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Mechanical properties and water sorption of two experimental glass ionomer cements with hydroxyapatite or calcium fluorapatite formulation

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In this study the mechanical behavior and water sorption (Ws) of experimental glass-ionomer-cements (GICs) with hydroxyapatite (HA) or calcium fluorapatite (CFA) prototype formulations were examined. Specimens from two experimental and one commercially available GIC were prepared in three protocols; (1) according to the manufacturer's instructions, (2) with coating and (3) with heat application. The specimens were stored in distilled water or artificial saliva at 37°C for 7- and 30-days. Flexural strength (FS), Vickers hardness (VHN) and Ws of GICs were evaluated. Experimental GICs showed higher FS values than commercial GIC ($p<0.001$). Higher FS and VHN values were observed when GICs were prepared according to manufacturer's recommendation. FS was affected only by GIC-type ($\eta^2=0.027$), whereas VHN was affected by GIC-type ($\eta^2=0.331$), treatment-protocols ($\eta^2=0.067$), storage-medium ($\eta^2=0.100$) and increased storage-duration ($\eta^2=0.317$). The tested parameters did not significantly influence the Ws of all tested GICs ($p>0.05$). The GICs with HA or CFA formulations might represent a promising approach due to their FS, VHN and Ws characteristics.

Keywords: Glass ionomer cement, Hydroxyapatite, Fluorapatite, Calcium fluorapatite, Mechanical properties

INTRODUCTION

Glass ionomer cements (GICs) have been widely used in clinical dentistry since 1971. They can be used as a lining, bonding, luting, sealing or restorative material. Compared to the conventional restorative materials such as resin-based composites, the advantages of GICs can be listed as fluoride release, anticariogenicity, biocompatibility, similar thermal expansion coefficient with dental hard tissues, direct adhesion to enamel and dentin without requiring an additional adhesive agent, and ease of use[1-5]. On the other hand, their low fracture toughness, slow setting reaction and moisture sensitivity are regarded as the main drawbacks of these cements[6].

GICs are formed by an acid-base reaction of alumino-silicate glass and an aqueous solution of polyalkenoic acid and set in two stages; the gelation phase which generally takes 10 min after mixing followed by the hardening phase including the slow release of the Ca^{2+} and Al^{3+} within the matrix and the formation of aluminum salt bridges[7]. The material becomes very sensitive to water uptake that may soften the surface in the first stage, while it is very susceptible to dehydration during the second step[8]. Early water exposure or dehydration significantly alters the final mechanical strength of the restorations[4].

To overcome the disadvantages mentioned above several attempts have been tried over the years. To avoid the problems within the early stage, protection of the GIC's surface is recommended. Petroleum jelly, different types of varnishes or light-cured resins have been used to sustain moisture levels in GICs. Recently, nanofilled, resin based light cured self-adhesives were introduced to improve the esthetics and physical properties of GICs. The main purpose of coating is, by covering the top surface of the restoration to protect against to saliva or dehydration until the setting reaction is completed and to increase wear resistance[8,9].

Furthermore, heat application by a light-curing unit during setting has been also suggested. Heat application is supposed to accelerate the setting reaction of GICs and thus getting over the initial critical setting period before exposure to saliva[10,11].

Considerable studies have been continued to enhance the mechanical or biological characteristics of GICs by incorporating several additives such as chlorhexidine, nanoclays, amino-acids, fibers, metallic powders, bioactive glass particles, montmorrilonite clay, hydroxyapatite (HA) and fluorapatite (FA) to the GIC[12-17].

Recently, it has shown that HA has promising advantages in restorative dentistry, with its hardness similar to natural tooth, intrinsic radiopaque response and biocompatibility. HA has been reported as a successful reinforcement material for adhesive bone cements and resin composites[18,19] and has been found to interact with *via* carboxylate groups in the polyacid of GICs[20].

In previous studies, the researchers added HA with nano particle sizes and different weight percentages (10–28%) to GIC powder or polyacid components at different P/L ratios (1.00, 1.25, 1.75, 2.33, 2.50, 3.60) by mixing procedures experimentally and it was shown that the addition of HA to GIC can increase its flexural strength (FS) while maintaining its compressive strength and simultaneously enhancing fluoride ion release[18,21,22]. Porous, spherical HA particles were found to be the most effective in this regard[16,17,23].

Other variables include the powder to liquid ratio, which in the case of GICs has a direct bearing on the concentration of reinforcing glass particles in the set

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material. The concentration of reinforcing glass particles together with the presence of voids produced either by air inclusions or inadequate wetting of powder by liquid will have an influence on mechanical properties. Central to the ability to achieve an effective contact between powder and liquid and a set material with low porosity is the method chosen for mixing[24].

On the other hand, FA or fluoridated HA were shown as having excellent biocompatible properties[23]. It is envisaged that the presence of HA and FA in the GIC matrix have the ability to increase the mechanical and bond strenght of the resulting material. Therefore, the incorporation of HA or FA into GIC may not only improve the biocompatibility of GIC but also have the potential of enhancing the mechanical properties.

Additionally, the strength of GICs is affected by incorporated porosity and this is dependent on the method of mixing. Encapsulated materials have certain inherent advantages over hand-mixed materials. The manufacturer controls the ratio of components and the mixing is performed in a reproducible manner, which is normally quicker and cleaner than hand mixing. At the end of mixing the encapsulated material is often ready for immediate use by injecting directly from the capsule. For hand mixing, the ratio of powder and liquid is variable, due to the differences in cement powder packing densities achieved on rolling the scoop and the manner in which the bottle is held and the drop of liquid created. The vibratory action of the conventional mechanical mixing machines has been reported to incorporate increased porosity into some encapsulated luting cements and GI restoratives compared with their hand-mixed equivalents[24-26]. Recently for the study, prototype GICs having HA or calcium fluorapatite (CFA) already added by the manufacturer to the encapsulated forms were produced as trial materials.

Thus, the aim of this study was to verify if these HA or CFA containing formulated prototype encapsulated GICs show comparable performance to conventional GIC. The effect of coating, heat application, storage medium (artificial saliva and distilled water) and storage duration were also evaluated. The null hypotheses tested were that: (1) the prototype GICs would not show significantly better performances than conventional GIC in terms of mechanical properties (FS and Vickers hardness (VHN)) and water sorption (Ws), (2) application of coating, heating and aging would not change the above-mentioned properties, (3) storage in saliva or water (7 and 30 days) would not result in similar mechanical properties.

MATERIALS AND METHODS

The two prototype encapsulated GICs tested were the following: F9ap-sphere (GC, Tokyo, Japan) and F9ap-CFap (GC). Conventional glass ionomer restorative cement Fuji IX GP (GC) was used as control. The materials' properties were summarized in Table 1. Three treatment protocol groups were established: (1) as recommended by manufacturer (without coating-control group); (2) with coating and (3) heat application with LED curing unit (Translux Power Blue, Heraeus Kulzer, Hanau, Germany) without coating during setting.

Specimen preparation

Group 1 (n=120): The encapsulated GICs were tumbled

Table 1 Materials, manufacturer and chemical composition of glass ionomer cements

Materials	Type	Manufacturer	Composition
Fuji IX GP	Conventional encapsulated glass ionomer cement	GC, Tokyo, Japan	Powder: 95% by weight alumino-fluoro-silicate glass with 5% polyacrylic acid powder. Liquid: 50% distilled water, 40% polyacrylic acid, and 10% polybasic carboxylic acid. Powder/liquid ratio: 3.6/1.0
F9ap-sphere	Experimental encapsulated glass ionomer cement	GC	Powder: 87 wt% alumino-fluoro-silicate glass, 5 wt% polyacrylic acid powder, 8 wt% spherical hyroxyapatite Liquid: 50% distilled water, 40% polyacrylic acid, and 10% polybasic carboxylic acid. Powder/liquid ratio: 3.6/1.0
F9ap-CFap	Experimental glass encapsulated ionomer cement	GC	Powder: 87 wt% alumino-fluoro-silicate glass, 5 wt% polyacrylic acid powder, 8 wt% calcium fluorapatite. Liquid: 50% distilled water, 40% polyacrylic acid, and 10% polybasic carboxylic acid. Powder/liquid ratio: 3.6/1.0
EQUIA-coat	Low-viscosity nanofilled surface coating resin	GC	40–50% methyl methacrylate, 10–15% colloidal silica, 0.09% camphorquinone, 30–40% urethane methacrylate, 1–5% phosphoric ester monomer

for 5 s to aerate the powder inside the capsule before activation. They were then mixed for 10 s using a mixing device (Softly™, Acteon New Zealand and Australia, Rosebery, Australia) according to the manufacturer's instructions. Bar-shaped test specimens (2×2×16 mm^3) were made using a half-split stainless steel mold. The tested materials placed on a glass slab, and covered with a transparent matrix strip. Another glass slab was pressed gently over the mold with finger pressure to evenly spread the material. The glass slab and transparent matrix strip were removed after GIC were set and the excess material was removed using a 1200 grit silicon carbide paper (LECO, St. Joseph, MI, USA)[27].

Group 2 (n=120): Specimens of this group were prepared in the same way as group 1. Then the coating material (EQUIA-Coat, GC) was applied with a micro-brush. All surfaces of the specimens were coated with the material without any pressure and polymerized by a LED curing unit (Translux Power Blue) with irradiance of 1,000 mW/cm^2 for 20 s.

Group 3 (n=120): Specimens were prepared same as group 1. Glass slab was immediately removed after the spread of the GIC, while the strip was maintained. LED curing unit was placed on top of the GIC surface immediately, so that it was in contact with the transparent matrix strip. To produce heat along the top surface of GIC specimens, the LED curing unit irradiance was used for three light exposures (3×20 s) during the setting reaction.

Specimens were removed from the molds and stored either in 50 mL artificial saliva (n=60) or in distilled water (n=60) at 37°C, and stored for 7 (n=30) or 30 (n=30) days. The distilled water and artificial saliva were changed twice a week; the volume of solution was kept constant. The composition of artificial saliva used was; Na_3PO_4 (3.90 mM), NaCl (4.29 mM), KCl (17.98 mM), $CaCl_2$ (1.10 mM), $MgCl_2$ (0.08 mM), H_2SO_4 (0.50 mM), $NaHCO_3$ (3.27 mM) and distilled water with the pH adjusted to 7.2[28].

FS test

The specimens were immersed in distilled water at room temperature (22°C) during loading. FS was evaluated by a three-point bending test (in analogy to ISO 4049:2009) using bar-shaped specimens (2×2×16 mm^3) with a universal testing machine (LR 30K, Lloyd Ins., West Sussex, UK). Before bending testing, each specimen was gently dried. A load with a constant crosshead speed of 1 mm/min was applied until fracture and FS (σ) was calculated from the formula[29]:

$\sigma=(3Fl)/(2bh^2)$

F: the maximum load (N)

l: the distance between the supports (12 mm)

b: the width of the specimens (mm)

h: the height of the specimens (mm)

VHN test

To determine VHN, fragments of the three-point bending test were used. All specimens were wet grounded with 2500 and 4000 grit SiC paper (LECO). The VHN values were measured with a micro-hardness tester (Shimadzu HMV/2000, Shimadzu, Kyoto, Japan). Fifty kgf load was fitted for 30 s to make indentations on the coated sight of GIC surfaces. Five indentations with a 100 μm distance were performed on the center of each specimen and mean values were calculated.

Ws test

Additional 60 disc-shaped specimens with 6 mm diameter and 2 mm thickness per group were produced for Ws evaluation. The specimens were first transferred to a desiccator maintained at 37°C for 24 h. At the end of 24 h all the specimens were weighed and this weight was recorded as the baselines dry mass (M_1) (mg). Then, specimens were immersed in 10 mL of artificial saliva or distilled water at 37°C according to the testing group for 7 and 30 days. The test medium was freshly prepared and replaced in every 24 h. The specimens were removed from the storage media at the end of the storage period. The specimens stored in artificial saliva were washed in distilled water. After the visible moisture was removed, they were weighed again. The value was recorded as the mass (mg) after water storage (M_2). Finally, Ws was determined in $\mu g/mm^3$ using the formula as[30]:

$Ws=(M_2–M_1)/V$, where V is the specimen volume in mm^3.

Statistical analysis

The Kolmogorov-Smirnov test was applied to verify if the data were normally distributed. Results were compared with one-way ANOVA and Tukey's HDS *post hoc* test (α=0.05). A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect's strength of the parameters; GIC type, preparation protocols, storage medium and storage duration on the considered properties. The partial eta-squared statistic reports the practical significance of each term, based upon the ratio of the variation accounted for by the effect. Larger values of partial eta squared indicate a greater amount of variation accounted for by the model effect, to a maximum of 1.

RESULTS

The FS values and standard deviations of all groups were summarized in Table 2. Prototype GIC groups showed higher FS values than Fuji IX GP (Fig. 1a). This difference was found statistically significant (p=0.007). FS values were affected only from GIC material type (η^2=0.027, Table 3). The other parameters (preparation protocols: -coating or heating, -storage medium, -distilled water or artificial saliva and -storage duration —7 and 30 days—) did not affect the FS values. The highest FS values were observed when materials were prepared according to manufacturer's recommendations. The lowest FS values were observed when specimens were coated (Fig. 1b). Specimens stored in distilled water showed higher FS values than in artificial saliva (Fig. 1c). FS values of all tested GICs decreased with the

Table 2 Flexural strength (FS) was detailed in mean values (MPa) and standard deviations (SD)

GICs	Control (n=120)				Coat (n=120)				Heat (n=120)			
	Distilled water		Artificial saliva		Distilled water		Artificial saliva		Distilled water		Artificial saliva	
	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days
Fuji IX GP	9.2 (3.1)[a]	8.7 (0.3)[a]	11.5 (1.0)[a]	10.1 (1.0)[a]	11.7 (1.0)[a]	10.5 (1.0)[a]	11.9 (0.7)[a]	10.7 (0.6)[a]	11.8 (1.2)[a]	11.0 (1.0)[a]	11.3 (1.0)[a]	9.8 (1.1)[a]
Fuji 9ap-sphere	11.9 (0.8)[b]	20.8 (30.6)[b]	12.3 (0.5)[b]	11.1 (0.3)[b]	12.4 (0.5)[a]	11.3 (0.8)[a]	11.9 (0.6)[a]	10.5 (0.7)[a]	12.5 (0.8)[b]	11.3 (0.7)[a]	13.3 (0.6)[b]	12.6 (0.8)[b]
Fuji 9ap-CFap	12.9 (0.7)[b]	12.1 (0.6)[c]	12.4 (0.9)[b]	11.3 (1.9)[b]	12.7 (0.8)[b]	11.6 (1.2)[b]	13.3 (0.5)[b]	12.8 (0.6)[b]	12.1 (0.6)[a]	11.2 (0.8)[a]	13.3 (0.4)[b]	12.5 (0.5)[b]

*Same uppercase letter in same column indicates no significant difference (p<0.05).

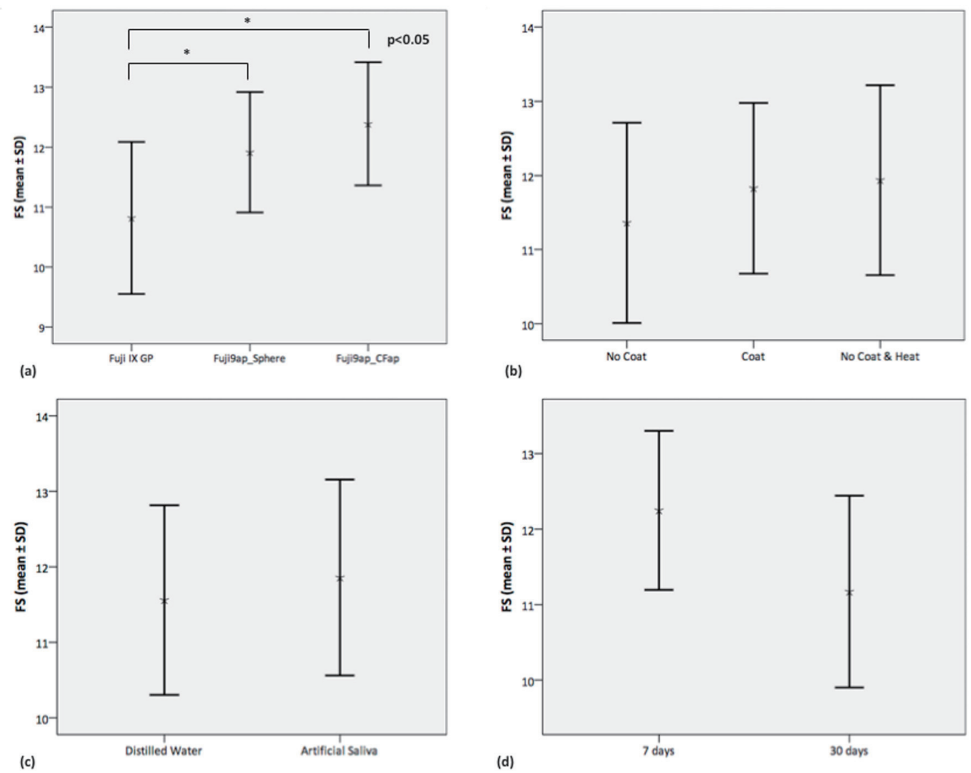

Fig. 1 Comparison of FS values according to (a) GIC types, (b) treatment protocols, (c) storage medium, (d) storage duration.

Table 3 Influence of GIC type, treatment protocol, storage agent and storage duration on flexural strength (FS), Vickers hardness (VHN) and water sorption (Ws)

	FS	VHN	Ws
GIC type	0.027	0.331	ns
Treatment protocols	ns	0.067	ns
Storage agent	ns	0.100	ns
Storage duration	ns	0.317	ns

The higher the partial eta-squared values, the higher is the influence of the selected variables on the measured properties (general linear model (η^2))
ns: non-significant.

prolonged storage time (Fig. 1d).

VHN values and standard deviations of all test groups are summarized in Table 4. The VHN values were affected by GIC material type (η^2=0.331), storage medium (η^2=0.100) and storage duration (η^2=0.317, Table 3). Fuji XP GP showed higher VHN values than experimental GICs (Fig. 2a) and higher VHN values were observed when the materials were prepared according to manufacturer's recommendation (η^2=0.067, Table 3, Fig. 2b). These differences were found statistically significant (p<0.001). Specimens received heat application showed lowest VHN values (Fig. 2b). Storage in artificial saliva showed higher VHN values than storage in distilled water (Fig. 2c). The VHN values were decreased when the storage duration was increased (Fig. 2d).

The Ws values obtained for tested materials are presented in Table 5. The tested parameters (GIC type, preparation protocols, storage medium and storage duration) did not significantly affect the Ws values (Table 3).

Table 4 Vickers hardness (VHN) (N/mm^2) was detailed in mean values and standard deviations (SD)

GICs	Control (n=120)				Coat (n=120)				Heat (n=120)			
	Distilled water		Artificial saliva		Distilled water		Artificial saliva		Distilled water		Artificial saliva	
	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days
Fuji IX GP	172.8 (10.6)^a	152.2 (31.8)^a	166.5 (5.8)^a	143.2 (18.5)^a	145.1 (4.0)^a	127.9 (36.5)^a	160.1 (6.0)^a	135.3 (12.6)^a	144.5 (6.9)^a	128.8 (26.5)^a	157.2 (6.4)^a	131.6 (22.0)^a
Fuji 9ap-sphere	125.3 (5.2)^b	104.3 (11.2)^b	175.5 (7.9)^a	150.8 (29.5)^a	134.4 (8.0)^a	113.5 (16.1)^b	146.9 (5.3)^b	121.8 (16.9)^b	129.3 (6.3)^b	109.2 (16.1)^b	146.7 (6.8)^b	121.4 (22.4)^b
Fuji 9ap-CFap	130.9 (7.1)^b	110.9 (21.1)^b	128.8 (4.6)^b	103.7 (15.1)^b	129.4 (5.3)^b	109.8 (12.4)^b	131.1 (5.3)^b	106.3 (14.0)^c	120.9 (6.2)^b	100.6 (22.9)^b	141.1 (6.4)^b	116.7 (20.9)^b

*Same uppercase letter in same column indicates no significant difference (p<0.05).

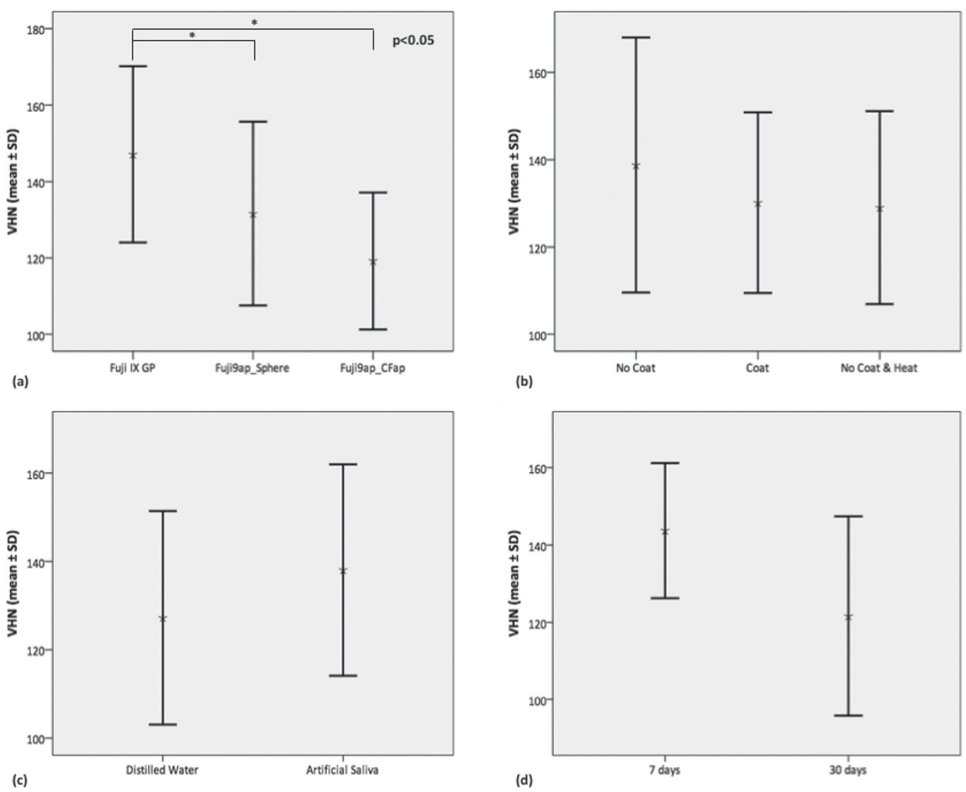

Fig. 2 Comparison of VHN values according to (a) GIC types, (b) treatment protocols, (c) storage medium, (d) storage duration.

Table 5 Water sorption (μg/mm^3) was detailed in mean values and standard deviations (SD)

GICs	Control (n=60)				Coat (n=60)				Heat (n=60)			
	Distilled water		Artificial saliva		Distilled water		Artificial saliva		Distilled water		Artificial saliva	
	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days
Fuji IX GP	36.8 (25.3)[a]	83.4 (8.1)[a]	24.6 (20.9)[a]	57.1 (44.2)[a]	54.1 (20.1)[a]	80.5 (8.3)[a]	44.4 (18.6)[a]	83.2 (29.2)[a]	36.0 (19.6)[a]	81.7 (4.7)[a]	44.4 (61.4)[a]	48.9 (43.3)[a]
Fuji 9ap-sphere	37.7 (12.2)[a]	92.2 (8.6)[a]	34.1 (18.3)[a]	68.5 (12.6)[a]	43.9 (17.8)[a]	93.8 (7.6)[a]	58.1 (22.1)[a]	119.8 (24.5)[a]	46.4 (14.6)[a]	93.6 (11.5)[a]	47.0 (23.2)[a]	77.6 (57.6)[a]
Fuji 9ap-CFap	42.0 (10.6)[a]	97.2 (4.0)[a]	56.3 (19.8)[a]	110.1 (23.0)[a]	44.8 (20.0)[a]	80.3 (40.9)[a]	59.4 (19.9)[a]	128.8 (30.9)[a]	42.5 (17.7)[a]	100.9 (6.1)[a]	42.8 (14.4)[a]	101.9 (29.2)[a]

*Same uppercase letter in same column indicates no significant difference (p<0.05).

DISCUSSION

Present study examined the effect of heat, coating, storage medium and aging on the mechanical behavior and Ws of two experimental GICs containing HA or CFA in comparison with a well-known commercial GIC. According to the manufacturer, these experimental GICs should present increased mechanic properties compared to traditional GICs.

In 1984, Yamamoto added HA to conventional GIC to improve the biocompability of GIC[31]. Later, Yap *et al.* showed that the addition of HA increased the hardness of GIC and recommended the use of this bioactive cement[21], Arita *et al.* reported improved mechanical strength of GIC, in the absence of resins or fillers by adding of HA whiskers[18].

On the other hand, Moshaverinia *et al.* added nanoparticules (100–200 nm) of HA and FA to GIC powder and the mechanical test results showed that both glass powders had higher strength compared with a commercial GIC while, GIC with FA had higher values compared with GIC with HA which can be related to the stability of FA and its lower dissolution rate[16]. In contrast to their study Lin *et al.* reported that incorporating of 25 wt% nano-fluroapatite or nano fluorohydroxapatite reduced the microtensile bond strength and shear bond strength of the experimental GIC[23].

The two experimental HA or CFA (8 wt%) containing with 3.6 P/L GICs tested in the study were not prepared by the authors but already prepared and encapsulated by the manufacturer. This amount is slightly below the recommended value of 12–28 wt% in the literature to improve the mechanical properties of the GICs[21]. In addition, Gu *et al.* reported that GICs containing 4 wt% HA particles exhibited enhanced mechanical properties in comparison with commercial GICs[32].

GI restoratives have an increased powder to liquid mixing ratio (2.7/1.0–3.6/1.0 g/g) compared with GI luting cements (1.8/1.0 g/g). The P/L ratio for Fuji IX and experimental GICs tested in this study was 3.6, such that more powder has to be incorporated into the liquid resulting in improve mechanical properties of these restorative GICs.

Hand-mixing has been reported to introduce operator induced variability due to the inaccurate dispensation of the powder and liquid constituents using scoop and dropper bottle systems. The volume of powder dispensed utilizing a scoop can vary due to the powder packing density achieved on filling the scoop and dropper bottles frequently dispense un-calibrated volumes of the liquid due to variations in the angle at which the bottle is held and the pressure applied to squeeze a drop. The variations in the powder to liquid mixing ratios utilized in clinical practice are further exacerbated when scoop and dropper bottle systems are not utilized and the constituents are mixed by 'eye' to the operators' desired consistency. As a result, the functional characteristics normally associated with hand-mixed luting cements prepared at the manufacturers' recommended powder to liquid mixing ratios are rarely achieved in clinical practice[33]. Taking these facts into consideration, the use of the GICs in the encapsulated forms in this study provided an advantage in terms of standardization of the results and reliability of the results.

FS test was frequently used to evaluate GICs in laboratory settings[34,35]. Arita *et al.*[18] and Moshaverinia *et al.*[16] examined the effect of the adding of HA or FA into the GICs powder and reported that, adding HA and FA improved the flexural and microstructural properties of GICs.

It was reported that particle size or quantity of additives could influence the mechanical strength of GICs. Nicholson *et al.* observed a progressive deterioration in the compressive fracture strength of experimental GICs with the increasing fine-grit HA particle content[36]. Lucas *et al.* showed that the HA substitution clearly increased fracture toughness of GIC[37], whereas Yap *et al.* indicated that, the incorporation of the HA powder resulted in a marked deterioration in the compressive fracture and diametral tensile strength following 24 h and 1 week water storage[21].

In the present study, experimental GICs showed higher FS values than Fuji IX GP. A chemical reaction

between the HA, glass powder and polyacid or the lower dissolution rate of FA may be the cause of increase in the flexural strength. Moreover, this increase in FS can be attributed to the specific properties of HA or CFA of the experimental GIC particles; such as the size of the particles, surface area, porosity of the surface and capacity of crystallinity.

All the tested GICs showed higher VHN values when prepared according to manufacturer's recommendation but Fuji XP GP showed higher VHN values than experimental GICs which is in accordance with the studies of Woolford[38], Menne-Happ, Ilie[11] and Dehurtevent *et al.*[39]. Both HA and CFA are involved in the acid-base reaction of GIC and react with inorganic/organic components of the GICs *via* their phosphate and calcium ions but the mechanical strength of these cements were seemed decreased. This is due to the gradual resorption of HA or FA particles incorporated into the cements after prolonged soaking in distilled water or artificial saliva. Resorption of HA or FA is time dependent and governed by the stability of the particles used. A previous study with a relatively lower crystallinity HA showed a significant decrease in the mechanical properties of GIC after 1 week[40]. It is possible to expect that HA or FA resorption may lead to the degradation of GIC interface, thus deteriorating the mechanical properties[32].

Matrix composition, the size of filler content and distribution, mixing method, and different immersion medium as well as the powder to liquid ratio could affect the water absorption of GICs[32,41,42]. Storage time and medium can be influential factors on Ws kinetics. Small molecular-sized HA or FA particles can gradually resorb in a time-dependent manner, which can also deteriorate the mechanical properties of GICs after prolonged soaking[32]. Moreover, water molecules can penetrate into the interpolimer chains thereby can cause deterioration of strength[43].

Water absorption levels of GICs tested in this study were within the similar range. Therefore, the effect of HA or CFA addition into the GIC composition could not be interpreted. Similarly, Aliping-McKenzie *et al.* reported that the Ws characteristics were found to be unaffected by the nature of the storage medium[41].

Water uptake or loss during the setting reaction would reduce the mechanical properties of GICs to preserve the balance between water uptake and loss[44,45]. It has been shown that the coating increases the FS *via* maintenance of the water balance and the inhibition of hygroscopic expansion, leading to less dimensional change and can also be beneficial in preventing the formation of surface porosities and cracks[46-49].

Bonifacio *et al.* investigated the effect of coating on a GIC (Fuji IX Extra) and reported significant difference in FS when coating was used[47]. On the other hand, Zoergiebel and Ilie examined the effect of coating on micro-mechanical properties of different GICs and reported a non-significant improvement in the hardness[50]. In the present study, coating did not improve the FS or VHN values of GICs. This result might be due to the chemical composition of the experimental GICs tested or the storage medium or storage duration of the specimens.

The setting process of GIC is characterized by an interaction between polyacid liquid and a glass powder. The use of heat is supposed to improve the mechanic properties by accelerating the matrix-forming reaction[38]. The heat energy can be supplied by LED, halogen lamp or ultrasonic excitation[11].

Woolford[38], Menne-Happ and Ilie[11] and Dehurtevent *et al.*[39] reported no-effect on mechanical properties, when materials were heated during setting reaction. On the other hand, Fabián Molina *et al.* reported that heating the GICs with an LED curing increased the biaxial FS value of GICs[51]. In the present study, heat application through the use of an LED 1,000 mW/cm^2 curing unit during setting did not show an improvement on the mechanical properties. This may also originate from the chemical formulation of the GICs used. In another study, it was reported that heat application enhances the reaction rate but does not influence the mechanical properties of the GICs[11].

Two different storage media were used in the present study and storage of GICs in artificial saliva showed higher VHN values than storage in water. Artificial saliva used in the experiment was composed of various chemical components simulating oral conditions. The higher VHN values may be due to salivary components, including calcium and phosphate diffusing into GIC structure. Okada *et al.* also investigated the effects of saliva and distilled water used as storage media and the storage period on the surface hardness of Fuji IX[52]. They reported that Fuji IX did increase in VHN with time at both storage conditions but the increase rate of saliva was higher than distilled water.

In the present study, VHN values of the all GICs were negatively affected from prolonged water storage in correlation with the study of Silva *et al.*[7]. On the other hand, Ellakuria *et al.* also examined the effect of storage time on microhardness of GICs and reported that the increase in storage time produced an increase in microhardness[53].

This study has highlighted the possible potential for improving the performance of GIC when using HA or CFA as reinforcement. The addition of HA or CFA in experimental GICs did not show better performances than the conventional GIC in terms of VHN. FS values of experimental GICs were higher than the conventional GIC whereas Ws values were similar for all tested GICs. Thus, the data support partly rejection of the first null hypothesis. Coating or heating did not influence the FS but VHN values of the GICs were affected by heat application. Aging decreased both of the mechanical properties. So, the second null hypothesis was also partly rejected. Storage in artificial saliva or distilled water did not show similar mechanical properties; thus, third null hypothesis was accepted but as this study was generated under laboratory conditions the results were far removed from clinical practice.

CONCLUSIONS

Within the limitation of this *in vitro* study the following conclusions were drawn:

1. Addition of HA or CFA to GIC may enhance the FS of GIC,
2. Inclusion of HA or CFA in GIC did not seem to improve the micro hardness of tested experimental GICs,
3. Ws was not affected by all tested parameters,
4. Coating or heating has no influence on FS of the tested GICs,
5. Microhardness of the GICs was seemed to be affected by heat application,
6. Aging seemed to affect FS and VHN negatively,
7. FS and VHN of the tested GICs could be affected differently from storage media.

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