Effect of Incorporation of Various Amounts of Nano-sized Hydroxyapatite on the Mechanical Properties of a Resin Modified Glass Ionomer

[1]Mahshid Mohammadi Basir [2]Mohammad Ataei [1]Mohammad Bagher Rezvani*[3]Parisa Golkar Taft

[1]Assistant Professor, Dept. of Operative Dentistry, Dental School, Shahed University, Tehran- Iran.
[2]Associate Professor, Dept. of Polymer, Petrochemical and Polymer Research Center of Iran, Tehran- Iran.
*[3]Corresponding Author: Assistant Professor, Dept. of Operative Dentistry, Dental School, Tehran University of Medical Sciences, Tehran- Iran. E-mail: p_golkar@tums.ac.ir

Abstract

Objective: Nano-sized hydroxyapatite nano particles (nHA) have optimal biological properties and by incorporating them into the restorative materials, we can benefit from these properties. The present study sought to assess the effect of incorporation of various amounts of nHA on the mechanical properties (compressive and flexural strengths) of a resin modified glass ionomer.

Methods: In this experimental study, a total of 252Fuji II LC improved GI samples were divided into 6 groups including a control group (0%) and the nHA groups (1%, 2%, 5%, 7% and 10% based on mass percent). Of the samples, 108 were fabricated for the flexural strength testing using a two-piece aluminum mold (2x2x25 mm) according to ISO standard 4049. In each group, a total of 18 samples in 3 subgroups (6 samples each) were fabricated. All samples were removed from the mold after 80 seconds of light irradiation. A total of 144 samples made for compressive strength testing using a two-piece brass mold (4x6 mm) according to ISO standard 9917. Thus, in each group, a total of 24 samples in three subgroups (8 samples each) were fabricated and removed from the mold after 80 seconds of light irradiation. After removal from the mold, all samples were stored in an incubator at 37˚C and 100% moisture and underwent flexural and compressive strength testing with the primary load of 2 N and crosshead speed of 0.5 mm/min^{-1}in a Zwick testing machine after one day, one week and one month. Data were analyzed using normal statistical tests of one-way ANOVA and Tukey's HSD (Post Hoc). In order to assess the correlation of time (in groups with various mass percentages of HAP) with understudy outcomes, one way ANOVA was employed and $P<0.05$ was considered statistically significant.

Results: Study results showed that incorporation of 5% nHA resulted in a significant increase in flexural strength after 30 days (17.4 MPa increase)($P<0.05$). Also, if the nHA weight percent exceeded 5%, flexural strength suffered a dramatic drop after one month(28.9 MPa reduction). This study also showed that addition of 5% NHAP significantly increased flexural elastic modulus after one month (2.2 GPa increase). Addition of NHAP to resin modified glass ionomer caused a small increase in compressive strength and compressive elastic modulus which was not statistically significant (about 1MPa increase).

Conclusion: Addition of nHA to resin modified glass ionomers (Fuji II LC improved) not only does not reduce compressive strength, but also can increase flexural strength which would be the greatest if nHA is added in an amount of 5%.

Key words: Resin modified glass ionomer, Nano-sized hydroxyapatite, Flexural strength, Compressive strength

Please cite this article as follows:
Mohammadi Basir M, Ataei M, Rezvani MB, Golkar Taft P. Effect of Incorporation of Various Amounts of Nano-sized Hydroxyapatite on the Mechanical Properties of a Resin Modified Glass Ionomer. J Dent Sch 2012;30(4):216-223.

Received: 14.10.2012 Final Revision: 19.11.2012 Accepted: 27.11.2012

Introduction:

Glass ionomer cement is among the most important dental cements which is popular for its biocompatibility, bacteriostatic property and double bond mechanism (ionic and micromechanical bonds)(1). However, its use is associated with problems like high technique

sensitivity and lower esthetics compared to composite resins. Furthermore, due to its low compressive strength and mechanical properties, it cannot be applied as a restorative material at areas under occlusal stress (2). Resin modified glass ionomers (RMGIs) are becoming increasingly popular due to their easier application, longer working time and superior mechanical properties (like flexural and compressive strengths) as well as keeping the advantages of the conventional types.

To date, several methods have been proposed to improve the strength characteristics of GI cements such as incorporation of various fillers like silver cermets and stainless steel powders with no good outcome under in-vitro and in-vivo conditions. Therefore, at present, the main focus in research is on improving the biological properties of this cement to be helpful in patients at high risk of caries. A new method for improving the properties of GI cements is addition of hydroxyapatite to the glass powder. Hydroxyapatite (HAP) is a type of calcium phosphate [Ca10(Po4)6(OH)2] which is used due to its similarity with the mineral content of enamel and dentin as well as characteristics like biocompatibility, bioactivity, low solubility in water and nontoxicity (3-5). Also, it is specifically important because of its potential for remineralization of primary carious lesions (6). Nano-sized HAPs have a higher degree of crystallinity and colloidal stability due to the smaller size and higher surface charge of particles that result in their improved strength and ease of application.

Gu et al, in 2005 incorporated a combination of nano-sized HAP and zirconium oxide (HA/ZrO2) with specific percentages into the conventional GI powder and reported higher compressive and tensile strengths in 4% and 12% volume percentages (7).

Moshaverinia et al, in 2008 incorporated nano-sized HAP into conventional GI powder and showed that addition of 5mass percent of this material caused a higher compressive, diametral tensile and biaxial flexural strengths compared to conventional cement (8).

It seems that addition of nano-sized HAP to glass ionomer improvesits biologic and mechanical properties. Thus, in this study we used nano-sized HAP as filler with optimal biologic characteristics to improve the mechanical properties of a resin modified glass ionomer cement. Nano-sized particles with specific mass percent in the form of needle-shaped particles (which have not been studied so far) were added to the light cure glass powder and their effect on compressive and flexural strengths and elastic modulus of the new cement was evaluated under in-vitro conditions. If no negative effect is observed on the mechanical properties, we can suggest addition of nano-sized HAP to this cement. This study sought to determine the effect of incorporation of various amounts of nano-sized hydroxyapatite particles on flexural and compressive strengths of a resin modified glass ionomer.

Methods:

This experimental study was conducted on 252 samples using hydroxyapatite nanoparticles (20090627, Nano Shell, India) and resin modified glass ionomer cement (Fuji II LC improved, GC Corporation, Tokyo, Japan). Nano-sized HAPs were weighed in specific amounts with digital balance (Mettler Toledo-AB 204) and added to the glass powder in order to reach the mass percent of nanoparticles in glass powder in the 6 test groups to 1%, 2%, 5%, 7% and 10% (0% in the control group, no nanoparticles). The obtained powder was mixed with a mortar and pestle for 20 minutes to achieve homogenous distribution of particles. The obtained powders were used to fabricate samples from the cements containing HAP. In each group, the powder according to the manufacturer's instructions (1 unit of liquid and 2 units of powder out of three mass percent) was mixed with liquid by a plastic spatula on a glass slab at room temperature and within a mixing time below 25 seconds. The prepared paste was used to fill up the related molds.

First phase- Fabrication of samples for flexural strength testing

In all 6 groups (one control, 5 test groups) the obtained paste was placed in a two-piece aluminum mold with 2x2x25 mm dimensions that had been prepared according to the ISO standard 4049. A glass slab was placed over the sample to compress the paste and eliminate any

possible void. The superior and inferior surfaces of the sampleswere light cured for 80 seconds using LED (light-emitting diode) light curing device (Demetron LC. SDS Kerr, USA) with 600 MmW/cm light intensity. By doing so, the entire length of the mold was irradiated 4 times and each time for 20 seconds. After completion of irradiation, the samples were removed from the mold, immersed in distilled water and stored in an incubator at 37˚C until testing. In order to assess the flexural strength, 108 samples were fabricated (18 in each group) out of which 6 were tested after one day, 6 after one week and 6 after one month by the Universal Testing Machine (Z2.5, Zwick, Germany) with the primary load of 2 N and crosshead speed of 0.5 mm/min^{-1}. Based on the obtained data and according to the formula $\alpha = \frac{3PL}{2dd^2}$ the flexural strength for each sample was calculated (α=flexural strength, P=maximum load at the point of flexural fracture, L=length of the support span, b=width of sample, d=diameter/thickness of sample).

Second phase- Fabrication of samples for compressive strength testing

In the second phase, in all 6 groups the mixed paste was placed in the two-piece brass mold with 4x6 mm dimensions (ISO standard 9917). After the placement of glass slab, the superior and inferior surfaces of each sample were irradiated for 20 seconds using the same LED light curing unit. After removing from the mold, samples were irradiated at each lateral surface for 20 seconds.

Samples were stored in an incubator until the conduction of the test as done in phase I. In order to measure compressive strength, 144 samples (24 sample in each group) were fabricated out of which 8 after one day, 8 after one week and 8 after one month were tested for compressive strength using Zwick Roell Testing Machine (primary load of 2N and cross head speed of 0.5 mm/min^{-1}). Based on the obtained data and the equation $CS = \frac{4P}{\pi d^2}$ where CS=compressive strength, P=maximum load at the point of compressive failure and d=diameter of the sample, compressive strength for each sample was calculated.

Third phase- Calculation of modulus of elasticity

Stress-strain curve for 252 samples was drawn using the device software. Modulus of elasticity was calculated for each sample (both compressive and flexural elastic moduli) based on the linear gradient of the curve.

Forth phase- Scanning Electron Microscopy (SEM) Analysis

Of each flexural strength test group, 2 samples were randomly selected (a total of 12) and after conduction of the test, were studied for evaluation of the microstructure of the obtained cement. Samples were prepared by the gold coating method and studied with SEM (Hitachi S-4160, model 180092, Tokyo, Japan).

The mean and standard deviation of strength and modulus of elasticity were calculated for each sample. In order to assess the distribution of data, a histogram with a normal distribution curve , for comparison of data, one way and two-way ANOVA and for evaluation of groups responsible for differences, Tukey's Post Hoc HSD test were used.

Results:

Results of statistical analyses (mean and standard deviation of flexural strength, flexural elastic modulus, compressive strength and compressive elastic modulus) for the 6 understudy groups in the two phases of the study are demonstrated in diagrams 1-4. The highest mean flexural strength (MPa) belonged to the group with 5% nano-HAP after one month. Addition of 1 and 2 weight percentnano-HAP to Fuji II LC (improved) light cure glass ionomer could not significantly improve its flexural or compressive strengths (about one MPa increase). Addition of 5% nano-HAP could significantly increase flexural strength and flexural elastic modulus ($P<0.05$)(17.4 MPa increase in flexural strength and 2.2 GPa increase in flexural elastic modulus) but had no significant effect on compressive strength or compressive elastic modulus (about one MPa increase). Addition of 7% and 10% nano-HAP could not cause any change in flexural or compressive strength or the related elasticmoduli compared to the control group (about 6 MPa increase)($P>0.05$). The

results of statistical tests revealed that addition of nano-HAP could not cause any significant difference in flexural or compressive strengths in any of the groups after one day but after one month, a significant increase was observed in flexural strength and flexural elastic modulus in the group with 5% nano-HAP ($P<0.05$)(17.4 MPa increase).As observed in the respective micrographs, in groups with up to 5%nHAP mixing of cement powder and liquid was almost complete and by increasing the HAP weight percent by up to 5% mixing was adequate resulting in subsequent improvement in strength (Figures 1 and 2).

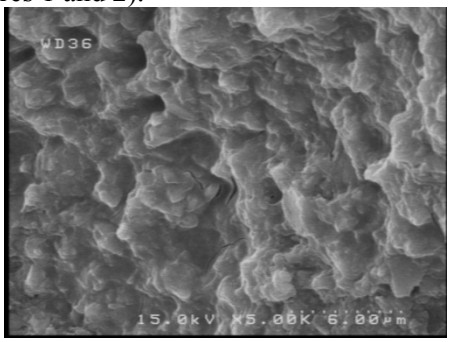

Figure 1- SEM micrograph of glass ionomer sample without nHAP (control group)

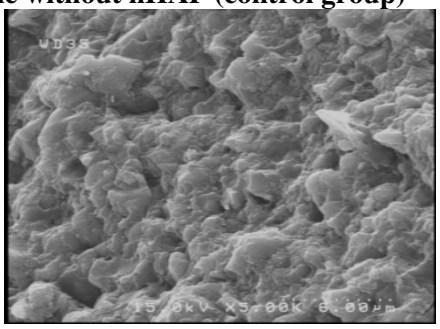

Figure 2- SEM micrograph of glass ionomer sample containing 5% nHAP

By increasing the weight percentage of nHAP (by 7% and 10%) a significant drop occurred in flexural strength properties and this reduction compared to the 5% group was statistically significant (11 MPa reduction)($P<0.05$). This reduction seems to be attributed to the agglomeration of nanoparticles at high mass percentages in the cement matrix that act as weak points. As observed in the respective micrographs, in 7% and 10% nHAP groups nanoparticles agglomerate and do not react adequately with cement powder (Figures 3 and 4).

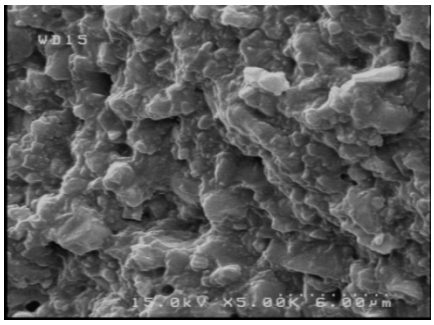

Figure 3- SEM micrograph of glass ionomer sample containing 7% nHAP

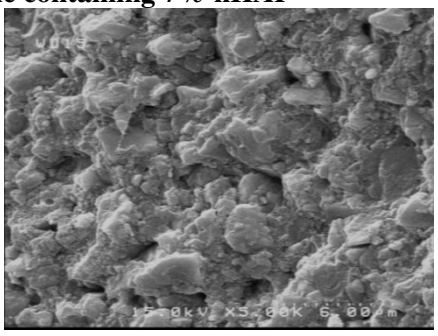

Figure 4- SEM micrograph of glass ionomer sample containing 10% nHAP

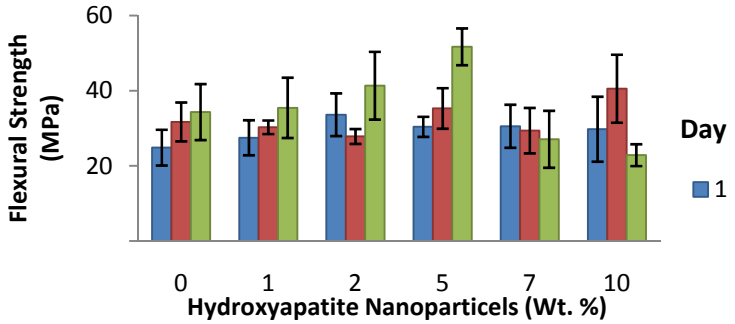

Diagram 1- The mean flexural strength (MPa) in the 6 understudy groups at three different time points (one day, one week and one month)

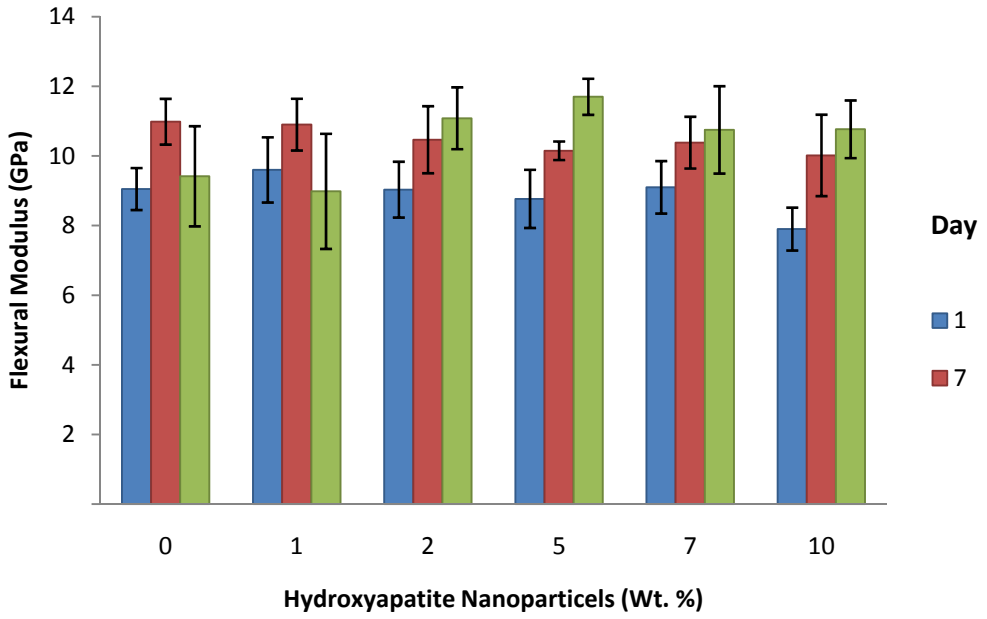

Diagram 2- The mean flexural elastic modulus (GPa)in the 6 understudy groups at three different time points (one day, one week and one month)

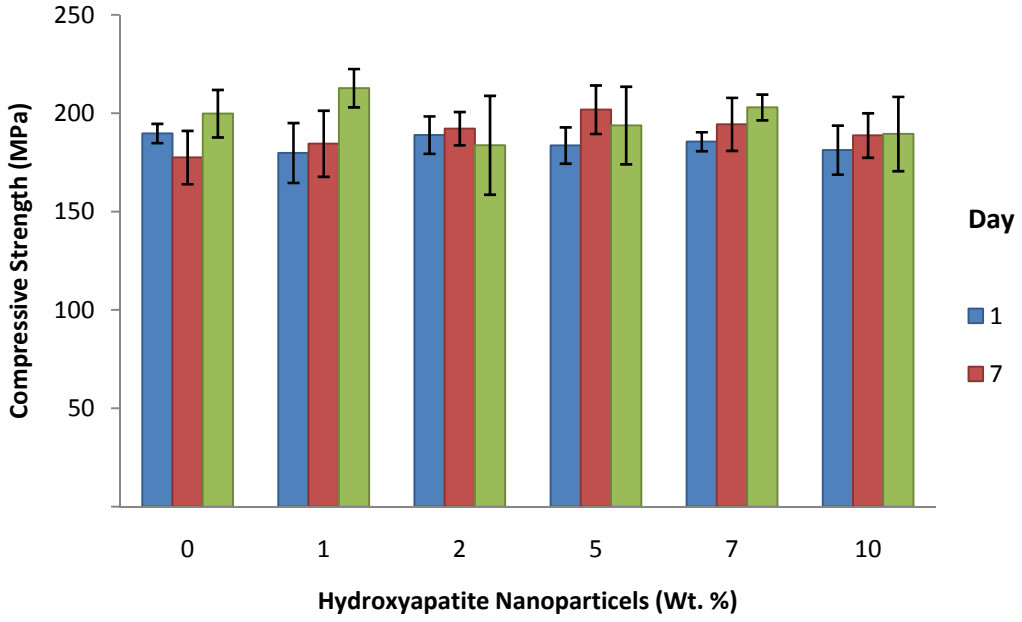

Diagram 3- The mean compressive strength (MPa) in the 6 understudy groups at three different time points (one day, one week and one month)

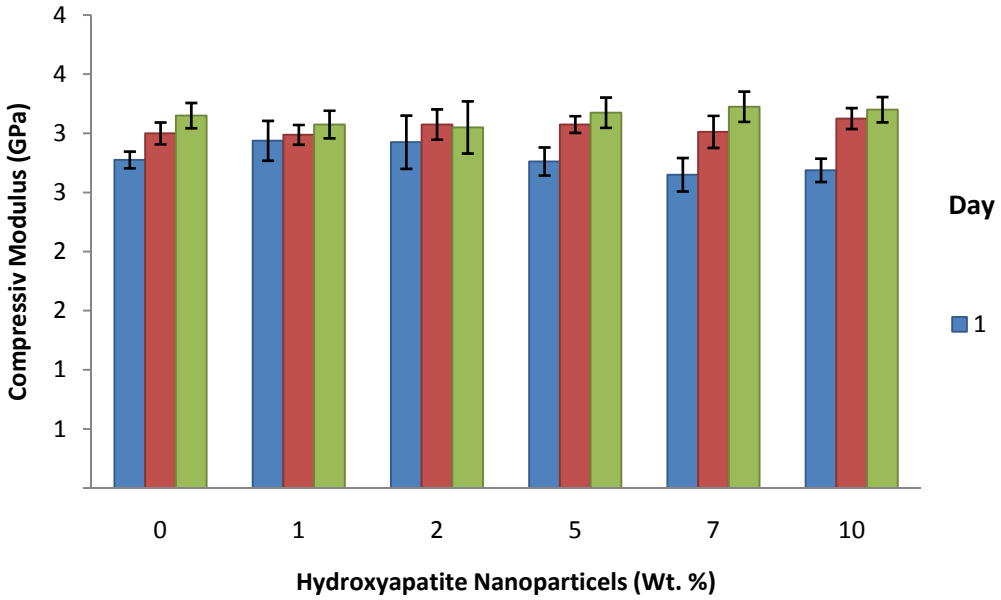

Diagram 4- The mean compressive elastic modulus (GPa)in the 6 understudy groups at three different time points (one day, one week and one month)

Discussion:

A contemporary idea for increasing the strength and improving the mechanical properties of glass ionomer cements is addition of different nanoparticles to the cement matrix. Glass ionomers containing hydroxyapatite were introduced to the field of dental materials a while ago. In the present study, we added hydroxyapatite nanoparticles to RMGI instead of the conventional glass powder. Nanoparticles due to their higher degree of crystallinity and colloidal stability have a greater reinforcing effect and easier application.

Results of the current study demonstrated that addition of 5% nanoparticles to the resin modified GI cement powder significantly increased the flexural strength and flexural elastic modulus of the cement compared to the control group as flexural strength increased from 34.3 MPa to 51.7 MPa and flexural elastic modulus improved from 9.5 GPa to 11.7 GPa.

Several studies have evaluated the incorporation of nanoparticles into the conventional GI cement but no study has evaluated addition of nano-sized HAP to the resin modified GI. At present, due to the characteristics like superior mechanical properties and easier application compared to the conventional type, resin modified GIs have numerous applications in operative dentistry and prosthodontics. Thus, the present study sought to assess the effect of addition of nano-sized HAP with high biologic properties to the resin modified GI cement.

In this study, results of the flexural strength test revealed higher flexural strength by increasing the weight percentage of nanoparticles up to 5%. Further increase, however, resulted in a reduction in flexural strength. Moshaverinia et al, in 2008 incorporatednano-sized HAP into the conventional GI powder and concluded that addition of 5% nano-sized HAP caused a higher compressive (177-179 MPa) and biaxial flexural strength compared to the original cement (26-28 MPa)(8). These results indicate a strong reaction between cement matrix and nanoparticles. Dissolution of nanobioceramicsin the acidic monomer leads to the release of calcium ions from the surface of nanoparticles and higher occurrence of crystallization reactions that eventually results in higher strength of the cement (9). In our study, we used resin modified GI instead of conventional GI. Also, Moshaverninia et al, (2008) in their study used granular nanoparticles whereas in the present study, we used nanoparticles manufactured by

Nano Shell company that according to the manufacturer, are rod-shaped. It seems that both the abovementioned issues are responsible for the difference in values obtained in the two studies.

In Gu et al, study in 2005 a combination of nano-sized HAP and zirconium oxide with specific volume percentages were added to conventional GI powder. They reported higher compressive and tensile strengths compared to the primary cement by addition of 4 and 12volume percentages (7). In our study, although after one week, compressive strength of the 5% group was significantly higher than that of the control group, no logical increasing trend was observed for the compressive properties. Studies have demonstrated that even addition of metal ions that are harder than HAP to the GI cannot result in significant improvement of compressive properties (10,11). It seems that using zirconium oxide nanoparticles due to their higher strength and modulus of elasticity compared to hydroxyapatite and glass particles and insolubility despite long water storage has resulted in a significant increase in the compressive strength of the mixture.

In the present study, addition of 7% and 10% nano-sized HAP reduced flexural strength. It seems that in percentages higher than 5% agglomerations of nanoparticles (agglomers) in the matrix act as weak points and reduce the mechanical properties of the mixture. Also, due to the opacity of HAP, insufficient penetration of light may also compromise the curing process of the resin portion of the cement and decrease its strength (12). Nanoparticles in high weight percentages act as non-reactive filler and may interfere with acid-base reactions as well (13).

Yap et al, in their study in 2002added various volume percentages of HAP powder to the conventional GI and observed no significant improvement in compressive strength. Also, a 20 MPa reduction occurred in the 28 volume percent group that is in accord with the present study results (14).

Evaluation of the effect of aging on strength properties revealed that cement strength gradually increased from day one to day 30 and this trend of increase in strength occurred by addition of nano-sized HAP by up to 5 weight percent. Mixing the glass powder and acidic monomer is still relatively complete and it seems that progression of acid-base reactions eventually results in improved strength (15). Furthermore, in groups with higher than 5% nano-sized HAP, resistance of cement decreased by longer water storage. By increasing the weight percent, greater number of defects and voids are observed in the material that increase water absorption and as weak points reduce the properties of the material (5). Santos et al, in 2002 evaluated the water absorption characteristics of composite resins containing HAP fillers and found that higher water absorption of samples containing filler can be due to the porosities and agglomeration of filler particles in the microstructure of cement which is in agreement with our study findings (16).

Within the limitations of this study, it appears that we may add 5% nano-sized HAP to the resin modified GI powder to improve its biological as well as flexural properties. Further studies are also required to evaluate other physical and mechanical properties of the obtained material.

Conclusion:

Within the study limitations, addition of 5% nano-sized HAP to Fuji II LC (improved) resin modified GI cement could significantly improve its flexural strength and flexural elastic modulus but had no significant effect on its compressive strength or compressive elastic modulus. Thus, it seems that by addition of 5% hydroxyapatite nanoparticles to GI we may improve its biological and mechanical properties.

Acknowledgment:

The authors would like to express their gratitude

to the Research Center of Shahed University, School of Dentistry for covering part of the expenses of this research project.

References:

1. Yoon SI, Lee YK, Kim YU, Kim MC, Kim KN, Kim SO, et al. The effect of hydroxyapatite on bonding strength between dental luting cement and human teeth. Key Engineering Mat 2005;284-286:935-956.
2. Mitchell CA, Douglas WH, Cheng YS. Fracture toughness of conventional resin modified glass ionomer and composite luting cements. Dent Mater 1999;15:7-13.
3. Kalita SJ, Bhardwaj A, Bhatt HA. Nano crystalline calcium phosphate ceramics in biomedical engineering Materials Science and Engineering 2007;27:441- 449.
4. Ferraz MP, Monterio FJ, Manual CM. Hydroxyapatite nano particles: A review of preparation methodologies. J Applied Biomat Biomech 2004;2:74- 80.
5. Sadat-Shojai M. Preparation of hydroxyapatite nanoparticles: comparision between hydrothermal and Solvo-treatment processes and colloidal stability of produced Nanoparticles in a dilute experimental dental adhesive. J Iran Chem Soc 2009;6:386-392.
6. Roveri N, Battistella E, Bianchi CL, Foltran I, Foresti E, Iafisco M, et al. Surface enamel remineralization: Biomimetic Apatite Nanocrystals and Fluoride ions different effects. J Nanomater 2009;Article ID 746383
7. Gu YW, Yap AU, Cheang P, Khor KA. Effects of incorporation of HA/ZrO(2) into glass ionomer cement. (GIC) Biomaterials 2005;26:713-720.
8. Moshaverinia A, Ansari S, Moshaverinia M, Roohpour N, Darr JA, Rehman I. Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements. Acta Biomater 2008; 4: 432 – 440.
9. Suchanek W,Yashima M,Kakihana M,Yoshimura M. Processing and mechanical properties of hydroxyapatite reinforced with hydroxyapatite whiskers. Biomaterials 1996; 17:1715-1723.
10. kilpatrick NM, Murray JJ, McCabe JF. The use of a reinforced glass– ionomer cement for the restoration of primary molars: a clinical trial. Br Dent J 1995;179: 175- 179.
11. Williams JA, Billington RW, Pearson GJ. The comparative strengths of commercial glass-ionomer cements with and without metal additions. Br Dent J 1992; 172: 279-282.
12. Sadat-Shojai M, Atai M, Nodehi A, Khanlar LN. hydroxyapatite nanorods as novel fillers for improving the properties of dental adhesives: Synthesis and application. Dent Mater 2010; 26: 471-482.
13. Nicholson JW. Hawkins SJ, Smith JE. The incorpordation of hydroxyapatite into glass-polyalkenoate ("glass-ionomer") cements: a preliminary study. J Mater sci: Mater Med 1994; 4: 418-42.
14. Yap AU, Pek YS, Kumar RA, Cheang P, Khor KA. Experimental studies on a new bioactive material: HAIonomer cements. Biomaterials 2002; 23: 955-962.
15. Lohbauer U. Dental glass ionomer cements as permanent filling materials? properties, limitations and future trends. Materials 2010; 3: 76 – 96.
16. Santos C, Clarke RL, Braden M, Guitian F, Davy KW. Water absorption characteristics of dental composite incorporating hydroxyaptite filler. Biomaterials 2002;23: 1897- 1904.