SOME PROPERTIES OF GLASS-IONOMER CEMENTS PREPARED BY SOL-GEL METHOD AND INCORPORATED WITH NANO-FLUORAPATITE

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ABSTRACT

Objective: To evaluate the compressive strength, diametral tensile strength, shear bond strength, and setting time of sol-gel formulated glass-ionomer cement (FGIC) (60%SiO_2, 35%CaO, 5%P_2O_5) with and without incorporation of nano-fluorapatite (nano-FAp) in comparison with commercial glass-ionomer cement (CGIC). **Material and methods:** The studied glass powder was prepared by sol-gel method and nano-FAp was added into the prepared glass powder with four different concentrations (1wt.%, 2wt.%, 3wt.%, and 4wt. %). A total number of 432 samples were used in this study. The prepared samples were grouped into six groups; group 1; CGIC (negative control), group 2; FGIC (positive control), group 3; FGIC/1wt.% Nano-FAp, group 4; FGIC/2wt.% Nano-FAp, group 5; FGIC/3wt.% Nano-FAp; and Group 6; FGIC/4wt.% Nano-FAp. Each group was subdivided into four subgroups of (18) samples each according to type of the test. The samples were characterized and mechanically tested for compressive strength, diametral tensile strength, shear bond strength, and setting time. One-way ANOVA tests was used to analyze data statistically significant is stablished at probability level of 0.05. **Rsults:** Prepared GIC recorded the lower compressive strength, diametral tensile strength, and shear bond strength, and the higher setting time when compared to the commercial GIC. While, these results improved with the increases of the concentration of the added nano-FAp from 1wt. % to 3wt. % and then decrease again at 4wt. %. **Conclusions:** The preparation of GIC with sol-gel method has lower compressive strength, diametral tensile strength, and shear bond strength, and longer setting time than GIC. However, the addition of 1-3 wt. % nano-FAp to the prepared GIC improve its mechanical properties and setting time. While the use of higher concentration than 3wt.% resulted in decrease in the tested properties.

KEYWORDS: glass-ionomer cement, nanofloroapatite, compressive strength, diametral tensile strength, shear bond strength, and setting time.

INTRODUCTION

Commercial glass ionomer cement (GIC) commonly used as an alternative restoration to amalgam in primary teeth as well as a restorative and lining material for permanent teeth owing to its favorable fluoride release, and its close matching of thermal coefficient , as well as due to its ability to adhere chemically to tooth, and its biocompatibility. However it has main shortcoming due to its lower mechanical properties [1, 2].

The preparation of glass powder via sol-gel method regarded as a good alternative to the

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popular melt and quench method due to utilizing oxide elements with a relatively low-temperature usually lower than its crystallization temperature through operating liquid chemical precursors to produce glasses-like ceramics with high purity and homogeneity [3].

Lately, marked enhancements were made in order to improve mechanical properties of the conventional GIC via addition of various nano-bioactive ceramic materials such as nano-fluoroapattite (nano-FAp) and nano-hydroxyapatite (nano-HAp) into glass ionomer cement [4-6].

However, fluorapatite commonalty has chemical structure comparable to hydroxyapatite, but fluorapatite has superior mechanical strength, sharper thermal stability, and lower acidic solubility in regard to hydroxyapatite [6, 7]. Also, it was implied that addition of sufficient amount of nano-FAp into the glass ionomer cement which supplied by sol-gel preparation method resulted in significant enhancement of its mechanical characteristics [3,8].

Hence, this study was carried out to assess the compressive strength, diametral tensile strength, shear bond strength, and setting time of GIC prepared by sol-gel method and effect of incorporation of nano-FAp with different percentages on these properties in regard to the commercially available GIC.

MATERIAL AND METHODS

The materials used in this study were, commercial glass ionomer cement powder (CGIC) and liquid (GC gold label, Tokyo, Japan), Sol-gel formulated glass ionomer cement (FGIC) (60% SiO_2, 35%CaO, 5% P_2O_5) and nano-floroapatite (Egyptian Nano Gate Company).

Grouping of samples:

A total number of 432 samples were used in this study. The samples were divided into six groups according to modifications:

Group1: CGIC powder mixed with commercial GIC liquid.

Group 2: FGIC powder mixed with commercial GIC liquid.

Group 3: FGIC powder 1wt.% nano-FAp powder mixed with commercial GIC liquid.

Group 4: FGIC/2wt.% nano-FAp powder mixed with commercial GIC liquid.

Group 5: FGIC/3wt.% nano-FAp powder mixed with commercial GIC liquid.

Group 6: FGIC/4wt.% nano-FAp powder mixed with commercial GIC liquid.

Each group was subdivided into four subgroups of (18) samples each according to type of the test (compressive strength, diametral tensile strength, and shear bond strength, and setting time).

Preparation of glass powder by sol-gel method:

Glass powder by sol-gel method was prepared in physics Department, Faculty of Science, Boys, Cairo, Al-Azhar University, Egypt. For preparation of 100gm of sol gel FGIC powder (60%SiO_2, 35%CaO and5% P_2O_5) various reagents and solutions with specific concentration were selected as a source supply of SiO_2, CaO and P_2O_5 (all chemicals used were manufactured by Sigma-Aldrich, St. Louis, MO, USA). The reagents and solutions were mixed together in electrical magnetic stirrer with continuous stirring in the following order: 26.134ml Tetra Ethyl Ortho Silicate (TEOS), 23.384ml distilled water, and 4.19ml nitric acid (HNO_3) together in ethanol at 1500.rpm for 45 minutes, then 1.204ml Tetra Ethyl Phosphate (TEP) and 8.507gm calcium nitrate tetra hydrate {Ca $(NO_3)_2 \cdot 4H_2O$} were added to mix and allowed to react for further 45 minutes. After that, all reagents were left under continuous magnetic stirring for 60 minutes to complete hydrolysis. Finally, 4.19ml ammonia solution (as gelation catalyst) was dropped into the mixture and manually flipped with glass rod to prevent the formation of bulked gel [3].

Thereafter, each prepared gel was left to dry at 100° C-120° C for 2 days and then sintered at 580° C for 2 hours in electrical oven. Then, the sintered powder was ground into fine powder in laboratory mortar and pestle and then was passed through a sieve with a mesh number 325mesh to give particle size less than 45um [3].

Preparation of modified sol-gel glass powder:

Nano-fluorapatite (Sigma-Aldrich, St. Louis, MO, USA) were added to the previously synthesized glass powder with percentage of 1 wt. %, 2 wt. %, 3 wt. % and 4 wt. % via using a sensitive digital balance (KERN ABJ 220-4NM, KERN & SOHN GmbH, Balingen – Germany) and then mechanically mixed with dental amalgamator (HL-AH G5 Dental Digital Amalgamator, Italy) for 30 s, separately to obtain a homogenous distribution of the incorporated nanoparticles[8].

Characterization of unmodified and modified sol-gel glass powder:

Characterization of the unmodified and modified powders was made by X-ray diffraction (XRD) {Siemens D5000} to identify the nature of glass (amorphous or crystalline). Also, Fourier transform infrared (FTIR) spectroscopic analysis (Thermo scientific™ Nicolet™ iS™ 50 FTIR) was used to determine the functional group.

Sample preparation:

The samples were prepared using a special designed Teflon mold with diameter and height of 3 mm X 6 mm for compressive test, and 6mm X 3 mm for diametral tensile test. [9, 10] The conventional GIC powder and the prepared unmodified and modified glass powder were mixed with commercial glass ionomer liquid according to the manufacturer instructions. Then, each mixed cement was placed in the Teflon mold on glass plate and covered with celluloid strip and pressed with another glass plate and left for setting and then stored in distilled water for 24 hours prior to testing. [9, 10]

This test was conducted in Department of Dental Biomaterial, Faculty of Dental Medicine, Boys, Cairo, Al-Azhar University. The prepared samples were loaded on the Lloyd mechanical testing machine at cross head speed of 1 mm/min. The samples were placed vertically with flat end between the two opposite metal plates. The load was applied until the sample was crushed and the peak force required to fracture each sample was recorded in Newton from stress strain curve. The compressive strength was calculated in (MPa) using the following equation: $CS = 4P/\pi d^2$; Where (CS) is the compressive strength (MPa), (P) is the load at the fracture point (N), (d) is the diameter (mm) of the sample and (π) is a constant = 3.14 [9].

Diametral tensile strength test:

This test was conducted in Department of Dental Biomaterial, Faculty of Dental Medicine, Boys, Cairo, Al-Azhar University. This is an alternative testing method for brittle materials which can easily fracture at the grips during testing. The ultimate tensile strength (UTS) of a brittle material is determined through compressive testing. In this test, the disc sample was mounted on the Lloyd mechanical testing machine and the load was applied to the samples using a cross head speed of 0.5 mm/min applying a compressive force on the samples until fracture. The diametral tensile strength was calculated in (MPa) using the following equation's = $2P/\pi dt$; Where (DTS) is the diametral tensile strength (MPa), (P) is the load (N) at the fracture point, (d) is the diameter (mm) of the samples, (t) is the height (mm) of the samples and (π) is a constant = 3.14 [10].

Shear bond strength test:

This test was conducted in Department of Dental Biomaterial, Faculty of Dental Medicine, Boys, Cairo, Al-Azhar University. Ten human permanent mandibular molars those freshly extracted and has no decay, crack or structure deformities were collected and stored in normal saline until use.

After removing any tissue tags the teeth were cleaned with pumice. Then, the roots of each tooth were embedded in chemically-cured acrylic resin block made by poly vinyl chloride (PVC) tube of 1.5 cm length and 2 cm diameter. The occlusal surface of each tooth was grinding and flat occlusal dentine surface was obtained. After that, cylindrical samples (5mm length x 2mm diameter) of GIC were constructed over the flat dentine surface using special Teflon mold and storage in distilled water for 24hour. Then, the shear bond strength was done via material testing machine at cross head speed 1/2 mm per minute [11].

Setting time test:

Vicat's apparatus was used for testing the setting time of the GIC samples. Samples were prepared using Teflon mold of 8mm X 10mm X 5mm in dimensions via mixing the powder, with glass ionomer liquid according to the predetermined powder/liquid ratio. A digital stopwatch was used to record the different testing times. The initial and final setting were calculated from the following equation; initial setting time = T2-T1 and final setting time=T3-T1; Where; T1 =Time at which liquid was first added to cement, T2 =Time when needle failed to penetrate the cement for about 0.5 mm measured from the bottom of the mold, and T3 =Time when the needle was failed to make an impression [12].

Statistical Analysis:

PASW Statistics 17 (SPSS Inc., Chicago, IL, USA) soft wear was used for all statistical tests with level of significance level at 0.05. ANOVA test were used to compare the means of the recoded values followed by pair wise comparison of means between the tested groups.

Characterization of the sol-gel prepared cement:

XRD analysis:

The XRD patterns of prepared glass powders (a) exhibit no diffraction peaks were observed indicating amorphous structure of prepared glass powder. While, the XRD pattern of the prepared glass powders with nano-FAp (b, c, d, e) showed markedly broader peak at $2\theta = 33^0$ with slight shift of this peak to the right-hand side in the fluoridated samples which indicates the substitution of OH with F ions in the apatite structure. This shift has been related to the a-axis contraction caused by smaller size of F ions compared to OH ions (Figure 1).

FTIR analysis:

The peak located at 467 cm-1 is characteristic to bending vibration mode of Si – O, also peaks at 875 cm-1 and 1099 cm-1 corresponding to symmetric stretching vibration of Si – O, respectively, asymmetric stretching vibration of Si – O – Si bridges. The presence of phosphate in glass structure
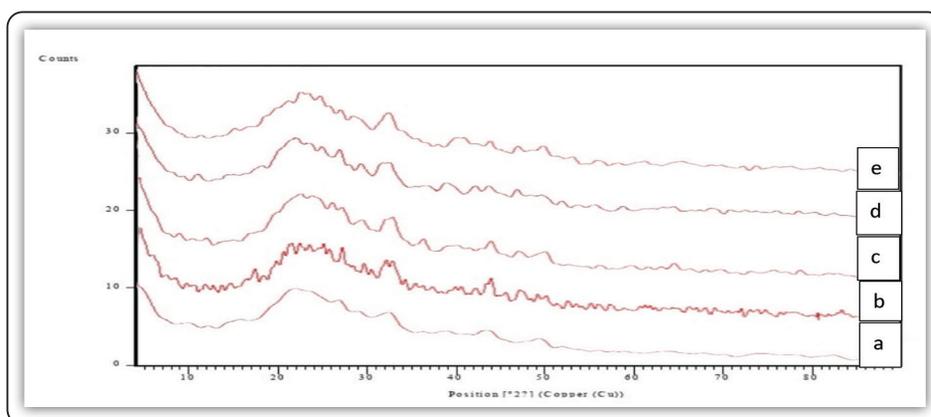
FIG (1) XRD patterns of different prepared glass powders.

was evidenced by the peaks located at 565 cm-1 encountered in case of P – O bending vibrations of PO_4^{3-} structure. The high Ca_2^+ content also causes the formation of a band at 1432 cm-1. The broaded band located at 3441 cm-1 corresponds to the stretching vibration of hydroxyl (O - H) common especially in case of silanol groups (Si – OH) and chemically bound water presents in the $SiO_2 – Ca_O – P_2O_5$ glass structure. The presence of H_2O molecules in the same glass structure has been confirmed by the peak at 1638 cm-1. Peaks located at 1384 cm-1 are characteristic to nitrate groups present in the structure of glass, through the use of Ca $(NO_3)2$ $\cdot 4H_2O$ as a precursor in the synthesis of this material On the other hand, the small peaks at 2426, and 2923 cm-1 spectrum are related to presence of C-H (υ) group and were weakly observed. Moreover, the analyzed composition powder had a broad and well-

defined peak at 3441 cm-1 which represent Si-OH group was observed. On the other hand, the nano-FAp modified groups revealed that the small peak at 2426 cm-1 spectrum is related to presence of C-H (υ) group and was absent in 3% and 4% Nan-FAp modified groups (Figure 2).

Compressive and diametral tensile strength results:

The statistical results of compressive and diametral tensile strength showed that, the difference between all tested groups were statistically significant and the commercial GIC recorded the higher compressive and diametral tensile strength when compared to the prepared GIC. The addition of nano-FAp significantly increase the compressive and diametral tensile strength of the prepared cement until percentage of 3% then it decreased again over this percentage as shown in tables 1 and 2.
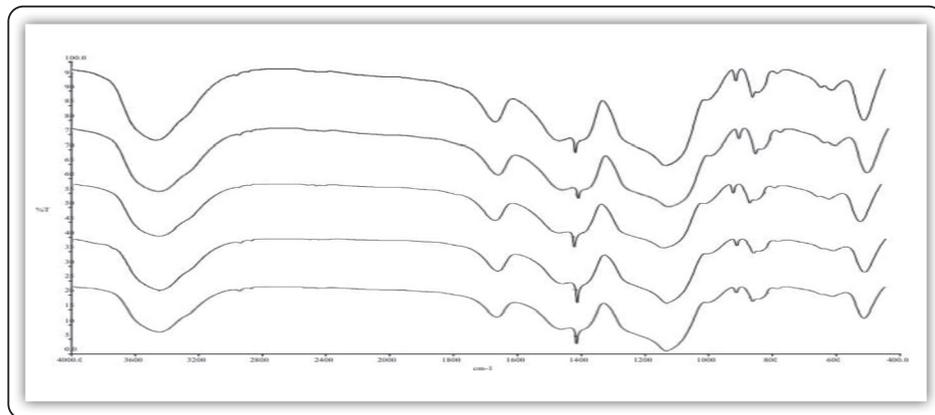
FIG (2) FTIR spectra the prepared glass powders.

TABLE (1) Comparison of compressive strength (MPa) of all tested groups.

Compressive strength	Group A	Group B	Group C	Group D	Group E	Group F
Mean ± SD	55.92±4.01	36.89±1.56	38.57±3.91	39.29±5.53	46.29±5.84	46.00±13.14
F test	5.608					
P value	0.001*					
P1		0.001*	0.001*	0.001*	0.033*	0.028*
P2			0.697	0.579	0.037*	0.043*
P3				0.868	0.082	0.093
P4					0.113	0.127
P5						0.947

*; *Significant at p < 0.05.*

TABLE (2) Comparison of diametral tensile strength (MPa) of all tested groups.

Diametral tensile	Group A	Group B	Group C	Group D	Group E	Group F
Mean ± SD	9.84±0.95	5.91±0.49	6.53±1.21	7.27±2.40	8.17±2.45	7.38±1.51
F test	3.408					
P value	0.018*					
P1		0.001*	0.004*	0.022*	0.126	0.028*
P2			0.564	0.212	0.043*	0.178
P3				0.493	0.132	0.429
P4					0.398	0.915
P5						0.459

*; Significant at p < 0.05.

Shear bond strength results:

The results of shear bond strength of the tested groups revealed that; the difference between all tested groups was statistically significant and the commercial GIC showed the higher of shear bond strength when compared to the prepared GIC and the incorporation of fluorapatite significantly improve the of shear bond strength of the prepared cement until percentage of 3wt.% then it decreased again over this percentage (Table 3).

Setting time results:

The results of setting time in the present study revealed that; the difference between all tested groups were statistically significant and the commercial GIC showed the lower setting time when compared to the prepared GIC and the incorporation of fluorapatite significantly decrease the setting time of the prepared cement with increase the percentage of nano-FAP (Table 4).

TABLE (3) Comparison of shear bond strength (MPa) of all tested groups.

Shear bond strength	Group A	Group B	Group C	Group D	Group E	Group F
Mean ± SD	9.42±0.52	3.55±1.70	4.52±1.68	5.11±0.59	6.46±0.27	5.86±0.77
F test	17.776					
P value	0.001*					
P1		0.001*	0.001*	0.001*	0.001*	0.001*
P2			0.170	0.032*	0.001*	0.002*
P3				0.393	0.009*	0.061
P4					0.061	0.283
P5						0.392

*; Significant at p < 0.05.

TABLE (4) Comparison of setting time (min.) of all tested groups.

Setting time	Group A	Group B	Group C	Group D	Group E	Group F
Mean ± SD	6.85 ± 0.91	14.15±3.34	13.10±2.76	12.85±3.20	9.75±2.13	9.27±0.68
F test	6.794					
P value	0.001*					
P1		0.001*	0.001*	0.001*	0.070	0.125
P2			0.500	0.404	0.008*	0.004*
P3				0.870	0.038*	0.019*
P4					0.053	0.028*
P5						0.759

*; Significant at $p < 0.05$.

DISCUSSION

The sol-gel method serves as a suitable easier alternative to the traditional melt and quench method for production of GIC this because its relatively low- synthesis temperature which utilize temperature usually below the temperature of crystallization of oxide elements via using liquid chemical precursors to produce glass-like ceramic with high homogeneity and purity [3] However, a comparison between sol-gel and melt and quenched prepared glasses showed a similar compositions, structure and atomic correlations. [13] Therefore, the sol-gel synthesis method was selected in this study for production of glass powder of the tested GIC.

Moreover, the sol-gel production method which use for the synthesis the glass powder which used in the present study depends mainly on the chemical precursor such as tetra ethyl ortho silicate (TEOS) and calcium nitrate tetra hydrate that have higher solubility rate in an organic solvent and can easily transform into the essentially reactive chemical forms [14]. Furthermore, in this study the prepared glass powder was developed as phosphate-based glasses quaternary system with low SiO_2 content that were successfully prepared by using phosphorus precursor (P_2O_5) which dissolved completely in anhydrous ethanol [13, 15].

In the present study the nano-FAp was selected to add to the prepared glass to modify its mechanical properties this because it was suggested that the addition of crystalline nanoparticle into GIC could improve the mechanical properties of the modified cement compared with the original GIC[16].However, it is important to control the amount of fluoride in the apatite lattice to attain the best physical performance [17]. As it was found that the increase of fluoride content could affect negatively the physical performance of the modified cement [17, 18] .Therefore, in the present study the nano-FAp were added to the prepared glass with percentage between (1-4wt. %) to determine the proper concentration of the nano-FAp that improve the performance of the prepared glass without any adverse effect.

The results of the present study showed that the synthesized glass has significant lower compressive and diametral tensile strength when compared to the commercial GIC. This may be because of shrinkage of the gel that occurs while the liquid is removed from the pores that can affect the strength of the network and also plays an important role in the gel structure. In addition, the reduction of gel volume is equal to the volume of evaporated liquid and generally changes of structure such as volume, weight, and density occurs[19].

However, the increase of compressive and tensile strength in the modified glass (in the presence of fluorapatite nanoparticles) was due to the formation of crystal phases in the amorphous structure of glass[6]. Moreover, the combination of glass particles with larger particle size and fluorapatite particles with smaller one led to a wide distribution of particle size [20]. This might cause a high packing density of the combined particles within the glass ionomer matrix, and therefore, a high mechanical strength [6] .Similarly, Barandehfard et al reported that addition of fluorapatite crystals led to improved compressive strength and diametral tensile strength of GICs via formation of saline bridges and cross-linking between organic and non-organic networks[21, 22].

Also, the results of the present study showed that the prepared GIC has significant lower shear bond strength as compared with the commercial GIC. This may be because of its low compressive strength and its lower diametral tensile strength. These results agree with the studies reported previously[23, 24]. On the other hand, fluorapatite or fluorided HA were increase the shear bond strength of the modified glass with the increase of the percentage of added Nano-fluorapatite particles. This because the reaction mechanism between HA and GIC may be similar to that of adhesion of the conventional GIC to enamel and dentin as the interaction of apatite found in the tooth structure with the polyacrylic acid produces polyacrylate ions[21, 25].

However, the decrease in compressive strength, diametral tensile strength and shear bond strength with incorporation of nano-FAp higher than 3 wt. % is due to a decrease in bond strength between ceramic and polymeric constituents of GIC [22]. Moreover, it could be due to the incorporation of excess nanoparticles which decrease the intersection between the particles and ionomer network, and thus, fluorapatite could not react with the ionomer to form the crosslinking network [21]. Also, nanoparticles with a large specific surface area tend to form agglomerates and this effect can make nanoparticles more difficult to uniformly disperse into polymer matrix, resulting in a strength reduction [6].

Moreover, the results of setting time of the prepared GIC in the present study showed significant increase in the setting time when compared to the commercial GIC. This may be because of the sol–gel glass was able to masking the process of hardening of the GIC, which is resulted by the cationic release from the alumino-fluorosilicate (AFS) glass granules which associated with the acid–base reaction [26]. The reason for this is that the cationic release from sol–gel glass is lower than that of AFS glass, thereby arbitrate the acid–base reaction of GIC [27].

However, the results of incorporation of fluorapatite ceramic nanoparticles in the newly synthesized glass (sol-gel glass) resulted in the decrease of its setting time along with the increase of the concentration of fluorapatite ceramic nanoparticles. This because of the nanoceramics have a higher specific area than the commercial glass powders; thus, they entered the reaction sooner than the rest of the other glass powders and caused a decrease in the setting times [21].

CONCLUSIONS

Within limitation of this study the following conclusions could be drown;

1. Formulation of GIC with sol-gel method decrease in compressive strength, diametral tensile strength, and shear bond strength, and longer setting time than commercial GIC.

2. Incorporation of nano-FAp 1-3wt. % to sol-gel formulated GIC improves its mechanical properties and setting time.

3. Incorporation of nano-FAp 4wt. % decrease in the tested properties of sol gel formulated GIC.

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