Original Articles

Physical Properties of White Portland Cement with Bismuth Oxide Modified by Chitosan and Calcium Chloride

Bovorn Kongsangdao[1], Oranart Matangkasombut[2], Chootima Ratisoontorn[3], Mettachit Navachinda[4] Sakanus Vijintanawan[5], Anchana Panichuttra[3]

[1]Department of Operative Dentistry, Faculty of Dentistry, Chulalongkorn University, Bangkok, Thailand

[2]Department of Microbiology and Center of Excellence on Oral Microbiology and Immunology, Faculty of Dentistry, Chulalongkorn University, Bangkok, Thailand

[3]Department of Operative Dentistry, Faculty of Dentistry, Chulalongkorn University, Bangkok, Thailand

[4]Department of Preventive Dentistry, Faculty of Dentistry, Naresuan University, Phitsanulok, Thailand

[5]Department of Oral Maxillofacial Surgery, Faculty of Dentistry, Mahidol University, Bangkok, Thailand

Abstract

This study compared some physical properties of White Portland cement with bismuth oxide dissolved in a distilled water (control), 1% chitosan solution, 6% calcium chloride solution and chitosan-calcium chloride mixture solution. A compressive strength, setting time, water solubility and acid erosion were tested at first and 21st day. The data was analyzed using one-way ANOVA. The control group showed the lowest compressive strength at both first and 21st day and also the longest initial and final setting time. The chitosan-calcium chloride mixture solution group achieved the highest compressive strength at first day, the fastest initial and final setting time, the least water soluble at 21st day, and the least acid erosion. The 6% calcium chloride solution group showed the highest compressive strength at 21st day and the least water soluble at first day. However, the 6% calcium chloride solution group had the greatest acid erosion property. The 1% chitosan solution group and the combination group resulted in the highest water soluble at first day. In addition, the control and 6% calcium chloride solution groups also showed the highest water soluble at 21st day. Adding either or both chitosan and calcium chloride affected the compressive strength, setting time, water solubility and acid erosion. The addition of these 2 substances may improve the physical properties of the Portland cement.

Keyword: Calcium chloride, Chitosan, Physical property, Portland cements

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Correspondence to:

Anchana Panichuttra, Department of Operative dentistry, Faculty of Dentistry, Chulalongkorn university, 34 Henri-Dunant Road, Wangmai, Pathumwan, Bangkok, 10330 Thailand. Email: anchana.p@chula.ac.th, Tel: 02-218-8795

Introduction

Bioceramic is a biocompatible ceramic compound because of its similarity to a biological hydroxyapatite. It also shows an osteoconductive effect to a promote bone formation[1] and available for using in dentistry under various trade names such as ProRoot® MTA (Dentsply Endodontics, Tulsa, USA), MTA Angelus (Angelus Soluções Odontológicas, Londrina, Brazil).

Mineral trioxide aggregate (MTA) was first described in a dental scientific literature in 1990s and has been used mainly for endodontic applications.[2] Studies on the MTA reveal a good sealing ability, biocompatibility and bioactivity. Several review articles have described the use of the MTA for many applications such as a pulp capping material, pulpotomy, root end filling, root repair material and apexification.[3-6] However, MTA has some clinical implications including a discoloration potential, presence of toxic elements in the material composition, difficult handling characteristics, long setting time and high material cost.[3-6]

Portland cement (PC) and MTA shared the same based compositions. The possibility of clinical use of Portland cement has been considered as an alternative to MTA.[7] Previous studies showed that White ProRoot® MTA and two commercial White Portland cements mixed with bismuth oxide had a comparable chemical constituent, physical properties and biocompatibility to osteoblastic cells.[8,9]

Recently, a special attention has been made toward natural materials because of their biocompatibility and low toxicity.[10] Chitin is mainly found in exoskeleton of crustaceans and also in some fungi.[11] Chitosan is a chitin derived polymer which is produced by a de-acetylation of chitin. Many biomedical applications have been applied for chitosan to promote wound healing, calcium absorption, osteoinductivity and tissue regeneration.[12] The chitosan was also mixed with several calcium rich cements including the calcium phosphate cement, gypsum and concrete cement to improve mechanical properties, physical properties, antibacterial properties and regenerative enhancement.[13-15]

In addition, calcium chloride ($CaCl_2$) is the most common accelerating agent used in calcium-rich cement for reducing setting time[16] and improving the physical properties[17] by accelerating the hydration and the crystallization process.

Regarding to many interesting characters of White Portland cement (PC) such as low price, comparable physical and biological properties to MTA, adding the chitosan and calcium chloride as additives to PC may be effective in terms of enhancement of physical properties. Therefore, the aim of this study was to investigate the physical properties of White Portland cement with bismuth oxide modified by the chitosan and $CaCl_2$.

Material and Methods

Preparation of materials

Powder preparation

Thai Portland cement (TPC) type I brand Tiger Decor for Terrazzo's work normal setting time formula (Siam Cement Group, Bang Sue, Bangkok, Thailand manufactured to Thai industrial standard no.133 2556) was selected as a precursor. The cement was mixed with extra pure 99% dibismuth trioxide powder (BO; LOBA CHEMIE, Mumbai, INDIA) by a milling machine with ratio 4(TPC):1(BO) for 24 hours.

Liquid preparation

Liquid parts were prepared into 4 groups as shown in the table 1.

Table 1 Detail of liquid part of each group

Group	Liquid components
Control	Distilled water
1%CS	1% Chitosan in 1% acetic acid solution
6%CC	6% Calcium chloride in distilled water
1%CS + 6%CC	1% Chitosan and 6% Calcium chloride in 1% acetic acid solution

The chitosan solution was prepared by dissolving 1700 kDa with 90% degree of deacetylation chitosan powder (Marine Bio Resources, Muang, Samutsakhon, Thailand) into 1% acetic acid solution. The calcium chloride and combination solution were prepared by dissolving calcium chloride dehydrate powder (Merck KGaA, Darmstadt, Germany) into distilled water and chitosan in 1% acetic acid solution. These concentrations were chosen according to a pilot study which revealed maximally dissolved chitosan and calcium chloride power in solvents.

The mixing of power and liquid were made in ratio 3:1 respectively with a cement spatula on a glass slab within 60 seconds to achieve smooth consistency.

Physical properties testing

The method of testing compressive strength, setting time and acid erosion testing were modified from international organization for standardization (ISO) 9917-1: 2007 (standard for water-based dental cements). The water solubility testing method was modified from ISO 6876: 2012 (standard for root canal sealing material) All physical properties testing 10 samples in each group .

Compressive strength measurement

The 10 cylindrical specimens in each group were prepared by stainless steel split mold (4 mm-diameter and 6 mm-height as shown in figure 1A) and kept at 37°C and 100% humidity for 24 hours. Then specimens were removed from the mold, specimens with visible voids and defect were excluded. The included specimens were grinding with a wet 400 grade silicon carbide paper and kept in distilled water at 37°C. At 24 hours and 21st day, the samples were picked up and placed in desiccator chamber for an hour before testing. The compressive strength was measured by Universal Testing Machine (LR10K; LLOYD Instruments, Bognor Regis, West Sussex, England) with crosshead speed 1mm/min^{-1}. The compressive strength was calculated by using the fracture load (N) divided by the specimen's cross-section area and recorded in MPa.

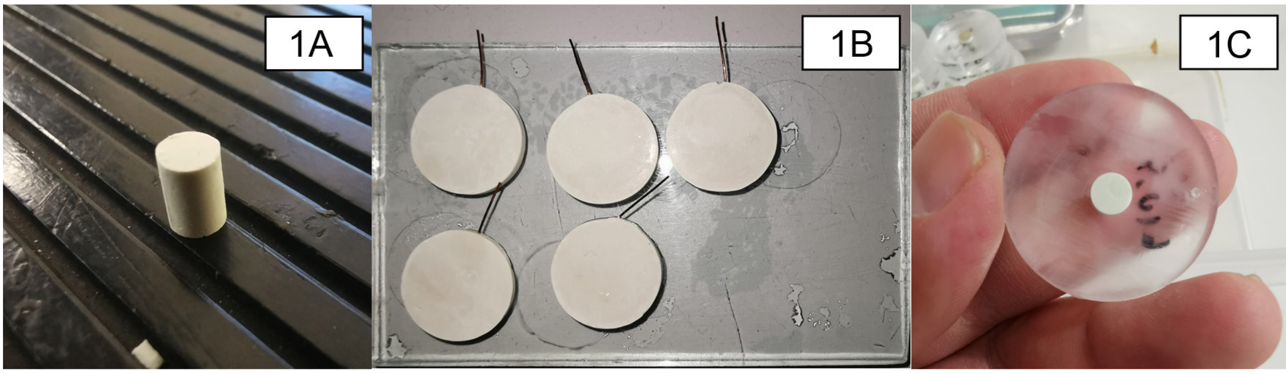

Figure 1 *Show the specimen of compressive strength (1A), water solubility (1B) and acid erosion (1C) testing method.*

Setting time measurement

Ten samples in each group were tested. Setting time was determined by using the Gilmore needle method. The freshly mixed cement of each group was placed into stainless steel mold (8 x 10 x 5 mm) and conditioned at more than 90% humidity and 37°C. The needle mass of 100 g and 400 g were used to determine initial setting time and final setting time respectively. The setting time is the total time from the start of mixing until the time when needle failed to make a completed circular indentation in the cement.

Water solubility measurement

The 20 cylindrical specimens in each group (20 mm-diameter and 1.5 mm-height with 6 mm copper wire insertion as shown in figure 1B) were prepared and storage in a condition of more than 90% humidity and 37°C for 24 hours. The included specimens were polished and dried in the oven at 105°C for 3 hours and cooled in the desiccator.

Glass bottles (W_i) and specimens (W_s) were weighted before testing. The specimen was then individually placed into the bottle containing 50 ml of distilled water, then it was transferred to the incubator chamber at 37°C. At 24 hours and 21st day, ten specimens were removed from the water and the bottle of water was placed in the hot air oven to evaporate the water, then cooled down. The bottles of water were weighted again as W_f). Water solubility at 24 hours and 21th day were calculated with this given equation; (W_f - W_i) x 100 / (W_s).

Acid erosion measurement

Ten samples in each group were tested. This test consisted three parts; preparation of eroding solution, preparation of specimens and measurement of acid erosion.

Preparation of eroding solution

Dissolved 16.54 g of lactic acid and 1.84 g of sodium lactate in 2,000 ml of deionized water for 18 hours before using. pH of the solution was controlled at 2.74 ± 0.02.

Preparation of test specimens

The cement was filled in a hole of the specimen holder (cement space Ø5 x 2 mm as shown in figure 1C) and maintained at 37°C with a relative humidity of at least 90%. After 24 hours, the specimens were polished using the abrasive paper with continuous water irrigation until acquired flat surface and the thickness of specimen and specimen holder were within 5 µm difference.

Measurement of acid erosion

The thickness of specimen was measured at the center. The average thickness of specimen holder was measured at 4 points. The difference between these two thicknesses was called D_0.

The specimen was immersed in 30 ml of the eroding solution. After 24 hours, the specimen was removed and rinsed with deionized water. The specimen was again measured the thickness at the center. The difference between the specimen thickness and specimen holder thickness was called D_t.

Eroding depth (D) was calculated with following equation: $D = D_t - D_0$

Statistical and data analysis

Data were statistically analyzed using IBM SPSS Statistics for Windows, Version 22.0 (IBM, Armonk, NY, USA). All data were represented as mean ± standard deviation. The data of each group was plotted and the distribution curve was analyzed together with the Kolmogorov-Smirnov test with *p* value = 0.05. Compressive strength (MPa), setting time (minutes), water solubility (% mass loss), and depth of eroding sample (mm) were performed using One-way ANOVA (*p* = 0.05) followed by Tukey's test to evaluated the effect of each additive to control.

Results

Compressive strength at 1st and 21st day

The result was displayed in figure 2. The control group showed the lowest compressive strength at both 1st and 21st days *(p<0.001).* The 1%CS+6%CC group had the highest compressive strength at 1st day *(p<0.001).* The 6%CC group showed the highest compressive strength at 21st day *(p<0.001).*

Initial and final setting time

The result was displayed in figure 3. The control group had the slowest initial and final setting time *(p<0.001).* The 1%CS+6%CC group had the fastest initial and final setting time *(p<0.001).*

Solubility at 1st and 21st day

The result was displayed in figure 4. At 1st day, the 1%CS and 1%CS+6%CC group showed the greatest percent mass loss while the 6%CC group had the least solubility *(p<0.001).* At 21st day, the control group and 6%CC group showed similar result which was the highest percent mass loss *(p<0.001).* The 1%CS+6%CC group had the lowest soluble at 21st day *(p<0.001).*

Acid erosion

The result was displayed in figure 5. The 6%CC group showed the highest eroding depth while the 1%CS+ 6%CC group was the least eroded *(p<0.001).*

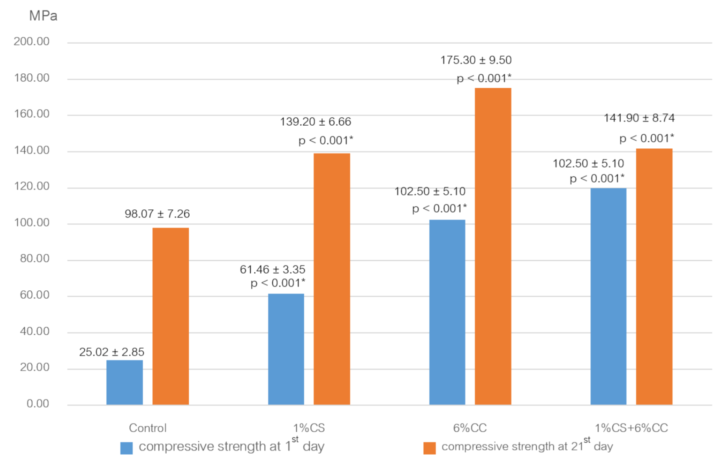

Figure 2 *The mean compressive strength at* 1^{st} *and* 21^{st} *day of each group expressed as mean MPa ± SD*
**represents a significant change compared with the control at p < 0.05*

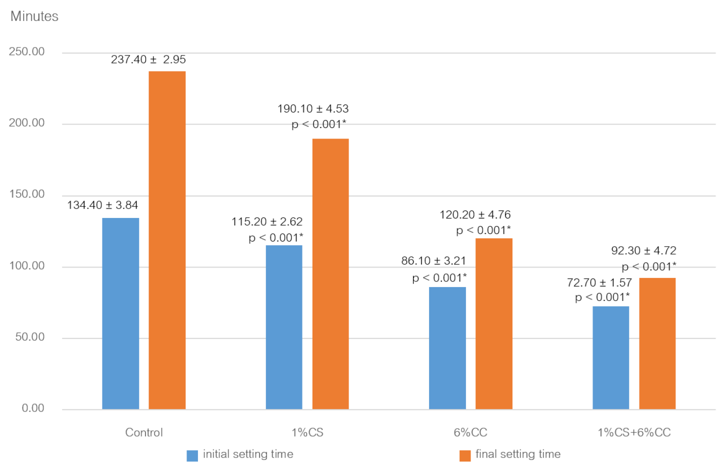

Figure 3 *The mean initial and setting time of each groups expressed as mean minutes ± SD*
** represents a significant change compared with the control at p < 0.05*

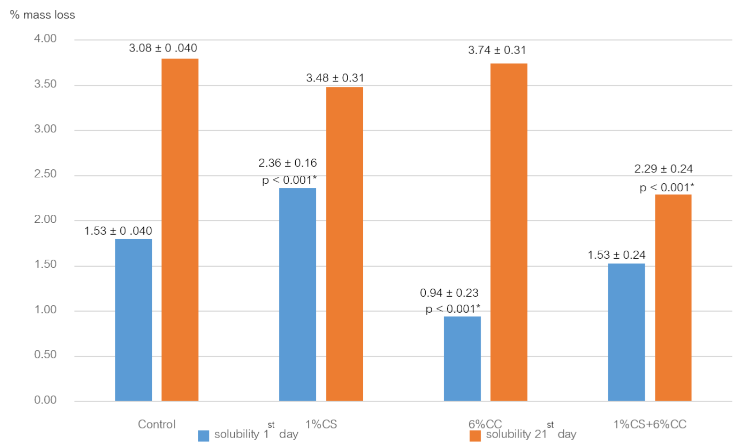

Figure 4 *The mean water solubility at* 1^{st} *and* 21^{st} *day of each group expressed as mean % mass loss ± SD*
** represents a significant change compared with the control at p < 0.05*

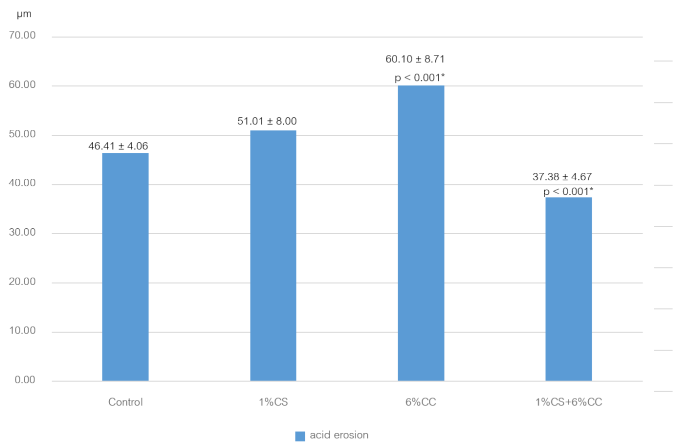

Figure 5 *The mean acid erosion of each group expressed as mean μm ± SD*
** represents a significant change compared with the control at $p < 0.05$*

Discussion

Bioceramic cement was used as several dental materials such as a root end filling, root repairing and pulp capping materials. Mineral trioxide aggregate (MTA) is one of the bioceramic material which is considered as a gold standard material for an apical root-end surgery, perforation reparation, pulp capping and root-end fillings because of superior biocompatibility and good sealing ability.[18,19] However, it has some disadvantages including a long setting time, high material cost and excessive early solubility.[3-6]

There are many additives such as a methylcellulose and $CaCl_2$ which were able to enhance the physical properties of the bioceramic cement.[16] The $CaCl_2$ is an accelerator of the setting time and the methylcellulose is used to increase washout resistance.[16,20] Present study attempted to develop better biomaterial from Portland cement (PC) which contained similar based compositions as MTA including dicalcium silicate, tricalcium silicate and tricalcium aluminate.[17] PC uses the hydration process for its setting or hardening reaction. Most of the hydration process occurs during first 3-4 weeks, although complete hydration may even take 1-2 years.[21,22] Therefore, we tested at 2 times, first day based on (ISO) 9917-1: 2007 (standard for water-based dental cements) and 21st day compared to Torabinejard's studies.[23] Even though the physical properties were tested by one examiner, the SD value was in an acceptable range according to the same study[23].

Several studies showed comparable physical properties between these two materials.[20,23-26] PC exhibited slightly lower compressive strength at first day, but the compressive strength of PC was higher after 21 days.[23] Initial and final setting time of PC was faster than MTA.[24, 25] PC showed lesser soluble at first day but higher at 21st day.[26]

Chitosan was added to PC to improve mechanical and biological properties. It is linear polysaccharide composed from glucosamine and N-acetyl glucosamine subunit. The proportion between these units is called the degree of de-acetylation. A molecular weight and degree of de-acetylation (DDA) determined properties of the chitosan because they increased amino and hydroxyl groups.[27] These functional groups can improve mechanical properties of cement because they were active binding sites to calcium ion from calcium rich cement. The functional groups formed crosslinking between cement crystalized particles and improved cement cohesion which is called "cement glue"[28]. And also promote cementogenesis, periodontal regeneration and promote initial attachment of osteoblasts and fibroblast.[29-31]

The compressive strength was improved after adding chitosan to the PC. The chitosan was hypothesized to chelate the calcium ion from modified PC to form a stronger interfacial transition zone around calcium silicate hydrate gel during a crystallization process. It also removed an excess water from a hydration process and refined cement pores.[15,31] The crosslinking between PC and chitosan made cement denser and increased a strength to modified PC. The result was similar to previous study which added the chitosan fiber combined with a gelatin to the calcium phosphate cement. They also found that the chitosan formed a chemical bond and mechanical interlocking to the cement particles so the cement was improved a flexural strength.[32]

However, chitosan is considered as a cement retarder because it can interrupt an ionic balance of cement components during the setting process.[33] It coated anhydrous surfaces of cement particle and prevented an initial attack by water.[34] Panahi *et al.* added chitosan to the cement which prolonged final setting time and decreased compressive strength.[35] In contrast, the present study found the chitosan solution slightly reduced the initial and final setting time. Similarly, Kamali *et al.* found significantly shorter setting time and stronger compressive strength.[34]

The different properties of cement may be resulted from the difference cement coating ability.[20,30] The coating property is increased by lower molecular weight and lower concentration of chitosan. Both Panahi's and Kamali's studies were used 2%, high concentration of medium molecular weight chitosan so their cements had less retarder effect.[34,35] They assumed that optimum chitosan gel layer on the cement surface may bind the metal ion in cement solution and act as nucleation site for the setting process which increased the compressive strength.

Calcium chloride ($CaCl_2$) is a soluble salt admixture which accelerates hydration process of the calcium rich cement.[36] It has been used as cement setting accelerator in dental materials such as Biodentine®. Previous studies use 2-15% calcium chloride mixing with PC and MTA.[37-40] We selected 6% $CaCl_2$ because it was the highest concentration that the chitosan completely dissolved without any precipitation from pilot study. Our study found that 6% $CaCl_2$ significantly increased the compressive strength, reduced the initial and final setting time and decreased the water solubility at first day. Similarly, Bortoluzzi *et al.* found that 10% calcium chloride added to MTA and PC significantly reduced the setting time, decreased the water solubility and increased the pH.[37] They suggested that a penetration of $CaCl_2$ in the pores of the cements, which strongly accelerated the hydration of silicates, led to faster crystallization process and shorter setting time.[37] Similar to Rapp P *et.al* and Torkittikul *et al*, they found that the compressive strength of modified PC was increase when added 1-8% $CaCl_2$ however the higher concentration than 8% $CaCl_2$ decreased the compressive.[38,39] There are two reasons explaining the greater compressive strength after adding $CaCl_2$. First, adding the $CaCl_2$ increases calcium silicates components that mainly responsible for the compressive strength of cement. Second, density of the cement paste is decreased. The ions and water can easily penetrate through the cement particles so greater rate of cement hydration is achieved which gives high early strength.[39-42] In contrast, some previous studies found $CaCl_2$ decreased the compressive strength of the MTA.[16,40,41] The different outcomes may cause by the different concentration of $CaCl_2$ and types of cement that affected the setting process and compressive strength.

Adding $CaCl_2$ to the chitosan solution prevented the retarder effect of chitosan which made thicker but less sticky cement paste. The chelated chitosan solution was thickened the cement paste liked chitosan solution but not made in difficult to blend and less sticky cement paste. Previous study mixed the chelated chitosan with $CaCl_2$ to an oil well cement. They found the thickening time reduction of the cement paste.[43] Faster setting time was described by some of the hydroxyl and amine groups of chitosan bid to the calcium ion and arranged to bridging polymer network chitosan calcium complex. These networks enwrapped the cement and water. Subsequently, it created the cluster of cement and water spreading throughout the cement slurry.[43]

The solubility of set root canal sealer should not be exceed 3% by mass according to ISO 6876-2012 (root canal sealing material standard). The solubility of modified PC in this study was less than standard. This property is one of multifactorial that make the three-dimensional hermetic seal which prevent reinfection of root canal system.[44,45] Nevertheless, the limitation of this study is that only some physical properties were investigated. Further research into the study of other physical properties including bacterial leakage, solubility in tissue fluid, pushout resistance and biocompatibility are suggested.

Conclusion

Adding either or both chitosan and calcium chloride affected the compressive strength, setting time, water solubility and acid erosion. These two substances may be option to improve some physical properties of cement.

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Conflict of interest statement

No conflict of interest in connection with this article.

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