Journal of Iranian Medical Council, Volume 7, Issue no. 1
http://dx.doi.org/10.18502/jimc.v7i1.14206

Original Article

Check for updates

Effects of Incorporation of Titanium Dioxide Nanoparticles on Mechanical Properties of Conventional Glass Ionomer Cement

Narges Panahandeh[1], Elham Hasani[1], Saeed Safa[2]*, Mojtaba Hashemi[1] and Hassan Torabzadeh[3]

1. Dental Research Center, Research Institute of Dental Sciences, Shahid Beheshti University of Medical Sciences, Tehran, Iran
2. Young Researchers and Elite Club, South Tehran Branch, Islamic Azad University, Tehran, Iran
3. Iranian Center for Endodontics research, Research Institute of Dental Sciences, Shahid Beheshti University of Medical Sciences, Tehran, Iran

Abstract

Background: Due to the poor mechanical properties of Glass Ionomer Cement (GICs), their use is limited to low stress-bearing areas. This study aimed to assess the effect of the addition of Titanium Dioxide (TiO_2) nanoparticles on the flexural strength and surface hardness of GIC.

Methods: In this *in vitro* study, 3, 5, and 10 wt.% TiO_2 nanoparticles were added to Fuji II conventional GIC powder. The purity and composition of the as-synthesized titania were investigated by using XRD and FT-IR tools. The homogeneity of powder particles within the used matrix was evaluated under a Scanning Electron Microscope (SEM).

Results: The SEM micrographs confirmed the homogenous mixing of TiO_2 nanoparticles with GIC powder.

Conclusion: Nevertheless, the flexural strength of experimental groups was not significantly different from that of the control group (p=0.384). However, the surface hardness of experimental groups was decreased in comparison with that of the control group (p<0.001).

Keywords: Glass ionomer cements, Hardness, Roughness, Titanium dioxide nanoparticles

*** Corresponding author**
Saeed Safa, DDS
Young Researchers and Elite Club, South Tehran Branch, Islamic Azad University, Tehran, Iran
Tel: +21 2297 4546
Email: safa1493@gmail.com

Received: Feb 27 2023
Accepted: Jun 14 2023

Citation to this article:
Panahandeh N, Hasani E, Safa S, Hashemi M, Torabzadeh H. Effects of Incorporation of Titanium Dioxide Nanoparticles on Mechanical Properties of Conventional Glass Ionomer Cement. *J Iran Med Counc*. 2024;7(1):99-106.

Introduction

Glass Ionomer Cements (GICs) bond to tooth structure and base metals and have cariostatic properties due to fluoride release potential, coefficient of thermal expansion close to that of tooth structure, translucency, biocompatibility and low toxicity (1). GICs have been reinforced to obtain more favorable mechanical properties by addition of different metal fillers, ions and other components (2). Addition of hydroxy ethyl methacrylate or bisphenolglycidyl methacrylate to GIC increases its compressive strength, hardness, modulus of elasticity and resistance to dissolution (3). It was mentioned that incorporation of hydroxyapatite and fluorapatite nano ceramic particles into GIC can increase its mechanical properties and enhance its bond strength to dentin. However, addition of barium sulfate to GIC significantly decreases its compressive strength and surface hardness (4-6).

Metal oxides such as zinc oxide and Titanium Dioxide (TiO_2) are among inorganic antimicrobial agents that have been suggested for addition to dental materials to confer antimicrobial properties (7). TiO_2 is an inorganic filler with properties such as optimal biocompatibility, no toxicity, antibacterial activity and favorable optical, physical and electrical properties (8). Evidence shows that addition of TiO_2 to composite resins improves their microhardness, flexural strength and antibacterial activity (9). Also, it was informed that addition of TiO_2 nanoparticles to GIC significantly increased its compressive and flexural strengths, fracture toughness, hardness and antibacterial activity against *Streptococcus mutans* without compromising the fluoride release potential and it was concluded that titanium incorporated GIC could be used in stress-bearing areas. Moreover, addition of TiO_2 nanoparticles to GIC did not affect its biocompatibility when human gingival and periodontal ligament fibroblasts were used as the culture medium (9).

According to Elsaka *et al*, addition of TiO_2 nanoparticles to GIC can enhance antibacterial properties of GIC. Thus, these cements can be used in Class II cavities as a liner to benefit from their antibacterial properties, which are important particularly in the gingival margin (9-14).

However, it is obvious that this type of recommendation (*i.e.,* using in Class II cavities) cannot be advised solely based on few studies. Thus, this study aimed to assess the effect of addition of different concentrations of TiO_2 nanoparticles on mechanical properties of GIC.

Materials and Methods

In this *in vitro*, experimental study, TiO_2 nanoparticles in 3, 5 and 10wt% concentrations were added to Fuji II GIC powder (GC Corporation, Tokyo, Japan).
A group without TiO_2 was also considered as control.

Preparation of TiO_2 nanoparticles

TiO_2 nanoparticles were prepared using sol-gel technique. First, a solution of 13.3 *mL* of titanium isopropoxide in 100 *mL* of isopropanol and a solution of 20 *mL* of double distilled water in 100 *mL* of isopropanol was prepared. These solutions were stirred for 2 *hr* and then the second solution was gradually added to the first solution in a dropwise fashion within 6 *hr*. After mixing, isopropanol was separated from the solution and 200 *mL* of double distilled water was added to the residual solution. The pH of the solution was adjusted to 1.5 using 1M nitric acid. The solution was refluxed at 343°*K* for 24 *hr* and then placed in an ultrasonic bath for 2 *hr* at room temperature. Sol at room temperature was gradually converted to gel and the gel was dried and calcined in a furnace at 673°*K* with a temperature rise rate of 1 *K/minute* for 3 *hr* (10).

Preparation of nano TiO_2 glass ionomer

For evaluating the mechanical properties, TiO_2 and Fuji II GIC powders were weighted on a digital scale (AL-104; Acculab, USA) with 0.0001*g* accuracy. TiO_2 nanoparticles measuring 5 wt% of the entire powder were placed on a mixing and the same amount of GIC powder (10 wt% of the powder) was added to TiO_2 nanoparticles and manually mixed by a plastic spatula. After homogenous mixing, GIC powder was added (20 wt% of the powder) and mixed to obtain the desired concentrations. The required amount of liquid was also weighted by the digital scale. Mixing procedure was carried out as manufacture's instruction. Three groups with 3, 5 and 10 wt% concentrations of TiO_2 nanoparticles added to GIC and one control group without TiO_2 were prepared (15).

Characterizations

X-ray Diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were performed to study the crystal structure and purity of TiO_2 nanoparticles by using PW1800 Philips and Nicolet 6700, respectively. For the FTIR test, a little amount of the prepared TiO_2 powder was added with KBr (1 wt.% composite) and completely mixed. Also, a control sample (without TiO_2) was prepared. Afterwards, the powders were pressed (100 *Kg*) within standard sample holder and rapidly measured in the standard range of FTIR (400-4000 cm^{1-}). For XRD test, about 0.2 *g* of the powder was pressed and the final pellet was placed in the sample holder for test. The Scanning Electron Microscope (SEM) was used to assess the surface morphology and degree of dispersion of nanoparticles within Fuji II GIC powder. For depicting the SEM images, a negligible amount of powder was ultrasonically dispersed in acetone. Afterwards, the suspension was dripped many times on to a steel sample holder and kept to dry for SEM imaging.

Flexural strength test

A stainless steel mold (2×2×25 *mm*) was used. A clear polyester strip was placed on a glass slab and the mold was placed over it. The mold was filled with GIC and another strip was placed over it and a glass slab was placed on the top. Gentle pressure was applied for the excess cement to leak out. Five samples were fabricated for flexural strength test in each group and rested at 37°*C* for 15 *min*. The samples were removed from the mold and immersed in distilled water and stored at 37°*C* for 24 *hr* and one week (PL-455, Peco, Pooya Electronic Co., Tehran, Iran). Prior to testing, the sample dimensions were measured by a digital caliper with 0.01 *mm* accuracy.

A universal testing machine (STM-20, Zwick Roell, Ulm, Germany) was utilized for three-point bending test for measurement of flexural strength, and 50±16 *N* load was applied at a crosshead speed of 0.5 *mm/min* until fracture. Maximum load at fracture was recorded and flexural strength value was calculated using the following formula: Flexural strength=3 $FL/2bh^2$

Where F is the maximum load at failure in Newtons (*N*), L is the distance between the two levers in *mm* with 0.01 *mm* accuracy, b is the width of sample in millimeters and h is the height of sample in *mm* (15).

Hardness test

For measurement of surface hardness, a stainless steel mold was used to fabricate samples with 6 *mm* diameter and 2 *mm* height. The samples were fabricated as explained above and placed in a Vickers hardness tester (HVS 1600-6100, Buehler testing Inc., Germany) with 0.025 µ accuracy. The surface of the samples was first inspected using 125× magnification to choose a smooth area. An indentation was created by applying 300 *g* load for 15 *s*. The created indentation was then measured at ×125 magnification and the surface hardness was calculated using the following equation: HV=1.8544 *f/d2* where F is the indentation load and d is the mean diameter of the indentation. Each sample was subjected to 10 indentations with 1.5 *mm* distance. Thus, a total of 20 values were obtained for each group and the mean value was reported as surface hardness. Vickers hardness number was measured at 24 *hrs* and one week (15).

Statistical analysis

Data were analyzed using descriptive and analytical statistics via SPSS version 21 (IBM Corp., Armonk, New York, USA). Kolmogorov-Smirnov test was applied to assess normal distribution of data. Two and One-way ANOVA was used to compare the groups in terms of flexural strength and hardness. Tukey's test and t-test were used for pairwise comparisons. $p<0.05$ was considered statistically significant (15).

Results

Figure 1 shows the XRD patterns of the as-synthesized TiO_2 nanoparticles. As can be seen, the characteristic peaks related to anatase phase TiO_2 centered at diffraction angles of 25.41, 37.97, 48.15, 55.11 and 62.81 are observable. The morphology and particle size distribution of the crystallized TiO_2 nanoparticles are shown in the Figure 2A. The semi spherical nanoparticles with a narrow size distribution could be appropriate for better distribution of this filler. Nevertheless, one can see a major aggregation tendency due to surface forces which shows the importance of mixing stage for fabrication of the composite samples.

SEM micrographs (Figure 2) showed 5% TiO_2 group

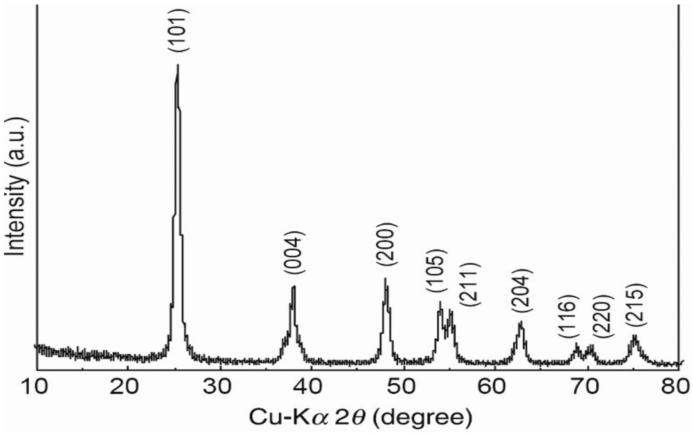

Figure 1. The XRD pattern of the as-synthesized TiO_2 nanopowder.

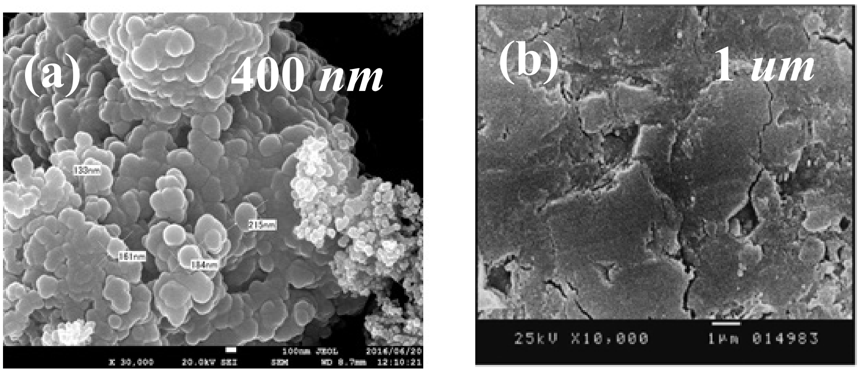

Figure 2. The SEM micrographs of (a) bare TiO_2 nanoparticles and (b) the cross cut of the GiC/5 wt.% TiO_2 composite.

had uniform distribution of TiO_2 nanoparticles in the form of granules in the matrix. Also, surface morphology of nanoparticles in 5% TiO_2 group indicated higher degree of uniformity and smoothness and fewer cracks compared to the control group.

The FTIR of control and 5wt% TiO_2 incorporated samples are shown in figure 3. The peaks appeared at 3446 cm^{-1} are assigned to the OH- dangling groups. The other peaks appeared at middle of the plots (between 1000-2000 cm^{-1}) are well assigned to the characteristic peaks of GIC. The peaks generally observable at low wavenumbers (<800 cm^{-1}) are generally attributed to the strong covalent band like Ti-O, Si-O and *etc*. Thus, one can conclude that due to the presence of intrinsic Si-O band in GIC, the Ti-O and Si-O characteristic bands are superimposed and hardly can be deconvoluted.

Flexural strength

Table 1 shows flexural strength of the four groups at 24 *hr* and one week. Normal distribution of flexural strength data was confirmed by Kolmogorov Smirnov test. Two-way ANOVA was applied to assess the effect of concentration of TiO_2 and time on flexural strength ($p<0.05$). The results showed that time had no significant effect on flexural strength ($p=0.60$) while concentration had a significant effect on flexural strength ($p<0.001$).

The interaction effect of time and concentration on flexural strength was not significant ($p=0.232$). Pairwise comparison of the groups using Tukey's HSD test (Table 2) indicated that 3% TiO_2 and control groups were not significantly different ($p=0.780$). Moreover, 5 and 10% TiO_2 groups showed no significant difference ($p=0.384$). However, 5%

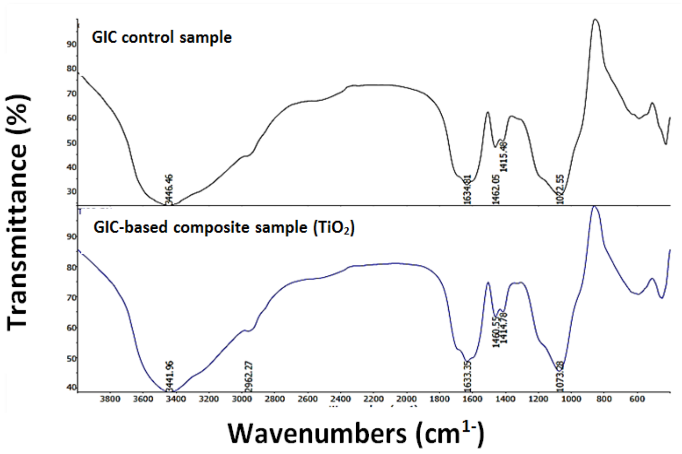

Figure 3. FTIR of GIC (control group) and the composite sample containing 5% TiO_2.

group exhibited significantly higher flexural strength in comparison with that of 3% and control groups ($p<0.05$).

Surface hardness

Table 1 shows surface hardness of the four groups at 24 *hr* and one week. Kolmogorov-Smirnov test demonstrated that data were normally distributed ($p>0.05$). Two-way ANOVA revealed that the addition of 3, 5 and 10% wt TiO_2 nanoparticles decreased hardness. The interaction effect of time and concentration of TiO_2 on hardness was also significant ($p<0.001$). One-way ANOVA was applied to compare the four concentrations and independent t-test was applied to compare the two time points for each concentration. At 24 *hr*, a significant difference was noted in hardness of the four concentrations ($p<0.001$). Pairwise comparison of concentrations at this time point by Tukey's test showed that 5 and 10% concentrations were not significantly different ($p=0.938$) while other comparisons showed significant differences ($p<0.05$). Surface hardness of the four groups was significantly different at one week ($p<0.001$). Pairwise comparison of the groups represented that 10% concentration had the lowest hardness ($p<0.001$) with significant differences with 3 and 5% TiO_2 groups. Also, 3% TiO_2 group had less hardness than 5% TiO_2 group at one week ($p<0.001$). Comparison of time points for each concentration showed significant differences between 24 *hr* and one week for all concentrations ($p<0.001$). Groups with 3 and 5% concentrations at one week showed higher

Table 1. Mean flexural strength and surface hardness of the groups at 24 *hr* and one week (n=5)

Storage Time	TiO_2 Concentration (wt.%)	Flexural strength (Mpa) Mean±SD	Surface hardness (VHN) Mean±SD
24 *hr*	3	8.26±2.45	25.06±3.73
	5	17.53±2.96	35.02±4.85
	10	11.96±6.38	34.24±3.59
	Control	10.66±1.65	54.43±4.67
1 week	3	10.50±3.04	36.43±9.36
	5	14.34±3.70	45.32±7.54
	10	14.84±1.25	16.12±4.28
	Control	11.08±3.96	40.27±3.09

Table 2. Pairwise comparison (Tukey's test) of the groups in terms of flexural strength

TiO_2 Concentration (wt. %)	TiO^2 Concentration (wt. %)	Mean difference	Std.Error (%)	p-value
3%	5%	-6.55	1.569	0.001
	10%	-4.01	1.569	0.070
	Control	-1.48	1.569	0.780
5%	10%	2.53	1.569	0.384
	Control	5.07	1.569	0.014
10%	Control	2.53	1.569	0.386

Table 3. Pairwise comparison of surface hardness in the four groups at 24 *hrs* and one week

Storage Time	TiO_2 Concentration (wt.%)		Mean difference	Std. Error	p-value
24 hr	3%	5%	-9.95	1.344	<0.001
		10%	-9.17	1.344	<0.001
		Control	-29.37	1.344	<0.001
	5%	10%	0.78	1.344	0.938
		Control	-19.41	1.344	<0.001
	10%	Control	-20.19	1.344	<0.001
1 week	3%	5%	-8.89	2.077	<0.001
		10%	20.30	2.077	<0.001
		Control	-3.84	2.077	0.258
	5%	10%	29.20	2.077	<0.001
		Control	5.05	2.077	0.080
	10%	Control	-24.15	2.077	<0.001

hardness than 24 *hr* while 10% TiO_2 and control groups showed higher hardness at 24 *hr* compared to one week (Table 3).

Discussion

This study evaluated the effect of addition of different concentrations of TiO_2 to GIC on its hardness and flexural strength. The results indicated that the mean flexural strength of the four groups was not significantly changed but incorporation of TiO_2 resulted in lower hardness.

Flexural strength test was used to assess the mechanical properties of TiO_2-reinforced GIC. This test is superior to compressive strength test for assessment of mechanical properties of many brittle dental materials such as cements (11). It was also suggested that since fracture in GIC matrix occurs as the result of shear and tensile loads in atomic scale, compressive strength test cannot be suitable for assessment of mechanical properties of these materials (12). This study showed that incorporation of 5% TiO_2 resulted in a higher flexural strength in comparison with that of control and 3% groups. This is in line with the study of Elaska *et al* (9) who added TiO_2 nanoparticles to GIC and demonstrated that flexural strength of 3% and 5% TiO_2 groups was higher than that of the control group. This increase attributed to the small size of these particles since they fill the gaps between GIC powder particles and cause additional bonds in polyacrylic polymer, reinforcing the GIC. On the other hand, Garcia *et al* (13) incorporated 3 and 5 wt% TiO_2 nanoparticles to conventional GIC and reported a reduction in flexural strength. They believed that nanoparticles may not be mixed homogenously with GIC powder and some weak bonds may form between nanoparticles and GIC matrix.

According to Wang *et al* (14), Vickers hardness test is more suitable for measurement of microhardness of brittle or very hard substances such as ceramics. Our results showed a significant increase in hardness of 5% TiO_2 group compared to the control group at one week while the hardness of 3 and 10% TiO_2 groups slightly but not significantly decreased compared to the control group. At 24 *hr*, no significant difference was noted in hardness of 5 and 10% TiO_2 groups but the difference in this regard among other groups was statistically significant such that the control group had the highest and 3% TiO_2 had the lowest surface hardness, followed by 5 and 10% groups. Garcia *et al* (13), reported that addition of TiO_2 to conventional GIC decreased its hardness, which was in line with our findings. They reported this reduction to be due to the absence of glass particles on the surface. In other words, nanoparticles were not uniformly distributed and mainly accumulated on the surface. In contrast, Elaska *et al* (9), showed an insignificant increase in surface hardness of 5% TiO_2 GIC compared to the control group. They attributed this finding to the interactions in the matrix causing greater reactions between the liquid (acid) and nanoparticles. Similar to our study, by an increase in concentration of nanoparticles, hardness of GIC decreased. It can be proposed that by an increase in concentration of nanoparticles, risk of agglomeration of nanoparticles increases and thus, their mechanical properties such as hardness decrease.

Since agglomeration of TiO_2 nanoparticles has been suggested as a possible reason for reduction in hardness, future studies are required to try mixing the TiO_2 nanoparticles with GIC powder using a tube shaker. Also, silanizing agents such as polydimethyl silane can be used for silanization to decrease the likelihood of agglomeration of TiO_2 nanoparticles.

Conclusion

Addition of 3 and 10 wt% TiO_2 nanoparticles to conventional GIC did not cause a significant change in flexural strength but decreased the surface hardness. 5% TiO_2 significantly increased the flexural strength; however, a reduction in surface hardness was observed.

Conflict of Interest

The authors declare that there is no conflict of interest.

References

1. Hojati ST, Alaghemand H, Hamze F, Babaki FA, Rajab-Nia R, Rezvani MB, et al. Antibacterial, physical and mechanical properties of flowable resin composites containing zinc oxide nanoparticles. Dent Mater 2013 May 1;29(5):495-505.

2. Culbertson BM. New polymeric materials for use in glass-ionomer cements. J Dent 2006 Sep 1;34(8):556-65.

3. Hibino Y, Kuramochi KI, Harashima A, Honda M, Yamazaki A, Nagasawa Y, et al. Correlation between the strength of glass ionomer cements and their bond strength to bovine teeth. Dent Mater J 2004;23(4):656-60.

4. Palmer G, Jones FH, Billington RW, Pearson GJ. Chlorhexidine release from an experimental glass ionomer cement. Biomaterials 2004 Oct 1;25(23):5423-31.

5. 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 (GIC). Acta Biomater 2008 Mar 1;4(2):432-40.

6. Prentice LH, Tyas MJ, Burrow MF. The effect of ytterbium fluoride and barium sulphate nanoparticles on the reactivity and strength of a glass-ionomer cement. Dent Mater 2006 Aug 1;22(8):746-51.

7. Dizaj SM, Lotfipour F, Barzegar-Jalali M, Zarrintan MH, Adibkia K. Antimicrobial activity of the metals and metal

oxide nanoparticles. Mater Sci Eng C Mater Biol Appl 2014 Nov 1;44:278-84.

8. Yu JX, Li TH. Distinct biological effects of different nanoparticles commonly used in cosmetics and medicine coatings. Cell Biosci 2011 May;1(1):1-9.

9. Elsaka SE, Hamouda IM, Swain MV. Titanium dioxide nanoparticles addition to a conventional glass-ionomer restorative: influence on physical and antibacterial properties. J Dent 2011 Sep 1;39(9):589-98.

10. Mahshid S, Askari M, Ghamsari MS. Synthesis of TiO2 nanoparticles by hydrolysis and peptization of titanium isopropoxide solution. Journal of materials processing technology. 2007 Jul 6;189(1-3):296-300.

11. Walls AW. Glass polyalkenoate (glass-ionomer) cements: a review. J Dent 1986 Dec 1;14(6):231-46.

12. Prosser HJ, Powis DR, Wilson AD. Glass-ionomer cements of improved flexural strength. J Dent Res 1986 Feb;65(2):146-8.

13. Garcia-Contreras R, Scougall-Vilchis RJ, Contreras-Bulnes R, Sakagami H, Morales-Luckie RA, Nakajima H. Mechanical, antibacterial and bond strength properties of nano-titanium-enriched glass ionomer cement. J Appl Oral Sci 2015 May;23:321-8.

14. Wang L, D'Alpino PH, Lopes LG, Pereira JC. Mechanical properties of dental restorative materials: relative contribution of laboratory tests. J Appl Oral Sci 2003;11:162-7.

15. Panahandeh N, Torabzadeh H, Aghaee M, Hasani E, Safa S. Effect of incorporation of zinc oxide nanoparticles on mechanical properties of conventional glass ionomer cements. J Conserv Dent 2018 Mar;21(2):130.