Original Article

pISSN, eISSN 0125-5614
M Dent J 2019; 39 (3) : 199-205

Radiopacity of Biodentine, Bio-MA, and calcium silicate-based cement added with different radiopacifiers

Piyawat Vibulcharoenkitja, Danuchit Banomyong, Supachai Sutimuntanakul

Department of Operative Dentistry and Endodontics, Faculty of Dentistry, Mahidol University, 6 Yothi Street, Rachathewi, Bangkok 10400 Thailand

Objective: To investigate the radiopacity of two commercial calcium silicate cements (CSC)—Biodentine and Bio-MA—and experimental CSC containing one radiopacifier—zirconium oxide (Zr), barium sulfate (Ba), tantalum oxide (Ta) or bismuth oxide (Bi) according to International Organization for Standardization (ISO) 6876:2012.

Materials and Methods: Biodentine and Bio-MA were mixed according to the manufacturers' instructions. CSC powder was added 20% by weight of radiopacifier in a blending machine. The powder was mixed with distilled water with a ratio of 0.5 g per 0.18 ml. The disc-shaped material, 6 mm in diameter and 1 mm thick, was formed in a mold. CSC without radiopacifier was used as a control. The disc was placed alongside 0.5-mm increment aluminium (Al) step wedge and irradiated with x-ray 60 kV, 8 mA, 0.016 msec on a digital receptor. Radiopacity of materials were compared with the aluminium step wedge using ImageJ program and transformed into mm of Al.

Results: Bio-MA radiopacity was 6.59±0.39 mmAl and was significantly higher than other investigated materials (p<.01). The radiopacity in mmAl of CSCs with the addition of radiopacifiers were CSC/Ba 2.52±0.14, CSC/Zr 2.90±0.05, CSC/Ta 3.39±0.10, CSC/Bi 5.42±018, and the control group was 0.99±0.06. They were all significantly different from each other (p<.01). Biodentine radiopacity was 2.34±0.20 mmAl which was significantly lower than other groups (p<.05) except CSC/Ba (p>.05).

Conclusion: Radiopacity of Bio-MA, CSC/Bi, and CSC/Ta were greater than 3 mmAl and were clinically acceptable as recommended by ISO 6876:2012.

Keywords: Bio-MA, biodentine, calcium silicate-based cement, radiopacifiers, radiopacity

How to cite: Vibulcharoenkitja P, Banomyong D, Sutimuntanakul S. Radiopacity of biodentine, bio-ma, and calcium silicate-based cement added with different radiopacifiers. M Dent J 2019; 39: 199-205.

Introduction

Portland cement (PC) or calcium silicate cement (CSC)-based endodontic root repair/filling materials have been widely used for root perforation repair, retrograde or orthograde filling [1]. Root repair/filling material should be radiopaque for the evaluation of filling quality [2,3]. Radiopacity unit is commonly measured in millimeter of aluminium thickness [4]. The International Organization for Standardization (ISO) recommended that the radiopacity of root canal sealing material should be at least 3 mm of aluminium thickness (mmAl) (ISO 6876:2012) [5].

Radiopacity of CSC (1.62±0.29 mmAl) [6] and PC (0.86-2.02 mmAl) [7,9] were insufficient to use as endodontic material. The addition of a high atomic-number (Z) compound, namely a radiopacifier, increases material radiopacity. Various radiopacifiers are used in dental materials such as zirconium oxide, barium sulfate, tantalum oxide or bismuth oxide. An addition of 20% of zirconium oxide in CSC increased radiopacity to 5.09-5.2 mmAl [10,11]. Biodentine *(Septodont,*

Correspondence author: Supachai Sutimuntanakul
Department of Operative Dentistry and Endodontics, Faculty of Dentistry, Mahidol University,
6 Yothi Road, Ratchathewi, Bangkok 10400 Thailand
Tel: +66 (0)2 200 7825 Ext. 13 E-mail: supachai.sut@mahidol.ac.th
Received : 24 July 2019 Accepted : 7 October 2019

Saint Maur des Fosses, France) is a commercial CSC with 5% zirconium oxide with radiopacity at 2.8-3.3 mmAl [12-14]. Barium sulfate is a radiopacifier in gutta percha and endodontic sealers. PC with 20% barium sulfate radiopacity was 1.48 mmAl [15]. Adding 20%tantalum oxide in PC, the radiopacity increases to 2.78 mmAl [15]. Bismuth oxide was the radiopaque material in the first generation of CSC, ProRoot MTA *(Dentsply, Tulsa Dental Products, Tulsa, OK, USA)* with radiopacity at 6.4±0.06 mmAl [16]. Camilleri *et al.* [6] reported that radiopacity of CSC with 20% bismuth oxide was 6.83±0.48 mmAl. Bio-MA *(M-Dent/SCG, Bangkok, Thailand)*, and a calcium silicate cement composed of bismuth oxide, has been used for similar purposes as ProRoot MTA [1]. Recently, a study on the high-purity of calcium silicate powder in substitution of PC has been developed. The radiopacity of pure CSC is too low to use clinically by itself, then a proper radiopacifier is required. The aim of this *in vitro* study is to evaluate the radiopacity of Biodentine, Bio-MA, and the purified CSC which contained with one of the following radiopacifiers—zirconium oxide, barium sulfate, tantalum oxide or bismuth oxide.

Materials and methods

Preparation of materials and samples

The main composition and radiopacifiers of Biodentine, Bio-MA and CSCs in this study were shown in Table 1. CSC without radiopacifier was used as a control. The encapsulated powder of Biodentine was added with five droplets of liquid, and was then triturated in a trituration machine *(Septodont, Hangzhou Sifang Medical Apparatus Co. Ltd., Zhejiang, China)* at 4,000 rpm for 30 sec. Bio-MA powder was mixed homogeneously with a calcium chloride-containing liquid, in a powder-liquid ratio of 1 g : 0.35 ml. The CSC powder was prepared by mixing purified calcium silicate powder *(Alfa Aesar, Thermo Fisher Scientific, Ward Hill, MA, USA)* with 20% by weight of a radiopacifier- zirconium oxide *(Riedel-de-Haën™, Loughborough, United Kingdom)*, barium sulfate *(Alfa Aesar)*, tantalum oxide *(Alfa Aesar)* or bismuth oxide *(Scharlau, Scharlab, Barcelona, Spain)*. The radiopacifier was mixed in calcium silicate powder by the geometric dilution method. In brief, the calcium silicate powder and radiopacifier, 3 g of each, were mixed in a close chamber of a blending machine for 5 min. Then, 6 g of calcium silicate powder was added and mixed for another 5 min. Finally, an additional 3 g of calcium silicate powder was mixed for 5 min to obtain a total 15 g of the material. The mixed experimental CSCs were kept in a close container with desiccant until the experiment started. CSCs and the control were mixed with distilled water in a powder-liquid ratio of 1 g : 0.36 ml.

The mixed material was swept and carried by a cement spatula into a stainless steel mold, 6-mm internal diameter and 1-mm thick, on a glass slab and condensed with an amalgam plugger *(Thomson, Miltex Inc., York, PA, USA)*. Material surface in the mold was covered and pressed with a glass slit to create a flat, smooth-surface disc. Five discs with 1±0.01 mm thickness from each group *(measured by Digimatic Caliper, Seiko Instruments Inc., Chiba, Japan)* were stored in a container with 95% relative humidity at room temperature for 7 days to allow complete set of material.

Radiopacity investigation

Radiopacity of the materials was evaluated according to ISO 6876:2012 [5]. Samples in the mold were placed beside an aluminium step wedge, which had 0.5-mm thickness difference between the steps (Figure 1). Both samples and step wedge were laid on a digital x-ray phosphor plate size 2 *(DIGORA® Optime, KaVo Kerr, Tuusula, Finland)* and was x-ray irradiated *(X-MIND DC, Acteon, Olgiate Olona, Italy)* at 60 kV, 8 mA, 0.016 msec with a fixed 30 cm distance between the x-ray tube and the target plate. Irradiated phosphor plate was scanned by an imaging-plate scanner *(SOREDEX DIGORA® Optime, KaVo Kerr)*, and the radiographic image was saved as TIFF file.

Table 1 Powder, liquid, and radiopacifiers of Biodentine, Bio-MA, and experimental CSCs.

Groups	Compositions		
	Powder	Liquid	Radiopacifier
1. Biodentine	Tricalcium silicate, calcium carbonate, water reducing agent	Water-based liquid with $CaCl_2$	Zirconium oxide
2. Bio-MA	Tricalcium silicate, dicalcium silicate, tricalcium aluminate	Distilled water with $CaCl_2$	Bismuth oxide
3. CSC/Zr	Calcium silicate powder	Distilled water	Zirconium oxide
4. CSC/Ba	Calcium silicate powder	Distilled water	Barium sulfate
5. CSC/Ta	Calcium silicate powder	Distilled water	Tantalum oxide
6. CSC/Bi	Calcium silicate powder	Distilled water	Bismuth oxide
7. CSC (Control)	Calcium silicate powder	Distilled water	-

CSC: calcium silicate cement, Zr: zirconium oxide, Ba: barium sulfate, Ta: tantalum oxide, Bi: bismuth oxide, CaCl2: calcium chloride

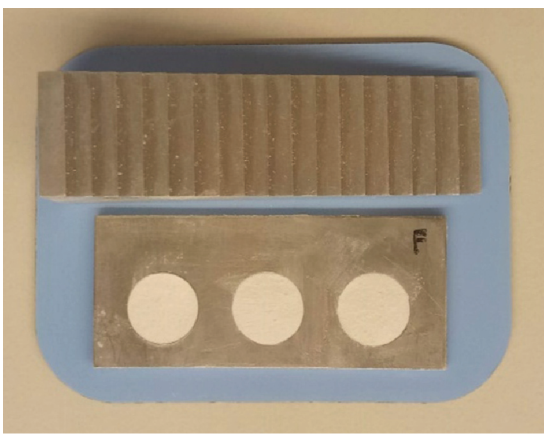

Figure 1 An aluminium step wedge with thickness from 0.5 mm to 9 mm was a radiopacity reference of evaluation materials.

The grey value of investigated materials and aluminium step wedge in the radiographic image were measured by ImageJ program *(National Institutes of Health, Bethesda, MD, USA)*. The 'Oval' tool was selected for the circular area at the center of the disc and the 'Rectangular' tool was for the rectangular area at the center of the aluminium step. The average grey value of the selected area was automatically showed when using the 'Measure' tool. The average grey values of the disc and aluminium step wedge were calculated to transform the grey value of materials into mm of aluminium thickness (mmAl) by the following formula:

$$\text{Radiopacity (mmAl)} = \frac{(m\text{-}b) * t}{(a\text{-}b)} + C$$

m = grey value of the material

b = grey value of the aluminium step wedge below m

a = grey value of the aluminium step wedge above m

t = different thickness between steps of aluminium step wedge, which was 0.5 mm

C = mmAl of the step wedge immediately below m

Means and standard deviations of radiopacity from each material were calculated and were descriptively compared with the clinically acceptable level at 3 mmAl [5].

Results

Means and standard deviations of radiopacity of investigated materials were shown in Table 2 and Figure 2. The Shapiro-Wilk test indicated that the data were normally distributed and the Levene's test revealed of non-homogeneity of variance. The Welch Analysis of Variance and the Games-Howell test were used to compare radiopacity between groups, at a significant level of .05. Bio-MA had 6.59±0.39 mmAl radiopacity that was significantly higher than the other materials ($p<.01$), while calcium silicate material without a radiopacifier was 0.99±0.06 mmAl, the lowest radiopacity. The radiopacity value in mmAl of experimental CSC with radiopacifiers increased in the ascending order (low to high) as follows—CSC/Ba 2.52±0.14, CSC/Zr 2.90±0.05, CSC/Ta 3.39±0.10, and CSC/Bi 5.42±0.18. Radiopacity of these CSC/radiopacifiers groups were significantly different from each other ($p<.01$). Biodentine radiopacity was 2.34±0.20 mmAl and was significantly lower than that of CSC/radiopacifiers ($p<.05$), but was not significantly different from CSC/Ba ($p>.05$).

Table 2 Means and standard deviations of radiopacity (mmAl) of investigated materials.

Groups	Mean ± SD (mmAl)
Gr1 Biodentine	2.34 ± 0.20^a
Gr2 Bio-MA	6.59 ± 0.39^b
Gr3 CSC/Zr	2.90 ± 0.05^c
Gr4 CSC/Ba	2.52 ± 0.14^a
Gr5 CSC/Ta	3.39 ± 0.10^d
Gr6 CSC/Bi	5.42 ± 0.18^e
Gr7 CSC	0.99 ± 0.06^f

Different superscript letters indicate statistically significant difference among the groups ($p<.01$).

Discussion

The radiopacity investigation was based on the ISO standard 6876:2012 [5], with minimal modifications to improve the reliability of testing. Firstly, a 0.5 mm-increment aluminium step wedge was used instead of a standard 1.0 mm-increment. The smaller increment between the steps provided more details of the radiopacity level, and provided more accuracy of radiopacity comparison. Secondly, a digital phosphor imaging plate reduced the variations of conventional film processing [17].

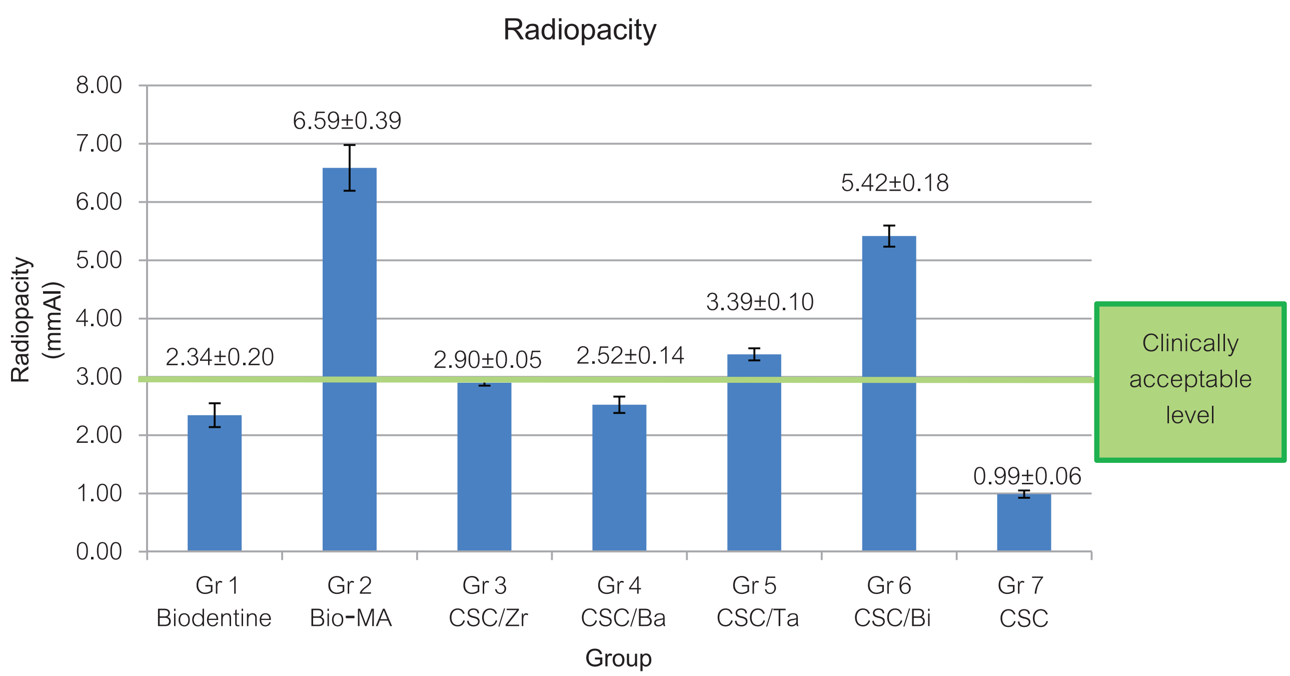

Figure 2 Means and standard deviations (mmAl) of radiopacity of investigated materials and clinically acceptable radiopacity level.

Moreover, the digital radiographic data was easily transferred and analyzed in the software. Lastly, the ImageJ program automatically averaged the grey values of the selected area. The comparison of data reading between material and reference step wedge were more accurate and reliable than the subjective decision from the visual reading.

Atomic number (Z) of material plays a significant role in radiopacity [6]. Grey scale on radiographic image is varied in proportion to the x-ray photons exposed to the target receptor. The unexposed area appears as whiteness or radiopaque area [18]. X-ray photons disappear when hitting and transferring the energy to the inner shell electrons of the element. An element with a higher atomic number contains more inner shell electrons that block more photons, resulting in higher radiopacity. In this study, the radiopacifiers including zirconium oxide (Z=40), barium sulfate (Z=56), tantalum oxide (Z=73), and bismuth oxide (Z=83) were added in the experimental CSC. The results showed that the radiopacity generally increased when the atomic number of the radiopacifier was higher. However, the radiopacity of CSC/Zr was higher than CSC/Ba, although the atomic number of Zr was lower than Ba. In fact, the radiopacity does not only rely on the atomic number, but also depends on the arrangement or density of atom [19]. The atomic number of barium sulfate (Z=56) is higher than zirconium oxide (Z=40). One unit-volume of barium sulfate is about 346.8 $Å^3$, while that of zirconium oxide is about 142.4 $Å^3$. In these volumes, barium sulfate as well as zirconium oxide has 4 element atoms [20,21]. Barium sulfate occupied 2.4 times volumetric space larger than zirconium oxide. In an equivalent volumetric space, the density of zirconium atoms is higher than barium atoms, which the x-ray photons have a chance to hit the zirconium atoms approximately as twice as the barium atoms. With this reason, zirconium oxide is able to block x-ray photons better than barium sulfate and provides the higher radiopacity.

ISO proposed that the radiopacity of root repair/filling material should not be less than 3 mmAl for radiographic interpretation [3,5]. Pure CSC ($CaSiO_3$) contains low-Z value elements, Ca (Z=20), Si (Z=14), and O (Z=8), and the radiopacity was lowest among the tested materials. Adding a high Z-value radiopacifier into CSC increased the radiopacity significantly. However, only bismuth oxide and tantalum oxide provided the radiopacity above 3 mmAl, which is a clinically acceptable level.

Bio-MA with bismuth oxide had the highest radiopacity and was significantly higher than CSC/Bi, which contained the same amount of the bismuth oxide. This might be the difference in the main ingredients of these two cements. Bio-MA consisted of PC—calcium silicate, calcium aluminate, and calcium aluminoferrite, while calcium silicate was pure CSC [22]. The radiopacity of PC was 1.54-1.73 mmAl [9,23] and was higher than the 0.99 mmAl radiopacity of pure CSC.

Radiopacity of Biodentine was significantly lower than CSCs contained with a radiopacifier except CSC/Ba. The main ingredient of Biodentine is tricalcium silicate with 5%/w of zirconium oxide as a radiopacifier [24]. Low content of zirconium oxide in Biodentine resulted in less radiopacity than that of CSC with 20% of zirconium oxide. Nevertheless, the radiopacity of Biodentine (2.34±0.20 mmAl) was lower than the 3 mmAl standard value but was still clinical accepted.

Radiopacity of CSC was markedly improved by the addition of either bismuth oxide or tantalum oxide, and was higher than the acceptable level. With the addition of bismuth oxide, tooth discoloration might be of concern [25,26], while tantalum oxide is a rare earth element with a relative high cost. The radiopacity of CSC with barium sulfate or zirconium oxide was slightly below the recommended standard. To improve the radiopacity if the amount of radiopacifier increases, the active ingredients will be reduced which might compromise the material properties such as push-out strength [16] and compressive strength [27]. The combination of radiopacifiers in a proper ratio might be a solution for acceptable radiopacity and will not affect the material properties.

In the biological point of view, radiopacifiers with good biocompatibility were generally selected. Tantalum oxide and zirconium oxide were inert and not leached out from the set material [28,29]. Bismuth oxide could induce discoloration, but cellular biocompatibility was confirmed [7,30,31]. Barium sulfate was commonly used in the medical field as a contrast media for gastrointestinal tract diagnosis [32]. However, these new CSC materials with the radiopacifiers must be tested to confirm their important physical properties and biocompatibility.

Conclusion

Bio-MA (6.59±0.39 mmAl) had the highest radiopacity among the investigated materials. Radiopacity of Biodentine was 2.43±0.20 mmAl. The addition of a radiopacifier—zirconium oxide, barium sulfate, tantalum oxide or bismuth oxide into the CSC increased the radiopacity in the ascending order—CSC/Ba (2.52±0.14 mmAl), CSC/Zr (2.90±0.05 mmAl), CSC/Ta (3.39±0.10 mmAl), and CSC/Bi (5.42±0.18 mmAl) The radiopacity of Bio-MA, CSC/Bi, and CSC/Ta were greater than 3 mmAl and were clinically acceptable as recommended by ISO 6876:2012.

Acknowledgements

This research is supported by Postgraduated Research Scholarship Mahidol University, Thailand.

The authors would like to thank Assist. Prof. Dr. Chulaluk Komoltri (Office of Research and Development, Faculty of Medicine, Siriraj Hospital, Mahidol University, Thailand) and Dr. Sittichoke Osiri (Department of Operative Dentistry and Endodontics, Faculty of Dentistry, Mahidol University, Thailand) for their assistance in the statistical analysis in this study. Finally, I also would like to thank you Mr.Alan Navarro (FERCAP Research Fellow, WHO-TDR Clinical Coordination and Training Center) for the language approval.

References

1. Parirokh M, Torabinejad M. Mineral trioxide aggregate: a comprehensive literature review--Part III: Clinical applications, drawbacks, and mechanism of action. *J Endod* 2010; 36: 400-13.
2. Sjogren U, Hagglund B, Sundqvist G, Wing K. Factors affecting the long-term results of endodontic treatment. *J Endod* 1990; 16: 498-504.
3. Beyer-Olsen EM, Orstavik D. Radiopacity of root canal sealers. *Oral Surg Oral Med Oral Pathol* 1981; 51: 320-8.
4. Watts DC, McCabe JF. Aluminium radiopacity standards for dentistry: an international survey. *J Dent* 1999; 27: 73-8.
5. International Organization for Standardization (ISO). Dentistry - Root Canal Sealing Materials. London, UK: British Standards Institution 6876; 2012.
6. Camilleri J, Gandolfi MG. Evaluation of the radiopacity of calcium silicate cements containing different radiopacifiers. *Int Endod J* 2010; 43: 21-30.
7. Kim EC, Lee BC, Chang HS, Lee W, Hong CU, Min KS. Evaluation of the radiopacity and cytotoxicity of Portland cements containing bismuth oxide. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2008; 105: e54-7.
8. Saliba E, Abbassi-Ghadi S, Vowles R, Camilleri J, Hooper S, Camilleri J. Evaluation of the strength and radiopacity of Portland cement with varying additions of bismuth oxide. *Int Endod J* 2009; 42: 322-8.
9. Chanin S, Sutimuntanakul S, Jeeruphan T. Comparison of radiopacity ot Thai white Portland cement with different radiopaque materials (High Grad Dip Project Report). *Mahidol University*. 2011.
10. Agarwal R, Nikhil V. The comparison of physicochemical properties of new and established root canal sealers. *Endodontology* 2016; 28: 97-101.
11. Cutajar A, Mallia B, Abela S, Camilleri J. Replacement of radiopacifier in mineral trioxide aggregate; characterization and determination of physical

properties. *Dent Mater* 2011; 27: 879-91.
12. Tanalp J, Karapinar-Kazandağ M, Dölekoğlu S, Kayahan M. Comparison of the Radiopacities of Different Root-End Filling and Repair Materials. *Sci World J* 2013; 2013: 1-4.
13. Lucas CP, Viapiana R, Bosso-Martelo R, Guerreiro-Tanomaru JM, Camilleri J, Tanomaru-Filho M. Physicochemical Properties and Dentin Bond Strength of a Tricalcium Silicate-Based Retrograde Material. *Braz Dent J* 2017; 28: 51-6.
14. Grech L, Mallia B, Camilleri J. Investigation of the physical properties of tricalcium silicate cement-based root-end filling materials. *Dent Mater* 2013; 29: e20-8.
15. S. Coomaraswamy K, J. Lumley P, M. Shelton R, P. Hofmann M. Evaluation of Different Radiopacifiers for an MTA-Like Dental Cement. *Key Eng Mater* 2008; 361-363: 885-8.
16. Camilleri J. Evaluation of the physical properties of an endodontic Portland cement incorporating alternative radiopacifiers used as root-end filling material. *Int Endod J* 2010; 43: 231-40.
17. Anas A, Asaad J, Tarboush K. A Comparison of intra-oral digital imaging modalities: Charged Couple Device versus Storage Phosphor Plate. *Int J Health Sci (Qassim)*. 2010;4:156-67.
18. Torres JP, Sariol HC, Yperman J, Sauvanell ÁB, Carleer R, Campa JN. A novel X-ray radiography approach for the characterization of granular activated carbons used in the rum production. *J Anal Sci Technol* 2018; 9: 1-15.
19. Chen C, Hsieh SC, Teng NC, Kao CK, Lee SY, Lin CK, et al. Radiopacity and cytotoxicity of Portland cement containing zirconia doped bismuth oxide radiopacifiers. *J Endod* 2014; 40: 251-4.
20. Colville AA, Staudhammer K. A Refinement of the Structure of Barite. *Am Mineral* 1967; 52: 1877-80.
21. Smith DK, Newkirk W. The crystal structure of baddeleyite (monoclinic ZrO2) and its relation to the polymorphism of ZrO2. *Acta Cryst* 1965; 18: 983-91.
22. Settawacharawanich S, Sutimuntanakul S, Phuvaravan S, Plang-ngern S. The chemical composition and physicochemical properties of a Thai white Portland cement (M.Sc. Project Report). *Mahidol University*. 2006.
23. Jeeruphan T, Sutimuntanakul S, Jainuch J. Radiopacity of Thai White Portland Cement Added with Bismuth Oxide in Different Ratio (High Grad Dip Project Report). *Mahidol University*. 2008.
24. Camilleri J, Sorrentino F, Damidot D. Investigation of the hydration and bioactivity of radiopacified tricalcium silicate cement, Biodentine and MTA Angelus. *Dent Mater* 2013; 29: 580-93.
25. Camilleri J. Staining Potential of Neo MTA Plus, MTA Plus, and Biodentine Used for Pulpotomy Procedures. *J Endod* 2015; 41: 1139-45.
26. Kang SH, Shin YS, Lee HS, Kim SO, Shin Y, Jung IY, et al. Color changes of teeth after treatment with various mineral trioxide aggregate-based materials: an ex vivo study. *J Endod* 2015; 41: 737-41.
27. Saghiri MA, Gutmann JL, Orangi J, Asatourian A, Sheibani N. Radiopacifier particle size impacts the physical properties of tricalcium silicate-based cements. *J Endod* 2015; 41: 225-30.
28. Camilleri J, Cutajar A, Mallia B. Hydration characteristics of zirconium oxide replaced Portland cement for use as a root-end filling material. *Dent Mater* 2011; 27: 845-54.
29. Camilleri J, Sorrentino F, Damidot DJCOI. Characterization of un-hydrated and hydrated BioAggregate™ and MTA Angelus™. *Clin Oral Investig* 2015; 19: 689-98.
30. Chaimanakarn C, Sutimuntanakul S, J J. Subcutaneous tissue response to calcium silicate-based cement (M.Sc. Project Report). *Mahidol University* 2014.
31. Torabinejad M, Parirokh M. Mineral trioxide aggregate: a comprehensive literature review--part II: leakage and biocompatibility investigations. *J Endod* 2010; 36: 190-202.
32. McKee MW, Jurgens RW Jr. Barium sulfate products for roentgenographic examination of the gastrointestinal tract. *Am J Hosp Pharm* 1986; 43: 145-8.