Original Article

Study of Methods to Improve the Physical Properties of Bioceramic Cement

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Abstract

This study aimed to investigate the effect of particle size, the addition of various concentrations of calcium chloride and calcium tungstate on the physical properties of white Portland cement. White Portland cement with two different particle sizes (12 and 5 Microns) were used as the main component. Calcium chloride with various concentrations was added as an accelerator, and calcium tungstate was used as a radiopacifier. The ISO 6876:2012 and ISO 9917-1:2007 standard testing protocol were applied for setting time, compressive strength and radiopacity evaluation. White Portland cement with calcium tungstate showed the radiopacity of 4.2 mmAl. Calcium chloride accelerated the setting time but also decreased the compressive strength. The dose dependent effect of 5 %, 10 %, 15 %, 20 %, 25 % and 30 % calcium chloride on setting time and compressive strength was not in a linear pattern. Small particle size Portland cement with 15 % calcium chloride provided a short setting time with acceptable compressive strength.

Keywords : Bioceramic cement, Calcium chloride, Calcium tungstate, Particle size, Physical property

Date: Oct 8, 2020 **Revised Date:** Oct 26, 2020 **Accepted Date:** Feb 2, 2021

Doi: 10.14456/jdat.2021.22

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Introduction

Since the introduction of commercial Mineral Trioxide Aggregate (MTA) in 1998, it has been widely used in dentistry. MTA fulfills many of the ideal properties of endodontic materials partly because of its hydraulic nature and the formation of calcium hydroxide, as a by-product of the hydration process. However, some physical properties such as a long setting time and causing tooth discoloration raise concern among clinicians regarding its usage in some clinical situations.

MTA is a derivative of Portland cement with both having a similar composition; mainly tricalcium silicate and dicalcium silicate, except for the presence of bismuth oxide as a radiopacifier in MTA.[1] Studies have shown that Portland cement has similar physical properties[2] and a biological response[3] to MTA. The physical properties of Portland cement have been improved by various methods such as adding an accelerator, plasticizer and radiopacifier. Calcium chloride has been added to accelerate the setting

process of Portland cement.[4-6] Studies showed the decreased setting time ranging from 20 % to 68 % with the addition of a calcium chloride concentration from 2 % to 10 %[4-7], but a decreased compressive strength was also observed.[5-7] The most suitable percentage of calcium chloride to be added to Portland cement to provide the acceptable physical properties is still unknown.

In principle, the reduction of particle size of a powder reactant should result in a high surface area, and should promote the setting reaction. Ha and co-workers[8] investigated the effect of the particle size of various commercial MTA and Portland cement on setting time. The correlation between a faster setting time and a smaller size particle of MTA and Portland cement was reported. However, different commercial brands are composed with different compositions which can influence the physical properties of the materials. The real effect of particle size on the setting time of the materials should be found by grinding materials to smaller particle size. Comparing the setting time between the large and small particle sizes of the same material will show the accurate effect.

MTA contains bismuth oxide which acts as a radiopacifing agent. It has been reported that bismuth oxide is a causative factor of tooth discoloration. Calcium tungstate provides acceptable radiopacity, and therefore is suggested as a substitution to bismuth oxide as a radiopacifier.[9] Though, its potential interference with the physical properties of Portland cement should be examined.

The purpose of this study was to investigate the effect of particle size, the addition of various concentrations of calcium chloride and calcium tungstate on the setting time, compressive strength and radiopacity of white Portland cement.

Materials and Methods

This study used white Portland cement (Date of manufacturer June-2019, Tiger décor, The Siam White Cement CO., LTD, Thailand) as a main component. Calcium chloride and calcium tungstate were used as an accelerator and a radiopacifier, respectively.

Preparation of small particle size Portland cement

Fifty grams of white Portland cement and 100 ml of Acetone were put into the Planetary Mill Pulverisette 6 machine (Fritsch, Idar-Oberstein, Germany). The grinding process was performed by the machine with the use of a zirconia ball (1 centimeter in diameter) at the speed of 500 rounds/minute for 60 minutes. The ground materials were oven-dried at 110°C for 24 hours. The ground cement was examined by using the particle size analyzer (Malvern Panalytical, Mastersizer 2000: Downers grove, IL 60515, USA). After grinding, the particle size was reduced from 12 to 5 microns.

The experimental groups were divided into five main groups.

Group 1: MTA

Group 2: White Portland cement + calcium tungstate

Group 3: White Portland cement + calcium tungstate +various concentration of calcium chloride

Group 4: Small particle size white Portland cement + calcium tungstate

Group 5: Small particle size white Portland cement + calcium tungstate + various concentrations of calcium chloride

The powder and liquid ratio of MTA and white Portland cement was 3:1 (by weight). Calcium tungstate was added to the white Portland cement at the ratio of 1:4 (by weight). Calcium chloride was mixed into distilled water at various powder-liquid ratios to provide the concentration of calcium chloride at 5, 10, 15, 20, 25 and 30 % (by weight).

Setting time evaluation

Setting time was evaluated following the protocol described in the ISO 6876[10] and ISO 9917-1 standard[11].

Initial setting time

The gypsum molds with an inner diameter of 10 mm and a thickness of 1 mm were stored at 37°C and 95 % humidity for 24 hours before testing. The materials were mixed and filled in to the molds to create ten samples for each experimental group. Setting time was determined with a Gillmore needle test. The indentor needle with a flat end tip of 2 mm in diameter was placed vertically on the sample surface with a load of 100 g at the rate

of 1 mm/min. The indentation test was repeated every 30 seconds until no indentation was observed on the cement surface. The initial setting time was the time from mixing cement to the time when the needle marks could not be observed on the cement surface. All testing was conducted in a cabinet with controlled temperature and humidity (37°C and 95 % humidity).

Final setting time

The cements were mixed and compacted into stainless steel rectangular molds with the dimension of 10 mm x 8 mm and 5 mm deep. Each experimental group contained ten samples. The testing procedures were similar to the initial setting time test but with a different indentor needle size and load (a flat-end needle with a diameter of 1 mm/with the load application of 400 g). The final setting time was the duration of time that elapsed from the start of mixing to when the indentor needle failed to make an indentation in the material.

Compressive strength evaluation

The compressive strength was determined according to the methods recommended by the ISO 9917-1. The cement was mixed and packed into the metal split mold (internal dimension 6 mm high, 4 mm diameter), and then was stored in the cabinet at 37°C with a relative humidity of at least 90 % for 24 hours. The test specimens were removed from the metal split mold and were subjected to test. Each experimental group contained ten samples. The compressive strength was measured by a Universal Testing Machine (LR10K, LLOYD Instruments, England), with a crosshead speed of 1 mm per minute. A compressive load was applied along the long axis of the test specimens. The maximum force when the test specimen fractures was recorded, and calculated for the compressive strength in megapascals (MPa).

Radio-opacity evaluation

The radiopacity was determined according to the method recommended by ISO 6876:201210. There were three experimental groups: MTA, white Portland cement and white Portland cement mixed with calcium tungstate (at the ratio of 1:4 by weight). Each experimental group contained six samples. The test specimens were mixed with distilled water with the powder to liquid ratio of 3:1 by weight. After mixing, the test materials were placed into a ring mold (internal diameter of 10 mm, height 1 mm). The fully-set specimen was placed in the center of the x-ray film adjacent to the step wedge, and was irradiated with X-rays at 65 kV at a target-film distance of 300 mm. After developing, fixing and drying the exposed film, the density of the image of the specimen was compared with the aluminium step wedge. The radio-opacity equivalent of the specimens was expressed in millimeters of aluminium (mmAl).

Statistical Analysis

Data were statistically analyzed by analysis of variance (ANOVA) and Tukey post hoc test. A *p* value of less than 0.05 was considered statistically significant.

Results

Table 1 *Setting Time of Experimental and Control Groups*

liquid	OPC		SPC		MTA	
	Initial setting time (min)	Final setting time (min)	Initial setting time (min)	Final setting time (min)	Initial setting time (min)	Final setting time (min)
Distilled water	89.50 ± 2.37 ^{A}	121.80 ± 2.66 ^{a}	25.80 ± 1.75 ^{AA}	44.60 ± 1.51 ^{aa}	115.90 ± 3.35	159.50 ± 2.32
5% $CaCl_2$	76.00 ± 2.75 ^{B}	100.00 ± 1.89 ^{b}	22.80 ± 1.75 ^{BB}	39.50 ± 2.46 ^{bb}	-	-
10% $CaCl_2$	69.30 ± 1.89 ^{C}	87.80 ± 2.15 ^{c}	21.70 ± 1.64 ^{BB}	38.60 ± 1.35 ^{bb}	-	-
15% $CaCl_2$	36.00 ± 1.25 ^{D}	60.90 ± 1.79 ^{d}	14.40 ± 1.43 ^{CC}	23.90 ± 1.37 ^{cc}	-	-

Table 1 *Setting Time of Experimental and Control Groups (cont.)*

liquid	OPC		SPC		MTA	
	Initial setting time (min)	Final setting time (min)	Initial setting time (min)	Final setting time (min)	Initial setting time (min)	Final setting time (min)
20% $CaCl_2$	33.00 ± 2.31 ^{E}	52.80 ± 1.62 ^{e}	8.50 ± 1.08 ^{DD}	17.80 ± 1.93 ^{dd}	-	-
25% $CaCl_2$	29.70 ± 2.00 ^{F}	39.00 ± 1.25 ^{f}	7.60 ± 1.07 ^{DD}	17.70 ± 1.34 ^{dd}	-	-
30% $CaCl_2$	24.60 ± 1.17 ^{G}	34.30 ± 1.64 ^{g}	7.40 ± 0.97 ^{DD}	16.70 ± 1.16 ^{dd}	-	-

OPC, Original size white Portland cement; SPC, Small size white Portland cement; MTA, Mineral trioxide aggregated; CaCl2, Calcium chloride. Results are shown as mean ± standard deviation for ten samples in each group. In the same column, different letter indicates statistically significant differences (p < 0.05)

Setting time

Table 1 illustrates the setting time of all OPC, SPC and MTA samples. OPC and SPC mixed with distilled water showed a shorter setting time than MTA ($p<0.05$). The reduction of particle size resulted in the shorter setting time when comparing between the SPC and OPC groups ($p<0.05$). The addition of calcium chloride caused the reduction of setting time. In general, at the same concentration of calcium chloride, SPC exhibited a shorter setting time than OPC ($p<0.05$). The OPC group, the higher percentage of calcium chloride added, the shorter setting time was observed. With the addition of 30 % calcium chloride, the setting time was reduced to as much as 70 % (initial setting time of 24 minutes and the final setting time of 34 minutes). The setting time of SPC with the addition of 5 % and 10 % calcium chloride was not statistically significantly different (there was a reduction of setting time by 10-15 %). The higher concentration of calcium chloride can further reduce the setting time. However, the setting time of SPC with the addition of 20 %, 25 % and 30 % of calcium chloride was not significantly different (there was a reduction of setting time by 60 %).

Compressive strength

The mean and standard deviation of compressive strength at 24 hours of all samples are presented in Table 2. OPC and SPC mixed with distilled water exhibited higher values of compressive strength in comparison to MTA ($p< 0.05$). The addition of calcium chloride to OPC and SPC decreased the compressive strength. At 20%, 25% and 30% calcium chloride, the compressive strength of OPC and SPC were significantly lower than the MTA group.

Table 2 *Compressive strength of Experimental and Control Groups*

Liquid	OPC (MPa)	SPC (MPa)	MTA (MPa)
Distilled water	62.75 ± 5.04 ^{A}	66.29 ± 10.36^{a}	50.93 ± 10.95
5% $CaCl_2$	44.68 ± 4.03 ^{B}	62.08 ± 6.89 ^{a}	-
10% $CaCl_2$	42.48 ± 2.42 ^{B}	42.86 ± 6.26 ^{b}	-
15% $CaCl_2$	41.20 ± 3.01 ^{B}	41.36 ± 4.46 ^{b}	-
20% $CaCl_2$	37.56 ± 9.42 ^{C}	39.09 ± 3.56 ^{c}	-
25% $CaCl_2$	36.09 ± 4.00 ^{C}	39.14 ± 7.04 ^{c}	-
30% $CaCl_2$	35.44 ± 4.35 ^{C}	38.22 ± 6.67 ^{c}	-

OPC, Original size white Portland cement; SPC, Small size white Portland cement; MTA, Mineral trioxide aggregate; $CaCl_2$, Calcium chloride. Results are shown as mean ± standard deviation for ten samples in each group. In the same column, different letters indicate statistically significant differences (p<0.05)

Radiopacity

The radiopacity values of MTA, White Portland cement and White Portland cement with the addition of calcium tungstate are presented in Table 3. MTA showed the highest radiopacity among tested specimens ($p<0.05$). White Portland cement with the addition of calcium tungstate was significantly more radiopaque than just White Portland cement ($p<0.05$).

Table 3 *Radiopacity of Experimental and Control Groups*

Materials	Mean ± Standard deviation (mmAl)
White Portland cement	1.01 ± 0.01 [a]
White Portland cement with Calcium tungstate	4.32 ± 0.25 [b]
MTA	6.78 ± 0.18 [c]

Results are shown as mean ± standard deviation for six samples in each group.

Different letters indicate a statistically significant difference ($p < 0.05$)

Discussion

For decades, MTA has been considered as the gold-standard material for various endodontic treatment procedures such as perforation repair, root-end retrograde filling, apexification and vital pulp therapy, due to its good physical, chemical and biological properties. However, in some clinical situations such as endodontic surgery with root-end filling, the extended setting time of MTA may increase the high rate of washout and a possibility of blood or serum contamination during setting. In cases of vital pulp therapy, with the application of the fast setting bioceramic cement, the treatment can be completed within one visit. To date, researchers have attempted to improve the properties of bioceramic materials such as adding the accelerator agents to decrease the setting time[4,12], adding the plasticizer to improve the handling properties[13], and etc.

The guidelines for testing the physical properties of dental materials have been provided by two organizations namely; the International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM). The ISO 6876[10] and 9971-1[11] are quite similar to ASTM C 26614 in terms of the weight (100 and 400 grams) and test methods using the Gillmore needle type. ISO 6876 uses a parameter similar to the defined initial setting time of ASTM C 266, and the ISO 9971-1 uses a parameter similar to the defined final setting time of ASTM C 266. As described by Shen and coworkers[15], this study used ISO 6876 to determine the initial setting time and ISO 9971-1 to establish the final setting time.

Portland cement is considered as a much cheaper alternative material to MTA. However, it still requires some modifications to improve its physical properties. In this study, White Portland cement was grounded by the grinding process of the Planetary ball mill machine, and the particle size was reduced from 12 to 5 Microns. When mixed with water, SPC exhibited a shorter setting time than OPC (60 % difference) ($p<0.05$). This finding is in agreement with the study of Ha and coworkers[8] which showed that the smaller size particle resulted in a faster setting. The possible explanation is that the increased surface area enhances the setting reaction.

Bioceramic materials used for endodontic treatment should provide adequate radiopacity in order to aid diagnosis and treatment. In this study, MTA showed the radiopacity of 6.7 mmAl which is comparable with the study of Torabenejad and co-workers.[16] Portland cement showed the radiopacity of 1.01 mmAl which is not sufficient to allow distinction from dentine (radiopacity of 1.7 mmAl).[9] Adding calcium tungstate to Portland cement increased the radiopacity from 1.01 mmAl to 4.3 mmAl, which is higher than the requirement of ISO 6876: 2012 of 3 mmAl.[10]

Calcium chloride has been added to Portland cement as an accelerator. It increases the hydration rate, thereby accelerating the setting time.[7] It is hypothesized that as the progress of hydration, the area of hydrated tricalcium silicate paste gradually increases due to the formation of hydration product such as calcium silicate hydrate gel and calcium hydroxide, and the addition of calcium chloride would accelerate this increasing rate.[17] Though, there is no explanation for the mechanism. Another possible mechanism is that calcium chloride penetrates the pores of the cement, and accelerates the hydration of silicate leading to faster crystallization.[4] The information regarding the dose dependent effect of calcium chloride on setting time is limited. Most studies investigated the setting time of only one concentration of calcium chloride per study such as at 5 % or 10 %.[4,8] Only the study by Kogan *et al.,* 2006[5] showed the dose dependent effect. The addition of 3 % calcium chloride did not reduce the setting time but the addition of 5 % calcium chloride decreased the setting time by 50 % (from 50 minutes to 25 minutes). Results from our study showed that increasing the concentration of calcium chloride did not always further decrease the setting time. The addition of calcium chloride at a concentration of 20 % and more (25 % and 30 %) to SPC showed similar results with the decreased setting time by approximately 60 % (approximately 8 minutes for initial setting time and 17.5 minutes for the final setting time).

In this study, the compressive strength was evaluated to determine whether the calcium chloride had an adverse effect on the mechanical properties of Portland cement. The compressive strength of MTA at 24 hours was 51 MPa which was higher than the reported value of 40 MPa.[16] The possible explanation is the difference of the test methods between two studies. This study followed the guidelines of ISO 9917-1: 2007[11] which recommended the tested specimen with the dimension of 6x4 mm, and the cross-head speed was 1 mm/minute. The published study in 1995 by Torabenejad and coworkers[16] cited the reference of ISO 6896: 1986 (Specification for dental root canal sealing materials)[14], and the prepared specimen had the dimension of 12x6 mm with no information on the loading application. The addition of calcium chloride decreased the compressive strength which is similar to other studies.[5-7] The dose dependent effect of the addition of various concentrations of calcium chloride was investigated by Kogan and coworkers[5] and this study. The addition of 3 % calcium chloride reduced the compressive strength by 30 %, and the higher concentration at 5% calcium chloride did not further reduce the compressive strength.[5] Our results showed that increasing the concentration of calcium chloride decreased the compressive strength but not in a linear pattern. At the 15 % concentration of calcium chloride, Portland cement showed a lower compressive strength of 41 MPa, (reduction by 35 %) but was not statistically significantly different from MTA (51 MPa). Increasing the concentration of calcium chloride to 20 % and higher reduced the compressive strength to the values of 35-38 MPa (reduction by 40 % and more) which was significantly lower than MTA. Similar to other studies, a low compressive strength of 19.9, 37.2 and 41.5 MPa with the addition of 5 %, 10 % and 2 % calcium chloride respectively were reported.[5-7] The limitation of this study is that the compressive strength was evaluated only at one day after mixing without repeating at twenty-one days as conducted by Torabinejad and co-workers.[16] The compressive strength increased from 40 MPa to 67 MPa after 21 days.[16] Therefore, in this study, it is possible to observe higher compressive strength with the longer observation periods.

The question is "What is the proper concentration of calcium chloride to be added to Portland cement? ISO 9917-1 (2007)11 provided the requirement for water-based cement. Depending on the usage of the materials, high compressive strength is compulsory for restoration and lower compressive strength for base/liner. Therefore, one specific formulation of cement may not be suitable for all kinds of dental procedures. In vital pulp therapy, it will be beneficial to patients if the treatment could be completed within one visit. According to the results, the addition of 15 % of calcium chloride to SPC provided a setting time

of 15 minutes which will allow the placement of restorative material on top of the cement at the same visit. At this concentration of calcium chloride, SPC exhibited the acceptable compressive strength (not significantly different to MTA). However, the limitation of this study is that only setting time and compressive strength were investigated. Other aspects of the physical properties such as solubility should be examined in future research.

Conclusion

The small size particles of white Portland cement set faster than the original size particles of white Portland cement. The addition of calcium tungstate to the Portland cement provided the acceptable radiopacity at 4.3 mm Al. Calcium chloride accelerated the setting time but also decreased the compressive strength. The dose dependent effect of the addition of 5 %, 10 %, 15 %, 20 %, 25 % and 30 % calcium chloride on setting time and compressive strength was not in a linear pattern. The small size particles of Portland cement with the addition of calcium tungstate and 15 % calcium chloride provided a short setting time with acceptable compressive strength.

Acknowledgements

This work was supported by The Chulalongkorn Academic Advancement into Its 2nd Century Project. The authors thank Dr.Thanakorn Wasanapiarnpong and Dr.Chalermkwan Makornpan from the Department of Materials Science, Chulalongkorn University, for their advice and help with the material preparation. The authors deny any conflict of interest related to this study.

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