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Degree of Conversion of Resin-Modified Glass Ionomer Cement Containing Hydroxyapatite Nanoparticles

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ABSTRACT

Objectives: Hydroxyapatite (HA) nanoparticles are used to improve the physical and mechanical properties of glass ionomers (GIs). This study aimed to assess the effect of addition of different weight percentages of nano-HA on degree of conversion (DC) of Fuji II LC GI cement using a spectrometer.

Materials and Methods: In this in vitro experimental study, 30 samples were fabricated of Fuji II LC (improved) GI cement in six groups (n=5) containing 0%, 1%, 2%, 5%, 7% and 10wt% nano-HA. The obtained paste in each group was subjected to Fourier-transform infrared spectroscopy (FTIR) before curing to assess the monomer to polymer DC percentage. The paste was then light-cured and underwent FTIR again. One-way ANOVA was applied to compare the DC percentage of different groups. Pairwise comparisons were performed using the Tukey's test.

Results: The DC was 57.88±0.57% in 0%, 60.04±0.63% in 1%, 66.92±0.54% in 2%, 65.5±0.71% in 5%, 51.49±0.24% in 7% and 50.09±0.32% in 10% nano-HA group. The difference in DC among the groups was statistically significant ($P<0.0001$). The highest DC was noted in 2% nano-HA and the lowest DC was found in 10% nano-HA group. Pairwise comparisons revealed significant differences between the groups in DC ($P<0.0001$).

Conclusion: Increasing the weight percentage of nano-HA to 2% increased the DC but increasing the nano-HA weight percentage over 5% decreased the DC of resin-modified glass ionomer cement (RMGIC). The highest DC was noted in 5w% and 2w% nano-HA groups. Thus, 5w% and 2w% nano-HA can be used to improve the DC of RMGIC.

Keywords: Nano-Hydroxyapatite; Polymerization; Fuji II LC cement improved

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INTRODUCTION

The unique properties of glass ionomer (GI) cements such as fluoride release potential, the ability to chemically bond to tooth structure, and a coefficient of thermal expansion similar to that of tooth structure have made them a suitable material with extensive applications in restorative dentistry [1]. Despite the advantages of GI cements, they have limited clinical application due to shortcomings such as brittleness, limited mechanical properties and low wear resistance [2]. To overcome these limitations while maintaining the optimal properties, resin-modified GI cements (RMGICs) were introduced to the market, which have easier application, longer working time and higher initial strength [3]. RMGICs cannot be used in areas under occlusal stresses due to having weaker mechanical properties than composite resins. Some strategies have been suggested to improve the cross-linking and physical properties of RMGICs such as addition of metal particles, zirconia, alumina, glass, carbon fiber and hydroxyapatite (HA) to their composition [4,5].

In the recent years, nanotechnology has been employed to improve the properties of materials without compromising their optimal characteristics. Use of nanoparticles improves the efficacy and clinical service of materials in long-term. HA nanoparticles have high solubility and can result in deposition of mineral ions such as calcium and phosphate into enamel defects. They confer resistance to demineralization as such, and improve the bond strength of restorative materials to tooth structure [6].

Needle-shaped nano-HA particles enhance optical and biological properties, increase bond strength and simplify the application of cements. These particles are biocompatible and bioactive, and have low solubility in water [7,8].

Degree of conversion (DC) is an important factor affecting the clinical service of resin-based materials [9,10]. DC is highly variable in resin compounds and depends on the composition of resin matrix, filler percentage, particle size, intensity and duration of light radiation, and the concentration of inhibitor and initiator [11]. Inadequate polymerization causes problems such as microleakage, postoperative tooth hypersensitivity, caries recurrence, susceptibility to degradation, discoloration, reduction of mechanical properties, and adverse effects on dental pulp [12]. Several methods are available to determine the polymerization depth and DC such as the scratch test, measurement of microhardness, light microscopy and spectroscopy. Also, Fourier-transform infrared spectroscopy (FTIR) is among the most accurate tests for this purpose [13].

Considering the optimal chemical bond of GI cements to the tooth structure, and the fact that the tooth structure is mainly composed of HA, it seems that incorporation of nano-HA into the composition of GI cement may improve its properties. This study aimed to assess the effect of addition of nano-HA on DC of RMGIC in vitro using spectroscopy. The null hypothesis was that the mean DC of RMGICs reinforced with different weight percentages of nano-HA would be the same.

MATERIALS AND METHODS

Fuji II LC (improved) RMGIC (GC, Tokyo, Japan) along with different weight percentages of nano-HA were used in this in vitro, experimental study. Nano-HA (Nanoshell, Punjab, India) as a natural form of calcium apatite with $Ca10(Po4)6(OH)2$ chemical formula was weighed by a digital scale and added in desired amounts to RMGIC powder until the percentage of nano-HA in GI powder reached 1w%, 2w%, 5w%, 7w% and 10w%. The powder was then mixed using a mortar and pestle. The light-cure RMGIC was applied into plexiglass mold and exposed to infrared light of FTIR spectrometer (Nicolet IS 10; Thermo Scientific, Madison, WI, USA). The spectra of each sample were recorded, with the accumulation of 16 scans with a resolution of 4 cm^{-1}. The absorption intensity of peaks was in the range of 400- 4000 cm^{-1}. The device drew a graph using the respective software.

To fabricate 1w% nano-HA samples, 0.05 g of nano-HA powder and 4.95 g of GI powder were required. The required amount of nano-HA for the fabrication of samples in other experimental groups was calculated as such.

The powder mixture was gently stirred for 20 seconds using a mortar and pestle to achieve a homogenous mixture of particles. The prepared powders were stored in dark glasses until the time of fabrication of samples. The powders were then mixed with liquid according to the manufacturer's instructions (powder to liquid ratio of 3.2:1). The obtained paste was condensed in plexiglass molds measuring 5 mm in diameter and 5 mm in thickness. The molds were first lubricated with petroleum jelly. Excess material was removed using a microbrush. The paste was then condensed and placed on a glass slab. The paste was condensed in the mold from one side using a metal spatula to prevent void formation. Next, another glass slab was placed over it and slightly compressed in order for the excess cement to leak out and obtain a smooth surface. The samples were then subjected to spectrometer. The glass slab was then removed and the samples were light-cured (Blue Phase; Woodpecker, China) from both sides (20 seconds from each side) with a light intensity of 1000 mW/cm^2. Next, the samples were subjected to FTIR. Change in DC was calculated in different groups using the formula below:

$$\text{DC}=1-\frac{Area\ of\ C{=}C\ band\frac{polymer}{area}of\ C{=}O\ band\ (polymer)}{Area\ of\ C{=}C\ band\frac{monomer}{area}of\ C{=}O\ band\ (monomer)}\times\ 10$$

Statistical analysis:

One-way ANOVA was applied to compare the groups in terms of DC. Pairwise comparisons of the groups in terms of DC were carried out using the Tukey's test. Type 1 error (alpha) was considered to be 0.05.

RESULTS

One-way ANOVA showed significant differences in DC of the groups containing different weight percentages of nano-HA ($P<0.0001$, Table 1) such that by an increase in weight percentage of nano-HA particles added to RMGIC from 0% to 2%, the DC increased.

By further increase in weight percentage of nano-HA particles from 5% to 10%, the mean DC of RMGIC decreased. Pairwise comparisons of the groups by the Tukey's test also revealed significant differences between the groups in DC ($P<0.05$).

DISCUSSION

Researchers have used methods to enhance the mechanical properties of GI cements without affecting their biocompatibility. Addition of nano-size metal particles, fibers and fillers is among the tested methods for this purpose.

Although GI cements are biocompatible, attempts have been made to improve their properties to convert them into a biologically active cement. One strategy to achieve this goal is to add HA nanoparticles to these cements to increase their remineralization potential and decrease their microleakage in dental cavities [14,15].

Evidence shows that addition of nano-HA to GI cements improves their physical properties. Nano-HA particles are soluble in acidic solutions and are therefore, eliminated after mixing of powder with these solutions. Thus, in GI powder containing nano-HA mixed with poly-acid liquid (GI cement liquid), calcium ions are released from the surface of nano-HA particles and consequently, higher rates of acid-base and cross-linking reactions occur in the structure of cement and result in formation of a stronger cement [16]. Nanoparticles have higher degree of crystallinity and colloidal stability and thus, they have stronger reinforcing effects and easier application. In the present study, nano-HA particles were added to light-cure RMGIC (Fuji II LC improved) due to having biological properties and structure similar to the mineral structure of the tooth, and the DC was then measured.

Nuri Sari et al. [5] assessed the effect of addition of nano-HA on shear bond strength of ceramic brackets bonded with RMGIC and reported that addition of 5% nano-HA had no negative effect on shear bond strength of RMGIC, but addition of 10% nano-HA decreased the bond strength. By an increase in percentage of nano-HA, accumulation of filler particles and porosities increase, which lead to

Table 1: RMGICs containing different percentages of nano-hydroxyapatite (HA) particles (n=5)

Nano-HA percentage	0%	1%	2%	5%	7%	10%
Mean (standard deviation) degree of convergence %	57.88 (0.57)	60.04 (0.63)	66.92 (0.54)	6505 (0.71)	51.49 (0.24)	50.09 (0.32)

higher water sorption, because they do not have a strong bond to the matrix and excess water can penetrate in-between the particles and matrix and decrease the bonding properties [5]. Poorzandpoush et al. [17] evaluated the wear of RMGICs containing different weight percentages of nano-HA following toothbrushing and showed that addition of up to 10w% nano-HA increased the wear resistance of Fuji II LC RMGIC. The greatest reduction was noted following addition of 2w% and 5w% nano-HA. Mohammadi Basir et al. [18] assessed the effect of incorporation of nano-HA into the composition of RMGIC and demonstrated that combination of relatively large glass particles and small nano-HA particles enhanced the dispersion of particles in the mass and its compressibility due to filling of micro-pores. It also improved the mechanical properties such that the compressive strength did not decrease and the flexural strength increased. Flexural strength reached its maximum level following addition of 5w% nano-HA. In other words, the reactions between the cement matrix and nanoparticles lead to dissolution of nano-bioceramics in the acidic monomer, and result in release of calcium ions from the surface of nanoparticles. They also increase the frequency of crystallization reactions, and consequently improve the strength of cement [18].

According to the current results, increasing the weight percentage of nano-HA particles added to RMGIC powder from 0% to 2% increased the DC of cement while by increasing the weight percentage of nano-HA particles added to RMGIC powder from 5% to 10%, the DC of cement decreased. Therefore, it seems that addition of 5% and higher concentrations of nano-HA decreases the DC of RMGIC.

Physical and mechanical properties of RMGICs are influenced by their DC. The process of polymerization depends on the radiation energy received by the photo-initiator and its break-down into active components. Light penetration into systems containing fillers depends on the passage of light through the matrix and fillers as well as the difference in the refractive index of the matrix and filler [19]. Since chemical reactions have a slower pace than physical reactions, free radicals formed by the chemical component may become trapped in the polymer network. Thus, increase in DC is generally limited [9].

The acid-base and methacrylate curing reactions in RMGICs can generate free radicals due to curing or redox reactions. It seems that addition of hydrophilic nano-HA particles with high surface area increases the acid-base ionic reactions and salt formation in RMGIC, and ionic bonds are formed between the carboxylic acid of GI and calcium ions on the surface of nano-HA particles [20]. However, by an increase in percentage of nano-HA added to GI, light may not be able to penetrate well into the cement, which may be one reason for reduction of DC in presence of 7w% and 10w% concentrations of nano-HA. At such high concentrations, the cement liquid would not suffice for effective preservation of nano-HA particles, considering their smaller size and higher effective surface area compared with larger-size glass particles. Therefore, increasing the weight percentage of nano-HA particles added to the cement weakens the bond and compromises the adhesion between the particles and ionomer matrix. In other words, nano-HA particles in higher weight percentages interfere as fillers with acid-base reactions. On the other hand, by an increase in weight percentage of nano-HA particles, the effective occupied surface by them increases and thus, the viscosity of cement increases as well. As the result, the mixing process of powder and liquid becomes more difficult and non-homogenous samples are fabricated. Researchers justified that by addition of nano-HA in high percentages to GI powder, agglomerates in the matrix would serve as weak points and decrease the mechanical properties of the mixture. Moreover, due to the opacity of HA, light may not be able to adequately penetrate into the cement, and the curing process is impaired as such [21]. As the light scattering increases, its intensity decreases. Thus, the process of polymerization is impaired. Moreover, oxygen present in nanoparticle agglomerates may prevent the polymerization of radicals [22].

Addition of nano-HA particles to GI powder results in dispersion of a wide range of particle sizes and improves the mechanical properties of the cement. The mean size of GI particles is 10 to 20 µm. Thus, they can fill the gaps between the GI particles and serve as a reinforcing agent in the composition of GI cements. On the other hand, presence of fluoride in fluorapatite crystals can increase the fluoride release potential of GI cements [23]. Most studies on the DC of composite resins have been conducted on bis-GMA as the main monomer in their composition. The chemical formula of bis-GMA includes two aromatic rings (aliphatic carbon-carbon double bond or open chain and aromatic bond). Previous studies on this topic reported a peak at 1638^{cm-1} for the aliphatic double bond and an internal standard peak at 1608^{cm-1} for double bonds present in the aromatic ring [24,25]. However, in assessment of RMGICs, bis-GMA is not present and hydroxyethyl-methacrylate (HEMA) is the main monomer in their composition. Since HEMA does not have an aromatic ring in its formula, the internal standard peak at 1608^{cm-1} can be used for this purpose [26]. Therefore, similar to previous studies [26,27], the internal standard wavelength used in this study was the carbon-oxygen double bond at 1712^{cm-1} (with a peak at 1636^{cm-1}). This value has also been defined as the reference corresponding to the methacrylate group. This technique has been used to determine the efficacy of curing of non-aromatic resins as well [26].

CONCLUSION

We concluded that by an increase in weight percentage of nano-HA to 2%, DC of the cement increased. The highest DC was noted following addition of 2% nano-HA to RMGIC powder.

CONFLICT OF INTEREST STATEMENT

None declared.

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