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INFLUENCE OF TITANIUM DIOXIDE INCORPORATION ON THE COMPRESSIVE STRENGTH OF MODIFIED CALCIUM SILICATE-BASED CEMENT

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ABSTRACT

Aim: The aim of this investigation was to evaluate the effect of incorporating titanium dioxide (TiO_2) particles on the compressive strength of modified calcium silicate-based cement (CSC).

Methods: The modified calcium silicate-based cement (CSC) used comprised 80 wt% white Portland-limestone cement and 20 wt% bisthmus oxide, as a radioopacifier. Incorporation of the 300-nm TiO_2 particles was done in the following concentrations: 0% (CSC group), 1% (CSC + 1%TiO_2 group), 3% (CSC + 3%TiO_2 group) and 5% (CSC + 5%TiO_2 group). Cylindrical specimens, 4 mm in diameter and 6mm in height, were prepared in split, teflon moulds; ten specimens were done for each group (n=10). Specimens were left to set for 7 days under wet conditions. Compressive strength testing was, then, done using an Instron testing machine. Data were analyzed using one-way analysis of variance (ANOVA) followed by Tukey post hoc test for pair-wise comparison. Statistical significance (α) was set at 0.05.

Results: There was no statistically significant difference among the four groups regarding compressive strength (p=0.162).

Conclusion: Within the conditions of this investigation, the incorporation of nano-scale TiO_2 particles within a concentration range of 1 to 5 % does not seem to affect the compressive strength of the modified calcium silicate-based cement having white Portland- limestone cement as the main cementitious component.

KEYWORDS: Calcium silicate-based cement; titanium dioxide; nanoparticles; limestone; compressive strength.

INTRODUCTION

Calcium silicate-based cements (CSCs) have contributed to a great extent in endodontics especially with cases that can be considered of high difficulty e.g. root perforations, root resorption and immature teeth (1). Nowadays, CSCs include a wide variety of formulations according to the cementitious phase component(s) and the types of additives included (2,3). CSCs used in endodontics have been classified into

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Portland cement (PC)-based cements e.g. mineral trioxide aggregate (MTA), and tricalcium silicate (TCS)-based cements (4). Of the several endodontic clinical applications of CSCs, some require that the material has favourable mechanical properties where the material is exposed to masticatory forces as well as the forces of compacting overlying restorations, e.g. vital pulp therapy applications, regenerative endodontic procedures and furcation perforation repair; this is a drawback with CSCs (5,6).

Several factors seem to affect the mechanical properties of CSCs including the material's composition (2,3,7–10), particle size distribution (10–15), the water-to-powder (W/P) ratio(5), the condensation pressure, (16) the technique of mixing and placement and the curing conditions (5,16,17). One of the ways to improve the mechanical properties of CSCs is by modifying the material's composition either through substituting integral components that could weaken the material structure with alternatives that retain or enhance the material's mechanical properties (7,12,18) or the addition of new components to improve its physical properties e.g. silver, calcium carbonate and titanium dioxide nanoparticles (8,10,15).

Titanium oxide (TiO_2) has been widely used, especially in its nanoparticulate form, in different daily-life aspects including cosmetics, food products, implanted biomaterials, pigments, paints, paper, pharmaceuticals and concrete industry. This is due to its versatile properties including being a white-coloring agent, having photocatalytic effects, showing chemical stability and insolubility, and having antibacterial activity in addition to its reinforcing effects (19–23). TiO_2 has, also, been incorporated in different dental materials, e.g. composite resins, glass ionomer cements, and sealers, for purposes of enhancing mechanical properties, physicochemical properties, antimicrobial activity, biocompatibility and radiopacity (19,24–26).

Few studies have investigated the effects of TiO_2 on the properties of endodontic materials, usually CSCs (7,8,18,27). Despite not contributing much as a radiopacifier to CSCs (7,18), it has been recently shown that the incorporation of 1% TiO2 to MTA could enhance both its compressive and push-out bond strength (8) without adversely affecting its biocompatibility (27). It was, thus, of interest to further assess the effect of adding TiO_2 on their mechanical properties of different types of CSCs. And so, the objective of this investigation was to examine the effect of incorporating different concentrations of nano-scale TiO_2 particles on the compressive strength of a modified CSC having Portland-limestone cement as its main cementitious component.

MATERIALS AND METHODS

Particle size distribution of the TiO_2 powder

The particle size distribution analysis of a commercially-available TiO_2 powder (Titanium [IV] oxide [Titanium dioxide] ADWIC, El Nasr Pharmaceutical Chemicals Co., El Minya Cement Co., ARE) was carried out using the dynamic light scattering method (DLS) utilizing a dynamic light scatter analyser (ZetaSizer Nano ZS, Malvern Instruments Limited, Worcestershire, UK) which has a range of 0.3nm-10μm. The powder sample was diluted in deionized water before analysis and tested in stoppered glass cuvettes. The samples were measured at 25 ˚C for 60 s.

Preparation of the materials

The constituents of the experimental, modified calcium silicate-based cement (CSC) used in this investigation were: 80% by weight white Portland-limestone cement (Royal White Portland-Limestone Cement, ES 4756-1/2013 & BS EN 197-1/2011, CEM II/ B-LL 42.5N, ARE) and 20% by weight bisthmus oxide (Bi_2O_3; Fine Chemicals Co., India) as a radioopacifier (4:1 wt/wt). TiO_2 was added to the modified CSC at concentrations of 1% (0.01g added to 1g CSC), 3% (0.03g added to 1g CSC) and 5% (0.05g added to 1g CSC) by weight. All cements were mixed with sterile, distilled water at a water-powder ratio of 1:3.

Preparation of specimens

Specimens were prepared by casting cement pastes into cylindrical, split, teflon moulds (Figure 1). A three-piece assembly containing three moulds was constructed with an external brass ring and two internal, teflon halves (Figure 1). The dimensions of each cylindrical mould were 4 mm in diameter and 6 mm in height following the ISO 9917-1: 2007 standard specifications (14). The assembly was placed on a glass slab and the cement mixtures were placed in increments into the moulds using an amalgam carrier and compacted using an amalgam condenser to secure dense, uniform specimens minimizing air entrapment to decrease porosity. Once full to excess, the material above the mould margins was scraped off with the edge of a glass microscopic slide to leave a flat uniform surface. Within 3 min of the start of mixing, two glass slides were placed one on each flat side of the assembly and all were clamped, to keep the material under pressure, then transferred to a cabinet maintained at 37°C/95±5% humidity up to 3 times the initial setting time. The clamp and the glass slides were then removed. The cements, while still secured in their moulds, were kept to set for 7 days at 37°C (14). During this period, the cements were kept under moistened conditions by being wrapped in 4x4-gauze pieces dampened with distilled water in closed containers so that one gauze piece was above and another beneath the moulds containing the cement specimens. Specimens were, then, carefully unmoulded under light pressure and visually checked for any air voids or chipped edges with defective specimens being discarded. The flat ends of intact specimens were wet finished using 600-grit sandpaper to obtain parallel surfaces. Ten specimens were obtained for each cement-type group (*n*=10) as follows: Group "**CSC**", modified calcium silicate cement alone (Control); Group "**CSC+1%TiO_2**", CSC with added 1 % TiO_2; Group "**CSC+3% TiO_2**", CSC with added 3 % TiO_2; and, finally, Group "**CSC+5% TiO_2**", CSC with added 5 % TiO_2.

Compressive strength measurement

Compressive strength evaluation was done using a universal testing machine (Instron 3365, Instron®, MA, USA). The applied force was 5 kN at a crosshead speed of 1 mm/min in a direction parallel to the longitudinal axis of the specimen using a stainless steel rod attached to the upper movable compartment of the device until the cement was crushed (Figure 2). The device recorded force in

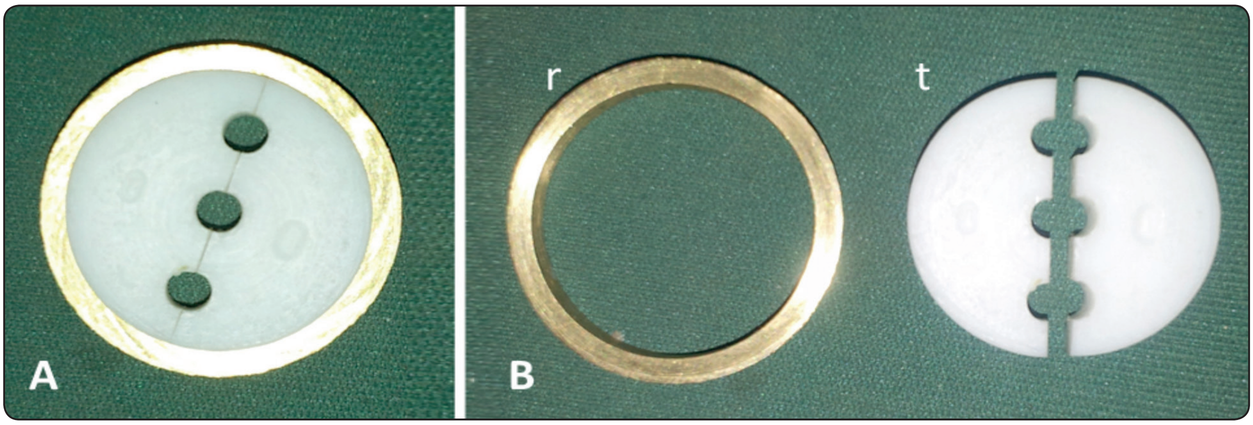

Fig. (1) The three-piece split mould used for preparing specimens in (A) an assembled and (B) disassembled form consisting of an outer brass ring (r) and two inner Teflon complementary halves (t).

Fig. (2) The specimen in position in the Instron testing machine for compressive strength testing.

Newton (N) which was converted to megapascal (MPa) using the following equation: Compressive strength= $4p/\pi d^2$, where ***p*** is the maximum load (in N), **d** is the mean diameter of the specimen (in mm) and π is a constant (3.14).

Statistical analysis

The mean and standard deviation values were calculated for each group. Data were explored for normality using Kolmogorov-Smirnov and Shapiro-Wilk tests and showed normal distribution. One-way ANOVA test was used to compare more than two non-related samples followed by Tukey *post hoc* test for pair-wise comparisons. The significance level (α) was set at 0.05. Statistical analysis was performed with IBM® SPSS® Statistics Version 20.0 for Windows (IBM Corp., Armonk, NY, USA).

RESULTS

Particle size distribution of TiO_2

The particle size pattern of distribution for the TiO_2 powder is presented in Figure (3). One peak existed for the frequency distribution of particle sizes which corresponded to 295.9 d.nm. The polydispersity index (PdI) was 0.309. The average TiO_2 particle size was approximately 300nm.

Compressive strength testing

Figure (4) illustrates the mean values of the compressive strength of the four cements. The mean and standard deviation values for **CSC**, **CSC+1%TiO_2**, **CSC+3%TiO_2** and **CSC+5%TiO_2** groups were 41.73 (± 10.38), 35.65 (± 8.40), 34.10 (± 5.77) and 36.02 (± 8.17) respectively. There was no statistically significant difference in compressive strength among the four groups (p=0.162).

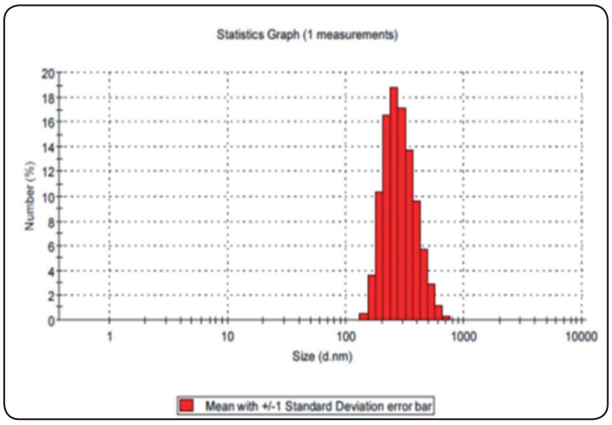

Fig. (3) Particle-size distribution of the titanium oxide powder used in this study.

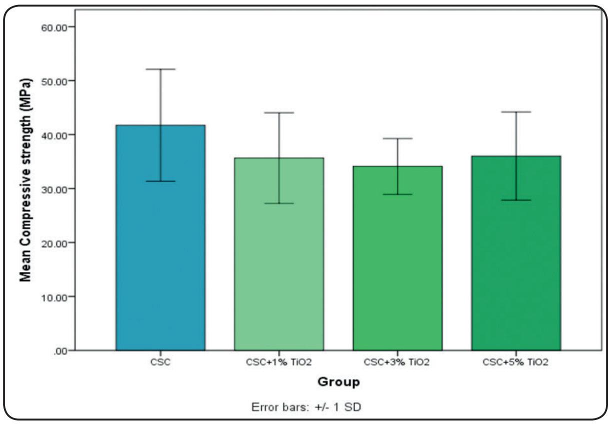

Fig. (4) Compressive strength (in MPa) of modified calcium silicate-based cement (**CSC**) alone or on the addition of 1 % TiO_2 (**CSC+1% TiO_2 group**), 3 % TiO_2 (**CSC+3% TiO_2 group**) or 5 % TiO_2 (**CSC+5% TiO_2 group**).

DISCUSSION

With low mechanical properties being a drawback with CSCs used in endodontics, enhancing the materials' strength is, thus, required, especially when used in certain load-bearing clinical applications as occurs with repairs for furcation perforations, pulp capping and regenerative endodontics. Various attempts have been explored to reinforce CSCs via modifying mixing and placement techniques, particle size distribution or composition e.g. through adding nanoparticles (5,8,10,15,16). Several studies have investigated the effect of different types of nanoparticles, such as nano-silica (11), zeolite-silver-zinc (9), nano-silver (10), nano-calcium carbonate (15) and nano-TiO_2(8), on the mechanical properties of CSCs with varying results. The aim of this investigation was to evaluate the effect of adding different concentrations (1%, 3% and 5%) of commercially-available TiO_2 nanoparticles on the compressive strength of modified CSC comprising 80% Portland-limestone cement and 20% Bi_2O_3.

The compressive strength of a CSC is the highest vertical compressive force it tolerates before fracture. It is associated with its stage of hydration, indicating setting reaction and stability of the material, and is affected by the CSC's type, W/P ratio, additives, condensation pressure and the mixing and placement techniques (5,6,14,16). It is important to assess this property in materials subjected directly or indirectly to mastication forces or condensation forces of overlying restorative materials as they are mainly compressive in nature (28). The measurement of compressive strength was done after 7 days of material setting in the present study as it is the time at which the material is commonly exposed to the extra forces of condensation of the overlying restorative materials, in addition to those of masticatory forces, if a two-visit endodontic approach is to be used. It is, also, a commonly-studied time point for the mechanical properties of CSCs in the endodontic literature (14,29). Due to the limitations of the existing standards for assessing the compressive strength of the CSCs used in dentistry, studies may undergo modifications to the method of testing typical to ISO 9917-1: 2007 specifications (14). The dimensions of the specimens in the present study followed those of the ISO 9917-1; 2007 in which cylindrical specimens had a diameter of 4mm and a height of 6mm; these are the dimensions commonly used in CSC studies (14,29).

The manipulation variables, including the mixing technique, condensation pressure and placement technique as well as the curing environment, whether dry or moist or in the presence on blood, influence the mechanical properties of CSCs (4,5,14,16,29). In the present study, one operator prepared the specimens in order to standardize mixing, condensation pressure and placement techniques across groups; specimens of all groups were kept to set in their moulds under pressure during initial setting. The presence of moisture improves the properties of endodontic CSCs including their compressive strength (4,14), so all specimens were stored with their exposed surfaces in contact with gauze soaked in distilled water in closed containers till the time of testing.

Nanomaterials exist in nature and are synthesized for use in daily life (23,30). Nanoparticles are considered one form of nanomaterials (30). Several definitions have been used for nanoparticles (22,23,30). The European Union (EU) defines nanoparticles as particles having one or more external dimensions within the size range of 1 to 100 nm; other definitions, however, are presented by the International Organization for Standardization (ISO) and several other organizations; the definition of a nanomaterial, however, has been liable to discussion and modification (22,23). Since most of the characteristic properties of nano-sized materials begin to show at dimensions smaller than 1000 nm (1 μm) (30), a broader definition of nanoparticles has, also, been adopted (24,30–32). Nanoparticle dimension, however, is recognized as being fundamental to their toxicity where particle toxicity has been shown to consistently increase as particle size decreases (20), thus, larger-range nanoparticles can be considered biologically safer to use; in the present study, 300-nm TiO_2 particles were used. The most notable property about nanoparticles is the significant increase in surface area relative to a given mass where a decrease in particle size quite increases surface area. One application to this is with fillers considered as reinforcing agents, where smaller-sized particles provide strengthening effects for plastics and cements within optimum concentration levels (19,22,24,33).

Based on the findings of the present study, the addition of TiO_2 in the range of 1 to 5 % did not seem to affect the compressive strength of the modified calcium silicate-based cement having Portland-Limestone cement as its base despite a trend towards a decrease in strength with increased concentration. This finding is in partial agreement with previous studies (9,11,15), while is in disagreement with others (8,33). The addition of 8% and 10% nano-silica did not affect the compressive strength of MTA (11). However, the addition of 5% and 10% nanoparticulate calcium carbonate (15) and zeolite-silver-zinc nanoparticles (9) had adversely affected the compressive strength of MTA. On the other hand, Samiei et al. (8) showed that the addition of 1% TiO_2 to MTA improved its compressive strength. Similarly, it was reviewed that the addition of TiO_2 nanoparticles to cementitious materials can improve their mechanical properties, particularly at early ages, within optimum levels ranging from 1 to 3% (33). Differences among studies could be attributed to differences in the type, particle size and concentration of the nanoparticles added, the cement formulations used and the study methods.

Particle size can have a role in determining the mechanical properties of CSCs (13,14). Generally speaking, the smaller the particle size, the better improved the mechanical properties (14). Saghiri et al. (13) showed better compressive strength of MTA when adding nano-Bi_2O_3 as radio-opacifier compared to regular-sized Bi_2O_3. On the other hand, Silva et al. (12) found similar effect of microparticulated and nanoparticulated zirconium oxide as radiopacifying additives to calcium silicate cement. Another study has, also, shown that both 21-nm and 350-nm TiO_2 nanoparticles improved the compressive strength of Portland cement particularly at early ages (31). Many nanomaterials, however, may not behave much differently from their larger counterparts (22).

Finely-ground mineral powders can enhance hydration rates of cement through the "filler effect" which is mainly attributed to the increased surface area by fine particles providing extra nucleation sites for the resultant reaction products, thus, accelerating hydration which could affect cement properties especially at early age e.g. setting time, compressive strength (21,34). Filler can, also, have a strengthening effect on cements due to its modification of its pore structure where large pores decrease, while small, more favourable ones increase resulting in denser, stronger structures (21,33-35). A certain concentration of filler is, however, required, to achieve optimum results beyond which material's mechanical properties may not be improved or even be adversely affected (33). Fillers can be nano-sized, e.g. nanosale TiO_2 particles, or microsized, e.g finely-ground calcium carbonate (limestone) particles (21,34).

Titanium dioxide (TiO_2), or titania, is a naturally-occurring oxide that is one of the whitest-existing materials, thus, usually used as a pigment in food and medicinal products, and its nanoparticles are among the most-commonly produced and used worldwide due its favourable properties including its stability, both chemically and biologically, its easy and affordable production and its environmental safety (21,31). TiO_2 particles have, also, been used in dental materials, including endodontic materials, for different purposes e.g. as a radiopacifier, pigment, filler or antibacterial agent, with variable concentration requirements according to its function (8,18,19,25,26). TiO_2 nanoparticles have been, also, used as fillers for calcium silicate cements influencing several properties including setting time, porosity and mechanical properties through modifying particle size distribution (21,33,34) and through accelerated cement hydration (21,31). The optimum concentration to achieve the most favourable mechanical properties is, however, affected by several variables including the curing age, the type and amount of the cementitious material and nanoparticle size. (15,21,33,34). Several explanations have been proposed as to the reasons of the adverse effects that could occur on exceeding the optimum concentration levels. One explanation is that the TiO_2 nanoparticles tend to agglomerate due to the lead to strong van der Waals force among nanoparticles with the creation of weak spots within the material bulk (15,21)**.** Another explanation is that the large surface area of the small particles could increase the water requirement of the cement to obtain a workable mix; this could increase the water/powder ratio which could adversely affect mechanical properties. An increase in concentration than optimum, however, can get cement particles coated by excess TiO_2 particles that can hinder cement-water reaction which could decrease material strength (5,15).

Calcium carbonate (limestone) has become a constituent of several calcium silicate cements (3,4,36). In the field of construction engineering, finely-ground limestone is used as an additive to Portland cement as a filler where it accelerates tricalcium silicate hydration through acting as a nucleation sites for calcium silicate hydrate, thus, shortening the initial setting time and improving strength especially at early age (4,15,34,36). Similarly, calcium carbonate has been added as filler to some endodontic CSCs e.g. Biodentine, MM MTA and MTA Caps, reducing setting time through a similar mode of action (3,4). In the present study, the cementitious phase of the used CSC is a composite cement of Portland cement and finely-ground limestone. A previous study comparing TiO_2 nanoparticles to micro-sized calcium carbonate particles as inert additives to Portland cement demonstrated that both similarly affect the early-age properties of the cement and that the early-age properties are rather affected by the particle size and dosage of inert fillers rather than their type where particles less than 3μm show similar behaviour (34).

In the present study, simultaneous co-existence of two types of fillers, nano-scale TiO_2 particles and micro-scale limestone particles, occurred within the cement. Both have a common effect, the filler effect, through which the pores in the cement are filled and pore size in the cement is refined to less harmful forms. An optimum filler concentration is, however, required beyond which the cement's properties do not get further enhanced or could, even, be adversely affected. This could explain, at least partly, the findings in the present study where the compressive strength tended to decrease despite without statistical significance as the already-existing, relatively-inert filler within the cement (limestone) made the additional incorporation of another inert filler (nano-scale TiO_2 particles) ineffective in enhancing the early-age compressive strength. The incorporation of TiO_2 particles may still, however, be beneficial to CSCs through enhancing other properties e.g. the antibacterial activity (19) which warrants further studies.

Within the conditions of this investigation, it could be concluded that the incorporation of nano-scale TiO_2 particles within a range of 1 to 5 % does not seem to affect the compressive strength of the modified calcium silicate-based cement having white Portland- limestone cement as the main cementitious component; this could imply that nano-scale TiO_2 particles may not be an effective strengthening agent to endodontic CSCs materials containing calcium carbonate.

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