



Original Article

The effect of moisture conditions on the constitution of two bioceramic-based root canal sealers



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KEYWORDS

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Abstract *Background/purpose:* Intraradicular moisture is not standardized and alters the sealing properties and adhesion of root sealers. The aim of this work was to evaluate the effect of different moisture on the constitution of bioceramic sealers.

Materials and methods: The sealers were evaluated before mixing, and after setting using X-ray diffraction (XRD), Energy Dispersive Analysis (EDX) and Scanning Electron Microscope (SEM) techniques. Twenty four extracted teeth were prepared and assigned to four groups according to the moisture conditions: (1) dry: using ethanol as final irrigation, (2) normal: using paper points until the last one appeared dry, (3) moist: using a Luer adapter for 5 s followed by 1 paper point, and (4) wet: the canals remained totally flooded. The roots were filled with MTA Fillapex[®] and Endosequence[®] BC and kept in phosphate buffer solution at 37 °C for 10 days. Each root was sectioned transversally and longitudinally. The sealers harvested from longitudinal sections were analysed using XRD. Whilst the transverse sections were analysed using SEM/EDX.

Results: The XRD analysis showed MTA Fillapex composed of Bismuth trioxide, calcium silicate and tricalcium aluminate. The intensity of peaks in the wet condition was reduced. Endosequence BC contained mainly calcium silicate, calcium silicate hydrate, zirconia and calcium hydroxide. The wet condition showed a small increase in hydrated calcium silicate. The EDX analysis showed changes in the elemental concentrations with different moisture conditions. The surface morphology differed with different moisture conditions.

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Conclusion: Tested sealers have different constitution that not affected by the degree of moisture. However, it changed their relative quantity.

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Introduction

Recently, attention has been given to root canal sealers containing calcium silicate, mainly Mineral Trioxide Aggregate (MTA). MTA has an extensive range of dental applications such as root-end filling, pulp capping and root-repair materials.¹ It has good physical and biological properties including alkaline pH, chemical stability, nontoxicity and biocompatibility.^{2–4} It is also a bioactive material and its bioactivity is attributed to its ability to produce hydroxyapatite in the presence of phosphate-buffered saline (PBS).^{5,6} The suggested mechanism for the formation of hydroxyapatite is initiated by release of calcium hydroxide from MTA which interacts with a phosphate-containing solution to produce calcium-deficient apatite through an amorphous calcium phosphate phase.⁷ The drawback of MTA is that it is not easy to handle.⁸ Thus, modifications to its original formulation have been suggested to improve its physicochemical and mechanical properties.^{8,9}

MTA Fillapex (Angelus, Londrina, PR, Brazil) is a MTA-based sealer. It is composed of salicylate resin, diluting resin, natural resin, bismuth trioxide, nanoparticulated silica, MTA (tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferritesilicate), and pigments. This sealer shows appropriate physicochemical properties.^{3,10} According to the manufacturer, the setting reaction of MTA Fillapex is not a polymerization reaction however, it is a complexation reaction and it is promoted by the presence of moisture in the dentinal tubules.

Endosequence BC (Brasseler, Savannah, USA); also known as iRoot SP (Innovative Bioceramix, Vancouver, Canada); is a bioceramic-based root sealer. It is composed of calcium silicate, calcium phosphate, calcium hydroxide, and zirconium oxide. The components of Endosequence BC are similar to MTA with addition of calcium phosphate. This sealer is a hydraulic sealer and requires the presence of water to set and harden. The manufacturer claims that, this sealer is able to form hydroxyapatite during the setting which creates an ultimate bond between dentinal wall and the sealer.¹¹

The phosphate-containing solution exists in living tissue fluid. Nevertheless its amount varies from intraradicular to periradicular tissue. Moreover, the intraradicular moisture is not standardized and it could vary widely according to the root anatomy and among clinicians.¹² Different levels of residual moisture in the root canal have been shown to alter the sealing properties and adhesion of root sealers.^{12,13} This could be related to the alteration of the setting reaction. The aim of this study is to evaluate the constitution of two commercially available bioceramic-based root canal sealers (MTA Fillapex and Endosequence

BC) based on the effects of different moisture conditions on its surface morphology and their ability to form hydroxyapatite.

Materials and methods

Analysis of unset sealers

The paste of both MTA Fillapex and Endosequence BC sealers were evaluated by X-ray diffraction XRD (PANalytical-EMPYREAN), operated at 45 kV and 40 mA with monochromated Cu K α radiation. X-ray data were collected at 2 θ values from 10° to 70° at a rate of 0.01° per minute. Energy Dispersive Analysis (EDX) and Field Emission Scanning Electron Microscope (SEM, Low Vacuum Operating Mode, Quanta FEG 250, Holland) with $\times 1000$ magnification was used to evaluate the microstructure morphology and elemental components of unset sealers.

Analysis of set sealers in mould

MTA Fillapex and Endosequence BC were injected directly into the plastic mould of 10 mm diameter and 2 mm height. Ultrasonic vibration was used to avoid air entrap. Two specimens were made for each sealer. The moulds were kept in an incubator at 100% humidity and 37 °C for 10 days prior to evaluation using XRD, FESEM and EDX.

Analysis of set sealers in simulating clinical situation

24 extracted, single-rooted central incisors teeth were disinfected by using 0.5% Chloramine T trihydrate solution for one week. The teeth were radiographed buccolingually and mesiodistally. The criteria of selection of the teeth included single, relatively straight canals, completely formed canals and patent foramina. The anatomical crowns of the selected teeth were removed with a separating disc at the level of the cemento-enamel junction perpendicular to the long axis of the root canal to standard root canal length for all specimens (16 mm). All root canals were prepared with ProTaper rotary files (Dentsply Maillefer; Ballaigues, Switzerland). The master apical file was set to finishing file F4 (size 40 and taper 0.06). After preparation, the canals were rinsed with 17% EDTA for 1 minute followed by 10 mL distilled water to remove all chemicals and overflow of distilled water was confirmed by visual inspection at the coronal access and by extrusion through the apical foramen. The roots were randomly assigned to the following 4 groups (n = 6) to evaluate the effect of

different intraradicular moisture conditions according to previously published study.¹³

Group 1 (Dry canal): after the removal of excess distilled water with paper points, the canals were dried with 95% ethanol using a tuberculin syringe with a 30-G blunt-tip needle, carried to the working length. Ethanol was left in the canal for 10 s. Excess ethanol was removed with paper points, after which the roots were stored at 37 °C to ensure complete dryness. **Group 2 (Normal moisture):** The canals were dried with paper points until complete dryness of the last point was confirmed visually. **Group 3 (Moist):** The root canals were dried with a Luer vacuum adapter (Ultradent Products Inc, South Jordan, USA) for 5 s. The adapter was operated at low vacuum with gentle up and down motion followed by drying with 1 single paper point for 1 s. **Group 4 (Wet):** The root canals were

left totally flooded with water to observe possible incorporation of moisture into the sealers.

For each moisture condition, the specimens were further subdivided according to the type of sealer used ($n = 3$). The roots were filled with sealers according to the manufacturer's instructions. Then, the specimens were stored individually in sterile plastic vials containing (Phosphate Buffer solution) PBS (OmniPur, Calbiochem, USA) at 37 °C to simulate oral cavity situation for 10 days. PBS was changed after 5 days.

Then each root was sectioned, horizontally at 1 and 2 mm from filling terminus with diamond disc to get two cross-sections per specimen. Subsequently, the rest of the root was grooved longitudinally in buccolingual direction and split into two halves by wedging a fine chisel into the groove and then carefully twisting the chisel. Gutta-percha

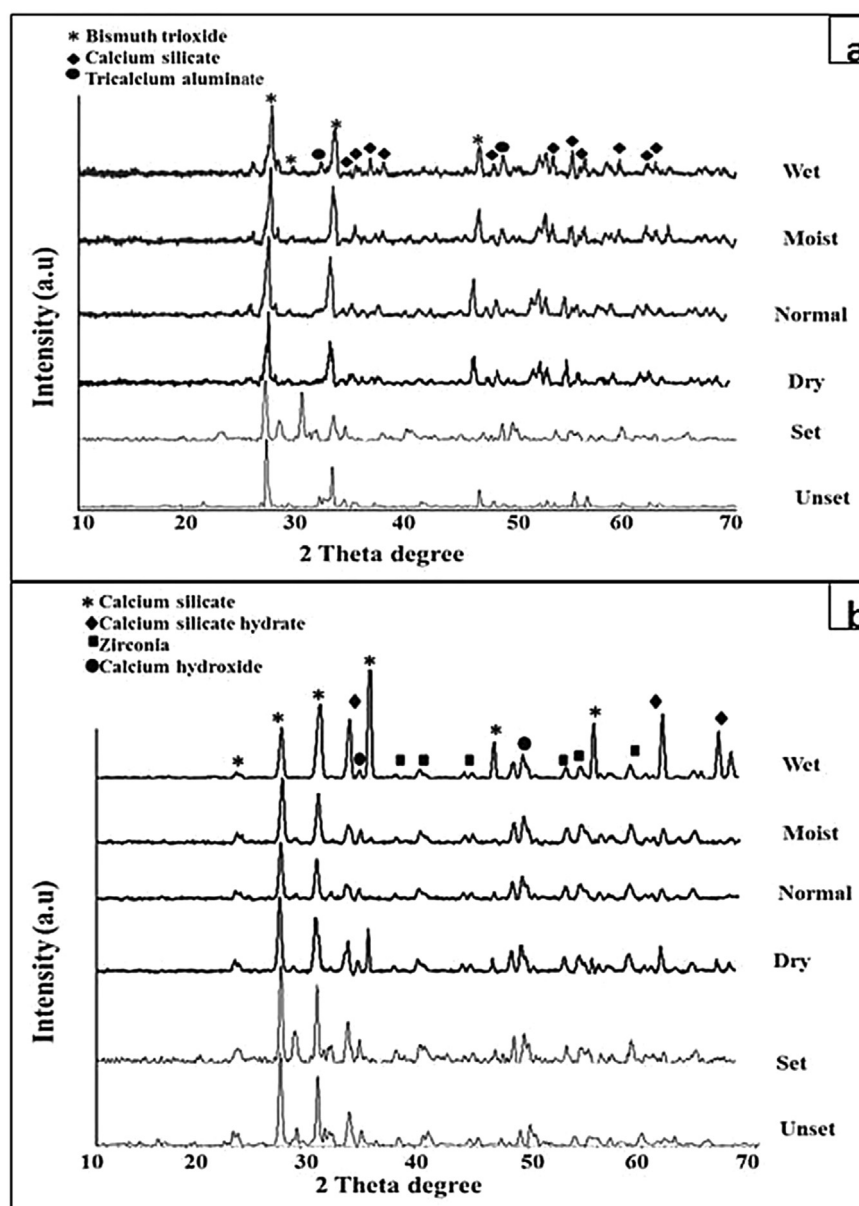


Figure 1 XRD analysis of sealers. a) MTA Fillapex. b) Endosequence BC sealer.

cones were fitted and used as indicators to best gauge the groove depths and to prevent the intrusion of the cutting disk and or debris into the sealers. The sealers were retrieved from the longitudinal sections and subjected to XRD to define the phases of the sealers. The cross-section of the root was evaluated by FESEM and EDX with $\times 1000$ magnification to evaluate the microstructure morphology and elements in the interfacial adaptation area between sealer and dentine.

Results

The XRD analysis (Fig. 1) showed MTA Fillapex composed of bismuth trioxide (JCPDS, 027-0053) calcium silicate (JCPDS, 027-0088) and tricalcium aluminate (JCPDS, 38-1429). The intensity of XRD peaks in the wet condition was reduced compared to other moisture conditions and this could be an indicator of reduce amount of MTA Fillapex in wet condition. Endosequence BC contained mainly calcium silicate (JCPDS, 027-0088), calcium silicate hydrate (JCPDS-020355), zirconia (JCPDS, 0899066) and calcium hydroxide (JCPDS, 4-0733). However, wet condition revealed a small increase in hydrated calcium silicate based on higher peaks intensity.

FESEM (Fig. 2) of unset MTA Fillapex showed homogenous matrix with small irregular particles interspersed with some elongated needle-like fillers. After setting in mould the fillers became more obvious. Endosequence BC revealed presence small fillers that became obvious after setting. Fig. 3 revealed that in dry, moist and wet conditions the fillers of MTA Fillapex reduced and the crystalline particles also. Additionally, with wet condition the sealer had cracks

(Fig. 3g). In normal condition the MTA Fillapex sealer appeared well crystalline. Endosequence BC had less crystalline particles and cracks in the surface with dry condition. Whereas with normal, moist and wet conditions the crystalline particles of sealer were obvious. Endosequence BC sealer also had showed no cracks with good adaptation to dentine and the penetration of sealer to dentinal tubules was noticeable with wet condition (Fig. 3h).

EDX (Table 1) showed MTA Fillapex composed mainly of carbon (C), oxygen (O), silica (Si), aluminium (Al) and calcium (Ca). Endosequence BC composed mainly of carbon (C), oxygen (O), silica (Si), calcium (Ca) and zirconium (Zr). However, changes in the elemental concentration were detected after setting and with different moisture conditions. MTA Fillapex has no phosphorus (P) before and after setting in mould. However, in simulating clinical situation, the phosphorus (P) was detected and the ratio was 1.7 for dry condition which is similar to hydroxyapatite (HA), normal condition was 1.96, moist condition was 1.57 and wet 1.54 that was not similar to the ratio of HA but it could be calcium phosphate. Also in Endosequence BC no phosphorus was detected before and after setting in mould. However, in extracted teeth Phosphorus (P) was identified and the ratio was 2.37 for dry, 1.92 for normal, 3.29 for moist, and 4.60 for wet and these ratios are not similar to that of HA.

Discussion

Hydrophilicity of root sealers is a favourable property as it increases the sealer flow and subsequently enhances the micromechanical interlocking.¹⁴ However, it can also

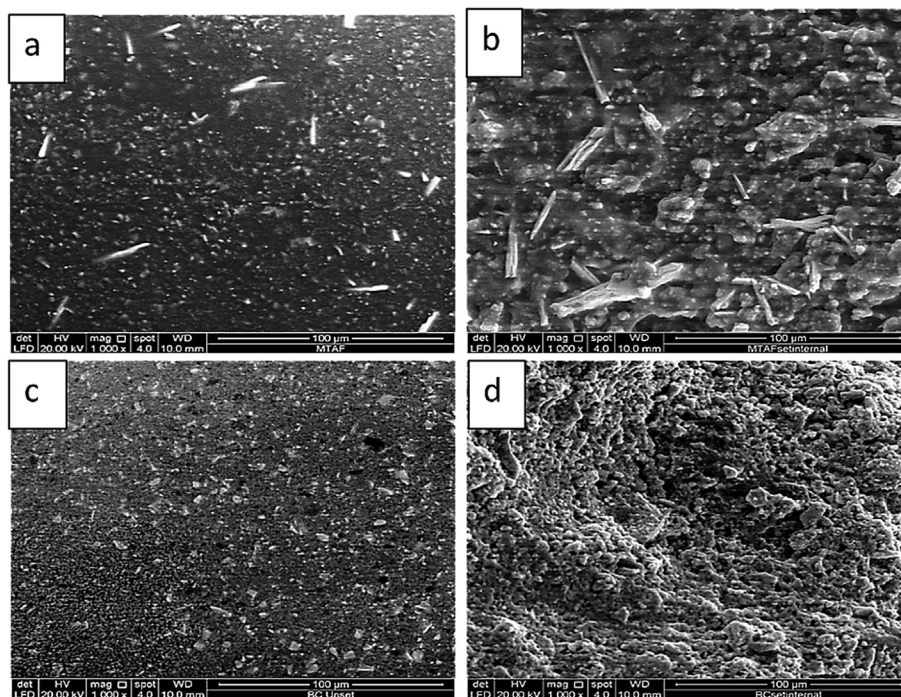


Figure 2 Scanning electron images of both sealers before and after setting ($\times 1000$). a) Unset MTA Fillapex showing small irregular particles interspersed with some elongated needle like particles. b) The elongated needle-like particles became more prominent after setting of MTA Fillapex. c) Scanning electron image of unset Endosequence BC showing small irregular crystalline particles. d) The crystalline particles became more obvious after setting.

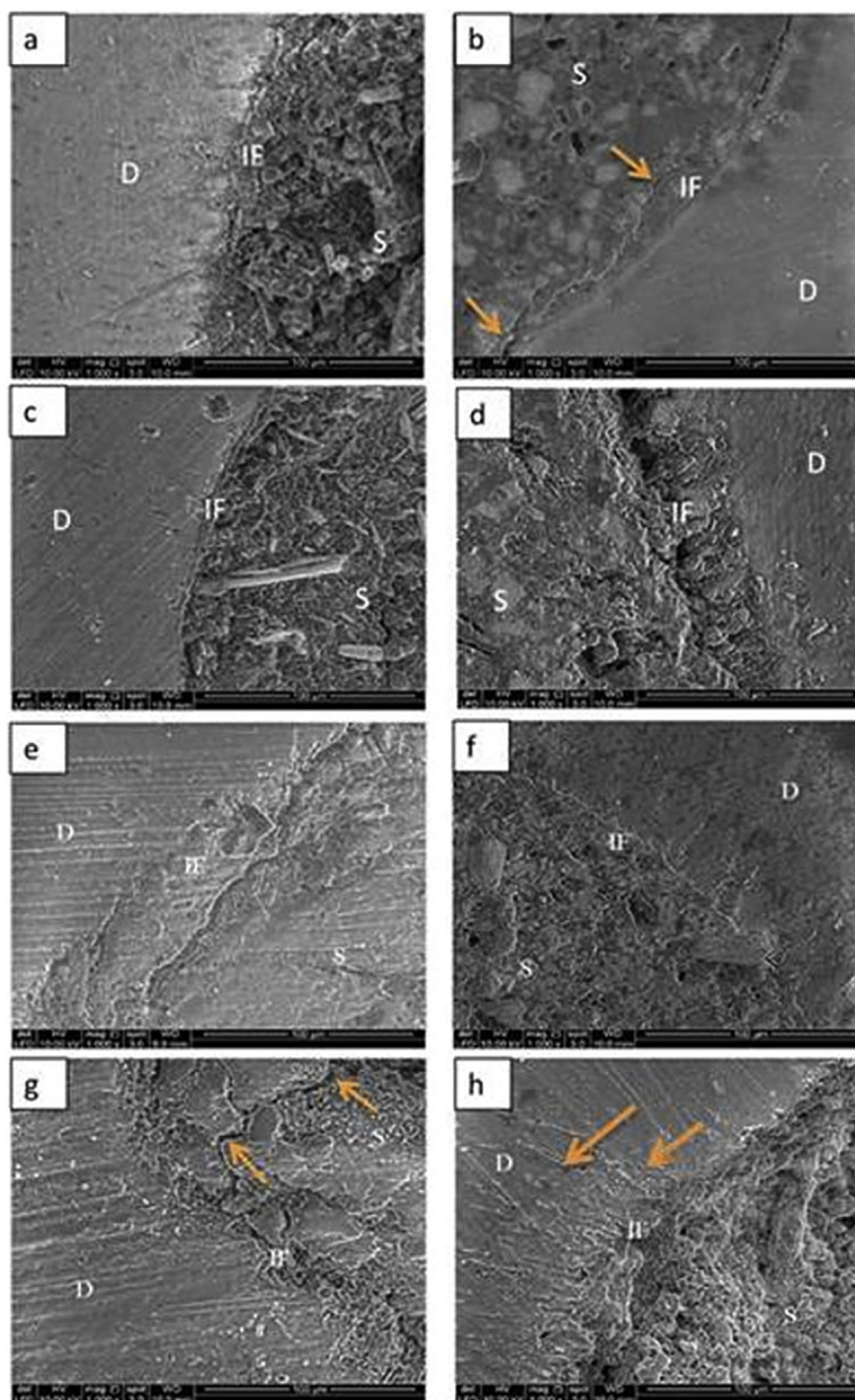


Figure 3 Scanning electron images of both sealers in different moisture conditions ($\times 1000$). S: sealer, D: Dentin, I: interfacial area. MTA Fillapex revealed the particles and adaptation of sealer and it reduced with different moisture conditions a) dry, c) normal, e) moist and g) wet (cracks are arrowed). Endosequence BC showed the particles and adaptation was improved with increased moisture b) dry (cracks are arrowed), d) normal, f) moist and h) wet (penetration of sealer to dentinal tubules are arrowed).

increase the solubility of the sealer.¹⁵ The intraradicular moisture is not clinically standardized.¹² Hence four different moisture conditions were applied in this study. Normal and moisture condition could occur clinically whereas two extreme scenarios (dry and wet) were also involved for research purposes. Three stages of analysis

were performed to notify the changes occurred of sealers compared to its initial status. Analysis of the constitution of sealers showed that both materials are different even with presence of calcium silicate in both.

The manufacturer of Endosequence BC stated that it does contain calcium phosphate; but neither calcium

Table 1 Semiquantitative elemental composition (atomic %) of sealers.

Sealer	Status	C	O	Ca	P	Bi	Ti	Al	Si	Zr	S	Mg	Ca/P
MTA Fillapex	Unset	63.77	25.21	3.58	—	—	0.36	0.29	2.58	—	4.21	—	
	Set	58.62	28.7	4.94	—	2.49	0.27	0.54	2.89	—	1.55	—	
	Dry	37.83	44.73	4.13	2.42	—	0.25	0.7	9.55	—		0.39	1.71
	Normal	43.86	42.24	5.4	2.75	—	—	0.67	4.68	—		0.4	1.96
	Moist	35.68	46.81	10.18	6.5	—	0.42	—	0.41	—		—	1.57
	Wet	18.84	54.57	15.53	10.07	—	0.39	—	—	—		0.6	1.54
Endosequence BC	Unset	42.16	44.62	6.07	—	—	—	—	1.77	5.38		—	
	Set	31.27	51.24	8.77	—	—	—	—	2.84	5.88		—	
	Dry	18.22	60.91	13.45	5.67	—	—	—	1.75	—		—	2.37
	Normal	25.15	52.15	13.2	6.89	—	—	—	1.7	0.44		0.47	1.92
	Moist	24.87	55.55	9.85	2.98	—	—	—	2.02	4.73		—	3.29
	Wet	18.46	49.77	26.1	5.67	—	—	—	—	—		—	4.6

phosphate nor phosphorus element was identified by XRD and EDX respectively. This is in agreement with a previous study¹⁵ and it was referred to the small quantity of calcium phosphate in the sealer. Moreover, carbon element was identified on Endosequence BC surfaces but the manufacturer did not report it.¹⁵ No aluminium was found in EDX and this confirmed the statement of the manufacturer that Endosequence BC is an aluminium-free calcium silicate sealer. In the third analysis stage, phosphorus element was detected. The calcium/phosphorus ratio was not equivalent to that of calcium phosphate or HA. This could have been due to the nature of root canal environment as PBS is limited inside the canal and presence of this solution is essential for formation of apatite structure.⁷ FESEM revealed more crystalline form of sealer with moist and wet and this was probably due to the presence of nano-calcium silicate that is the hydrophilic component and exhibits minimal or no shrinkage.¹⁶ Endosequence BC showed less adaptation to dentinal wall with dry condition and this is in accordance with a previous study.¹³ This could be attributed to excessive desiccation that may remove the water residing in the dentinal tubules which in turn obstruct effective penetration of hydrophilic sealers and thus compromise the quality of adaptation to the dentinal wall.¹³ Although a totally wet condition represents an extreme experimental scenarios that should be avoided in the clinical situation, it was apparent that Endosequence BC sealer could better tolerate this condition to some extent. This might be advantageous in clinical practice where a standardized degree of residual moisture may be difficult to achieve in all regions of the root canal.

For MTA Fillapex, Bismuth was too little to be detected with EDX before setting or after setting inside root canal this is in agreement with previous study.¹⁵ Nevertheless, XRD and FESEM both showed the obvious presence of trioxide Bismuth that added presumably to make the materials radiopaque for dental use.¹⁷ Identification of phosphorus inside root canal with different moisture could indicate that the bioactivity of MTA Fillapex has similarity to MTA. And the presence of PBS enhances production of apatite-like structure⁶ that is not confirmed to be hydroxyapatite. Unlike Endosequence BC, MTA Fillapex can tolerate dry condition and it showed good adaptation with no apparent crack in dry condition. This can be attributed to its resin components and its complexation setting reaction that requires only water molecule to

hydrate the CaO and it has an intrinsic process of self-acceleration. Even in dry condition, this water molecule could be obtained from the environment during application of MTA Fillapex or from the storing media. Normal condition was the suitable condition for MTA Fillapex sealer as the crystalline forms was recognizable and good adaptation. However, wet condition decreased the quantity of compounds and altered the crystalline microstructure. This could be explained by inability to displace water in a totally wet root canal, and entrapment of water droplets decrease the monomer conversion, leading to incomplete resin polymerization and decreased bonding and adaptation of MTA Fillapex to the dentinal wall.¹³

Even both examined sealers are MTA-based, hydrophilic sealers and their setting is promoted by presence of water, their constitutions and response to dentin moisture were dissimilar.

Within the limitation of this study, the following conclusion was drawn. MTA Fillapex and Endosequence BC sealers have dissimilar constitution. And the degree of moisture does not affect the chemical components of the sealers. However, it changed its relative quantity and adaptation to the root dentin.

Conflicts of interest

The authors have no conflicts of interest relevant to this article.

Acknowledgment

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