



## Evaluation of micro surface structure and chemical composition of two different calcium silicate–containing filling materials

Kadriye Demirkaya,<sup>1</sup> Şeyda Erşahan,<sup>2</sup> Gökhan Suyun,<sup>1</sup> Selçuk Aktürk<sup>3</sup>

<sup>1</sup>Department of Endodontics, Health Sciences University Faculty of Dentistry, Ankara, Turkey

<sup>2</sup>Department of Endodontics, İstanbul Medipol University Faculty of Dentistry, İstanbul, Turkey

<sup>3</sup>Department of Physics, Muğla Sıtkı Koçman University Faculty of Science, Muğla, Turkey

**Objective:** To investigate and compare the composition and micro surface structure of two different calcium silicate–containing filling materials using energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM).

**Methods:** The materials investigated included DiaRoot BioAggregate (BA) and MTA Angelus (MTA-A). After mixing, each filling material was placed into cubes of 3 mm<sup>3</sup>. The hardening samples were compressed and broken and these samples were used for SEM examination. For elemental analysis and chemical composition, some samples were powdered and EDX was performed.

**Results:** EDX findings indicated that the major constituents of BA included calcium, oxygen, tantalum, and silicon. The chemical structure of MTA-A was similar to that of BA except for the absence of tantalum (radiopacifier). In addition, MTA-A contained some elements, e.g., aluminum, sodium, potassium, phosphorus, iron, rubidium, and strontium in trace amounts. The chemistry of compounds of BA filling material is more biologically compatible as a restorative material. In SEM images, BA was noted to be granular and almost spherical and particles of all sizes were observed. MTA-A was detected as a porous structure; its particles were granular, but locally planar layers were also detected.

**Conclusion:** The mineralogical composition of BA was different from that of MTA-A. As opposed to MTA-A, BA did not contain tricalcium aluminate phase and it included tantalum oxide as a radiopacifier. SEM images of MTA-A represented a more porous surface structure than that of BA. In light of these findings, BioAggregate seems to be a more suitable root-end filling material in terms of mineral content and surface structure.

**Keywords:** BioAggregate; chemical composition; MTA Angelus; surface structure.

A number of materials has been developed by various manufacturers for use as root-end filling materials. The first material to be developed specifically for this purpose was mineral trioxide aggregate (MTA). Although MTA is considered to have ideal properties, its usage remained limited due to its high-cost, difficult handling

characteristics, long setting time, and the potential of discoloration.<sup>[1]</sup> These shortcomings of MTA led to continuous efforts in developing the modified versions of MTA. In 2001, MTA Angelus (MTA-A, Angelus Dental Solutions, Londrina, Brazil) was introduced as an alternative to ProRoot MTA, the first MTA product, and used in cer-

**Correspondence:** Dr. Şeyda Erşahan, İstanbul Medipol Üniversitesi Diş Hekimliği Fakültesi Hastanesi, Birlik Mah., Bahçeler Cad., No: 5, Esenler, İstanbul, Turkey.

Tel: +90 212 – 440 10 00 e-mail: seydaersahan@hotmail.com

Submitted: February 22, 2018 Accepted: March 13, 2018

©2018 Turkish Endodontic Society



tain regions with its lower price. The chemical difference between ProRoot MTA and MTA Angelus is that MTA Angelus lacks calcium sulfate dehydrate as one of its main compounds, resulting in MTA Angelus having shorter setting time than ProRoot MTA (165 minutes for ProRoot MTA, while 10 minutes for MTA Angelus).<sup>[2,3]</sup> MTA Angelus is less radiopaque than ProRoot MTA because of the lower content of bismuth oxide in its composition.<sup>[3]</sup> Bio-Aggregate (BA, Innovative BioCeramix, Vancouver, BC, Canada) was released in 2007 as a bioceramic material, in which most of the constituents are similar to those in ProRoot MTA. It differs from MTA in being aluminum-free and containing calcium phosphate monobasic and tantalum pentoxide.<sup>[4]</sup> Aluminum-free content is one of the most significant features of BA since aluminum has a toxic effect on the human body.<sup>[5,6]</sup>

Clinically, the composition of the set material is important. Once placed and in contact with tissue fluids, root-end filling materials can leach trace elements and compounds that can affect the surrounding periapical tissues.<sup>[4]</sup> Energy-dispersive X-ray spectroscopy (EDX) is a powerful method used for identifying and characterizing the crystalline phase composition of the materials. Even though EDX analysis of the material, BA, has been previously performed, few studies have compared the major

constituents of this material with MTA-A.<sup>[5]</sup> The aim of this study was to characterize particle size and to investigate the micro surface structure and chemical composition of MTA-Angelus and DiaRoot BioAggregate using EDX and scanning electron microscopy (SEM).

## Materials and methods

Materials used in this study included white MTA Angelus (MTA-A, Angelus Dental Solutions, Londrina, Brazil) and DiaRoot BioAggregate (BA, Innovative BioCeramix, Vancouver, BC, Canada). The materials were mixed according to manufacturer's instructions. After mixing, specimens were prepared by placing the mixed materials into standard polyethylene tubes with an internal diameter of 3 mm and length of 3 mm. The tubes were placed on a glass slab (75 × 25 × 1 mm), slightly overfilled with freshly prepared materials and transferred to a chamber with 95% relative humidity and 37°C for a period corresponding to three times the manufacturer's recommended setting time. Nine homogeneous specimens of each material were created.

The morphological analysis of the outer surface of the materials was performed using a scanning electron microscope (JSM-6610; Jeol Ltd., Tokyo, Japan) at ×500 magnification, using an accelerating voltage of 20-25 kV and a

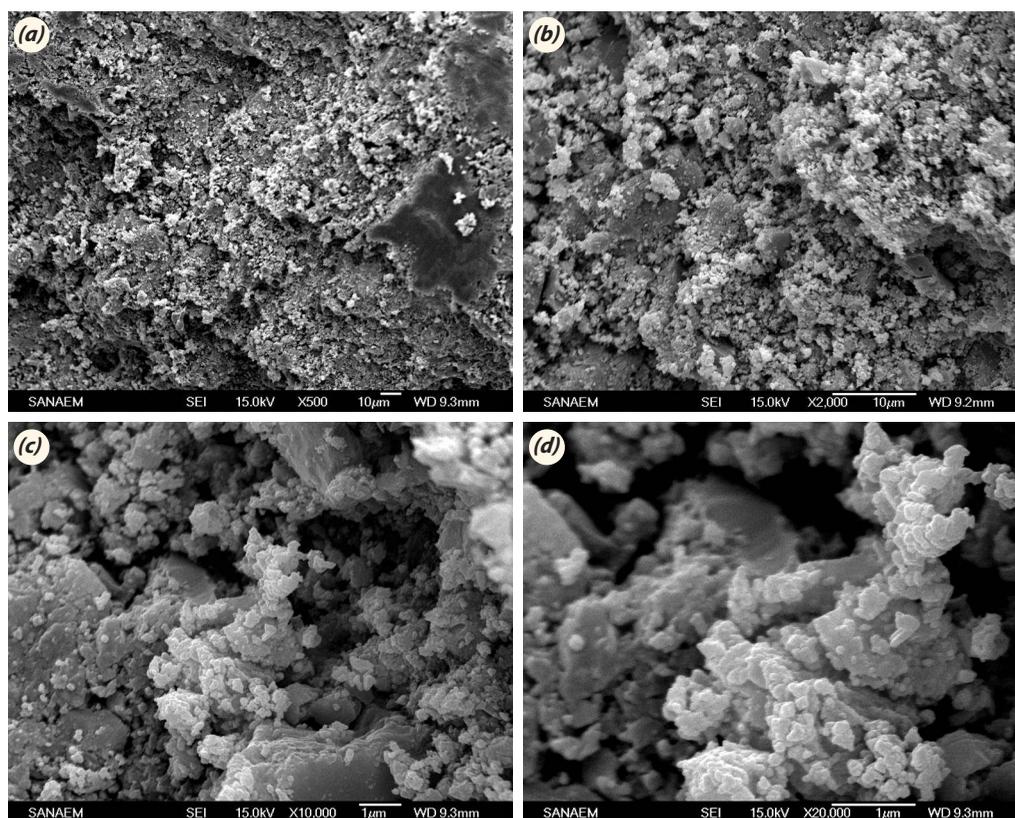


Fig. 1. (a-d) SEM images of BioAggregate surface.

working distance of 15 mm. The specimens were sprinkled on carbon double-sided tape over a metallic stub, critical-point dried, and sputter-coated with gold-palladium (Bal-Tec AG, Balzers, Germany). EDX was performed with the energy dispersive X-ray micro-analyser (EDAX; JEOL, JSM-840A, Tokyo, Japan) for examining the elemental composition of the tested materials. One EDX spectrum was collected from the central region of each specimen under the following conditions: 25 kV accelerating voltage, 110- $\mu$ A beam current, 10<sup>-6</sup> Torr pressure (high-vacuum), 130  $\times$  130  $\mu$ m area of analysis at  $\times$ 1000 magnification, 100 s acquisition time and 30%–35% detector dead time. The elemental analysis (weight % and atomic %) of samples was performed in nonstandard analysis mode using PROZA (Phi-Rho-Z) correction method. The elemental maps were archived by NETCOUNTS method, with high resolution, using the same detection-analysis-system (NSS Spectral Analyses System 2.3).

## Results

The results of EDX analysis are presented in Tables 1 and 2. The following concentrations of Ca were found in samples: BA, 43.2%; MTA-A, 45.7%. EDX profile on MTA-A revealed high concentrations of Ca, O, Si, and Al and traces of Na, K, P, Fe, Rb, and Sr, while the EDX

profile on BA revealed high concentrations of Ca, O, and Si and the presence of Ta. SEM images of the materials are shown in Figures 1a-d, 2a-d. Figures 1a-d show the micrographs from BA surfaces, while Figures 2a-d show the micrographs from MTA-A surfaces. Figures 1a-d indicate that BA was composed of granular powders of various oxides as presented by the chemical analysis shown in Table 1. As seen in Table 1, the chemistry of compounds are expectantly more biologically compatible as a restorative material. The appearance of unbound nature of powders are very characteristic of different powder sizes with which a strong bond is expected following the compaction process, improving the capacity of filling the intrinsic voids inside the compacted volume. This makes the filling less vulnerable to microleakage. Figures 2a-d show the fracture surface from MTA-A. The filling contains a significant amount of porosity of different sizes and appears to have a flaky structure owing to the different composition as seen in Table 2.

## Discussion

The identification of the major constituents or compounds present in a material is important as it contributes to the understanding of the material's physical, chemical, and mechanical properties. The use of EDX permits the identifica-

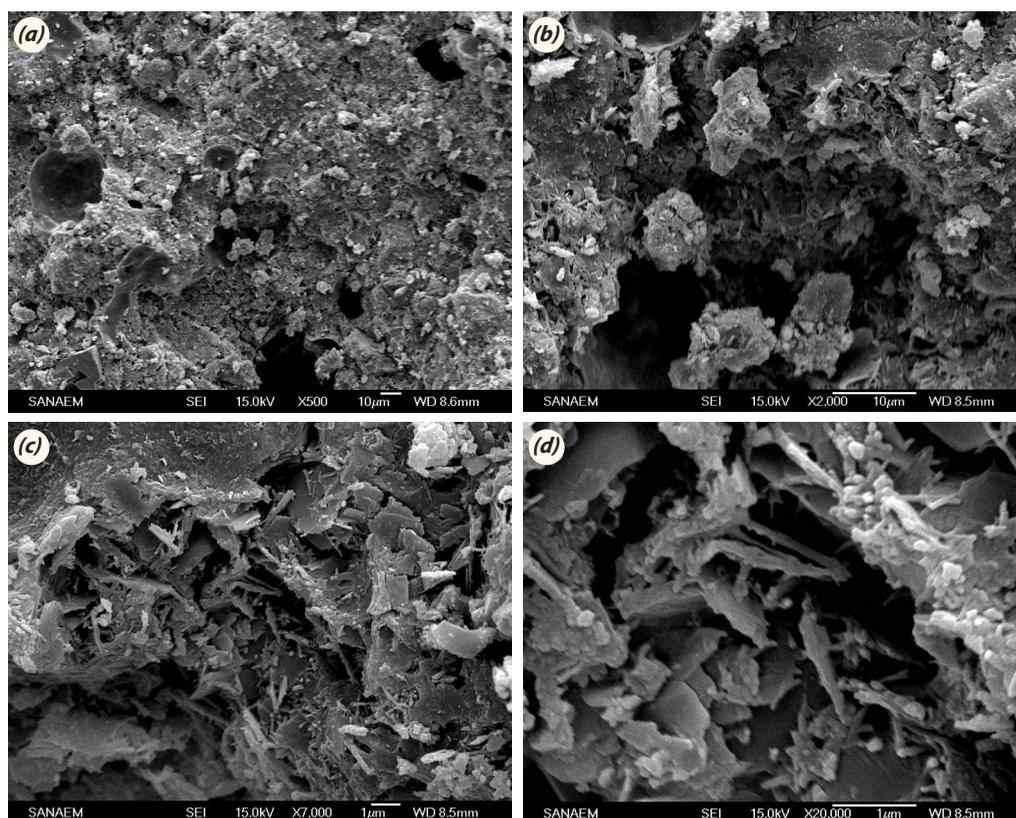


Fig. 2. (a-d) SEM images of MTA Angelus surface.

**Table 1.** EDX results of BioAggregate

Analyte	Compound formula	Measured (kcps)	Used (kcps)	Concentration (%)
O	O	0.029	0.029	25.019
Mg	Mg	0.060	0.060	0.068
Al	Al	0.044	0.044	0.041
Si	Si	6.769	6.766	9.313
P	P	2.799	2.799	1.421
Ca	Ca	20.461	20.461	43.217
Zr	Zr	1.057	1.057	0.412
Ta	Ta	7.308	7.308	20.509

**Table 2.** EDX results of MTA Angelus

Analyte	Compound formula	Measured (kcps)	Used (kcps)	Concentration (%)
O	O	0.029	0.029	26.831
Na	Na	0.038	0.038	0.157
Mg	Mg	0.095	0.095	0.122
Al	Al	1.838	1.838	1.913
Si	Si	4.070	4.070	4.759
P	P	0.025	0.025	0.009
K	K	0.021	0.021	0.043
Ca	Ca	19.511	19.511	45.701
Fe	Fe	0.072	0.072	0.258
Rb	Rb	0.648	0.648	0.041
Sr	Sr	0.577	0.577	0.296
Bi	Bi	117.723	117.723	19.870

tion of the major constituents or compounds present in a material. The materials investigated in this study included two commercially available tricalcium silicate-based cements (MTA-A and BA) manufactured by different companies. Both MTA-A and BA exhibited similar constituents (Ca, Si, and O). MTA-A and BA exhibited similar amounts of Ca (>40%), which explains their antimicrobial properties. Both material powders were composed of tricalcium silicate and included a radiopacifier phase, tantalum oxide, and bismuth oxide, respectively. All these phases were also verified by EDX analysis in this study. The absence of bismuth oxide in BA reduces the risk of tooth discoloration although with root-end filling materials, this is not a major clinical problem.<sup>[7]</sup> Our results indicate that both materials contained aluminum. Even though the manufacturer of BA claimed that it lacked aluminum in composition, we found that BA contained trace amounts of aluminum (0.041%). On the contrary, MTA-A contained higher levels of aluminum (1.913%) when compared with that of BA and contained the tricalcium aluminate phase as one of its main phases as opposed to BA. The presence of aluminum is not indicated in dental and biomaterials owing to the risk of Alzheimer's from excessive exposure to aluminum in close contact with human tissues.<sup>[8]</sup> The lack of heavy

element contamination in BA in comparison with that of MTA-A has been verified and this finding is in agreement with that of previous reports.<sup>[9]</sup> The EDX results obtained from BA and MTA-A samples in this study were largely similar to those by Park et al.<sup>[5]</sup> and Camilleri et al.<sup>[10]</sup> Considering these major differences between MTA-A and BA, it may be important to examine the differences between contents such as radiopacifiers, phases, and heavy elements in terms of toxicity and biocompatibility.

The external surface analysis of BA with SEM method demonstrated granular, spherical particles of approximately 7–10  $\mu$ . Particle sizes of both materials were similar, so that the surface available for hydration, handling properties, and material strength may not differ so much between the groups. While BA surface exhibited granular, spherical calcium silicate grains, MTA-A exhibited granular but plate-like planar images in some regions and also a more porous surface structure than that of BA. The higher material porosity of MTA-A in comparison with that of BA could result in a reduction in material strength. This is clinically undesirable as the increased porosity may attract more bacterial adhesion to the material surface.<sup>[11]</sup> Although both materials are used as a root-end filling material and thus are placed in nonstress-bearing areas, poor physical char-

acteristics will lead to material deterioration with possible dislodgement and loss caused by high solubility.

### Conclusion

The mineralogical composition of BioAggregate was different from that of MTA Angelus. As opposed to MTA Angelus, BioAggregate did not contain tricalcium aluminate phase and it included tantalum oxide as a radiopacifier. SEM images of MTA Angelus represented a more porous surface structure than that of BioAggregate. In light of these findings, BioAggregate seems a more suitable root-end filling material in terms of mineral content and surface structure.

**Conflict of interest:** None declared.

### 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. [\[CrossRef\]](#)
2. Tanomaru-Filho M, Tanomaru JM, Barros DB, Watanabe E, Ito IY. In vitro antimicrobial activity of endodontic sealers, MTA-based cements and Portland cement. *J Oral Sci* 2007;49:41–5. [\[CrossRef\]](#)
3. Oliveira MG, Xavier CB, Demarco FF, Pinheiro AL, Costa AT, Pozza DH. Comparative chemical study of MTA and Portland cements. *Braz Dent J* 2007;18:3–7. [\[CrossRef\]](#)
4. Grech L, Mallia B, Camilleri J. Characterization of set Intermediate Restorative Material, Biodentine, Bioaggregate and a prototype calcium silicate cement for use as root-end filling materials. *Int Endod J* 2013;46:632–41. [\[CrossRef\]](#)
5. Park JW, Hong SH, Kim JH, Lee SJ, Shin SJ. X-Ray diffraction analysis of white ProRoot MTA and Diadent Bio-Aggregate. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2010;109:155–8. [\[CrossRef\]](#)
6. Zhang H, Pappen FG, Haapasalo M. Dentin enhances the antibacterial effect of mineral trioxide aggregate and bioaggregate. *J Endod* 2009;35:221–4. [\[CrossRef\]](#)
7. Camilleri J. Color stability of white mineral trioxide aggregate in contact with hypochlorite solution. *J Endod* 2014;40:436–40. [\[CrossRef\]](#)
8. Forbes WF, Gentleman JF. Risk factors, causality, and policy initiatives: the case of aluminum and mental impairment. *Exp Gerontol* 1998;33:141–54. [\[CrossRef\]](#)
9. Camilleri J, Kralj P, Veber M, Sinagra E. Characterization and analyses of acid-extractable and leached trace elements in dental cements. *Int Endod J* 2012;45:737–43. [\[CrossRef\]](#)
10. Camilleri J, Sorrentino F, Damidot D. Characterization of un-hydrated and hydrated BioAggregate™ and MTA Angelus™. *Clin Oral Investig* 2015;19:689–98. [\[CrossRef\]](#)
11. Bentz DP, Garboczi EJ, Haecker CJ, Jensen OM. Effects of cement particle size distribution on performance properties of Portland cement-based materials. *Cem Concr Res* 1999;29:1663–71. [\[CrossRef\]](#)