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Journal of Materials Research and Technology
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Original Article

Influence of hydroxyapatite nanoparticles on the properties of glass ionomer cement

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ARTICLE INFO

Article history:

Received 29 August 2017

Accepted 15 January 2018

Available online xxx

Keywords:

Glass ionomer cement

Nano hydroxyapatite

S. mutans

Fluoride ion

Compressive

ABSTRACT

Glass ionomer cement (GIC) is an important restorative dental biomaterial which is utilized in filling, lining and adhesion restoration. The aim of this work is the enhancement of the mechanical, morphological, antibacterial and fluoride release properties of the glass ionomer cement by incorporation of different wt% of nano hydroxyapatite powder (HA). The result of this work refers to that, the addition of nano-HA to GIC enhance its fluoride ion release, compressive strength and antibacterial effect against *Streptococcus mutans* and the bacterial inhibition zone reached to about 8.6 mm when 8% HA wt% is used. This suggests that addition of nano-HA particles to GIC to produce GIC-HA hybrids which can be used as suitable materials for improving its fluoride ion release, mechanical properties and inhibiting residual bacteria in dentine.

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1. Introduction

Glass ionomer cement (GIC) was invented by Wilson and Kent [1] in 1969 and developed by Mclean and Wilson [2] in 1970, where GIC is a cement consisting of a basic glass and acidic polymer which sets by an acid–base reaction. GIC term covers two sub-groups which are glass–polyacenoate and glass–polyphosphonate [3,4].

In 1990s, the highly viscous conventional glass ionomer cement (C-GIC) was produced by a neutralization reaction between a basic calcium or strontium salt of fluoro-alumino-silicate glass powder with an electrolyte acidic water soluble

polymers and copolymers of acrylic, itaconic, maleic and vinyl phosphonic acids [5]. The freeze dried electrolyte acidic water soluble acidic polymers attacks the basic glass powder resulting in glass surface degradation and releasing of metal ions as Ca^{2+} , Sr^{2+} , Al^{3+} and non metal F^- . Carboxylic group of acidic polymers reacts with the released metal ions forming salts of polyacid which combine with silica hydrogels forming a cement matrix. Glass ionomer cement has a mortar form and is usually used as a filling material in dental treatments as base material or adhesive in the deciduous teeth restoration [6].

However, C-GIC has some deficiency in its mechanical properties because it is highly sensitive to moisture and its fast dehydration. These insufficient mechanical properties of C-GIC led to limitation of its applications in the non-stress bearing regions. For GIC strengthening and wear resistance

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<https://doi.org/10.1016/j.jmrt.2018.01.010>

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improving, several ways were carried out as; "Maiacle mix" was produced in 1980s by blending the silver amalgam with C-GIC [7]. Also "Ketac siver" was obtained by addition of Ag metal into GIC powder under the effect of high temperature. Silver modification of GIC properties did not achieve desired results in enhancement of the stress bearing areas harness and resistance [8,9]. Photo polymeric resin, which acts as strengthening material when meets a visible light was used to produce moisture protected resin-GIC (R-GIC). The produced R-GIC has a higher mechanical and resistance properties than C-GIC. Resin-GIC (R-GIC) can also be obtained via hydroxyethyl methacrylate (HEMA) or Glycidyl Methacrylate monomer (GMA) free radical polymerization producing poly(HEMA) or poly(GMA) bonded with the poly acid with a covalent bond resulting in insoluble material with both ionic and covalent bonds. Improvement of the mechanical properties of polymeric materials by nanoparticles incorporation was studied [10,11]. Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ is a natural mineral and called "bone mineral" and have feature properties that are favourable in dental restoration. It is utilized in enhancement of surface hardness, toughness and biocompatibility because Hydroxyapatite structure looks like natural tooth. Hydroxyapatite nanoparticles addition to R-GIC was used for production of materials similar to human hard tissues used in dental restoration [12,13]. The aim of this work is investigation the effect of hydroxyapatite nanoparticles addition on the mechanical, chemical, fluoride release and antibacterial properties of conventional glass ionomer restorative material.

2. Materials

Glass ionomer cement (GIC) supplied from Riva, SDI, Australia. GIC consists of two parts, (i) powder part composed of strontium fluoro-silicate glass powder, polyacid copolymer powder and pigments. (ii) Liquid part composed of acrylic acid copolymer, tartaric acid, water, accelerants and hardeners.

Nano-hydroxyapatite powder with molecular weight: 502.31 g/mol and particle size less than 200 nm, supplied from Sigma, Aldrich, Germany.

Mitis Salivarius agar medium, supplied from RalinBV, Netherlands, the agar media composed of Casein enzymatic hydrolysate, crystal violet, dextrose, dipotassium phosphate, peptic digest of animal tissue, sucrose and tryptan blue. *Streptococcus mutans* (*S. mutans*) from Microbiologics, Inc., USA, ATCC; 25127.

3. Methods

3.1. Preparation of C-GIC control sample [14]

Conventional self-cure glass ionomer cement (C-GIC) powder and liquid were mixed at a powder/liquid ratio of 2.17:1 (W/W) according to manufacturer instructions [14]. The Mixing of the powder and liquid was done using a metal spatula and a glass slab at room temperature. The mix was then placed in a pre-fabricated Teflon mould having 5 holes (10 mm in diameter and 2 mm in height), and then covered with a celluloid strip and a microscopic glass slab under hand pressure. The glass

ionomer was allowed to set at room temperature for 15 min, then the bottom of the mould was pushed upwards using finger pressure to remove the disc specimen. The excess material was removed, thereafter, gently with a scalpel.

3.2. Preparation of C-GIC-HA hybrid

Experimental material powder was prepared by mixing different wt% (1:10%) of nano-hydroxyapatite (HA) powder with GIC powder and evenly mixed. The nano-HA powder was mixed with GIC powder by a spatula on a glass slab. The powder containing 5 wt% nano-HA and liquid of GIC material were mixed according to manufacturer's instructions with a ratio of 2.17:1. Disc specimens were then prepared as described previously.

3.3. Evaluation of antibacterial activity in vitro materials [15]

3.3.1. Preparation of the culture medium

Culture media for *S. mutans*; Mitis Salivarius Agar was prepared according to manufacturer instructions as follows: 90 g Mitis Salivarius agar, and 200 g sucrose were dissolved in 1 l of distilled water. The medium was then heated to dissolve the components, then autoclaved at 121 °C. The medium was left to cool at 45 °C, after which 1 ml of 1% sterilized potassium tellurite solution and 5 µg Bacitracin were added. Sterile plates were poured with nearly 20 ml of the medium and the plates were allowed to dry for 24 h at room temperature, plates were then stored in the refrigerator at 4 °C.

3.3.2. Test method

The antibacterial spectrum of C-GIC-HA hybrids with different HA wt% samples were determined against the test bacteria by disc well-diffusion method on an agar plate [16]. Briefly incubated cultures of bacteria were swabbed uniformly on the individual plates using sterile cotton swabs on the Mitis Salivarius Agar, 50 µl of C-GIC-HA hybrid samples with different HA wt% were loaded in sterile disc, Plates were incubated at 37 °C for 24 h. The inhibition effect was verified by the presence of inhibition zones around the discs where the solution was deposited and sized for analysis and comparison.

3.4. Fluoride ion measurement

3.4.1. Specimen preparation

Ten discs specimens from control C-GIC and from each C-GIC hybrid (10 mm in diameter and 2 mm in height) were prepared using fabricated Teflon moulds. Specimens were stored at 37 °C for 25 h. Each specimen was immersed in 20 ml of deionized water in a closed plastic container at 37 °C. At the time of fluoride ion measurement, each specimen was removed from its container and the storage solution was collected for analysis. The discs were plotted dry and then placed in a new container with fresh 20 ml of deionized water [17].

3.4.2. Test method

Measurement of fluoride ions concentration were made using ion selective electrode [18], at 24 h, 48 h, 72 h, 7 days, 14 days and 28 days.

Results were calculated as the amount of fluoride per unit surface area of the specimen ($\mu\text{g}/\text{mm}^2$). Fluoride levels in ppm were obtained using the ion-selective electrode connected to a digital metre. Total fluoride in μg was calculated by multiplying the $1 \text{ ppm} = 1 \mu\text{g}/\text{ml}$ by the tested solution volume (20 ml). The total fluoride was then divided by the area of the sample disc to obtain the fluoride release in $\mu\text{g}/\text{mm}$ [19].

3.5. Compressive strength measurement

3.5.1. Specimen preparation

Ten cylindrical C-GIC specimens and from each C-GIC hybrid (6 mm in height and 4 mm in diameter) were made using pre-fabricated Teflon moulds and tested for compressive strength according to ISO 9917 [20]. The specimens were stored at 37°C for an hour and then immersed in a small container for incubation in water at 37°C for 7 days [21].

3.5.2. Test method

Compressive strength (CS) was assessed at 7 days after mixing. Wet specimens were placed in a vertical position with force incident on their long axis, and loaded in compression at a crosshead speed of 1.0 mm/min in a universal testing machine (Model WDW-20, Beijing Sinofound; Beijing, China), until fracture occurred. The CS was calculated by the following formula: $P/\pi r^2$, where P is the load at fracture, r is the radius of the specimen, and $\pi = 3.14$. The CS values [kgf/mm^2] were converted into Mega Pascal (MPa) as follows [22]:

$$\text{CS [MPa]} = \text{CS [Kgf/mm}^2] \times 0.09807$$

3.6. Scanning electron microscope (SEM)

Specimens for this study were cut from the samples. Specimen size was 10 mm diameter and it was circular in shape. These samples subjected to sputter coating (Edwards's model S140A) of gold ions to have a conducting medium. Sputter coated samples were scanned with JEOL Model JSM-T20 SEM.

3.7. Fourier transform infra-red (FT-IR)

FTIR was used for monitoring the chemical characterization and modification which occurred in the C-GIC after HA nanoparticle addition. Thus, the samples were analyzed

before and after HA addition with a FTIR spectrometer (Model 6100 Jasco, Japan). Each spectrum was obtained in the transmission mode with TGS detector and by using KBr method and represents (2 mm/s) co-added scans at the spectral region ranging from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} .

4. Results and discussion

4.1. Antibacterial effect

The antibacterial effect of C-GIC and its HA hybrids with different HA wt% against *S. mutans* bacteria is illustrated in Fig. 1. From the figure, it can be concluded that, the pure C-GIC almost did not record any inhibition zones when applied to *S. mutans* bacteria. The results also showed that, the increasing in HA wt% till 8% enhance the antibacterial effect of C-GIC-HA hybrid against *S. mutans* and the bacterial inhibition zone reached to about 8.6 mm.

4.2. Fluoride release measurement

It is known that nano HA particles have a large surface area due its small size, and its addition to C-GIC led to increasing the acid-base reaction activity, then, increasing the release of fluoride ion [23].

Fluoride ion release ($\mu\text{g}/\text{mm}^2$) was determined by immersion of C-GIC and its hybrids with different HA wt% in deionized water for 24 h, 48 h, 72 h, 7 days, 14 days and 28 days and the results are listed in Table 1 and illustrated in Fig. 2.

Table 1 – Fluoride ion release from C-GIC and its hybrids with different HA wt% for different immersion time.

Immersion time	HA wt%					
	0%	1%	3%	5%	8%	10%
24 h	0.12	0.11	0.10	0.10	0.09	0.09
48 h	0.09	0.15	0.16	0.18	0.21	0.21
72 h	0.06	0.09	0.18	0.20	0.27	0.26
7 days	0.05	0.08	0.22	0.29	0.30	0.30
14 days	0.06	0.08	0.14	0.19	0.36	0.30
28 days	0.05	0.07	0.10	0.12	0.24	0.25

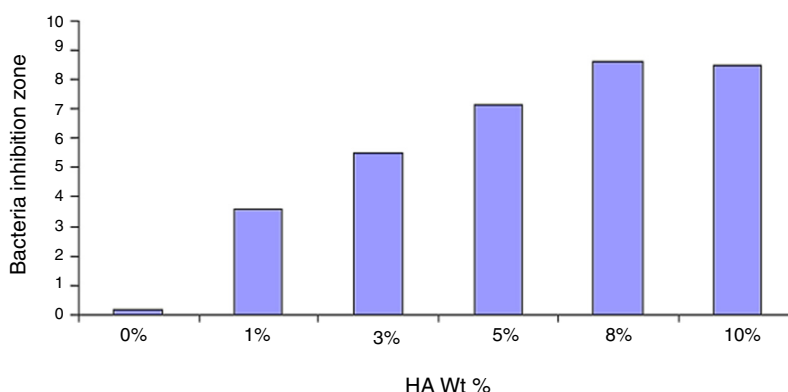


Fig. 1 – Effect of C-GIC and its HA hybrids with different HA wt% against *S. mutans* bacteria.

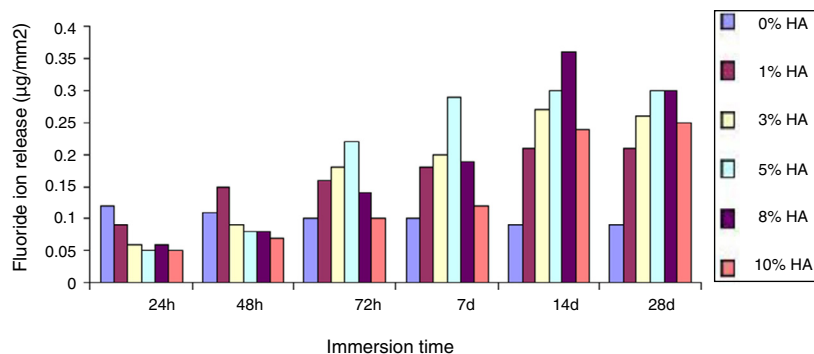


Fig. 2 – Fluoride ion release from C-GIC and its hybrids with different HA wt% for different immersion time.

Table 2 – Compressive strength (MPa) for C-GIC and its hybrids with different HA wt%.

	HA wt%					
	0%	1%	3%	5%	8%	10%
Compressive strength (Mpa)	136.49	141.58	147.12	149.72	147.75	149.70

From the data listed in the table and illustrated in the figure, it is clear that, the fluoride ion release from C-GIC is increased by HA addition till 8% HA wt% [24]. From the table it is also noted that, the control C-GIC has a highest value of F⁻ release after 24h where the highest value of F⁻ release for C-GIC-HA hybrids is directly proportional with HA wt%. This result attributed to the high ability of HA for ion exchange. This ion exchange ability permits the ionic exchange between OH⁻ ions in HA by ions with the same charge F⁻ (releasing from C-GIC surface degradation when freeze dried acidic polymers attacks the basic glass powder), therefore, F⁻ exchanged between C-GIC and HA [25].

4.3. Compressive strength measurement

Compressive strength is an important feature for C-GIC to be used as restorative material, distinctly in the process of mastication. This test is more suitable for the comparison of brittle materials, such as GIC which show relatively low tolerance when subjected to tension [26].

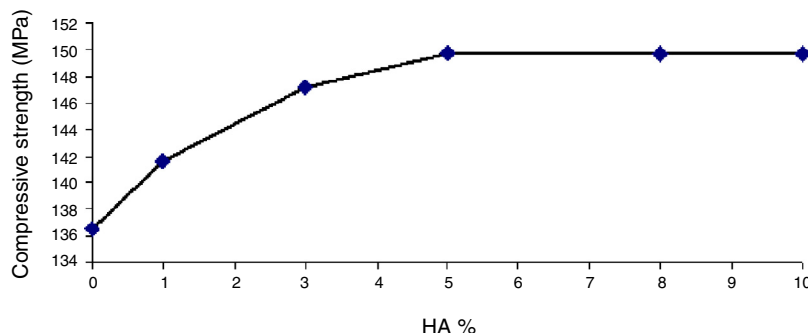


Fig. 3 – Compressive strength (MPa) for C-GIC and its hybrids with different HA wt%.

Mechanical properties of C-GIC and its hybrids with different HA wt% was determined by measuring the compressive strength in (MPa) for each sample. The results are listed in Table 2 and illustrated in Fig. 3.

The result indicated that, GIC with different HA wt% gave higher values for compressive strength when compared with C-GIC. This can be attributed to the influence of nano HA on each of GIC polysalt bridge formation level and its setting reaction, which improve mechanical properties of the obtained GIC material [27].

From the obtained results, it is clear that addition of nano-HA to C-GIC enhance its fluoride ion release, compressive strength and antibacterial effect against *S. mutans*. This suggests that adding nano-HA particles to GIC can be used as suitable materials for improving its fluoride ion release, mechanical properties and inhibiting residual bacteria in dentine.

4.4. Scanning electron microscope (SEM)

Fig. 4 illustrates the morphology examination of the C-GIC and its hybrid GIC-HA with 8% HA wt% using SEM analysis. From the figure it is clear that, the matrix surface cracking and degradation is caused by attacking of the freeze dried acidic polymers to the basic glass powder resulting of metal and non-metal ions releasing.

Furthermore, the increasing in the matrix degradation surface was observed in case of HA addition due to highly bonding between the matrix surface and HA nanoparticles, which means that, the strength of the GIC is increased by HA nanoparticle addition where the adsorption of HA by

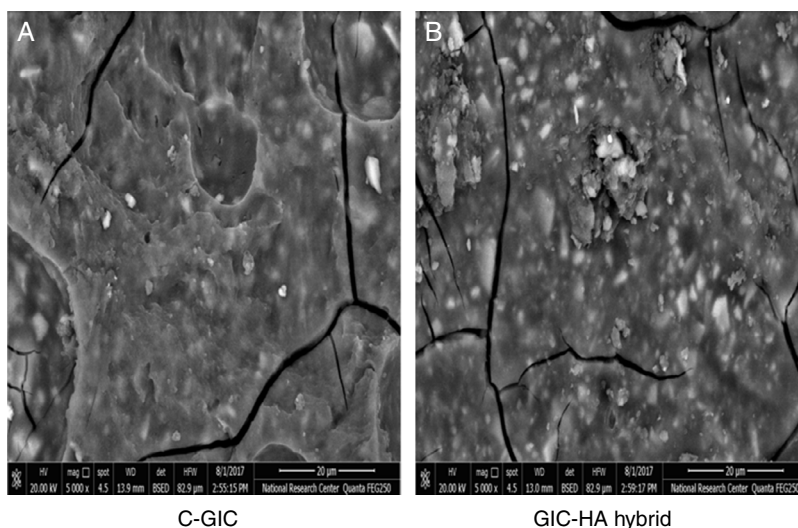


Fig. 4 – SEM of C-GIC and GIC-HA hybrid.

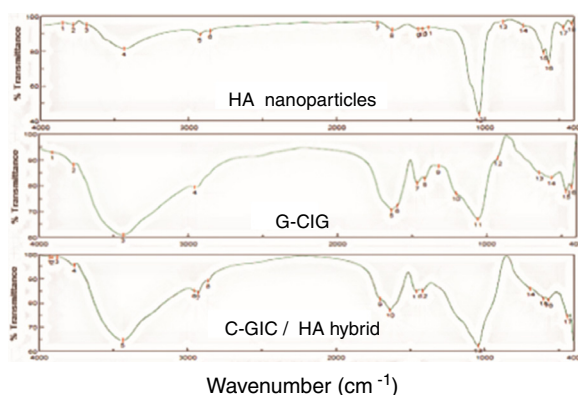


Fig. 5 – FTIR analysis for HA nanoparticle, C-GIC and GIC-HA hybrid.

the GIC surface is completed during CIG hardening reaction [28].

4.5. Fourier transform infra-red (FT-IR)

FTIR analysis of the C-GIC and its hybrid GIC-HA were obtained and illustrated in Fig. 5. From the figure, it can be concluded that, GIC-HA hybrid exhibited diffraction peaks at 2691 cm^{-1} which was characteristic for HA hydroxyl group the HA nanoparticles. Also, the GIC-HA hybrid exhibits HA phosphate vibration diffraction peaks at 1043 and 439 cm^{-1} . These results were an indication for the successfully embedding of HA nanoparticles into the C-GIC matrix [29].

5. Conclusion

Different wt% (1:10%) of nano-hydroxyapatite powder was successfully loaded to conventional glass ionomer cement (C-GIC) with different concentrations and produced GIC-Ha hybrids. The results showed that, addition of nano-HA to

C-GIC enhance its fluoride ion release. Compressive strength and antibacterial effect against *S. mutans* were also studied. The bacterial inhibition zone reached to about 8.6mm when 8% HA wt% is used. This suggests that adding nano-HA particles to GIC can be used as suitable materials for improving its fluoride ion release, mechanical properties and inhibiting residual bacteria in dentine. The C-GIC and GIC-HA were characterized by SEM and FTIR analysis in order to confirm the success of HA nanoparticle loading process.

Conflicts of interest

The author declares no conflicts of interest.

Acknowledgment

The author would like to acknowledge University of Tabuk for the financial support under research project number S1438-0011.

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