

Research Paper: Microhardness and Wear Resistance of Glass Ionomer Cements Modified by Chitosan and Nano-Hydroxyapatite



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ABSTRACT

Introduction: Despite the merits of glass ionomer cements (GICs), they suffer from weak mechanical properties such as low wear resistance. In this study, the mechanical properties of GICs after incorporating chitosan and nano-hydroxyapatite was investigated.

Materials and Methods: The samples were prepared in four groups, including non-modified GIGs (NMGIC, n = 5), chitosan incorporated GICs (CHGIC, n = 5), nano-hydroxyapatite incorporated GICs (nanoHAGIC, n = 5), and chitosan/nano-hydroxyapatite incorporated GICs (CH/nanoHA/GICs, n = 5). Long-term Vickers microhardness (VH) and wear rate of the samples after immersion in artificial saliva were measured.

Results: The results were analysed using one-way ANOVA followed by Scheffé's test ($P < 0.05$). Moreover, the microstructure of the samples was investigated via scanning electron microscopy. After 1 hour, the VH values of CH/nanoHA/GICs and CH/GICs were greater than nanoHA/GICs and non-modified GICs ($p < 0.001$). However, there were no statistical differences among VH values of all groups after 11 weeks ($p > 0.05$). Based on the wear tests, adding nanoHA or CH to GICs increased their wear rates, while introducing both of them decreased weight loss of GICs.

Conclusion: Within the limitations of the present study, introducing both nanoHA and CH to GIC enhances GIC's microhardness and wear resistance. Consequently, the addition of nanoHA and CH is a promising approach for improving mechanical properties of GICs.

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Introduction

Dental caries is caused by consecutive cycles of de- and remineralization of dental tissues at the interface between tooth surface and biofilm which occur due to release of acidic products produced by bacterial fermentation of carbohydrates into oral environment (1, 2). For altering or reversing these caries, fluoride products can be helpful because they inhibit demineralization and enhance remineralization of dental tissues (3). One of the most important restorative dental materials which have the ability to release fluoride ions are glass ionomer cements (GICs). Glass ionomer cements are the product of the acid-base reaction between the fluoro-aluminosilicate glass powder (base) and polyalkenoic acids family. Utilization of GICs is a promising approach in restorative dentistry (4, 5). Their thermal compatibility with tooth enamel, biocompatibility, low cytotoxicity, ease of use, anticariogenic properties, the ability to remineralize dental tissue due to fluoride release/uptake, chemical set reaction, and adhesion to moist tooth structure and base metals are considered as the most advantages of GICs(6-8).

The major limitation of GICs is their poor mechanical properties including low fracture toughness, and poor resistance to wear which may limit their applications in dentistry. Also they suffer from some drawbacks such as long setting times, short working times, and susceptibility to moisture contamination throughout the early stages of setting reaction(9-11).

Several attempts have been made to improve the mechanical properties of GICs. Generally, these modifications are classified into two categories including metal-modified-GICs (MMGICs) and resin-modified-GICs (RMGICs). These modified GICs, however, have some shortcomings, for instance the low strength of MMGICs and release of unreacted 2-hydroxyethyl methacrylate (HEMA) monomers in RMGICs which result in compromised biocompatibility in comparison to conventional GICs. Therefore, investigations for other ways to enhance conventional GICs to be continued(12-14).

Different biomaterials have been incorporated into GICs to improve their mechanical and anti-bacterial properties. A commonly used biomaterial for this purpose is hydroxyapatite (HA), which is a calcium phosphate bio-ceramic and one of the main constituents of teeth. Another biomaterial is chitosan (CH). CH is a natural bio-polyaminosaccharide, which has been examined in dentistry due to its unique properties such as possessing antibacterial effects against *Streptococcus mutans*. (15, 16).

In 2010, Lee et al(17) added 10% micro-HA and 10% nano-HA to the powder phase of conventional GICs and studied the changes of film thickness, setting time, and compressive strength. The results indicated significant improvement of the properties of the modified GICs as compared to non-modified GICs. In 2015, Ebrahim et al (18) modified the liquid phase of a commercial GIC with 5-50% v/v chitosan and investigated the changes of antibacterial properties against *Streptococcus mutans*. The results showed significant improvement of the antibacterial properties of the GICs by increasing the CH volume. In another study conducted in 2017(19), GICs were modified by adding 10% v/v chitosan to the liquid phase and 3% w/w TiO₂ nanoparticles to the powder phase. The antibacterial and mechanical properties of the dually-modified GICs were studied. The results demonstrated significant improvement of the antibacterial properties against *S. mutans*.

Furthermore, flexural and compressive strengths of the GICs were improved significantly.

In this study, the effects of introducing CH and nanoHA into GICs on long-term microhardness, wear rate, and microstructure of modified and un-modified GICs were evaluated. There are two null hypotheses: 1) The surface microhardness and wear resistance of GICs do not change after the addition of CH. 2) The surface microhardness and wear resistance of GICs do not change after the addition of nanoHA.

Methods and Materials

Materials:

In this study, powder/liquid Fuji IX GPs (LOT NOs. 9906141, 9905291, GC Corporation, Tokyo, Japan) was investigated. Low molecular weight chitosan (CAS-NO: 9012-76-4) and hydroxyapatite nanoparticles with mean particle size of 20nm (CAS-NO: 12167-74-7) purchased from Aprin Advanced Technologies Development company, Tehran, Iran.

Preparation of samples:

To modify GICs with nanoHA, GIC powder was mixed with nanoHA 5 wt. %. 0.1 ml of 0.2 mg/ml CH solution was added to 0.9 ml of GIC liquid to obtain GIC with 10% (v/v) CH solution. Four groups of modified and non-modified GICs were prepared (Table 1). After mixing powder and liquid of GIC with the ratio of 3.6 g/1.0 ml, the cements were placed in cylindrical moulds with 2 mm height and 10 mm diameter, pressed for 15 min, polished with 800, 1000, and 1200 grit papers respectively, de-moulded, and then immersed in artificial saliva at 37°C.

Table 1. Experimental study groups and their constituents

| Study group | Powder | Liquid |
|-----------------------------|---------------------------------------|------------------------------------------------------|
| NMGIC (n = 5) | Fuji IX GPs powder | Fuji IX GPs liquid |
| CHGIC (n = 5) | Fuji IX GPs powder | Fuji IX GPs liquid+ 10%(v/v) chitosan solution |
| nanoHAGIC (n = 5) | Fuji IX GPs powder+ 5 wt. % nanoHA | Fuji IX GPs liquid |
| CH/nano HAGIC (n = 5) | Fuji IX GPs powder+ 5 wt. % nanoHA | Fuji IX GPs liquid+ 10% (v/v) chitosan solution |

Morphological analysis:

One prepared sample of each group, was stored in artificial saliva for 24 h at 37°C, dried, fractured, gold-coated, and its morphology was observed by field emission scanning electron microscopy (FE-SEM, Hitachi 4160).

Surface microhardness analysis:

Surface microhardness of all samples (n=20) was determined by Vickers method with a hardness test machine (BAREISS, Germany) under conditions of a 200-gf load and dwell time of 15 seconds. Each sample indented three times. After immersion of samples for 1 hour, 24 hours, 1 week, 2, 3, and 11 weeks in artificial saliva, their surface microhardness values were determined.

Wear Test :

Wear tests were fulfilled with the pin-on-disc test machine. Samples (n= 12) were placed in a holder connected to the pin. The counter-acting disc was covered by a 1500 grit paper. The grit paper was replaced by a fresh one after each test. All samples were tested under constant 15N load and speed of 0.23 m/s for 400 m sliding distance at room temperature.

Statistical analysis:

Mean values and standard deviations of measured microhardnesses and weight losses were calculated. The Kolmogorov-Smirnov test was used for assessing the normality assumption of the data. One-way ANOVA followed by Scheffé's test was employed for statistical analysis with the level of significance set at $p < 0.05$. Statistical analysis was performed in IBM SPSS Statistics 25.

Results

Morphological analysis:

The micro-structure images of all samples are shown in Figure 1. The angular particles of fluoroaluminosilicate can be seen in Figure 1, A1 and A2. In NMGIC, lots of hollow bodies are seen. However, the number of these bodies decreased after 11 weeks. The agglomeration of HA nanoparticles in nanoHAGIC (Figure 1, B1 and B2) has led to the formation of spherical nanoparticles, which are distinguishable from angular fluoroaluminosilicate glass powder. In the case of CHGICs (Figure 1, C1 and C2), the amount of hollow spaces has been decreased in comparison to NMGIC. In CH/nanoHAGICs (Figure 1, D1 and D2), the number of spherical and angular particles have been reduced and the microstructure is more uniform.

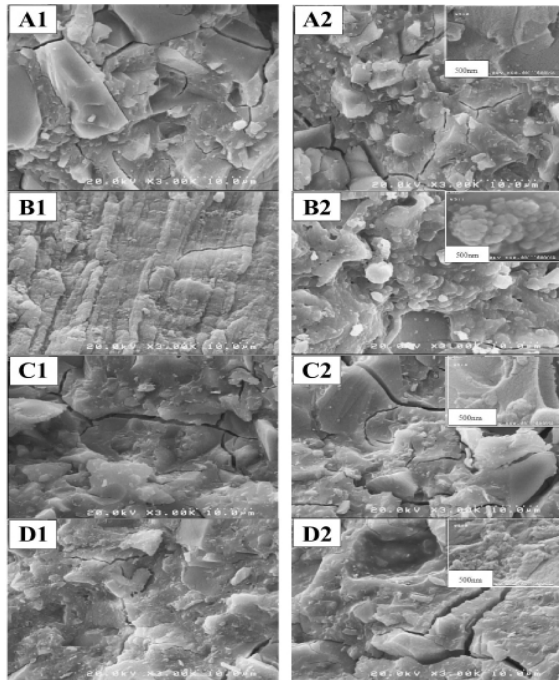


Figure 1. FESEM micrographs of NMGICs (A1, A2), nanoHAGICs (B1, B2), CHGICs (C1, C2), and CH/nanoHAGICs (D1, D2). Samples were immersed in artificial saliva for 48 hours (A1, B1, C1, D1) and 11 weeks (A2, B2, C2, D2).

Surface microhardness

The means of Vickers microhardness (VH) are presented in Table 2 and Figure 2. In the first hour, there is a significant increment for CHGICs and CH/nanoHAGICs in comparison to NMGICs ($p < 0.001$). After 3 weeks, the VH values of CHGICs and CH/nanoHAGICs were also higher than other groups. However, there were not any statistically differences among the groups after 11 weeks. Overall, nanoHA dropped the VH values in comparison to NMGICs and CH improved the VH of GICs.

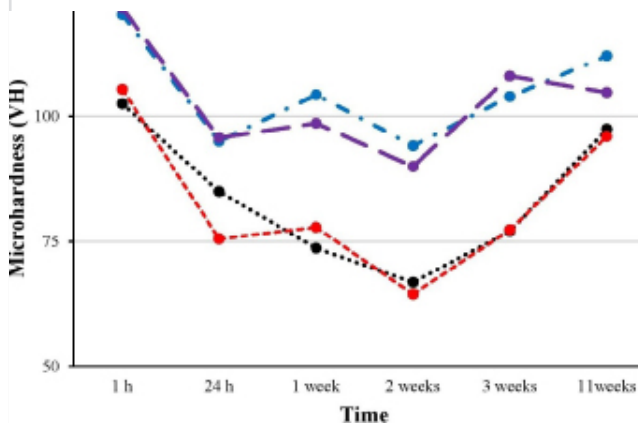


Figure 2. Vickers microhardness of NMGICs, nanoHAGICs, CHGICs, and CH/nanoHAGICs after immersing in artificial saliva.

Table 2. Vickers microhardness after immersing the samples in artificial saliva.

| Study group | NMGIC | nanoHAGIC | CHGIC | CH/nanoHAGIC |
|-------------|--------|-----------|--------|--------------|
| 1 h | 102.51 | 105.42 | 120.04 | 121.67 |
| 24 h | 84.95 | 97.49 | 95 | 95.72 |
| 1 week | 73.63 | 77.08 | 104.03 | 98.62 |
| 2 week | 66.08 | 64.44 | 94.12 | 89.97 |
| 3 week | 77 | 77.04 | 103.97 | 108.05 |
| 11 week | 97.42 | 95.96 | 112.11 | 104.77 |

Wear test:

The data of wear tests are presented as weight loss of samples per sliding distances (Figure 3). The highest and the lowest amount of weight losses belong to nanoHAGIC and CH/nanoHAGIC samples, respectively. The percentages of weight loss of CH/nanoHAGICs were decreased significantly in comparison to NMGICs ($p < 0.001$).

The percentage of wear rate for NMGICs is lower than nanoHAGICs and CHGICs; however, weight loss of CH/nanoHAGICs is lower than NMGICs ($p < 0.001$). It is found that, except for the second 100 m, wear resistance of CH/nanoHAGICs is significantly higher than NMGICs ($p < 0.001$). (Table 3)

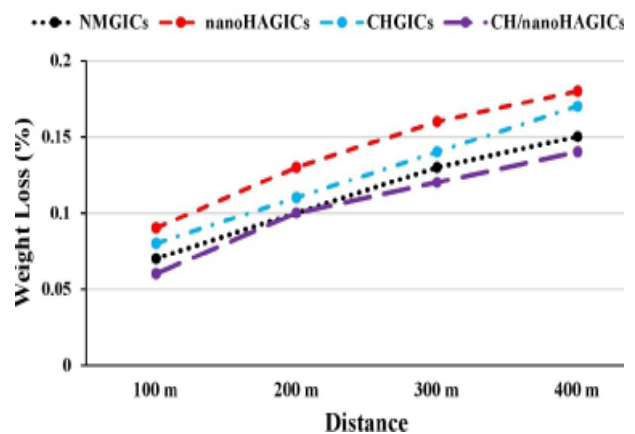


Figure 3. The weight loss percent of NMGICs, nanoHAGICs, CHGICs, and CH/nanoHAGICs after immersing in artificial saliva for 24 h as a function of sliding distance

Table 3. The weight loss percent of the samples after immersing in artificial saliva for 24 h as a function of sliding distance

| Study group | 100 m | 200 m | 300 m | 400 m |
|--------------|-------|-------|-------|-------|
| NMGIC | 0.07 | 0.1 | 0.13 | 0.15 |
| nanoHAGIC | 0.09 | 0.13 | 0.16 | 0.18 |
| CHGIC | 0.08 | 0.11 | 0.14 | 0.17 |
| CH/nanoHAGIC | 0.06 | 0.1 | 0.12 | 0.14 |

Discussion

Morphological studies revealed obvious structural changes caused by the addition of CH and nanoHA to GICs. In CHGICs the amount of the hollow spaces has been decreased as compared to NMGIC. This may indicate that the adhesion among the GIC components has been improved in the presence of CH. In nanoHAGIC, nHA particles has agglomerated and formed microparticles due to the poor miscibility of the nanoparticles within the matrix. In contrast, the uniform structure of CH/NHAGIC indicates strong interfacial interactions between the components.

Microstructure analysis of fractured surface of GICs provide more details about their microstructure and mechanical properties (20). All of the samples contain micro-pores, voids, and cracks. The cracks could be formed due to the dehydration of samples during preparation for FE-SEM. Since GICs contain water in their composition, the existence of fractures and cracks seems inevitable after dehydration(6, 21, 22). On the other hand, the cracks may be caused by fracturing of samples before the test.

Mastication imposes different kinds of forces to human teeth. As a result, measuring the hardness of tooth and dental restorative materials seems necessary because by assessing the hardness, we can learn about the distribution of masticatory strains throughout the tooth (23). Hardness of a material could be measured via a variety of different approaches and methods. One of the most common hardness test approaches is static indentation test which include several test methods such as Vickers test (24). In this study, a pattern for Vickers microhardness values of

each experimental GICs over time is obtained. As it is presented in Figure 2, nanoHAGICs and NMGICs follow almost the same pattern, as for CHGICs and CH/nanoHAGICs. After 1 h immersion in saliva, the VH of CHGICs and CH/nanoHAGICs have considerably increased in comparison to NMGICs ($p < 0.001$), although the VH values of all groups decreased during first three weeks. Again, after three weeks, the amounts of VH increased. Within 11 weeks, the total VH reduction percent of NMGICs, nanoHAGICs, CHGICs, and CH/nanoHAGICs were 4.96, 8.97, 6.88, and 13.89%, respectively. At the end of experimental time period, CHGICs had the highest VH. The low microhardness values attributed to nanoHAGICs in comparison to other modified GICs can be due to the aggregated nanoparticles. It has been shown that agglomeration of nanoparticles may reduce the mechanical strength of GICs, for these particles cannot interact with the polyacid (25).

Many studies claim that introducing nanoceramics may improve the mechanical properties of GICs (26-28); however, in this study, addition of nanoHA to GICs did not affect the VH significantly. Similarly, Gu et al. conducted an investigation on effects of incorporation of HA/ZrO₂ into GICs. The effects of addition of ZrO₂/HA and HA into GICs compared separately. They found that the mechanical properties of ZrO₂/HA are much better than HA-GICs; also, the values of HA-GICs hardness were even lower than the original GICs (29).

Yap et al. studied HA/Ionomer cements. They substituted 4, 12, and 28 vol % of fluoroaluminosilicate by crystalline HA particles, and measured the surface hardness after 1 day and 1 week. They observed that, for both time intervals, HA28 had the lowest hardness among all groups. The presence of greater amount of HA which is softer than glass particles as well as inadequate PAA to hydrolyze the HA/Ionomer powder mixture, may be lead to insufficient matrix formation which results in reduced resistance to indentations. Based on their conclusion, HA/Ionomer cements are considered as a promising materi-

al due their mechanical properties (30).

CH has many hydroxyl and acetamide groups which can form strong hydrogen bonds with hydroxyl groups of GIC and carboxyl groups of PAA. There are not any kinds of interactions between them. Therefore, this combination would be very appropriate for self-healing materials with improved properties including durability (15, 31). With respect to this fact, the higher amount of CHGICs hardness is justifiable. The formed hydrogen bond between PAA and CH increases the resistance of this sample to indentations.

With regarding the limitations of our study, it has found that immersion of all experimental groups of GICs in saliva has reduced surface microhardness. Ellakuria et al. measured the surface microhardness of conventional and RMGICs during 1 year storage in water. They reported a range of variations in VH values of RMGICs and conventional GICs. They, also concluded that the addition of resin did not improve the surface microhardness of GICs (32).

On the contrary, Shiozawa et al. evaluated the effect of immersion time of two kinds of GICs in CaCl₂. They found that by immersion of these GICs in CaCl₂ at the early stages of setting, their surface microhardness have increased (33).

Restorative dental materials should have the same or greater wear resistance than teeth. In order to measure wear rate in restorative materials, a variety of procedures has been proposed. These procedures are mainly based on the utilization of wear machines (direct methods) or measurement of mechanical properties related to wear, such as hardness or coefficient of friction (indirect methods). In most of the studies, wear resistance of the restorative materials is measured directly using an abrading point over the material (34-36). Similarly, in this study, wear measurement was performed by the use of a pin-on-disk machine.

According to Archad's law, wear resistance of a material is proportional to its hardness. Therefore, a substance with higher hardness has higher wear resistance or lower weight loss (37). In the present study, the weight loss

of the modified and non-modified GICs as well as the relation between microhardness and wear rate were investigated. The obtained data suggest two phases (Figure 3). The first phase (before 100 m) is related to high weight loss rate, and the second phase is associated with low weight loss rate (steady state wear procedure) (37). Considering microhardness data, nanoHAGICs and CH/nanoHAGICs follow Archad's law, but CHGICs doesn't follow the law. In other words, although the weight loss percentages of nanoHAGICs and CHGICs are lower than NMGICs, CH/nanoHAGICs have the highest microhardness and the lowest weight loss among all experimental groups.

Various factors including shape and size of glass particles, wear resistance of liquid constituent (polymeric part) and glass particles, as well as the adhesion between these two parts may influence the wear rate of GICs (38). It is found that introducing nanoHA particles or CH solution did not change the wear rate of GICs; however, adding both of them improved wear resistance of GICs significantly. This may be justified by their microstructures. As it is presented in Figure 1, the microstructure of CH/nanoHAGICs is more integrated than others. This may be due to the adhesion between glass particles and polymeric matrix. Therefore, the weight loss of these GICs is lower than the other samples.

Conclusion

Briefly, microhardness, weight loss, and microstructure of modified and non-modified GICs were studied. It was found that adding CH to GIC's solution enhances the microhardness, but does not improve the wear resistance. Moreover, nanoHA added to GIC's powder neither increased wear resistance, nor improved microhardness. Interestingly, adding both CH and nanoHA enhanced both the microhardness and wear resistance of GICs. Within the limits of this study, it can be concluded that incorporation of CH and nanoHA is a promising approach to enhance the mechanical properties of GICs. However, further investigations are required to

better understand the synergic effects of CH and nanoHA on the microstructure of GICs. It is also suggested to conduct future studies on optimizing the amounts of the fillers to obtain GICs with maximum improvement of properties.

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