	6.55

The cement formed by incorporating nano-sized HA particles at 6% by weight into the powder of GIC, manipulated with liquid at l/p ratio of 3:1 showed highest strength amongst the other groups.

Hence, 6% weight proportion of HA and I/p ratio of 3:1 was used in the future experiments for adding nano-sized HA to the commercially available GIC.

Flexural strength of different luting agents

Figure 4 and Table 2 summarize the average values of flexural strength of glass ionomer cement, resin modified GIC, adhesive resin and HA modified GIC.

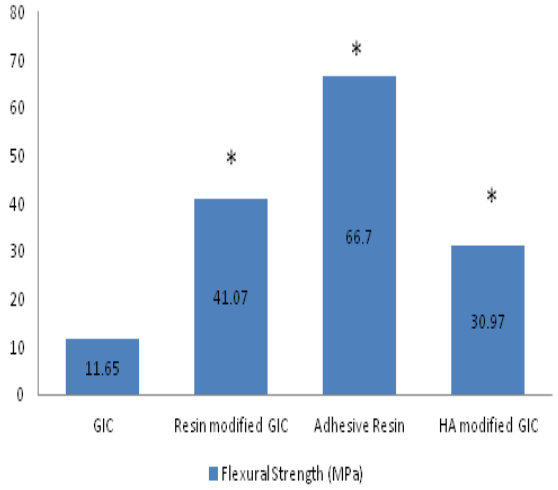

Figure 4- Graphical representation of the comparison of flexural strengths of luting agents. Significant difference between flexural strengths of GIC and other luting agents studied (* p<0.001)

Table 2- Mean with Standard Deviation values of flexural strengths of different luting agents.

Flexural strength(MPa)			
GIC	**Resin modified GIC**	**Adhesive Resin**	**HA modified GIC**
Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
11.65±5.63	41.07±11.50	66.7±5.26	30.97±5.90

Statistically significant difference was observed between the values of the flexural strength of all four cements. It was observed that, flexural strength of adhesive resin was highest(66.7 MPa) as compared to GIC which was lowest(11.65 MPa). Incorporating nano-sized HA to the GIC improved the flexural strength of GIC to 30.97 MPa. However, a difference of approximately 10 MPa was noted in the flexural strength of HA modified GIC(30.97 MPa) and resin modified GIC(41.07MPa).

Shear bond strength to dentin of different luting agents

Table 3 and Figure 5 summarize the fracture load and the shear bond strength to dentine of the four cements tested.

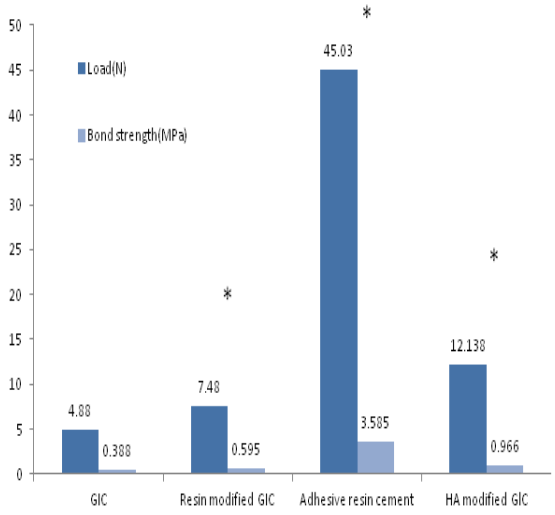

Figure 5- Graphical representation of the comparison of fracture load and shear bond strengths of different luting agents. Significant difference between fracture load and shear bond strengths of GIC and other luting agents studied (* p<0.001)

Table 3- Mean with Standard Deviation of the fracture loads and shear bond strengths of different luting agents.

Luting Agents	Fracture Load(N)	Bond strength(MPa)
	Mean ± SD	Mean ± SD
GIC	4.88±1.97	0.388±0.16
Resin modified GIC	7.48±5.00	0.595±0.399
Adhesive Resin	45.034±5.26	3.585±0.91
HA modified GIC	12.138±5.15	0.966±0.41

Fractured Surface Analysis using Scanning Electron Microscopy(SEM)

Surface analysis of the fractured dentine-cement interface was carried out by examining the fractured specimens under a scanning electron microscope at 500 X magnification. The presence or absence of residual cement on the dentine surface was used to classify the failures as cohesive or adhesive respectively. The conventional glass ionomer luting agent, HA modified glass ionomer luting agent and resin modified glass ionomer luting agent samples showed a cohesive ,failure with the presence of residual cement adhered to the tooth surface(Figure6,7,8) whereas the resin adhesive cement sample showed a cohesive failure(Figure 9).

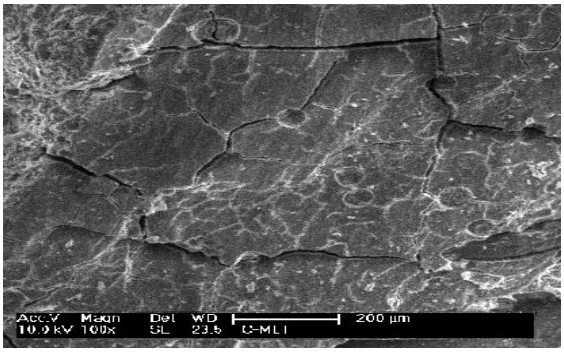

Figure 6 – Scanning Electron Microscope image of tooth-GIC interface.

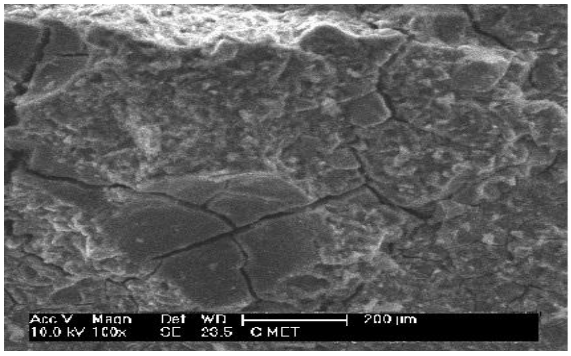

Figure 7- Scanning Electron Microscope image of tooth- HA GIC interface.

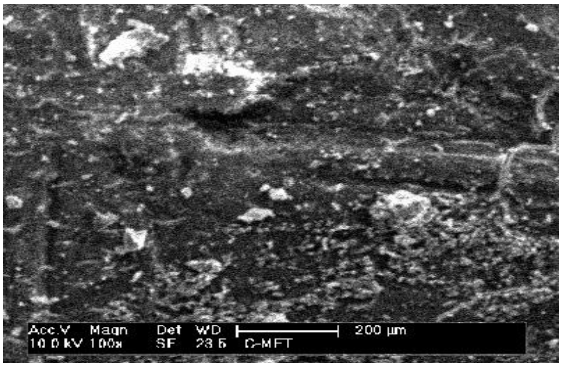

Figure 8-Scanning Electron Microscope image of tooth-Resin interface.

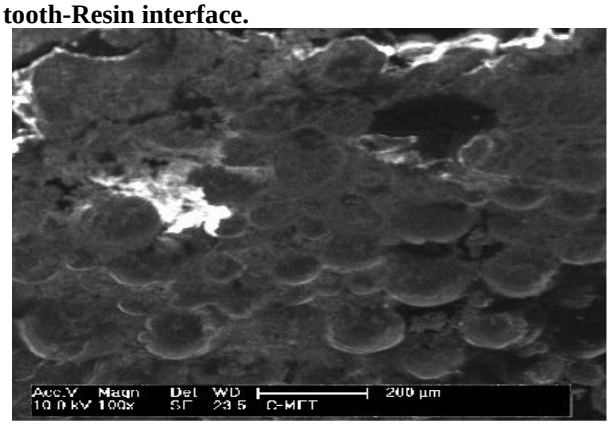

Figure 9- Scanning Electron Microscope image of tooth-Resin GIC interface.

DISCUSSION

The objective of this study was to improve the mechanical properties of glass ionomer luting agents using the chemical reactivity of hydroxyapatite with tooth and compare it with different luting agents commonly used in restorative dentistry. Hard tissues of vertebrates (bones, dentin, enamel) are natural composite materials, which contain hydroxyapatite (HA, $Ca_5 (PO_4)_3 OH$) together with protein, water and other organic substances, having a calcium to phosphorus ratio of 1.67.[39,40] Hydroxyapatite is always considered as a model compound of enamel due to its chemical similarity.[40] Therefore, the re-mineralization of enamel minerals by using synthetic apatite has always been suggested in dental research. HA is soluble in acidic solution and its solubility rate is rapidly increased with a pH below 2.0514.[41] Upon contact with polyacrylic acid, having pH of 1.23, calcium ions may get liberated from the surface of HA. A number of researchers have attempted to evaluate the effect of the addition of HA powders to restorative GICs.

The reaction mechanism between HA and GIC may be similar to that of adhesion of GIC to enamel and dentine, wherein, the interaction of apatite found in the tooth structure with the polyacrylic acid produces polyacrylate ions.[4] 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 ESCA(Electron Spectroscopy for Chemical Analysis) studies.[42] 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 aluminium phosphates and polyacrylates would form at the interface between the cement and HA(Figure 10). This layer is very resistant to acid and is difficult to break, hence, resulting in stronger bonds between the organic and inorganic network of the set cement.[43] Therefore, the incorporation of HA into GIC may improve its bonding characteristics to the tooth surface.

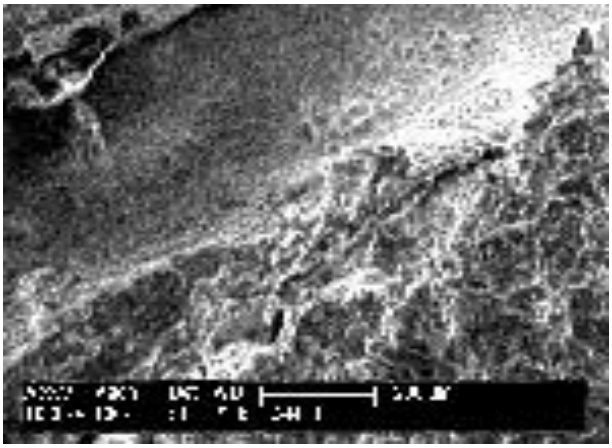

Figure 10- Scanning Electron Microscope image of the bonding interface between the tooth dentine and HA incorporated GIC luting agent.

HA modified restorative glass ionomer cements were first described by Nicholson et al[44] In 1993. Many studies have reported the effect of incorporating HA with varying compositions and crystallinity into restorative glass ionomers, to study the change in the mechanical behavior and fluoride release ability of resulting cement.[23,27-34] In a recent report by Arita et al[33], commercially available HA was used and four different morphologies of the same were incorporated into the glass powder in mass proportion of 8 percent. In the present study, the experimental hydroxyapatite was synthesized using co-precipitation technique and the synthesized precipitate was incorporated in mass proportion of 6 percent. The X-Ray diffraction analysis, FESEM and TEM images showed that HA particles were roughly spheroidal/ hexagonal in shape with size in the range of 80-150nm.

Considering the results from different manipulating combinations (Figure 11), it can be concluded that the chemical reaction taking place between the HA, glass powder and polyacid resulted in increase in flexural strength of the cement. The highest flexural strength was obtained at liquid to powder ratio of 3:1 with the addition of 6 percent HA to glass ionomer powder by mass. For the particle size being utilized in the study, further increase or decrease in the mass proportion of HA deteriorated the strength of the cement. Arita[29], Lucas[28] and Lee[32] reported that addition of HA to restorative GIC improved the flexural strength and bond strength to dentine. In this study the flexural strengths and the shear bond strengths of commercially available different luting agents (GC Fuji 1, RelyX™ luting plus, RelyX™ U200) were compared to those of experimental HA modified GIC. Flexural strength of RelyX™ U200 was observed to be the highest(66.7MPa). Significant difference in the flexural strength of HA modified GIC(30.97MPa) and GC Fuji 1 (11.65MPa) confirmed the chemical reactivity of HA with the glass powder and liquid of the glass ionomer cement. Shear bond test is probably more representative of the stress applied on the luting agents used for cementing dental restorations.[45] The shear bond strengths of HA modified GIC luting (0.966MPa) was observed to be more than that obtained with GC Fuji 1 (0.388MPa) and RelyX™ luting plus(0.595MPa). The results of the present study are in accordance with the previous studies who had reported enhancement of flexural strength and bond strength to tooth of the restorative glass ionomer cements. The flexural strength of the HA modified glass ionomer restorative cements had been reported to be in the range of 25- 30 MPa[33] while the shear bond strength in the range of 3.8-6.28 MPa.[28] The formation of an intermediate layer as a consequence of HA in glass ionomer matrix, resulted in stronger bond between the set cement and the tooth.

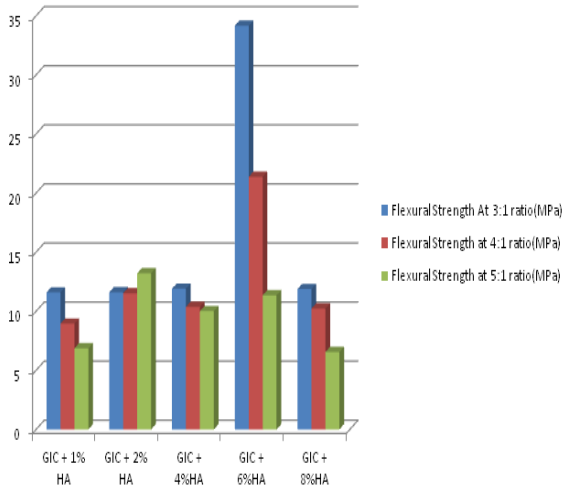

Figure 11- Graphical representation of the comparison of the flexural strength of different calibrations of HA incorporated GIC luting agents.

CONCLUSION

The results from this study demonstrated that the addition of 6 percent mass of HA of particle size 80-150 nm enhanced the flexural strength and shear bond strength of conventional glass ionomer luting agent when manipulated at a higher liquid to powder ratio of 3:1. Higher flexural and bond strengths of the experimental luting agent on comparison with those of commercially available luting agents, confirms the beneficial role of HA in glass ionomer matrix. This promising novel glass ionomer luting agent requires further investigation for its application in restorative dentistry.

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