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RESEARCH ARTICLE

X-Ray Diffraction Analysis of Various Calcium Silicate-Based Materials

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Background: The purpose of this study was to evaluate the composition of the crystal phases of various calcium silicate-based materials (CSMs): ProRoot white MTA® (mineral trioxide aggregate) (WMTA), Ortho MTA® (OM), Endocem MTA® (EM), Retro MTA® (RM), Endocem Zr® (EN-Z), Biodentine™ (BD), EZ-seal™ (EZ), and OrthoMTA Ⅲ (OM3).
Methods: In a sample holder, 5 g of the powder sample was placed and the top surface of the material was packed flat using a sterilized glass slide. The prepared slides were mounted on an X-ray diffraction (XRD) instrument (D8 Advance; Bruker AXS GmbH, Germany). The X-ray beam 2θ angle range was set at 10~90° and scanned at 1.2° per minute. The Cu X-ray source set to operate at 40 kV and 40 mA in the continuous mode. The peaks in the diffraction pattern of each sample were analyzed using the software Diffrac (version 2.1). Then, the peaks were compared and matched with those of standard materials in the corresponding Powder Diffraction File (PDF-2, JCPDS International Center for Diffraction Data). A powder samples of the materials were analyzed using XRD and the peaks in diffraction pattern were compared to the Powder Diffraction File data.
Results: Eight CSMs showed a similar diffraction pattern because their main component was calcium silicate. Eight CSMs showed similar diffraction peaks because calcium silicate was their main component. Two components were observed to have been added as radiopacifiers: bismuth oxide was detected in WMTA, OM, and EM while zirconium oxide was detected in RM, EN-Z, BD, EZ, and OM3. Unusual patterns were detected for the new material, OM3, which had strong peaks at low angles.
Conclusion: It was caused by the presence of Brushite, which is believed to have resulted in crystal growth in a particular direction for a specific purpose.

Key Words: Calcium silicate, Mineral trioxide aggregate, Root canal filling materials, X-ray diffraction analysis

Introduction

1. Background

Mineral trioxide aggregate (MTA) was developed at Loma Linda University in the 1990s for use as a root filling material[1]. It has been approved by the U.S. Food and Drug Administration (FDA) and marketed as ProRoot MTA® (Tulsa Dental Products, Tulsa, OK, USA)[2]. MTA was originally developed as a root end filling material, but its range of applications has been extended due to its excellent biocompatibility, sealing ability, and induction of hard tissue formation. It is used in various root canal treatment methods such as pulp capping, pulpotomy, apexogenesis, open apex to apical barrier formation, root perforation repair and canal filling[3-5].

ProRoot MTA® was the first commercially available and most widely used MTA-based material worldwide and has shown excellent biocompatibility in many previous studies[6]. However, ProRoot MTA® is limited by long setting time, poor handling, and discoloration of teeth[7,8]. Manufacturers have developed a variety of MTA-like materials namely, calcium silicate-based materials (CSMs)

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by varying the composition of the material to compensate for the drawbacks of the original MTA. As shown in Table 1, various CSM products are marketed in Korea with the approval of Ministry of Food and Drug Safety (MFDS).

X-ray diffraction (XRD) is a useful analytical technique for cement research. Major crystalline products can be identified in cement samples using XRD[4]. The highlight of this technique is that, for single crystalline phases, the XRD pattern is characterized by a unique set of peaks with a specific diffracted intensity (y-axis) and diffracted angle (x-axis). The measured peak set can be compared with the Powder Diffraction Data File (PDF) of interest, provided by the International Center for Diffraction Data (ICDD) database, to identify a specific materia[15].

In the early stages of the use of MTAs, XRD was used to compare the components of ProRoot® MTA with those of Portland cement or newly released MTA products[3-5,9].

The main components of MTA are tricalcium silicate, tricalcium aluminates, calcium silicate and bismuth oxide[4]. In another study reported that the presence of bismuth oxide, calcium silicate, calcium carbonate, calcium phosphate, and calcium silicate in MTA samples[9]. However, research on the components of various CSM products that have been used in Korea recently is lacking.

2. Objectives

The purpose of this study was to find an exact match for experimental peaks with known data available on the ICDD database in order to verify the presence or absence of certain materials in the investigated sample and clarify the difference in the chemical compositions of various CSM products used in Korea using XRD analysis.

Table 1. Other Root Canal Filling Materials Approved by Ministry of Food and Drug Safety (Classification Number: C10040.01)

No.	Item permission number	Product name	Model name	Manufacture/importer
1	00-90		METAPEX and 1 other	Meta Biomed
2	00-136		METAPASTE and 2 others	Meta Biomed
3	00-721		VITAPEX	Shinhung
4	04-261	PROROOT MTA	A040500000100 and 4 others	Dentsply Sirona Korea
5	05-988		CALCIPEX II	Shinhung
6	09-968		ORTHO MTA	BioMTA
7	10-800		820 MTA-Angelus Gray 1 g and 3 others	Osstem Implant
8	10-853		MTA WHITW 1G and 3 others	Sambudental
9	11-750		ENDOCEM MTA	MARUCHI
10	12-1133	RetroMTA-Ortho MTA II	RetroMTA-OrthoMTA II	BioMTA
11	12-1514		ENDOSEAL	MARUCHI
12	12-1515		ENDOCEM Zr	MARUCHI
13	14-2165	RetroMTA-Ortho MTA II	BIODENTINE	Shinwon dental
14	14-1792	MTA Cem, MTA, MTA Seal	MTA cem and 2 others	NEXOBIO
15	14-1858		Evofill Cartridge 23 g and 1 other	DiaDent
15	15-883	EZ-seal	EZ-seal	EZEKIEL
17	16-4273	MTA Cem	MTA Cem 1.0 and 2 others	NEXOBIO
18	16-4707		Well-Root PT	VERICOM
19	17-4592		OrthoMTA III-1	BioMTA
20	18-4131	ApexCal	598607AN and 1 other	Ivoclar Vivadent
21	18-4240		MTA 10 and 3 others	GENOSS
22	18-4353	New MTA Cem	MTA Cem 0.14 and 1 other	IL-CHUNG Dental
23	18-4410		New MTA Cem S	IL-CHUNG Dental
24	18-4613	ApexCal	598607AN and 1 other	META VISION
25	18-4956		DIA-ROOT BIO MTA 0.5 g	DiaDent
26	19-4152		DIA-ROOT BIO MTA 0.5 g	DiaDent

MTA: mineral trioxide aggregate.

Materials and Methods

1. Ethics statement

This study did not receive IRB as a material subject.

2. Study design

This study examined eight CSMs approved by the MFDS and used clinically in Korea as alternative root canal fillings: ProRoot white MTA® (WMTA; Densply, Tulsa, OK, USA), Ortho MTA® (OM; BioMTA, Seoul, Korea), Endocem MTA® (EM; MARUCHI, Wonju, Korea), Retro MTA® (RM; BioMTA), Endocem Zr® (EN-Z; MARUCHI), Biodentine™ (BD; Septodont, St.Maur-des-Fosses, France), EZ-seal™ (EZ; EZEKIEL, Taean, Korea), OrthoMTA III (OM3; BioMTA). Of these, OM3 is a new material not yet been released although it has been approved by the MFDS. In a sample holder, 5 g of the powder sample was placed and the top surface of the material was packed flat using a sterilized glass slide. The prepared slides were mounted on an XRD instrument (D8 Advance; Bruker AXS GmbH, Karlsruhe, Germany). The X-ray beam 2θ angle range was set at 10～90° and scanned at 1.2° per minute. The Cu X-ray source set to operate at 40 kV and 40 mA in the continuous mode.

3. Statistical methods

Each material has a characteristic diffraction pattern. Because cement is made up of several compounds, each sample can produce several peaks. The peaks in the diffraction pattern of each sample were analyzed using the software Diffrac.Suite Eva software (version 2.1; Bruker, Billerica, MA, USA). Then, the peaks were compared and matched with those of standard materials in the corresponding Powder Diffraction File (PDF-2, JCPDS ICDD).

Results

The XRD pattern of each sample is shown in Fig. 1. Similar XRD patterns appeared for the eight materials because they are all based on calcium silicate. Alite (Ca_3SiO_5) was predominant in most of the seven materials. In EZ, belite (Ca_2SiO_4) was detected. Bismuth oxide (Bi_2O_3) was detected as a radiopacifier in WMTA, OM, and EM, which were released earlier. Zirconium oxide (ZrO_2) was detected in the remaining materials: RM, EN-Z, BD, EZ, and OM3.

In EM, aluminum bismuth oxide ($Al_2Bi_{24}O_{39}$) and mayenite ($Ca_{12}Al_{14}O_{33}$) were detected. In addition, calcium carbonate ($CaCO_3$) was detected in BD, and bassanite ($2CaSO_4 \cdot H_2O$) was identified in EZ.

The new material, OM3, which has not yet been commercialized, showed a strong peak at a low 2θ angle of 11.7°, unlike other materials. This was observed due to the presence of Brushite ($CaHPO_4 \cdot 2H_2O$).

Discussion

MTA consists of Type 1 Portland cement containing 20 w% bismuth oxide for radiopacity, and for the first time, ProRoot MTA® was commercially manufactured[5]. Type 1 Portland cement contains four major phases; alite, belite, tricalcium aluminate ($Ca_3Al_2O_6$), and calcium alminoferrite (Ca_2AlFeO_5)[10]. Among them, alite and belite are the main phases in MTA[2,5,11,12]. Alite is the most important phase showing seven polymorphic crystal phases depending on the temperature, composition, or presence of impurities[13]. It has the advantage of undergoing hydration relatively quickly, reducing the setting time[13,14]. Belite is generally a b-polymorph, and its hydration reaction is relatively slow[5,14]. As a result, alite contributes to the strength for up to 28 days, while belite provides strength in the later stages[10]. Instead of undergoing a slow reaction, belite releases silicon ions during the reaction, shows high apatite formation activity and good bioactivity[14]. Camilleri et al.[11] reported that gray MTA contained both alite and belite, whereas white MTA contained only alite without belite. In this study, alite was identified as the main component in seven materials including WMTA, and belite was the main component in EZ only. RM and EN-Z had similar components to those of EZ except calcium silicate. The setting time for RM and EN-Z were 2 minutes and 30 seconds and 4 minutes, respectively, while EZ required a relatively long setting time of approximately 60 minutes[15,16]. Because of concerns of wash out, it is thought that alite was preferred for shortening the setting time and

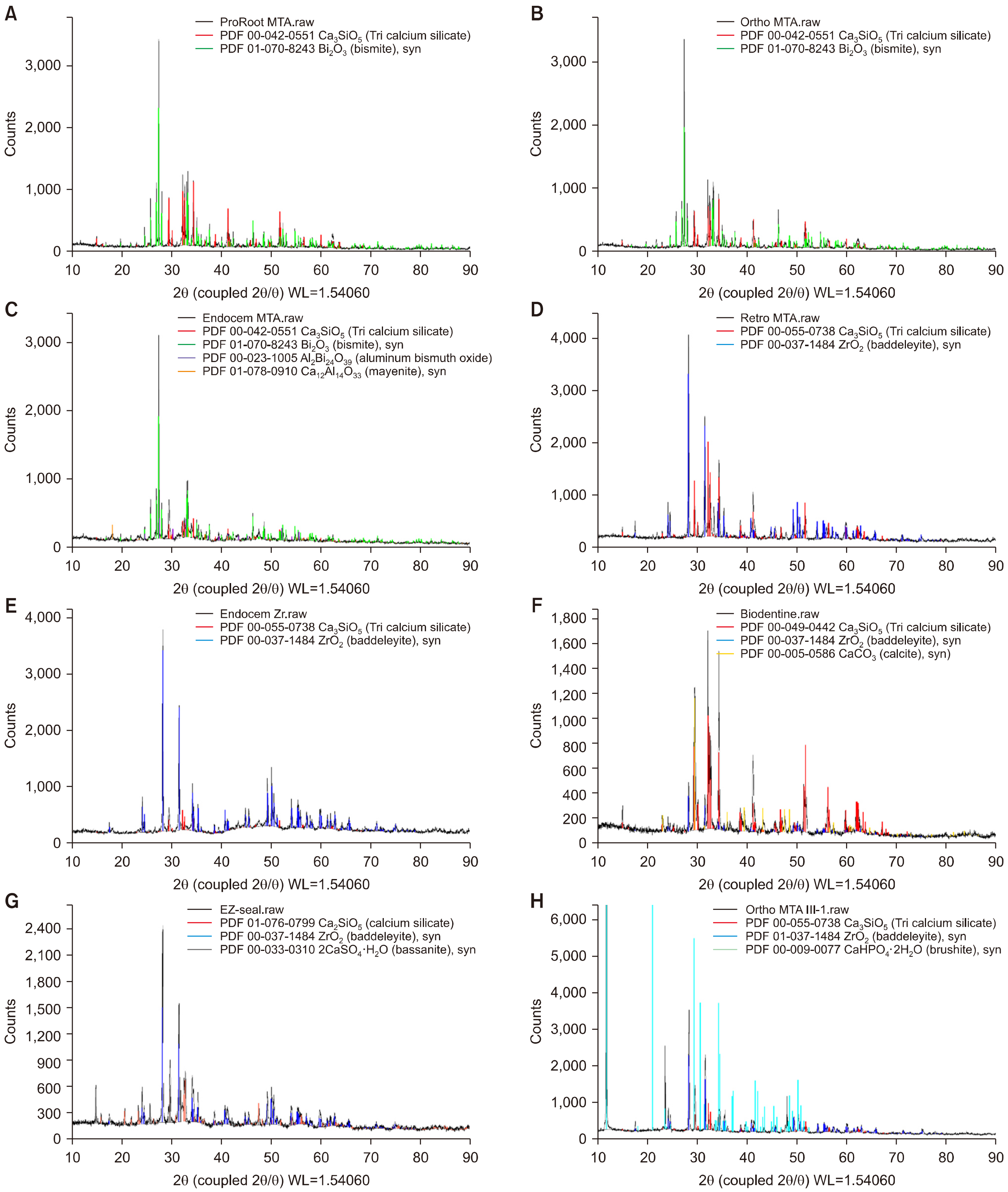

Fig. 1. X-ray diffraction patterns of calcium silicate-based materials showing peaks that represent the crystal phases present in each material. (A) ProRoot white MTA®, (B) Ortho MTA®, (C) Endocem MTA®, (D) Retro MTA®, (E) Endocem Zr®, (F) Biodentine™, (G) EZ-seal™, (H) OrthoMTA Ⅲ. MTA: mineral trioxide aggregate.

increase the initial strength.

Tricalcium aluminate had the fastest hydration rate among the main components of Portland cement and is thus, important for shortening setting time and improving initial compressive strength by promoting the hydration process therein[10,14]. However, it is rarely included in MTA due to concerns about the safety over the use of aluminum. Song et al.[9] reported that tricalcium aluminate was found in Portland cement but not in gray and white MTA. Similarly, in this study, tricalcium aluminate was not identified in any of the eight CSMs. Calcium aluminoferrite was not identified in the eight CSMs examined in this study, either. Since the ferrite phase contributes to dark colors in Portland cement, a white MTA with a reduced ferrite phase is preferred to improve aesthetic aspects[4]. The resulting strength is lower, but the slight decrease in compressive strength is not a significant issue because the MTA does not receive direct occlusal load when used as the root end-filling material[4]. Radiopacifiers are added to biomaterials to increase their radiopacity, making it easy to distinguish materials from anatomical structures in radiographs[17]. Bismuth oxide was used as the first radiopacifier in MTA[18]. In this study, bismuth oxide was identified in WMTA, OM and EM. However, zirconium oxide was detected, instead of bismuth oxide, in RM, EN-Z, BD, EZ, and OM3.

The use of zirconium oxide instead of bismuth oxide as a radiopaque material has many advantages. Among heavy metals, bismuth is unusual in that its toxicity is significantly lower than that of its neighboring metals in the periodic table, such as lead and thallium. However, it exhibits toxic properties and negatively affects the growth and proliferation of human dental pulp cells and reduces the biocompatibility of MTA[7,19]. Because bismuth oxide is dissolved in an acidic environment, when MTA is placed in an acidic environment such as inflammatory tissues, bismuth oxide is released and affects the precipitation of calcium hydroxide[7]. Bismuth oxide also has the disadvantage of delaying the setting reaction and causing tooth discoloration[20-22]. Due to these disadvantages of bismuth oxide, alternative radiopacifiers such as gold powder, silver alloy, zirconium oxide, and calcium tungstate have been proposed[14,17].

Zirconium oxide has been used as a biomaterial in dental and orthopedic fields because of its excellent physical properties and biocompatibility[17,21]. Zirconium oxide is a radiopaque due to its high atomic number and can be used as a radiopacifier in place of bismuth oxide[17]. Nanoparticles of zirconium oxide accelerate the setting time because they accelerate the degree of hydration of Portland cement and do not compromise the biocompatibility[20,21]. In terms of tooth discoloration, MTA containing zirconium oxide causes less discoloration than MTA containing bismuth oxide[22].

In this study, aluminum bismuth oxide ($Al_2Bi_{24}O_{39}$) and mayenite ($Ca_{12}Al_{14}O_{33}$) were included only in EM. Han et al.[20] also reported that EM showed a higher aluminum content than WMTA. This is due to the presence of pozzolan cement: the increase in aluminum content contributes to the reduction in the setting time[20]. Aluminum is rare, but it is likely to cause vitamin D-resistant osteomalacia, erythropoietin-resistant microcytic anemia, and central nervous system alterations[23]. In addition, studies have reported that aluminum is associated with Parkinson's and Alzheimer's diseases[14]. In fact, the aluminum contained in MTA has never been proven to be harmless to humans, but due to concerns about the inclusion of aluminum, manufacturers may have excluded aluminum-related components from their latest released products.

BD contains calcium carbonate ($CaCO_3$) as a filler material in powder components[24]. In this study, calcium carbonate was identified only in BD. Camilleri et al.[25] suggested that calcium carbonate acts as a nucleation site, forming reaction rims and improving hydration around them, thus resulting in dense microstructures. Therefore, BD shows a higher density and less porosity than conventional MTA. In addition, its physical properties are superior to those of the conventional MTA and its strength is similar to that of dentin, so it can be used as a core material[24,26]. Commercially available CSMs have similar constituents: therefore, their XRD patterns also exhibited similar features. OM3 is a product that is yet remains to be introduced to the market after MFDS approval. Unlike other materials, a strong peak was observed at a low 2θ angle of 11.7°. As a result of matching with the PDF provided by ICDD, it was conidered to have been caused by brushite ($CaHPO_4 \cdot 2H_2O$) grown in a specific crystal direction for a specific purpose. Brushite is a phosphate mineral and the precursor of hydroxyapatite (HA, $Ca_5(PO_4)_3OH$)[27]. HA is the major inorganic mineral in natural bones. Calcium and phosphate ions, which can accelerate bone growth and healing, are released during the transformation of Brushite into HA[27]. Other studies regarding Brushite cement have also shown that it is biocompatible and has great potential as a bone substitute and can act as a reservoir for calcium and phosphate ions in the re-mineralization of hard tissues[28,29]. Brushite cements have excellent bioresorbability and can be absorbed under physiological conditions such that newly produced woven bones replace Brushite cements[28,29]. OM3 may have been prepared with this advantage in mind.

1. Limitations

There is a limit to the research conducted by selecting products centered on materials currently used in dental clinic.

2. Generalizability

Eight CSMs showed similar diffraction peaks because calcium silicate was their main component. Two components were observed to have been added as radiopacifiers: bismuth oxide was detected in WMTA, OM, and EM while zirconium oxide was detected in RM, EN-Z, BD, EZ, and OM3. Unusual patterns were detected for the new material, OM3, which had strong peaks at low angles. This was caused by the presence of Brushite, which is believed to have resulted in crystal growth in a particular direction for a specific purpose. The number of MTA materials used in clinical fields is increasing, and there are differences between countries where they are used. Therefore, there is a limit to generalizing the product used as a research object to all products used in clinical practice.

3. Suggestions

Modified or newly developed materials from existing ones can be widely used if they overcome the weaknesses of previous products. In fact, MTA has been successfully modified in Portland cement and is widely used clinically. Careful research is needed before new materials with different components can be applied to clinical settings and investigations should be undertaken to verify if they can replace existing materials. In this study, OM3, a new material, was found to have add new components that were different from previous CSMs. OM3 should be investigated and evaluated to check whether its physical properties and biocompatibility are superior to that of existing materials and whether it can replace currently used materials. In the future, research on more diverse products will be needed.

Notes

Conflict of interest

No potential conflict of interest relevant to this article was reported.

Ethical approval

This study did not receive IRB as a material subject.

Author contributions

Conceptualization: So-Youn An and Youn-Soo Shim. Data acquisition: Myung-Jin Lee. Formal analysis: Youn-Soo Shim and Myung-Jin Lee. Funding: Youn-Soo Shim. Supervision: Youn-Soo Shim. Writing–original draft: So-Youn An. Writing–review & editing: Youn-Soo Shim.

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Data availability

The calcium silicate-based materials (CSMs) of MTA data can be obtained here: https://www.mfds.go.kr.

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