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RADIOPACITY OF TRICALCIUM SILICATE-WHITE PORTLAND CEMENT WITH BISMUTH OXIDE AND ZIRCONIUM OXIDE ADDITIONS FOR USE AS POTENTIAL MATERIALS FOR AN ENDODONTIC SEALER

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Radiopacity is one of the properties needed for intraoral dental materials. The root canal sealer should have sufficient radiopacity to provide a clear distinction between the material and the surrounding anatomical structure, which can only be performed by radiographic examination. Some radiopacifier materials that can be used are Bismuth Oxide (Bi_2O_3) and Zirconium Oxide (ZrO_2). Portland cement has the same characteristics as MTA; however, the lack of presence of bismuth oxide in Portland cement causes low radiopacity. This study investigates the radiopacity value of Tricalcium Silicate White Portland Cement (TS-WPC) by adding Bi_2O_3 and ZrO_2 with concentrations of 10, 15, 20, and 25 % respectively. A mixture of TS-WPC with Bi_2O_3 and TS-WPC with ZrO_2 was made using a simple solution method. After that, the radiopacity of all the samples and the control was tested. The results showed statistically significant differences in the radiopacity value between the groups ($p < 0.05$), and the post hoc test revealed that the highest radiopacity value was found in the TS-WPC Bi_2O_3 group of 25 %. In conclusion, adding a Bi_2O_3 and ZrO_2 radiopacifier at a concentration of 10, 15, 20, and 25 % can increase the radiopacity value of TS-WPC. TS-WPC with the addition of Bi_2O_3 has better radiopacity compared to ZrO_2.

INTRODUCTION

The selection of the appropriate sealer is critical to achieving a successful endodontic treatment. One of the requirements for an ideal endodontic sealer is to have sufficient radiopacity to distinguish it from the surrounding tissues, such as enamel, dentin, and bone. A Mineral Trioxide Aggregate (MTA) ceramics-based sealer was introduced as a root canal filling sealer which exhibits good physical, mechanical and biological properties.

Some other advantages of MTA-based sealers compared to other sealers include the ability to be used in teeth obturation with an open apex and repair of perforated lesions or damage due to resorption. The advantages result from the ability to harden in humid conditions and induce cementogenesis and dentinogenesis. MTA also has a strong bond with the dentin wall. Many studies have shown promising results from using MTA; however, the cost is less economical, making it limited to use in developing countries [1-7].

MTA and Portland Cement have similarities in composition except for the absence of the bismuth oxide (Bi_2O_3) content in Portland cement. This causes the radiopacity of Portland cement to be below the minimum radiopacity standardised by ISO 6876: 2012, thus Portland cement is not currently intended for clinical use [8, 9]. To overcome this, several studies have tried adding radiopacifier materials to Portland cement so its characteristics are like MTA. Radiopacifiers that are recommended for use on Portland cement are Bi_2O_3 and Zirconium Oxide (ZrO_2).

EXPERIMENTAL

Material and Methods

Preparation of materials and samples

The materials used in this study were Tricalcium silicate-white Portland cement (TS-WPC) (PT. Indocement, Cirebon, Indonesia), Bi_2O_3 (Shanghai Xinglu Chemical Technology Co. Ltd., Shanghai, China), ZrO_2 (Zirai Guangzhou Hongwu Material Technology Co., Guangzhou, China), distilled water, 99.9 % isopropanol, and commercial ProRoot MTA (Dentsply Maillefer, Ballaigues, Switzerland) was used as the control. Bi_2O_3 radiopacifier material concentrations of 10, 15, 20, and 25 % were mixed into the TS-WPC powders. A similar method is employed to make a mixture of TS-WPC and ZrO_2. Each mixture was dissolved in 99.9 % isopropanol and stirred for 30 min using a magnetic stirrer at a rotation speed of 200 rpm until it became homogeneous, then, it was transferred into tubes for centrifugation at 5000 rpm for 10 min. The supernatant was discharged, the pellet was dried in a vacuum for 60 min to evaporate the isopropanol, and dry powders were obtained. In particular, the synthesis of TS-WPC Bi_2O_3 25 % and TS-WPC ZrO_2 25 %, each weighing 2 g was mixed into the distilled water and stored in an incubator at 37 °C for 24 hours, then characterised using X-ray diffraction (XRD-Rigaku, Tokyo, Japan) to obtain detailed information about the crystallographic structures formed after hydration.

The TS-WPC Bi_2O_3 and TS-WPC ZrO_2 powder samples at 10, 15, 20, and 25 % concentrations were prepared by mixing with distilled water at a ratio of 1:0.37 until they became homogenous, then they were inserted into Teflon moulds (10 mm in diameter and 1 mm in height). A total of 45 samples were divided into nine groups with five samples in each group. Each sample was stored in an incubator at 37 °C for 24 hours, then a radiopacity examination was carried out. The ProRoot MTA sample as the control was prepared as recommended by the manufacturer.

Figure 1. Position of samples, aluminium step wedge, PSP.

Radiopacity examination

The method used in this study is that according to International Organization for Standardization (ISO) 6876:2012 to determine the radiopacity by comparing the materials and an 1100 series aluminium step wedge with different thicknesses (1 to 10 millimetres). The samples removed from each mould were positioned beside an aluminium step wedge on a size 2 photostimulable phosphor plate (PSP) (Figure 1). The X-ray tube of an Instrumentarium Focus 70 kV radiography machine, with a total infiltration of 2.5 mm Al and 7 mA (Instrumentarium Dental, PaloDEx, Oy Group, USA), was directed to a vertical position, perpendicular to the sample and the PSP with a fixed 30 cm distance between the X-ray tube and the target plate (ANSI / ADA 2000). The irradiated PSP was scanned by an imaging-plate scanner (ExpressTM Origo Scanner, Instrumentarium Dental, PaloDEx, Oy Group, USA), and digital radiographic images of each sample and the aluminium step wedge were obtained. This method was carried out on all the samples.

The digital radiographic images of each sample and each aluminium step wedge were evaluated using ImageJ software to determine the grey value. The radiographic images of each sample were entered into the ImageJ software (Figure 2).

The average grey values of each sample and each step aluminium wedge thickness were calculated to transform the grey value of materials into mm of aluminium thickness (mm Al) by the following the Equation [10]:

$$Radiopacity \text{ (mm Al)} = \frac{(m-b)\times t}{(a-b)} + c$$

where m is 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 the steps of the aluminium step wedge (1 mm), c mm Al of the step wedge immediately below m.

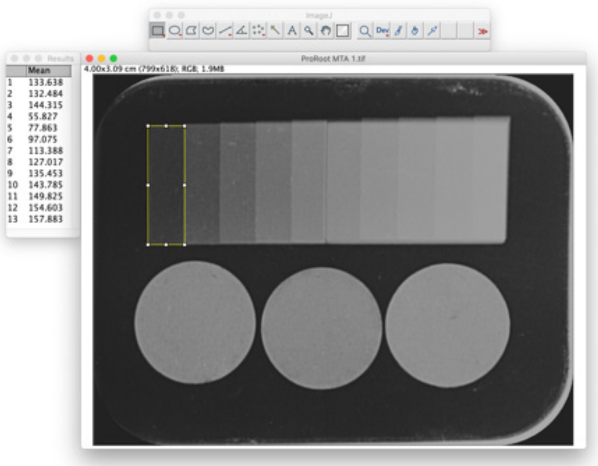

Figure 2. Determined grey value with the ImageJ software.

RESULTS AND DISCUSSION

Figure 3 shows the diffractogram profile from the XRD patterns of the 25 % ZrO_2 and Bi_2O_3 samples, and also the ProRoot MTA as the control. Two major peaks at a 2-theta angle of 18° and 34° identified as Portlandite were revealed in all the samples. The two peaks are referred to as ZrO_2 in the TS-WPC 25 % ZrO_2 sample. Meanwhile, three peaks were identified at a 2-theta angle of 25.5°, 27° and 33° as Bi_2O_3 from the TS-WPC 25 % Bi_2O_3 sample and the ProRoot MTA sample with high intensity compared to ZrO_2. Based on the diffractogram analysis of the TS-WPC 25 % Bi_2O sample, it can be concluded that the compounds have similarities with the ProRoot MTA.

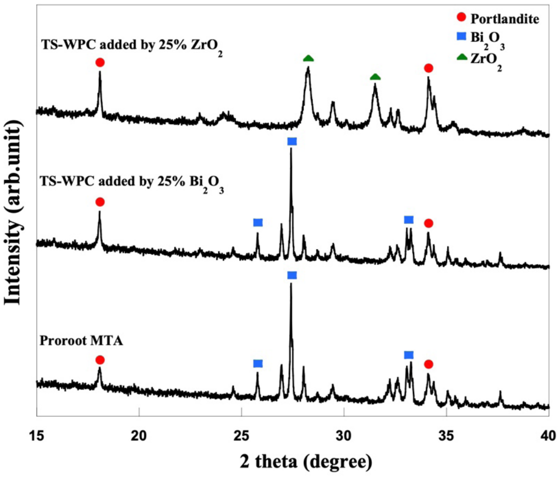

Figure 3. The XRD patterns of TS-WPC with the 25 % ZrO_2 addition, TS-WPC with the 25 % Bi_2O_3 addition and ProRoot MTA as the control.

The calculation of the mean radiopacity value of all the sample groups in Table 1 showed that group 4 (TS-WPC Bi_2O_3 25 %) has the highest average radiopacity value, and group 5 (TS-WPC ZrO_2 10 %) has the lowest average radiopacity value compared to the other groups. The average radiopacity value in all the groups showed an increase in the radiopacity value and followed the criteria set out in ISO 6876: 2012, the minimum recommended 3 mm Al, except for group 1 (TS-WPC Bi_2O_3 10 %) and group 5 (TS-WPC ZrO2 10 %) where the radiopacity values presented below 3 mm Al.

Table 1. Means (mm Al) and standard deviations of the radiopacity values in each group.

Groups of samples		Mean (mm Al)	Sample size	Standard deviation
Bismuth Oxide	1 (10 %)	2.94	5	0.30
	2 (15 %)	4.04	5	0.34
	3 (20 %)	5.13	5	0.25
	4 (25 %)	6.42	5	0.31
Zirconium Oxide	5 (10 %)	2.36	5	0.27
	6 (15 %)	3.10	5	0.17
	7 (20 %)	3.61	5	0.14
	8 (25 %)	4.41	5	0.51
ProRoot MTA	9 (Bi_2O_3 20 %)	6.08	5	0.54

The collected study data were then analysed using an analysis of variance (ANOVA) to determine the average radiopacity value in each group. In the results of the ANOVA test, the mean radiopacity value of each group showed a statistical significance in the mean radiopacity between the groups ($p < 0.05$), which means that each group gave a different radiopacity value.

The analysis was continued to determine the best group in increasing the radiopacity and the difference in the mean radiopacity values between the groups using independent t-tests. The independent t-test is a pairwise test, ordered from the lowest to the highest average radiopacity value. The test results indicated a statistically significant difference ($p < 0.05$) in the mean radiopacity value between the groups. There was no statistically significant difference ($p > 0.05$) in group 1 (TS-WPC Bi_2O_3 10 %) compared to group 6 (TS-WPC ZrO_2 15 %), group 2 (TS-WPC Bi_2O_3 15 %) compared to group 8 (TS-WPC ZrO_2 25 %), and group 9 (ProRoot MTA) compared to group 4 (TS-WPC Bi_2O_3 25 %). The results obtained using the independent t-test statistical analysis concluded that there are differences in the radiopacity value of the TS-WPC samples with the Bi_2O_3 addition and the TS-WPC sample with the ZrO_2 addition with the different concentrations. Based on the post hoc test, the highest radiopacity value was in group 4 (TS-WPC Bi_2O_3 25 %) and occupied the minimum ISO requirement of 3 mm Al.

The radiopacity of the sealer material, according to ISO 6876:2012, should have a radiopacity equivalent to not less than 3 mm of aluminium. In this study, the addition of the Bi_2O_3 and ZrO_2 radiopacifier to TS-WPC with a concentration of 10, 15, 20, and 25 % resembles the commercial product in the market, ProRoot MTA which contains 75 % Portland cement, 5 % calcium sulfate, and 20 % Bi_2O_3 [11, 12]. The average radiopacity values obtained in this study on the 15 %, 20 %, 25 % Bi_2O_3 TS-WPC samples and the 15 %, 20 %, 25 % ZrO_2 TS-WPC samples resulted in radiopacity values greater than 3 mm Al. In comparison, with the addition of a radiopacifier at a concentration of 10 %, the radiopacity value was less than 3 mm Al. This also occurred in the research of Djordje et al. in 2012 Bi_2O_3 and ZrO_2 were added at 20 % and 30 % as the radiopacifier materials to Portland cement, resulting in a radiopacity of more than 3 mm Al [13, 14].

The concentration of the radiopacifier that increases the radiopacity of TS-WPC following ISO 6876:2012 uses a minimum concentration of 15 % Bi_2O_3 and 15 % ZrO_2, which has a radiopacity value of more than 3 mm Al. This is supported by a study from Bueno et al. in 2009, which stated that adding at least 15 % Bi_2O_3 to TS-WPC provides sufficient radiopacity to be used as an endodontic sealer [15].

There was a difference in the radiopacity value between the TS-WPC group with the Bi_2O_3 addition and the TS-WPC group with the ZrO_2 addition, except for the 10 % Bi_2O_3 TS-WPC and 15 % ZrO_2 TS-WPC, 15 % Bi_2O_3 TS-WPC and 25 % ZrO_2 TS-WPC, the ProRoot MTA and 25 % Bi_2O_3 TS-WPC, there is no difference in the radiopacity value, based on a statistical analysis of the independent t-tests. The radiopacity value of 25 % Bi_2O_3 TS-WPC was not different from the ProRoot MTA. However, the radiopacity value of 20 % Bi_2O_3 TS-WPC was different from the ProRoot MTA, similar to the study of Hwang et al. in 2008 which examined the radiopacity of 75 % Portland cement with a 25 % Bi_2O_3 addition, which was equivalent to the radiopacity of the ProRoot MTA [16]. The atomic number of the material plays an essential role in the radiopacity.

The greyscale on the radiographic image varies in proportion to the X-ray photons exposed to the target receptor. The unexposed area appears as a white or radiopaque area [17]. 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. A study by Vibulcharoenkitja et al. in 2019 showed that the radiopacity generally increased when the atomic number of the radiopacifier was higher [10]. The radiopacity not only relies on the atomic number, but also depends on the arrangement or density of the atom. The atomic density of Bismuth is higher than the atomic density of Zirconium; it is able to block X-ray photons better than Zirconium and provides higher radiopacity. The radiopacifier of Bi_2O_3 has an atomic number greater than the atomic number of ZrO_2; for this reason, the radiopacity of Bi_2O_3 is higher than that of ZrO_2. It was proven in this study that the average radiopacity value of Bi_2O_3 TS-WPC is higher than ZrO_2 TS-WPC, and it can also be concluded that the best radiopacifier increasing the radiopacity of TS-WPC is 25 % Bi_2O_3 [10, 18].

This study proves and supports the potential of TS-WPC with the addition of a Bi_2O_3 and ZrO_2 radiopacifier as endodontic sealers. The results of this study prove that the TS-WPC with the addition of Bi_2O_3 and ZrO_2 radiopacifiers with different concentrations occupy one of the requirements for the ideal obturation material, which is the radiopacity property, by following the ISO criteria.

CONCLUSIONS

There is a difference in the radiopacity values of TS-WPC with the Bi_2O_3 addition and TS-WPC with the ZrO_2 addition at different concentrations. The study proves that the Bi_2O_3 and ZrO_2 concentrations of 10, 15, 20, and 25 % increase the radiopacity of the TS-WPC samples and the best radiopacifier for increasing the radiopacity of TS-WPC is 25 % Bi_2O_3, which slightly better compared to the commercial product.

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