

Research Article

Investigation the Compressive Strength of Glass Ionomer Cement Containing Hydroxyapatite Nano and Micro Particles

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Glass Ionomer Cements (GICs) are one of the most important dental restorative materials. Improvement of biological and mechanical properties of these materials has been taken into consideration. The aim of this work was to preparation and characterization of GICs by melting method and evaluation of adding Hydroxyapatite (HA) micro and nanoparticles on compressive strength of GICs. In this research, the ceramic part of GIC was prepared using melting method, and micro and nano-hydroxyapatite were synthesized from natural bone. HA micro and nanoparticles were added to GICs in different weight percents (0, 1, 3, 5 and 7 wt.%). The microstructure of synthesized products, chemical composition of the ceramic part of glass ionomer cement and the size and shape of HA nanoparticles were studied by Scanning Electron Microscopy (SEM), X-ray Fluorescence (XRF) and Transmission Electron Microscopy (TEM), respectively. The phase analysis of GICs composite was carried out by X-ray Diffraction (XRD) technique. Finally, the compressive strength of composite samples were determined and compared. TEM confirmed the nanometric scale of hydroxyapatite particles. Results of the compression test showed that adding HA micro and nanoparticles with the values of less than 5% by weight had no distractive effect on compressive strength of GICs. The final result of this research was gaining GICs containing HA micro and nanoparticles with improved equivalent mechanical properties. The improvement of GICs properties in dentistry applications can be achieved by adding bioactive materials like HA micro and nanoparticles.

Keywords: Glass ionomer cement; Hydroxyapatite micro/nanoparticles; Compressive strength

Introduction

Glass Ionomer Cements (GICs) are of the most important tooth-colored restorative materials used in dentistry. Since the GICs were introduced to the dental profession by Wilson and Kent in 1972, the use of these materials has been increased due to their exclusive properties such as proper biocompatibility with body's hard tissue, long-term fluoride release, the capability of absorbing and restoring fluoride, low thermal expansion coefficient, good adhesion to moist enamel and dentin without necessitating an intermediate agent and low cytotoxicity [1-3]. Despite the above mentioned advantages, this group of substances has some disadvantages which mainly include low mechanical strength and sensitivity to humidity that limit their applications [4,5]. Some efforts have been dedicated to improve the mechanical properties of conventional GICs which include reinforcement with metal powders [6], modification with resin [7], Incorporation with SiC whiskers/ short fibers [8,9], HA and fluoroapatite nanobioceramics [10], forsterite nanoparticles [3], etc.

Hydroxyapatite (HA) is one of the most important calcium phosphate bioceramics ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ chemical formula; Ca/P=1.67), and has a composition and crystal structure similar to apatite in the human dental structure and bone tissue [11,12]. In recent years, a number of studies have tried to assess the effect of HA

addition to the restorative dental materials such as GICs [13]. It was found that glass ionomer cements were interacted with HA through the carboxylate groups in the polyacid. Hence, the incorporation of HA into GIC powder composition can not only improve the biocompatibility of GICs, but also increase the mechanical properties [10,14].

Lee et al. [15] investigated the physical properties of resin-reinforced GIC modified with micro and nano-hydroxyapatite, and suggested that demineralization of enamel surface could be prevented by incorporating nano-HA into GIC.

On the other hand, studies on ceramic particles (or glass beads) reinforced polymers suggested that the particle size had effects on the mechanical properties of composites [16].

Therefore, the aim of this work was to synthesis micro and nano-hydroxyapatite from natural bone and *via* sol-gel method, respectively, and also investigate and compare the influence of HA particle size on the mechanical properties of GIC.

Materials and Methods

Preparation of ceramic part of Glass Ionomer Cement (GIC)

The analytical-grade of Aluminum Oxide (Al_2O_3 , Merck), Silicon

Table 1: Compositions, the abbreviations used for various experimental groups and compressive strength values (mean values \pm standard deviation) of micro and nano-HA-containing glass ionomer cement samples (mHG and nHG, respectively).

X	Composition					Compressive Strength (MPa)		
	Liquid Compositions	Polyacrylic acid copolymer					XnHG [#]	XmHG ^m
0 (GIC)	Powder Compositions	Strontium containing aluminum Fluorosilicate glass					46.10 \pm 3.39	46.10 \pm 3.39
	Chemical Composition	SiO ₂	Al ₂ O ₃	AlPO ₄	CaF ₂	SrF		
		39.00	25.50	16.50	12.00	7.00		
1	GIC- 1% HA					74.76 \pm 6.50	49.54 \pm 1.95	
3	GIC- 3% HA					61.7 \pm 0.40	50.95 \pm 0.35	
5	GIC- 5% HA					56.8 \pm 0.1	65.56 \pm 1.62	
7	GIC- 7% HA					37.75 \pm 1.46	41.31 \pm 3.64	

^m: Microparticles; [#]: Nanoparticles

Oxide (SiO₂, Merck), Fluoride Strontium (SrF, Merck), Aluminum Phosphate (AlPO₄, Merck) and Calcium Fluoride (CaF₂, Merck) were used as the starting materials for producing the ceramic part of glass ionomer by melting method.

First, a defined weight percentage of the mentioned oxides was prepared and mixed in a ball mill with aluminum balls for homogenizing the powders' mixture. Then the mixed materials were placed in an electric melting furnace, and heated for 3 hours with the rate of 5°C/min to reach the temperature of 1400°C. Finally, the as-obtained melted glass was cooled at ambient temperature, underwent shattering process in the ball mill for 5 h, and passed through a 200 mesh sieve in order to be defined as glass powder according to ASTM [17].

Producing of hydroxyapatite micro and nanoparticles

Microparticles of hydroxyapatite were obtained from natural bone. A femur of an adult bovine was obtained from a slaughterhouse and boiled in water for 12 h to render it aseptic and loosen any attached soft tissues. Then it was washed and cleaned carefully to remove visible tissues, fats and any other impurities on the bone surface. To remove the internal organic content (e.g. collagen) and water, the bone was then heated in an electric furnace under ambient conditions, at 700°C with 2 h holding time. The resulting white solid specimens were first ground and crushed with a mortar and pestle to produce a powder, and then sieved to obtain particle-size distribution less than 50 μ m. Bone powder was sterilized at 150°C for 1 h, rinsed in distilled water, and incubated in 1% phosphoric acid. Eventually, microparticles were rinsed again in sterile distilled water, and sterilized at 200°C.

A high energy planetary ball mill (Fretch Pulverisette 5), with a 125 ml zirconia *via* 1 and four 20 mm diameter zirconia balls at ambient temperature, was used to produce HA nanoparticles. Obtained HA microparticles in previous stage were ball milled for 20 h and finally sterilized at 200°C.

GIC-HA composites preparation

The glass ionomer- hydroxyapatite composites was fabricated through adding 1, 3, 5 and 7 wt.% of HA micro- and nanoparticles to the prepared glass powders. The specimens were transferred in to the aluminum mold after mixing of powder and liquid, and removed after 1 h.

Characterization

X-ray Fluorescence (XRF): X-ray fluorescence elemental analysis (XRF, Bruker, S4PIONEER, Germany) was used to confirm the presence of oxides in the final compound of glass ionomer powder.

Scanning Electron Microscopy (SEM): HA particles' morphologies and glass ionomer cement containing HA were mounted on aluminum SEM pins and coated with Au, and were investigated with scanning electron microscope (SUPRA 40 VP FE-SEM, Carl Zeiss AG, Germany) operated at an acceleration voltage of 20 kV.

Transmission Electron Microscopy (TEM): Transmission Electron Microscopy (TEM) was also employed to investigate the size and morphology of HA nanoparticles. A universal method for the preparation of TEM samples was applied to bioceramic ones. In this method, special holders were used in which the sample is embedded using epoxy glues.

X-ray Diffraction (XRD): X-ray Diffraction (XRD) technique (Philips X'Pert-MPD system with a Cu K α , 1.5418 Å) was used to analyze the structure of the prepared glass ionomer powder and the GIC-HA composites. The diffractometer was operated at 40 kV and 30mA at a 2 θ range of 10–90° employing a step size of 5s per step.

Compressive strength measurements

Cylindrical specimens were prepared using aluminum cylindrical shaped molds 4 mm in diameter and 6 mm in height for compressive strength test. The molds were filled with the material, flattened and gently pressed by hand in order to remove air bubbles from uncured cement paste. The specimens were removed from the molds after 30 min and conditioned in distilled water at 37°C for 24 h [18]. Five specimens were made for each test. The different experimental groups of GICs and their abbreviations are tabulated in Table 1.

Compressive strength test was performed on a screw-driven testing machine (Hounsfield, Model H25KS, England) with a cross-head speed of 0.5 mm/min.

Cylindrical specimens with 4 \pm 0.1mm diameter and 6 \pm 0.1mm height were prepared according to ASTM D695 (Table 1), and their compressive strength (CS; MPa) was calculated by the following equation:

$$CS=4P/\pi d^2 \quad (1)$$

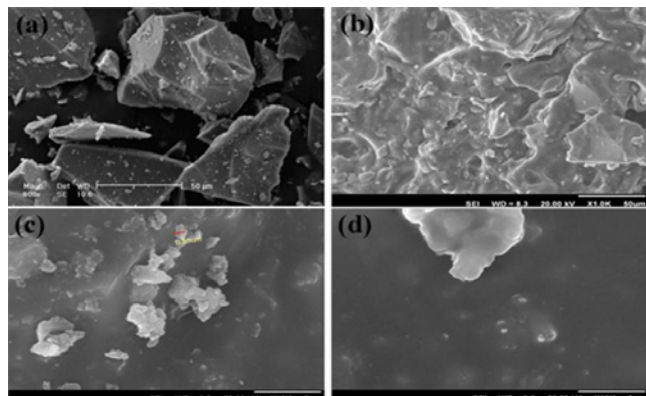


Figure 1: SEM images of (a) the ceramic part of glass ionomer cement, (b) ceramic part of glass ionomer cement mixed with polyacrylic acid liquid, (c) glass ionomer cement containing 5 wt.% hydroxyapatite microparticles and (d) glass ionomer cement containing 5 wt.% hydroxyapatite nanoparticles.

Where P is the load at fracture (N), and d is the diameter of the cylindrical specimen (mm).

Results and Discussion

Chemical composition of as-prepared glass ionomer

Glass ionomer powder composition analyzed by XRF is reported in Table 1. This result confirmed that the chemical compounds of the ceramic part of glass ionomer cement synthesized by the melting method were to a great extent similar to the expected weight rates.

The weight percentage of oxides was expressed by computer according to the elemental analysis and considering the assumption that all the elements are in oxidic form. These results showed that the composition of prepared GIC powder was in good agreement with reported composition for commercial type of GIC [19].

Scanning Electron Microscope (SEM)

SEM image of the ceramic part of GIC is shown in Figure 1a. From these images, it is found that the glass particles have irregular shapes and the size of less than 100 μm . Other researchers also reported the size of less than 100 micrometers for the glass particles produced through melting method [20].

Figure 1b shows the SEM micrograph of the integrated structure of glass ionomer (mixture of glass ionomer powder and polymer liquid (polyacrylic acid)). The relatively homogeneous and flat surface of glass ionomer is clearly observed in this image.

As it can be seen from the Figure 1c, hydroxyapatite microparticles were non-uniformly dispersed in glassy matrix of GIC.

Agglomerated hydroxyapatite semi-sphere nanoparticles (less than 150 nm) in a homogenous field of glass ionomer are observable in the SEM micrograph (Figure 1d). The same as many other nanocompounds, the agglomeration of hydroxyapatite nanoparticles is inevitable. These results showed a good agreement with the reports presented by other researches [10].

Transmission Electron Microscopy (TEM)

Results from TEM analyses for HA nanoparticles are shown in Figure 2. The TEM observations revealed that the powder particles of HA have prolate spherical and hexagonal morphology. However, the

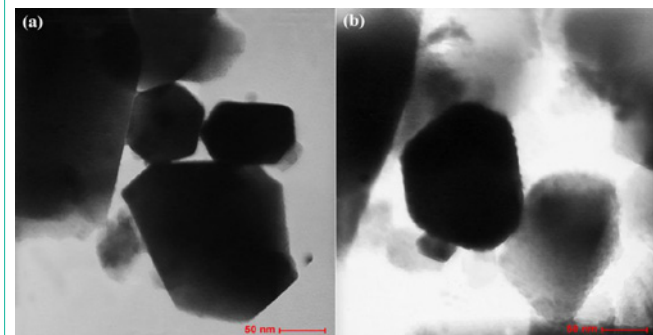


Figure 2: TEM images of HA nanoparticles.

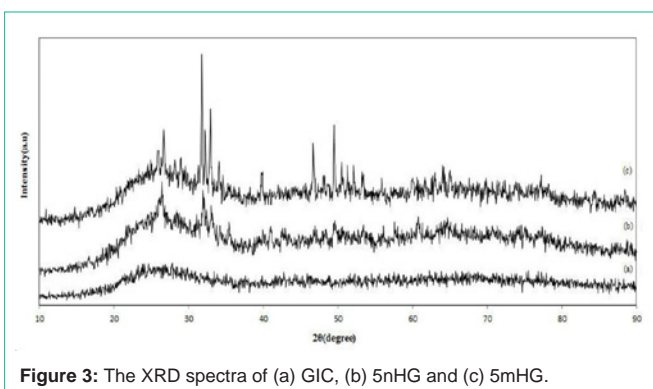


Figure 3: The XRD spectra of (a) GIC, (b) 5nHG and (c) 5mHG.

powders were not well dispersed, suggesting that the aggregation of powders occurred due to Vander Waals attraction [21].

The size of the hydroxyapatite particles as estimated from the TEM images ranged from 50 to 150 nm.

Phase analysis (XRD)

The XRD patterns of GIC powder, 5nHG and 5mHG are shown in Figure 3. The pattern of GIC (Figure 3a) did not contain diffraction peaks, indicated the internal disorder and the glassy nature of this material.

In addition, the XRD patterns of 5nHG and 5mHG showed the peaks related to HA particles in glass ionomer structure (Figure 3b and 3c). These results had a good agreement with the results reported by Moshavernia et al. [10].

Compressive strength measurements

The results of 7 days compressive strength values of the micro- and nano-HA containing glass ionomers are shown in Figure 4 and Table 1, and compared with GIC ones as the control group. The results showed that there was a significant difference between the compressive strength values of the micro- and nano-HA containing GIC samples and the control group.

In micro-HA-containing glass ionomer cement samples (mHG), the higher compressive strength value was observed for 5mHG sample (42% increases) (Figure 4). The same trend was observed for the nano-HA-containing glass ionomer samples (nHG) and the higher compressive strength value was observed in 1nHG sample (62% increases).

Increasing of compressive strength in presence of hydroxyapatite

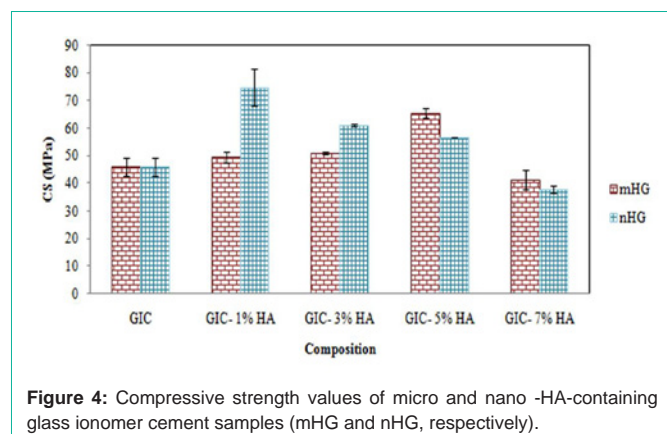


Figure 4: Compressive strength values of micro and nano -HA-containing glass ionomer cement samples (mHG and nHG, respectively).

particles is due to the formation of crystal phases in the amorphous structure of glass ionomer. In both micro- and nano-HA containing glass ionomers, with increasing of HA, the compressive strength of GIC is increased. In micro-HA containing glass ionomers, the maximum strength was observed in 5%wt and in nano-HA containing glass ionomers the maximum strength was observed in 1%wt of HA particles. Decrease of compressive strength in hydroxyapatite weight percentages upper than 5 and 1, is due to the decrease in bonding forces between the ceramic part and the polymeric matrix of GICs. In fact, the added hydroxyapatite particles act as a barrier and prevents from the complete bonding of the parts of glass ionomer cement [3,10,14].

Results also showed that the enhancement in compressive strength of nano-HA containing glass ionomers is more than micro-HA containing glass ionomers. In addition, when compared to micro-HA containing glass ionomers, in presence of HA nanoparticles, more compressive strength was observed in lesser amounts of HA. Large specific surface area can easily lead to particle agglomeration, which makes nanoparticles more difficult to be evenly dispersed into polymer matrix, thus resulting in a strength reduction [22].

Conclusion

Micro and nano-hydroxyapatite particles were successfully synthesized from natural bone. The addition of micro- and nano-HA into prepared conventional composition of GIC enhanced the compressive strength of the resulting cements. These bioceramics are therefore considered promising additives for glass ionomer restorative dental materials. However, the compressive strength increase in nano-HA containing glass ionomers was more than micro-HA containing glass ionomers. Moreover, in presence of HA nanoparticles, more compressive strength was observed in lesser amounts of HA.

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