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Physicochemical properties of three bioceramic cements

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Abstract: This study aimed to compare the physicochemical properties of MTA Angelus (MTA-A), MTA Repair HP (MTA-HP), and Biodentine (BD). Setting times (n = 7) were determined in accordance with ASTM C266–15. Solubility (n = 11), pH (n = 10), and calcium ion release (n = 10) were evaluated up to 28 days in accordance with ANSI/ADA specification no. 57. Radiopacity was assessed by ANSI/ADA (n = 10) and the tissue simulator method (n = 10). In both methods, the specimens were radiographed using an aluminum stepwedge and the digital radiographs were analyzed in Adobe Photoshop, determining the mean grayscale pixel values of the materials, of the 3-mm aluminum stepwedge, and of the dentin, the latter of which was analyzed on the tissue simulator. The data obtained from each test were statistically analyzed and compared ($p < 0.05$). MTA-A presented longer final setting time compared with the other materials. There were no significant differences in the mass values of materials during the experiment. All materials presented an alkaline pH. BD promoted greater calcium ion release in most of the experimental periods. All materials presented appropriate radiopacity. BD showed lower radiopacity than MTA-A in the tissue simulator method. All groups presented higher radiopacity in the tissue simulator when compared with the ANSI/ADA method. MTA-A, MTA-HP, and BD showed appropriate physicochemical properties and radiopacity, and were considered suitable to be used in clinical practice.

Keywords: Endodontics; Biocompatible Materials; Root Canal Filling Materials; Dental Materials.

Introduction

Mineral trioxide aggregate (MTA) had been initially developed for sealing root perforations and as a root-end filling material.[1] Due to its physicochemical[1] and biological[2] properties, it has been also indicated for vital pulp therapy[2] as an apical plug[3] and as a coronal barrier in the endodontic treatment of immature teeth.[4] MTA formulation comprises a powder – containing tricalcium aluminate, tetracalcium aluminoferrite, calcium sulfate, gypsum, and bismuth oxide – and distilled water.[5] White MTA Angelus (MTA-A) is slightly different from the original MTA, with a lower content of tetracalcium aluminoferrite and calcium sulfate.[6] More recently, bismuth oxide has been replaced with calcium tungstate as radiopacifier to avoid tooth discoloration from the reaction of bismuth

oxide with sodium hypochlorite and/or dentin collagen,[7] but the physicochemical properties of the new formulation still have to be studied.

Besides the risk of tooth discoloration, difficulties with handling[8] have encouraged the development of alternative materials. MTA Repair HP (MTA-HP) (Angelus, Londrina, Brazil) has been developed to provide higher plasticity. The main difference from the most recent formulation of MTA-A is the addition of an organic plasticizer to distilled water[9]. Recent studies have demonstrated that MTA-HP improves resistance to dislodgement and flowability,[9] maintaining the widely acclaimed biological properties of MTA.[6] However, other physicochemical properties of this material, including radiopacity, should be further investigated.

Biodentine™ (BD) (Septodont, Sair Maur de Fossés, France) is another alternative to MTA. It contains tricalcium silicate, dicalcium silicate, calcium carbonate, iron oxide, and zirconium oxide (powder), in addition to a liquid with calcium chloride (accelerator), water-soluble polymer, and a water-reducing agent.[10] Greater microhardness and resistance to compressive loading are some of the advantages of BD in comparison with MTA.[11] Studies evaluating biological properties[12] and antimicrobial activity[13] have also indicated favorable properties. On the other hand, there is no consensus on the radiopacity of BD when the ANSI/ADA method[14,15] is used; therefore, additional methods that evaluate radiopacity under the influence of osseous, dental, and soft tissue superimposition should be considered.[16]

In the standard method, the absence of tooth, bone, and soft tissue could alter the perception of radiopacity in dental materials, thus requiring the addition of radiopacifier to their compositions, potentially influencing other properties.[16,17] Previous studies have shown higher radiopacity of endodontic sealers using the tissue simulator block,[17,18] but to date, this method has not been used to evaluate bioceramic materials.

The present study aimed to compare baseline and final setting times, pH, solubility, and calcium ion release of MTA-A, MTA-HP, and BD. Moreover, the radiopacity of these materials was evaluated both by the ANSI/ADA and the tissue simulator methods.

Methodology

This study was approved by the local research ethics committee (protocol nº 2.940.053). Setting time, solubility, pH, release of calcium ions and radiopacity of MTA-A (Angelus, Londrina, Brazil), MTA-HP (Angelus, Londrina, Brazil), and BD (Septodont, Sair Maur de Fossés, France) were evaluated. All materials were prepared according to the manufacturers' instructions. The sample size was determined for each experiment by means of a calculation based on the results of previous studies.[16,17,19] BioEstat 5.0 statistical package (Mamirauá Foundation, Belém, Brazil) was used.

Setting time

The baseline and final setting times were evaluated according to ASTM C266–15 and ISO 6876:2012.[20] Plaster molds (n = 7) with an internal diameter of 10 mm (± 0.1 mm) and a height of 2 mm (± 0.1 mm) were filled with the mixed material. The specimens were maintained for 5 min in an incubator at 37°C with a relative humidity of 99 ± 5% before the baseline setting time measurements. Baseline setting time was measured with a Gillmore needle (diameter of 2 mm (± 0.1 mm), height of 5 mm, and weight of 100 g (± 5 g)) carefully lowered onto the surface of the specimen without any further pressure. This procedure was repeated every 60 s until an impression was no longer visible on the material surface, and the baseline setting time was then recorded. The final setting time (time elapsed from the beginning of mixing to the time at which no indentation was detected on the surface of the specimens) was determined with a larger Gillmore needle (diameter of 1 mm (± 0.1 mm) and weight of 456.5 g (± 5 g)).

Solubility

The solubility test (n = 11) was adapted from the American National Standard Institute/American Dental Association (ANSI/ADA) specification no. 57/2000[21] and ISO 6876:2012.[20] MTA-A, MTA-HP, and BD specimens were prepared using plastic molds with a height of 1.5 mm (± 0.1 mm) and an internal diameter of 7.75 mm (± 0.1 mm), as proposed by Carvalho-Júnior et al.[22] The molds were placed on a glass plate and filled with the mixed material.

Another plate was positioned over the specimens and then stored in an incubator at 37°C with a 95% relative humidity, using a setting time three times longer than at baseline, as recommended by the manufacturers (12 min for MTA-A and MTA-HP, and 15 min for BD). The specimens were unmolded and weighed on a precision scale with an accuracy of 0.001g (Sartorius 1801MPS, Göttingen, Germany) to determine their initial mass (P-0). After the baseline weight measurements, the specimens were immersed in 15-mL Falcon tubes (Labor Import, Osasco, São Paulo, Brazil), filled with 7.5 mL of deionized water, and maintained in the incubator (SXCR80, Sterilifer Ind. Com. Ltda., Diadema, Brazil) for 24 h. Subsequently, the specimens were removed from the incubator, slightly dried with absorbent papers, and placed in a drying chamber at 37 °C for 48 h. The specimens were then weighed in 72-hour shifts for 28 days. The specimens were maintained in the incubator throughout the weight measurements. Solubility was obtained by calculating the mass loss after the experimental periods in comparison with P-0.

pH and calcium ion release

For pH and calcium ion release analysis (n = 10), MTA-A, MTA-HP, and BD were inserted into 10 x 1.6-mm polyethylene tubes. After the baseline setting time (provided by the manufacturers), the specimens were inserted into 50-mL Falcon tubes (Cral Artigos para Laboratório Ltda, Cotia, São Paulo, Brazil.) containing 10 mL of deionized water (pH = 7.4). The specimens were stored at 37°C during the experimental period. The storage water was replaced at each endpoint (1, 3, 12, and 24 h and 7, 14, 21, and 28 days), and the collected water was analyzed for pH by using a pH meter (Digimed, Digicrom Analitica, Campo Grande, Brazil), previously calibrated with standard solutions with known pH (4 and 7). The calcium ion release assessment was performed in the same experimental periods used for pH analysis. The calcium levels of the collected specimen were analyzed by the colorimetric method using Arsenazo III.[23]

Radiopacity

The radiopacity of MTA-A, MTA-HP, and BD was evaluated by two methods. In the ANSI/ADA method (n = 10), the materials were prepared and placed in acrylic plates containing 4 x 1.5-mm rings. The filled rings were stored at 37°C (± 1) in 95% (± 5) humidity for 7 days until the materials were completely set. Afterwards, the specimens were radiographed using a phosphor plate[24,25] and an aluminum stepwedge.

Radiopacity was further evaluated using the tissue simulator developed by Gegler and Fontanella.[16] Briefly, to build the simulator, the maxillary anterior region of a human skull was split by sagittal osteotomy into two segments fixed with wax (Wilson, São Paulo, Brazil) in a plastic container (length of 56 cm; width of 52.5 cm; depth of 53.5 cm). Distances of 1 cm were established between the external surfaces of the buccal and palatal segments and the container walls. This space was filled with self-curing acrylic (Artigos Odontológicos Clássico, São Paulo, Brazil) that could simulate the soft tissues. A distance of 0.5 cm was established between the internal surface of the buccal bone and the internal surface of the palatal bone. The space was filled with wax, which was used to fix a human canine root with the previously prepared root canal. The root was inserted up to the point at which the cementum-enamel junction coincided with the level of the alveolar crest. To evaluate radiopacity in this tissue simulator, the materials were manipulated and introduced into polyethylene tubes (length of 10 mm and diameter of 1.5 mm; Abbott Lab do Brasil, São Paulo, Brazil) with a syringe to avoid bubbles (n = 12 for each cement). The filled tubes were stored at 37°C (± 1) in 95% (± 5) humidity for 7 days until the materials were completely set. Thereafter, they were individually placed in the root canal of a canine tooth in the tissue simulator and radiographed using a phosphor plate and an aluminum stepwedge (Figure).

In both methods, the radiographs were obtained using a radiographic unit (Timex 70C, Gnatus, Ribeirão Preto, Brazil) operating at 70 kV and 10mA, with a 0.1-s exposure time and a 30-cm focal distance set. The images were generated using a scanner (Dürr Dental SE) and then exported and saved in JPG format. The digital images were analyzed using Adobe Photoshop® CS5 (Adobe Systems, San Jose, USA). For the images obtained with the ANSI/ADA method, a standard-size square (400 pixels) was drawn at the center of the standard disc (material), and another

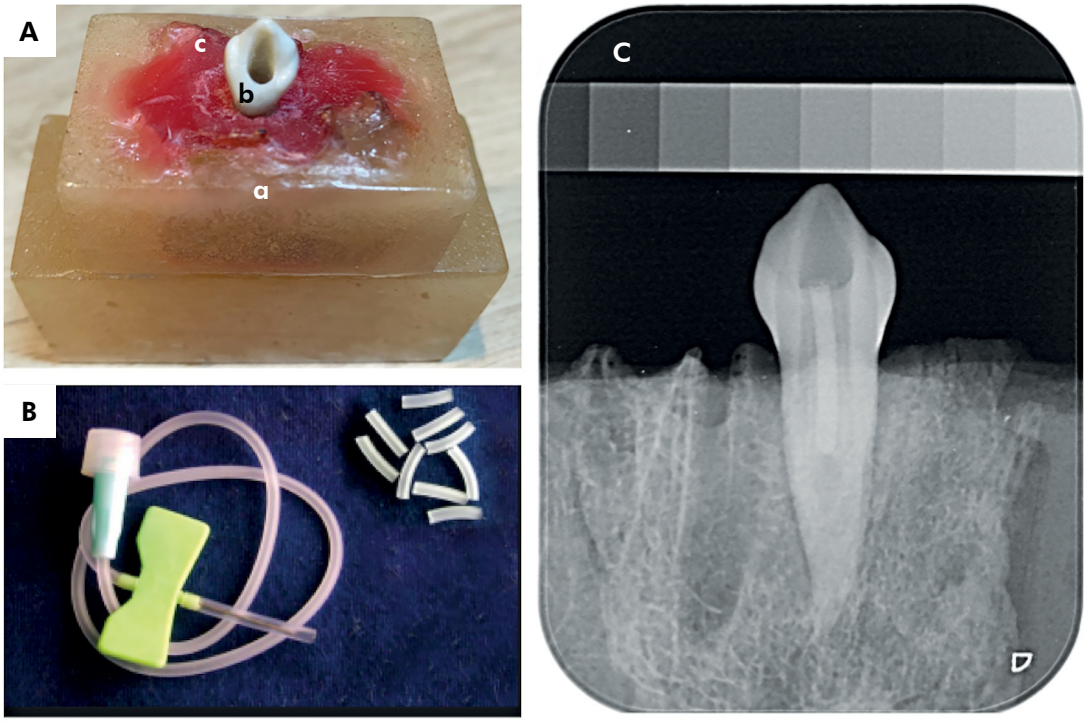

Figure. (A) Tissue simulator. Acrylic block simulating soft tissues and containing a fragment of osseous tissue (a) and a canine tooth (b) involved by utility wax to simulate periodontal ligament (c). (B) Polyethylene tubes into which the bioceramic cements were inserted. (C) Radiographic image of a polyethylene tube filled with Biodentine and inserted into a canine tooth in the tissue simulator, in addition to an aluminum stepwedge.

one was drawn in the third step, from left to right, of the aluminum stepwedge, equivalent to 3 mm of aluminum. In the simulator method, three standard-size squares (400 pixels) were drawn: one under the tube containing the material, another one under the dentin (both in the bone tissue overlap region), and the third one in the aluminum stepwedge at the same step described above. The mean and standard deviation of the grayscale pixel values of each selected area were measured and recorded using the histogram tool.

Data analysis

The statistical analysis was performed with GraphPad Prism 5.0 (GraphPad Software, San Diego, USA) ($\alpha = 0.05$). Baseline and final setting times were compared amongst the experimental groups using one-way ANOVA and Tukey's post-hoc test. The solubility of each material was evaluated throughout the experiment using repeated-measures ANOVA and Tukey's post-hoc test. Calcium ion release and pH were compared amongst the groups and the experimental periods by two-way ANOVA and Tukey's post-hoc test.

In both methods tested herein, radiopacity was compared amongst the groups using one-way ANOVA and Tukey's post-hoc test. The minimum radiopacity recommended by ANSI/ADA for the aluminum stepwedge (equivalent to 3 mm of aluminum) was used as a control for both methods. Besides, in the tissue simulator, dentin radiopacity was also used as a control. To compare the methods, the data were evaluated by Student's unpaired t-test.

Results

Baseline and final setting times of all tested materials are shown in Table 1. MTA-A presented a longer final setting time compared with MTA-HP and BD ($p = 0.0001$). There was no significant difference when evaluating the variability of mass values in the solubility test ($p < 0.05$). All the tested materials presented an alkaline pH – close to 10 – during the

experimental period. After 1 h, MTA-HP presented a more alkaline pH in comparison with MTA-A ($p < 0.05$). Both MTA-HP and MTA-A showed significantly greater calcium ion release after 21 days, while BD presented greater release of calcium ions from the third day ($p < 0.05$). BD promoted greater calcium ion release in most of the experimental periods, except after 1 h and 14 and 28 days ($p < 0.05$) (Table 1).

Table 2 summarizes the findings on radiopacity. All tested bioceramic cements showed higher radiopacity in the tissue simulator method as compared to the ANSI/ADA method ($p < 0.05$). In both methods, all materials presented higher radiopacity than 3 mm of aluminum stepwedge. In the tissue simulator, the three tested materials presented higher radiopacity than dentin. There were no significant differences amongst the materials when evaluating radiopacity through the ANSI/ADA method, while BD showed lower radiopacity than MTA-A when materials were evaluated in the tissue simulator ($p < 0.05$).

Table 1. Mean and standard deviation (± SD) of initial and final setting times (minutes), solubility expressed as mass loss (%) in relation to initial mass (g) and pH values measured in different experimental periods of MTA HP, BD and MTA-A.

Variable	MTA-HP	BD	MTA-A
Setting time			
Initial (min)	19.14 ± 1.46^{aA}	21.71 ± 1.60^{aA}	18.71 ± 8,60^{aA}
Final (min)	35.86 ± 2.19^{aB}	33.29 ± 4.31^{aB}	44.43 ± 2.82^{bB}
Solubility			
m-0	0.16 ± 0.01^{aA}	0.17 ± 0.02^{aA}	0.18 ± 0.01^{aA}
m-1	0.17 ± 0.01^{aA}	0.15 ± 0.05^{aA}	0.20 ± 0.22^{aA}
m-2	0.17 ± 0.01^{aA}	0.16 ± 0.01^{aA}	0.20 ± 0.22^{aA}
m-3	0.16 ± 0.05^{aA}	0.16 ± 0.01^{aA}	0.20 ± 0.02^{aA}
m-4	0.17 ± 0.01^{aA}	0.16 ± 0.01^{aA}	0.20 ± 0.02^{aA}
m-5	0.17 ± 0.01^{aA}	0.16 ± 0.01^{aA}	0.20 ± 0.02^{aA}
m-6	0.17 ± 0.01^{aA}	0.16 ± 0.01^{aA}	0.19 ± 0.02^{aA}
m-7	0.17 ± 0.01^{aA}	0.16 ± 0.01^{aA}	0.19 ± 0.02^{aA}
pH			
1h	10.11 ± 0.4^{aA}	10.14 ± 0.14^{abA}	9.82 ± 0.10^{bA}
3h	10.28 ± 0.13^{aA}	10.50 ± 0.44^{aA}	10.31 ± 0.09^{aA}
12h	10,16 ± 0,25 ^{aA}	10,26 ± 0,46^{aA}	10,28 ± 0,21^{aA}
12h	10,16 ± 0,25^{ABCa}	10,26 ± 0,46^{Aba}	10,28 ± 0,21^{BCa}
24h	10.20 ± 0.34^{aA}	10.19 ± 0.60^{aA}	10.27 ± 0.27^{aA}
7 days	10.33 ± 0.50^{aA}	10.52 ± 0.62^{aA}	10.55 ± 0.20^{aA}
14 days	10.68 ± 0.41^{aA}	10.87 ± 0.64^{aA}	10.99 ± 0.1^{aA}
21 days	10.86 ± 0.58^{aA}	10.83 ± 0.74^{aA}	10.92 ± 0.28^{aA}
28 days	10.87 ± 0.54^{aA}	10.79 ± 0.74^{aA}	10.76±0.45^{aA}
Calcium ions release			
1h	335.63 ± 102.56^{aA}	383.70 ± 30.77^{aA}	397.95 ±104.75^{abA}
3h	371.46 ± 24.70^{aA}	384.34 ± 11.34^{bB}	328.66 ± 42.13^{aA}
12h	349.96 ± 34.05^{aA}	383.19 ± 7.16^{bB}	337.15 ± 23.14^{aA}
24h	333.08 ± 48.43^{aA}	422.70 ± 5.44^{bC}	329.48 ± 51.54^{aA}
7 days	400.28 ± 26.40^{aA}	433.84 ± 8.07^{bB}	403.65 ± 20.73^{aA}
14 days	482.38±41.5^{aA}	421.55 ± 7.15^{bB}	414.22 ± 9.39^{abA}
21 days	573.56 ± 18.77^{aB}	591.95 ± 2.07^{bD}	576.73 ± 23.26^{aB}
28 days	570.87 ± 51.79^{aB}	579.83 ±50.31^{aB}	559.55 ± 60.30^{aB}

*Different lowercase letters in each row indicate significant difference amongst experimental groups ($p < 0.05$). Different capital letters in each column indicate significant differences among experimental periods ($p < 0.05$).

Table 2. Means and standard deviation of MTA-HP, BD, and MTA-A radiopacity (in grayscale pixel) (n = 10 per group).

Variable	ANSI/ADA		Tissue Simulator		Dentin
	Material	AL	Material	AL	
MTA-HP	91.95 ± 17.81 ^{Aa}	83.50 ± 10.01 ^{Ab}	192,5 ± 1.75 ^{Bab}	153,12 ± 0.88 ^{Bd}	181,17 ± 1.05 ^{c}
BD	94.38 ± 5.12 ^{Aa}	85.50 ± 10.00 ^{Ab}	191,1 ± 3.21 ^{Ba}	149,35 ± 0.90 ^{Bd}	180,10 ± 0.88^{c}
MTA-A	98.35 ± 12.9 ^{Aa}	88.10 ± 09.34 ^{Ab}	194,3 ± 1.37 ^{Bb}	157,13 ± 0.78 ^{Bd}	182,68 ± 0.98 ^{c}

Values with different superscript uppercase letters represent statistically significant differences between the radiopacity evaluation methods. Values with the same superscript lowercase letters were not statistically different when comparing the groups ($p < 0.05$).

Discussion

In the present study, the physicochemical properties of MTA-A, MTA-HP, and BD were investigated. Baseline setting time was evaluated to observe the suitability of the tested materials in clinical procedures performed in a single appointment, since a faster setting time reduces dislodgement after material placement.[26] The original MTA set after 2 h and 45 min[1], which has traditionally been considered a drawback. In agreement with previous studies,[9,27] the three tested materials showed adequate baseline setting time – about 20 minutes –, which was similar among the materials. Modifications in the original formulation such as absence of calcium sulfate[28] and bismuth oxide[9] have probably influenced this outcome.

With regards to the new formulation of MTA-A, although the values of baseline setting time were very similar to those found in other studies that have evaluated MTA-A with bismuth oxide,[9,27] the final setting time was longer in comparison with that of the other materials, probably due to differences in the formulations of the materials. MTA-HP differs from MTA-A mainly in the liquid component. The organic plasticizer of MTA-HP could have altered the water content after the mixing process, thus affecting setting time. In this regard, setting time is directly affected by moisture.[24] Moreover, higher surface area has been previously observed for MTA-HP in comparison with MTA-A, which correlates with smaller particle sizes and could accelerate the setting time.[29] In BD, the addition of calcium chloride in the liquid component has probably reduced the setting time.[30] Accordingly, it has been previously observed[30] that the use of calcium chloride is efficient in accelerating the setting of bioceramic materials.

Solubility and contamination before complete setting are concerns for materials with a longer final setting time.[26] On the other hand, the differences observed herein did not seem to affect MTA-A solubility. As a matter of fact, there were no significant differences in solubility amongst the materials throughout the experiment. The three silicate-based cements showed constant mass values and presented appropriate behavior - in accordance to ISO 6876[21] - proving their suitability as root repair materials, when in contact with body fluids. Calcium tungstate is insoluble in water, contributing to MTA-A and MTA-HP insolubility.[6]

An ideal bioceramic material should have alkaline pH and calcium ion release as early as possible, and these environmental conditions should be maintained for long periods. In this regard, an alkaline pH should contribute to the maintenance of an environment that is inhospitable to microbial growth[24,26] and, together with the presence of calcium ions, favor the mineralization process.[12,13] In the current study, MTA-HP showed greater pH than MTA-A after 1 h, but all the bioceramic materials sustained an alkaline pH throughout the 72-hour experimental period. BD showed a higher release of calcium ions earlier than did the other materials, also producing higher levels of ion release in most of the experimental periods. This feature could have an effect on previously described positive aspects of BD such as good biocompatibility, bioactivity,[32] and biomineralization.[33] Thus, the ability of BD to promote pulp mineralization in shorter periods than the other bioceramic materials has been suggested in an entire human tooth culture model.[10]

Among other characteristics, an ideal bioceramic material should be more radiopaque than dentin and tooth surrounding structures. In the current investigation, two methods for evaluation of

radiopacity were compared, showing that under the influence of tissue superimposition, bioceramic materials presented significantly higher radiopacity than when they were evaluated by the ISO-recommended method. The tissue simulator block has already been successfully used in studies on the diagnosis of external apical root resorption[16] and in the evaluation of radiopacity of root filling materials.[17,18] As with the present investigation, previous studies using the same tissue simulator used herein have shown higher radiopacity of endodontic materials than in the ISO-recommended method.[17,18]

Previous studies evaluating the radiopacity of bioceramic materials have used only the ISO-recommended method. In agreement with the current outcomes, Guimarães et al.[6] showed that MTA-HP meets the criteria recommended by ISO 6876:2012,[21] presenting similar radiopacity when compared to MTA-A. Note that, in that study, as well as in the other investigations on MTA Angelus radiopacity,[15,34] bismuth oxide was still used as radiopacifier. The current outcomes revealed that calcium tungstate was able to maintain suitable radiopacity of MTA-A in both methodologies used.

Conflicting results have been observed for BD radiopacity in previous investigations, which ranged from suitable[14,35] to inappropriate according to ISO[24]. The current results show that BD met the ISO criteria and, although it presents lower radiopacity compared to other materials, these differences are probably clinically irrelevant. As a matter of fact, in the present study, dentin presented lower radiopacity than did BD. The tissue simulator method employed herein has allowed evaluating radiopacity closer to what is observed clinically. Therefore, under the influence of tissue superimposition, radiopacity tends to be higher, confirming that BD can be employed in dental practice.

Conclusion

In conclusion, MTA-A, MTA-HP, and BD showed appropriate physicochemical properties and can thus be used in clinical practice.

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