Original Article

Setting time, mechanical and adhesive properties of magnesium oxide nanoparticles modified glass-ionomer cement

Arass Jalal Noori*, Fadil Abdullah Kareem

Department of Pedodontics, Orthodontics and Preventive Dentistry, College of Dentistry, University of Sulaimani, Sulaymaniyah, 46001, Iraq

ARTICLE INFO

Article history:
Received 6 October 2019
Accepted 4 December 2019
Available online 18 December 2019

Keywords:
Glass-ionomer cement
MgO nanoparticles
Compressive strength
Diametral tensile strength
Setting time
Shear bond strength

ABSTRACT

Nanoparticle modifications of glass-ionomer cement are interesting research subjects. This study investigated the effect of MgO nanoparticles on the setting time, compressive and diametral tensile strength, and adhesive properties of glass-ionomer cement. A conventional GIC was modified by the incorporation of MgO nanoparticles at 1%, 2.5%, 5%, and 10% (w/w) ratios with an unmodified GIC used as the control group. The data were analysed using a one-way analysis of variance (ANOVA) and Tukey’s HSD test (p < 0.05). Although the GICs with 1% and 2.5% MgO nanoparticles were still within the ISO standard range specified for the GIC setting time, increasing the MgO nanoparticle concentration significantly increased the setting time of the tested cement (p < 0.05). GICs with 1% MgO nanoparticles had the highest compressive and diametral tensile strength values. Increasing the nanoparticle content from 5% and more significantly decreased the cement strength (p < 0.05). The shear bond strength (SBS) of enamel and dentine showed statistically significant differences among the tested groups (p < 0.05). However, the addition of MgO nanoparticles up to 5% (w/w) did not have an unfavourable effect on the cement adhesiveness. Although cohesive and mixed type failure modes were more common than adhesive failure modes, no statistically significant associations were found between the failure mode and type of GIC (p > 0.05).

Within the limitations of this study, the current findings suggest that modifying GICs by incorporating MgO nanoparticles up to 2.5% (w/w) could be a promising restorative material for clinical dental applications.

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1. Introduction

Glass-ionomer cement (GIC) is a polymer-based cement and an indispensable dental biomaterial developed and introduced in the 1970s that has since been utilised in clinical applications as a filling, lining, and luting cement [1]. Glass-ionomer cement is used in clinical dental practise in
a variety of forms due to their unique fluoride-releasing properties and rechargeability potential, adhesion to tooth structures, biocompatibility, and low toxicity [1-3]. Glass-ionomer cement is the ideal restorative material for the management of dental caries according to the principles of minimally invasive dentistry, including atraumatic restorative treatment procedures [4-6]. However, despite their favourable properties, GICs suffer from shortcomings as low fracture toughness, low wear resistance, and dissolution due to water sorption that eventually weakens the cement, leading to secondary caries due to microleakage and bacteria growth [2,3,7].

Although GICs have fluoride release properties, they are not sufficiently potent to inhibit bacterial growth under fillings [8]. Furthermore, caries excavations based on minimally invasive techniques such as atraumatic restorative treatment may leave residual bacteria under the restorative after caries removal, causing recurrent caries and dental restoration failure [9]. A therapeutic benefit is gained when antimicrobial substances are used in association with glass-ionomer cement to eliminate residual infection, thus minimising the risk of recurrent caries and pulp damage [10]. Studies have investigated different antimicrobial additives to improve the antibacterial properties of glass-ionomer cement [2,11-13].

The accumulation and adhesion of oral bacteria to dental structures can cause dental caries [14], and antibacterial restorative dental materials can reduce the adhesion and proliferation of bacterial microorganisms at a very early stage, decreasing the development of carious lesions [15]. As a restorative cement, GICs should have specific physical and mechanical properties, and the addition of antibacterial substances should not jeopardise the required properties of restorative cement [2,16].

Several studies reported that nanomaterials can provide novel preventive and therapeutic strategies for the management of dental caries [17], notably for the reduction and control of dental plaque biofilms, improving the antibacterial properties of dental materials, and remineralisation of initial dental caries lesions. The application of nanoparticles with safe and biocompatible degradable compounds may be of significant benefit [18,19] as the biosafety and accumulation of non-biodegradable nanoparticles in different body organs remains a serious concern for the medical field, and the application of nanoparticles with safe and biocompatible degradable compounds is advantageous in this context [20]. Dental restorative materials have specific requirements that are necessary for a material to be suitable for clinical application [7]. One essential requirement is the biocompatibility of restorative material components, as the degradation products must be biocompatible and non-irritating to the surrounding tissues [7].

Magnesium oxide (MgO) nanoparticles are of interest for use in biomedical applications due to their antimicrobial properties against bacteria, spores, and viruses and have the advantage of non-toxicity, high thermal stability, biocompatibility, and low production costs [21-23]. MgO nanoparticles’ advantage over other nanoparticles is due to their biocompatibility and the biocompatibility of their biodegradable by-products (namely magnesium ion). The US Food and Drug Administration recognises MgO nanoparticles as harmless materials under 21CFR184.1431 [24].

Studying the physical properties of GICs modified by antimicrobial additives is a valuable approach as it is essential to maintain restorative material under ISO standards [25]. Furthermore, it is well-documented that the incorporation of nanosized particles may improve or alter the mechanical and physical properties of polymeric dental materials [26]. Therefore, maintaining the right balance among antibacterial activity and mechanical features is essential for any modified restorative material [11]. Recent studies reported the antibacterial effects and antibiofilm activity of magnesium oxide nanoparticles on a range of microorganisms, including oral bacteria such as the cariogenic species of Streptococcus mutans [27-29]. In a previous work, we investigated and reported the efficacy of MgO nanoparticles and MgO nanoparticle-modified GIC composites as an antibacterial restorative cement [30]. Because of the biocompatible and safe nature of MgO nanoparticles and their by-products [21], researchers opted to further investigate the effects of such nanoparticles on other GIC properties. The aim of the present paper was to investigate the influence of MgO nanoparticles on the setting time and mechanical, and adhesive properties of a glass-ionomer cement.

2. Materials and methods

2.1. Materials and sample preparation

Commercially available magnesium oxide nanoparticles (Nanjing Nanotechnology Co., Nanjing, China) were used for the modification of the GIC. The GIC used was in a powder/liquid form, 3M ESPE Ketac Molar Easymix glass-ionomer filling material, A3 shade (3M Deutschland GmbH, Neuss, Germany). GIC specimens were fabricated according to the manufacturer’s instructions, and the liquid/powder ratio of the modified GIC samples was maintained as described for the original GIC material. The powder/liquid ratio is one spoonful of powder and one drop of liquid. The powder for the experimental GIC groups was prepared by mixing the MgO nanoparticle powder with the GIC powder at weight/weight ratios of 1, 2.5, 5, and 10%.

2.2. Setting time

The net setting times of the cement were measured according to the ISO method for water-based dental cement (ISO 9917-1:2007) [31]. The setting time was recorded as the time elapsed between the start of mixing and the time when the flat-end needle (1.06 mm in diameter) of the indenter (400 ± 5 g) of a Gillmore apparatus (UTEST-Material Test Equipment Ltd, Ankara, Turkey) failed to make a complete circular indentation in the test material, as shown in Fig. 1. The original large indenter weight of the Gillmore apparatus was 453.6 g in weight and had to be reduced to 400 g for this test. The mean setting time of the tested groups was recorded from five replicate tests.
2.3. Compressive strength and diametral tensile strength tests

Samples for the mechanical tests (compressive and diametral tensile tests) were prepared using metallic moulds according to ISO specification 9917 (ISO 9917-1:2007) and the American Dental Association specification No. 27 [32].

Ten cylindrical samples (6 × 4 mm) for the compressive strength tests and 10 cylindrical samples (3 × 6 mm) for the diametral tensile tests were prepared for each sample group using a metallic mould and tested according to ISO specification 9917 [31,33]. The glass-ionomer cement was hand mixed and injected into the metallic mould. The specimens with the moulds were covered on both ends with a glass slide over clear acetate tape during the setting time with a 400 g weight pressing on it. This assembly was stored at 37°C for 30 min and then the specimens were removed from the moulds and immersed in a small plastic container containing 5 ml of distilled water for incubation at 37 ± 1°C for 24 h until testing [34]. For the compressive tests, the force load was applied along the long axis of the specimen and along the cross-sectional diameter for the diametral tensile strength tests at a cross-head speed of 0.75 mm min⁻¹ using a WP 310 materials testing UTM testing machine (G.U.N.T., Barsbüttel, Germany).

The compressive strength was computed via the following formula:

\[ \text{Compressive strength (MPa)} = \frac{4F}{\pi D^2} \]

where \( F \) = fracture load in newtons and \( D \) = diameter in mm.

The diametral tensile strength was computed via the following formula:

\[ \text{Diametral tensile strength (MPa)} = \frac{2F}{\pi DH} \]

where \( F \) = fracture load in newtons, \( D \) = diameter in mm, and \( H \) = height (thickness) in mm.

2.4. Shear bond strength tests

A total of 100 bovine incisor teeth were used in the present study (50 for each test group on enamel and dentine). The tissue remnants were cleaned using periodontal instruments, and the tooth crowns were separated from the roots just apical to the cementoenamel junction using a diamond fissure bur mounted on a high-speed dental handpiece under water cooling. The teeth were stored in distilled water and used within two weeks [35,36]. The crowns were embedded in PVC rings using self-curing acrylic resin with labial surfaces facing the outside of the ring. After the resin cured, the resultant cylinders were removed from the PVC tubes and stored in distilled water. The labial surfaces were prepared accordingly, with 50 samples for the enamel and 50 samples for the dentine group. For the enamel group, the enamel surfaces of the mid-coronal regions of the crowns were sequentially ground under water cooling with 320 and 600 grit silicon carbide papers. For the dentine group, the same sequential grinding was performed.

Fig. 1 – A: gillmore apparatus. B: specimen of the tested GIC for the setting time evaluation.

Fig. 2 – A special jig made to hold the samples during the SBS testing.
after the enamel was removed until a flat standard surface 1 mm deep into the dentine was observed [37].

A plastic mould (4 mm diameter × 5 mm height) was positioned and fixed on the prepared surfaces and then filled with the glass-ionomer cement. After the material set, the samples were stored in an incubator (100% humidity at 37 °C) for 24 h before the shear bond strength test.

The shear bond strength was measured on a low-force materials testing machine (MultiTest 1-d testing machine, Mecmesin Ltd, West Sussex, UK) operated at a cross-head speed of 1 mm/min. The samples were mounted in a custom-made jig, and the force of the GIC specimen debonding was applied through a knife-like mandrel that was positioned parallel to the surface of the samples at the junction of the GIC to the sample (Fig. 2.). The shear bond strength was expressed in MPa and calculated using the following formula:

Shear bond strength (MPa) = \( \frac{F}{A} \)

where F = failure load in newtons and A = bonded area (\( \pi r^2 \)) in mm².
2.6. The nanoparticles

Dentine (de-bonded electron spectrophotometry (Malvern, USA)) wholly inside the interface between the glass-ionomer and dentine (no observable glass-ionomer remained on the dentine surface), (2) cohesive failure if the fracture occurred inside the glass-ionomer or dentine, and (3) mixed failure if a mixture of both failure modes was observed (the fracture surpassed the interface into the glass-ionomer or dentine) [37].

2.5. SEM, FTIR and XRD analysis

The scanning electron microscopy were taken for the MgO nanoparticles and for the fractured unmodified and modified GIC samples using a CS 3200 LV CamScan scanning electron microscope (CamScan Electron Optics Ltd, Waterbeach, UK) accelerated at 25 kV. The structure of the MgO nanoparticles were investigated by X-ray powder diffraction (XRD) (PANalytical X’Pert PRO, Malvern Pananalytical Ltd, Malvern, UK) operating at 45 kV with a current of 40 mA using CuKα radiation (λ = 1.5406 Å) in the range of 30°–90°. FTIR spectrophotometry was used to investigate loading of the nanoparticles into the GIC matrix (PerkinElmer Inc., Waltham, MA, USA) in the range of 400–4000 cm⁻¹.

2.6. Statistical analysis

The data were tested using SPSS Statistical software version 25 for Windows (SPSS, Chicago, IL, USA). The normality of the data values was confirmed via the Shapiro-Wilk test (p > 0.05). One-way analysis of variance (ANOVA) was used to conduct the statistical analysis followed by Tukey’s HSD post hoc test for detecting significant differences between the groups. The chi-square test was used to detect any association between the failure modes and the type of GIC tested. A cut-off level of significance was set at 5% for all of the statistical analyses.

3. Results

Fig. 3 shows the mean (±SD) values of the setting time and the compressive and diametral tensile strength values with their statistical test results. An increase in the setting time was observed with the increasing amount of MgO nanoparticles in the experimental cement. The addition of MgO nanoparticles at concentrations of 2.5% and above resulted in a statistically significant increase in the setting time values (F(4, 20) = 145.218, p = 0.000). However, GICs with the addition of 1% and 2.5% MgO nanoparticles still fell within the specified range of the GIC setting time from 1.5 to 6.0 min according to the ISO standards [31]. The addition of MgO nanoparticles altered the GIC compressive and diametral tensile strength properties (p < 0.05). The addition of 1% MgO nanoparticles increased both the compressive (F(4, 45) = 59.265, p = 0.000) and diametral tensile strength (F(4, 45) = 2.874, p = 0.033) values for the GIC cement and was the strongest among all of the groups tested. Further increasing the amount of MgO nanoparticles led to a decrease in the cement strength. This effect was more noticeable with the addition of 5% and more of MgO nanoparticles.

The shear bond strength (SBS) of the enamel (F(4, 45) = 4.759, p = 0.003) and dentine (F(4, 45) = 5.979, p = 0.001) showed statistically significant differences between the conventional and modified GIC groups, as shown in Fig. 4. The
diffraction peaks matched well with the face-centred cubic structure of periclase MgO nanoparticles (JCPDS No. 87-0653). The major peaks at 2θ values of 36.9°, 42.9°, 62.3°, 74.8°, and 78.6° were indexed to the lattice planes of (111), (200), (220), (311), and (222), respectively. The diffracting pattern showed sharp, narrow and intense peaks that matched the crystalline structure of the MgO [38].

The Fourier transform infrared (FTIR) spectra of the MgO nanoparticles showed the detected bands in the 3400–3700 cm⁻¹ range from the FTIR spectra of the MgO nanoparticles were due to the O-H stretching bond vibrations from the absorbed water molecules, Fig. 9 [39]. The peaks at 1424 cm⁻¹ and 1485 cm⁻¹ were attributed to stretching of the carbonate ion and CO₃²⁻ species and the bending vibration of the water molecules [40]. Bands at 581 cm⁻¹, 850 cm⁻¹, and 890 cm⁻¹ corresponded to v1 and v2 stretching vibrations of the metal-oxygen bond [41,42], which corresponded to the presence of the MgO [43]. The FTIR spectra of both the control GIC and MgO nanoparticles modified GIC are shown in Fig. 10, and the presence of v1 and v2 stretching vibrations of the metal oxides in the FTIR spectra of the modified GIC indicates successful embedding of the nanoparticles in the GIC matrix [30].

4. Discussion

High powder ratio glass-ionomer cement is mainly used as a restorative material that yields higher strength materials to withstand the forces of occlusion [4,5,7,10]. Furthermore, micro-gaps may form at the tooth-restoration interface, leading to microleakage and restoration failure [44]. Therefore, restorative materials should ideally possess antibacterial properties to prevent bacteria-induced tooth sensitivity, pulpal irritation, and recurrent caries [15]. When choosing the type of antimicrobial agent to add to a restorative material, it is essential to consider that an ideal antimicrobial agent should provide effective antibacterial action without adversely affecting the mechanical and bond strength properties of the material [2,12].

Several modifications have been used to improve the antimicrobial, physical, and mechanical properties of GICs through the addition of varying materials and products, including different types of nanomaterials [2,8,45]. Our results confirm that the addition of MgO nanoparticles to glass-ionomer cement will have varying effects on the different physical and mechanical properties of the material.

Although the GICs with the addition of 1% and 2.5% MgO nanoparticles still fell within the specified range of the GIC setting time of under 6.0 min according to the ISO standards [31], the handling properties of the modified cement were moderately affected by increasing the amount of the MgO nanoparticles. This lengthening of the GIC setting time is attributed to the presence of magnesium ions in the modified cement, which may impede or interfere with the acid-base reaction, resulting in a rubber-like cement during setting, leading to a delay in the setting reaction speed and eventually affecting the cement strength [46]. It has been reported that magnesium oxide may act as a network modifier and an intermediate oxide in part concerning glass formation [47].
The compressive and diametral tensile strengths of the modified cement were comparable to those of the original glass-ionomer cement, and 1% MgO nanoparticle addition increased the strength. As permanent restorative materials, glass-ionomer cement (GICs) (both resin-modified and conventional self-cure versions) still have limitations when placed in stress-bearing restorations due to their relatively low fracture strength, toughness, and wear properties [3]. Nevertheless, this strength enhancement requires meticulous tuning of the quantity of nanoparticles added to the cement as the further increase in the amount of nanoparticles beyond the optimal level will adversely affect the dental cement’s physical and mechanical properties. These results are generally consistent with those reported by other studies that demonstrated that modifying GICs by the addition of nanoparticles is beneficial to a certain level and beyond that amount, the cement’s strength properties start to decline [11,45,47]. The reason that the GIC’s physical properties improved through the addition of nanoparticles might be due to the incorporation of these small nanoparticles in the voids present in the cement during the mixing procedure [12,48,49]. Moreover, nanoparticles may provide additional bonding sites for polyacrylic polymers, thereby reinforcing the GIC [50,51].

The adhesive properties of glass-ionomer cement on the surface of the tooth is an essential clinical advantage, and this property leads to the use of GICs to repair cervical erosion lesions and as pit and fissure sealants [1,52]. The current
study demonstrated a statistically significant difference in the effect of MgO nanoparticle addition to GIC cement and specifically above 5% w/w modification, leading to a decrease in the adhesiveness of the cement above this level. The chemical bonding of GIC to the tooth structure is caused by the reaction of phosphate ions in the dental tissue with carboxylate groups from the polyacrylic acid of the GIC [3]. The adhesive nature of GIC aids in the retention of the restoration within the tooth and reduces or eliminates marginal microleakage, which prevents micro-organisms from entering the space under the restoration [1]. Although cohesive failures were more common than the other types, different kinds of GIC debonding were observed with no specific preference in the amount of MgO nanoparticles that were added to the cement. Similar results are reported in the literature [53,54].

5. Conclusions

Within the limits of this study, modification of GIC by incorporation of MgO nanoparticles caused a direct increase in the cement setting time. GICs containing 1% MgO nanoparticles showed an improvement in the compressive and diametral tensile strength and the highest SBS values for both adhesions to enamel and dentin. Modifying GIC using MgO nanoparticles did not affect the failure modes during shear bond testing.

Conflicts of interest

The authors declare no conflicts of interest.

References


