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The effect of pH on surface hardness and microstructure of mineral trioxide aggregate

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Abstract

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Aim To evaluate the surface microhardness of mineral trioxide aggregate (MTA) specimens following exposure of their surface to a range of acidic environments during hydration. In addition, the morphological microstructure features of samples were studied by scanning electron microscopy (SEM).

Methodology White ProRoot MTA (Dentsply Tulsa Dental, Johnson City, TN, USA) was mixed and packed into cylindrical polycarbonate tubes. Four groups, each of 10 specimens, were formed using a pressure of 3.22 MPa and exposed to pH 4.4, 5.4, 6.4 and 7.4, respectively, for 4 days. Vickers microhardness of the surface of each specimen was measured after exposure. Four groups of two specimens were prepared and treated in the same way prior to qualitative examination by SEM. Data were subjected to one-way ANOVA and *post hoc* Tukey's test.

Result The greatest mean surface hardness values (53.19 ± 4.124) were observed following exposure to pH 7.4 with the values decreasing to 14.34 ± 6.477 following exposure to pH 4.4. The difference between these values at the 95% CI (33.39–44.30) was statistically significant ($P < 0.0001$). There were no distinct morphological differences between groups in terms of the internal microstructure. However, a trend was observed that the more acidic the solution, the more extensive the porosity of the specimens.

Conclusion Under the conditions of this study, surface hardness of MTA was impaired in an acidic environment.

Keywords: acid, microstructure, mineral trioxide aggregate, scanning electron microscopy, vickers microhardness.

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Introduction

Mineral trioxide aggregate (MTA) has shown potential as an endodontic material in several *ex vivo* and *in vivo* studies (Mitchell *et al.* 1999, Torabinejad & Chivian 1999, Moretton *et al.* 2000, Schmitt *et al.* 2001). It was first recommended as a material for repair of root perforations (Lee *et al.* 1993). It was then widely used as a root-end filling material (Torabinejad *et al.* 1993, Aqrabawi 2000) and for vital pulp therapy, including direct pulp capping and pulpotomy of immature teeth with vital pulps (apexogenesis) (Abedi & Ingle 1995, Torabinejad & Chivian 1999). In addition, because of its sealing ability, it was also suggested as an apical barrier in treatment of teeth with open apices and necrotic pulps (apexification) (Shabahang & Torabinejad 2000, Witherspoon & Ham 2001).

There are two types of MTA: grey and white. Asgary *et al.* (2006), in a qualitative X-ray analysis, stated that the absence of iron in white MTA was the main difference between the two types. Several authors have

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examined similarities between different types of MTA and Portland cement (Funteas *et al.* 2003, Asgary *et al.* 2004, Menezes *et al.* 2004, Dammaschke *et al.* 2005), the key difference being the addition of bismuth oxide to MTA as a radiopacifier (Camilleri *et al.* 2005a, Asgary *et al.* 2006).

Portland cement comprises of four main elements namely calcium, silicon, aluminium and iron that are extracted from the raw materials, limestone and sand in the form of calcium oxide (lime) and silicon dioxide (silica) (Eglinton 1987, Abdullah *et al.* 2002, Lawry *et al.* 2005, Camilleri & Pitt Ford 2006). The basic compounds involved are tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite (Islam *et al.* 2006).

The principal setting process of Portland cement is initiated on contact with water when a chemical reaction between water and cement begins; this is essentially a hydration reaction (Atkins *et al.* 1991, Baglioni *et al.* 2002). The hydration reaction is primarily controlled by aluminates that are the first compounds to react with water and cause the flash setting of the cement (Eglinton 1987). This stage is crucial to gain sufficient primary strength within the cement and is usually followed by hydration of the silicate phases (Eglinton 1987, Taylor 1997, Yazdani & Mckinnie 2004). The hydrated calcium silicate phases that comprise 70–80% of the cement contribute most to the binding power and strength of the material. During this process, fine hydrophilic particles react chemically with water and subsequently harden (Torabinejad *et al.* 1995, Ouki & Hills 2002, Camilleri *et al.* 2005b). Cement hydration connects the original cement particles together resulting in a colloidal gel that develops bonding properties and is responsible for its hardening (Yazdani & Mckinnie 2004, Bentz 2007).

The hydration rate is a characteristic of the progress of cement setting (Taylor 1997). Papadakis *et al.* (1999) and Ouki & Hills (2002) indicated that scanning electron microscopy (SEM) could be used to quantify the observable porosity as an indicator of cement hydration. Yi Min *et al.* (2003), in their study on the effect of hydration characteristics on compressive strength of Portland cement, reported that better hydration could enhance greatly its compressive strengths. Sufficient water is required during the setting of the cement to ensure a comprehensive hydration reaction.

In many clinical applications, MTA is placed in an environment where inflammation is present and where a low pH is likely (Malamed 1997). Torabinejad *et al.* (1995) demonstrated that MTA had a pH of 10.2 initially, which increased to 12.5 three hours after mixing. It is possible, however, that variations in the pH value of host tissues because of pre-existing pathological conditions at the time of MTA placement could effect its physical and chemical properties (Lee *et al.* 2004). For example, an acid pH in the environment may impede MTA setting (Torabinejad & Chivian 1999), and reduce its strength (Torabinejad *et al.* 1995) and hardness (Taylor 1997). Lee *et al.* (2004) stored MTA specimens in various pH solutions for 7 days and reported the mean Knoop microhardness values of MTA specimens. They indicated that specimens stored at pH 5 were weaker than those stored at higher pH. However, although in clinical situations MTA might be exposed to an acidic environment, extended immersion in acid does not simulate clinical conditions. Thus, to investigate further the response of MTA to acid under more relevant conditions, the present study was designed to evaluate the surface microhardness of white ProRoot MTA as an indicator of the setting process (Alexander 1972) following exposure to a range of acidic environments during hydration. In addition, the morphological microstructural features of samples were studied by SEM.

Materials and methods

The parameters investigated were surface hardness (Vickers microhardness), and assessment of morphological characteristics using SEM. The material investigated was the tooth-coloured formula of ProRoot MTA (Dentsply Tulsa Dental, Johnson City, TN, USA; LOT number 03081235).

Microhardness

The material was mixed according to the manufacturer's instructions. Each sachet containing 1 g of MTA was mixed with the recommended volume of water supplied by the manufacturer. The mixed material was weighed and then divided into four equal specimens that were packed into polycarbonate cylindrical tubes having an internal diameter of 6 mm and height of 12 mm.

Four groups each of 10 specimens were prepared using a pressure of 3.22 MPa applied for 1 min (Nekoofar *et al.* 2007). The samples were thus subjected to a constant vertical force that was translated

into a transverse and equally distributed pressure that compacted the MTA evenly into the cylindrical mould using a custom-made device containing a stainless steel piston with the similar internal diameter of polycarbonate cylindrical tubes (Nekoofar *et al.* 2007). A wet cotton pellet was placed onto the MTA within the polycarbonate tube and samples stored at room temperature (20 °C) within a glass vial for 4 days. The bottom of each vial contained a piece of 2 cm × 2 cm gauze that had been soaked in butyric acid buffered at either pH 4.4 ($n = 10$), 5.4 ($n = 10$), 6.4 ($n = 10$) or 7.4 ($n = 10$), respectively. The latter group acted as the control group. Based on pilot experimentation, the acid-soaked pieces of gauze were replaced with fresh acid-soaked gauze every 24 h to ensure a consistent pH during the experimental period. The openings of the glass vials were then covered by moist gauze and covered to ensure the presence of sufficient humidity inside the vials. After 4 days, the MTA specimens were removed from the moulds.

The surfaces exposed to acid on each specimen were then wet polished at room temperature using minimum hand pressure and silicon carbide-based sandpapers of varying particle size ('Wetordry™, 600-grit, 737 SF 'Tri-M-ite™' and 'Wetordry™, 1200-grit, 3 M; St Paul, MN, USA) to provide smooth surfaces for ease of indentation testing. By employing wet polishing and gentle pressure, the influence of sample processing on the structure and surface microhardness is minimized (Cross *et al.* 2000). The polished specimens were cleaned gently under light pressure distilled water to remove surface debris. To prevent dissolution or water sorption, the surfaces were dried gently by air spray. The Vickers microhardness test of each specimen was performed using a Mitutoyo microhardness tester MVK G1 (Mitutoyo Corp., Tokyo, Japan) and a square-based pyramid-shaped diamond indenter with a full load of 50 g for 5 s at room temperature that produced a quadrangular depression with two equal orthogonal diagonals in the polished surface of the cement. The angle between the opposite faces of the diamond indenter was 136°. Five indentations were made on the polished surface of each specimen at separated locations no closer than 1 mm to adjacent indentations or the specimen periphery. The diagonal of the resulting indention was measured immediately under the microscope and the Vickers microardness value displayed on the digital readout of the microhardness tester. The Vickers microhardness (HV) is calculated based on the following formula:

$$\mathrm{HV} = \frac{2F\sin\frac{136^\circ}{2}}{d^2} \quad \mathrm{HV} = 1.854\frac{F}{d^2} \text{ approximately}$$

where F = load/kg; and d = the mean of the two diagonals of the impression made by the indenter in millimetres. The mean value of the hardness value obtained was calculated to determine the hardness value for each specimen. Differences between the experimental groups were analysed by one way ANOVA and *post hoc* Tukey's test.

Scanning electron microscopy

For the microstructural morphological evaluations by SEM, eight specimens (two for each group) were prepared using the same pressure to condense the material and then stored for 4 days under the same conditions whilst exposed to either pH 4.4, 5.4, 6.4 and 7.4, respectively. To analyse the internal microstructure, the specimens were sectioned into two halves using a disposable surgical scalpel blade No. 15 to initiate the crack. The surfaces were sputter-coated with gold using a Polaron Sputter Coater (Quorum Technologies, Newhaven, UK) and specimens were analysed with an EBT1 (Electron Beam Technology) Scanning Electron Microscope (S.E.M Tech Ltd, Woodbridge, UK). The micrograph images from the SEM analysis showing the qualitative internal microstructure of the set MTA were evaluated at the same depth within the specimens in terms of the presence of microchannels and type of crystal formation.

Results

Microhardness

The results of the microhardness testing are shown in (Fig. 1). The greatest mean surface hardness values (53.19 ± 4.124) were observed following exposure to pH 7.4 with the values decreasing to 14.34 ± 6.477 following exposure to pH 4.4. The difference between these values at the 95% CI (33.39–44.30) was statistically significant ($P < 0.0001$). Mean surface microhardness values of 40.73 ± 3.15 and 37.75 ± 1.75 were observed following exposure to pH 6.4 and 5.4, respectively. Tukey's *post hoc* tests revealed that the difference between the values of specimens exposed to pH 6.4 and pH 5.4 at the 95% CI (−2.78 to 8.75) was not statistically significant. However, the difference between the Vickers microhardness values of other groups was statistically significant ($P < 0.001$).

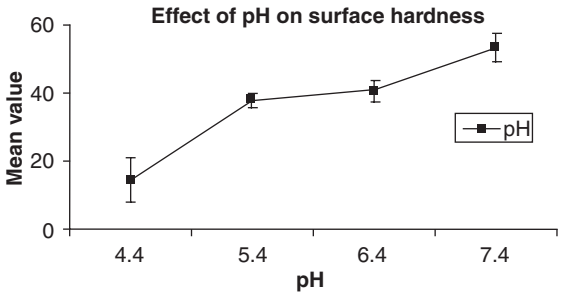

Figure 1 Mean surface microhardness of specimens. The greatest mean surface microhardness values (53.19 ± 4.124) and the lowest microhardness values (14.34 ± 6.477) were observed after exposure to pH 7.4 and pH 4.4, respectively ($P < 0.0001$). The difference between the values of specimens exposed to pH 6.4 and pH 5.4 at the 95% CI (−2.78 to 8.75) were not statistically significant.

SEM analysis

The internal microstructure of all specimens that were exposed to the various pHs revealed a variety of structures such as microchannels (Fig. 2), depressions caused by air bubbles (Fig. 3), pores (Fig. 4), asymmetrical crystalline formations in the form of laminated cross-stratified structures (Fig. 5), bundles of jagged needle like formations (Fig. 6) in a homogeneous matrix that was partially covered by a gel-form structure (Figs 7 and 8). In general, there were no distinct morphological differences between groups. Moreover, it was not possible to score each characteristic and thus compare them quantitatively between groups. However, specimens kept in contact with pH 7.4 butyric acid had distinctive crystalline structures embedded within a more uniform matrix partially covered by colloidal gel that may have been involved in the bonding of the various phases of the cement (Figs 2, 7 and 8). Specimens exposed to more acidic pH had extensive porosity (Fig. 4).

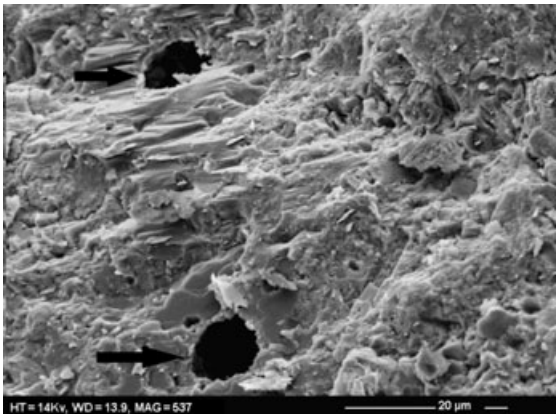

Figure 2 Scanning electron microscopy image of a specimen exposed to pH 7.4. Cross sections of two microchannels can be seen (original magnification ×537).

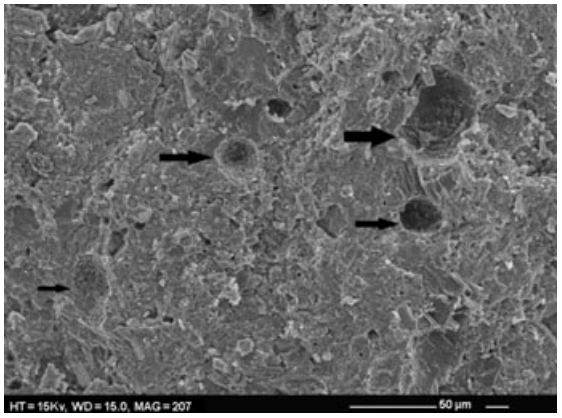

Figure 3 Scanning electron microscopy image of a specimen exposed to pH 6.4. Depressions caused by air bubbles can be seen (original magnification ×207).

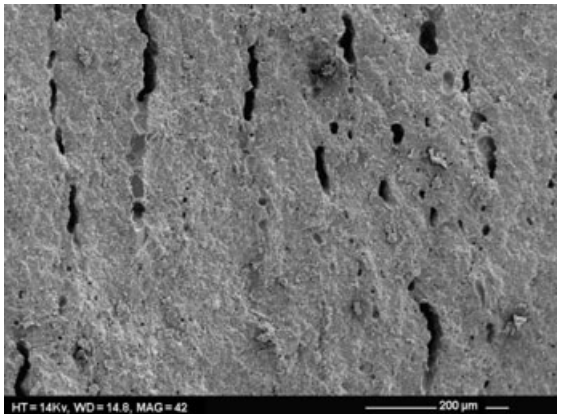

Figure 4 Scanning electron microscopy image of a specimen exposed to pH 4.4. Extensive porosity can be seen (original magnification ×42).

Discussion

Mineral trioxide aggregate has been shown to release soluble fractions (mainly calcium hydroxide) in both the short- (Fridland & Rosado 2003) and long-term (Fridland & Rosado 2005) sufficient to maintain the pH

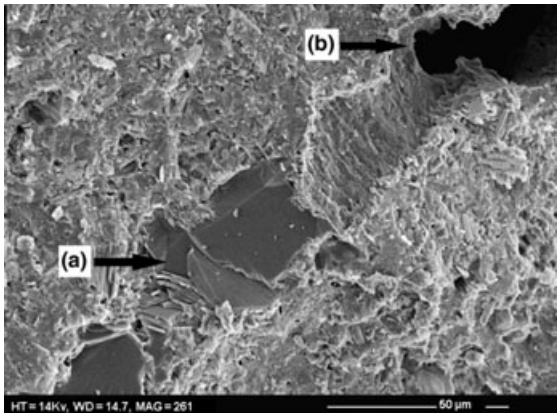

Figure 5 Scanning electron microscopy image of a specimen exposed to pH 5.4. Asymmetrical crystalline formations in the form of laminated cross-stratified structures (a) near the cross section of a microchannel can be seen (b) (original magnification ×261).

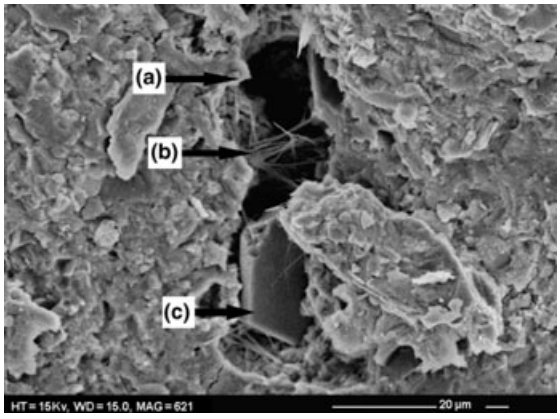

Figure 6 Scanning electron microscopy image of a specimen exposed to pH 4.4. A cross section of a microchannel (a), needle like (b) and laminated (c) crystalline formation can be seen (original magnification ×621).

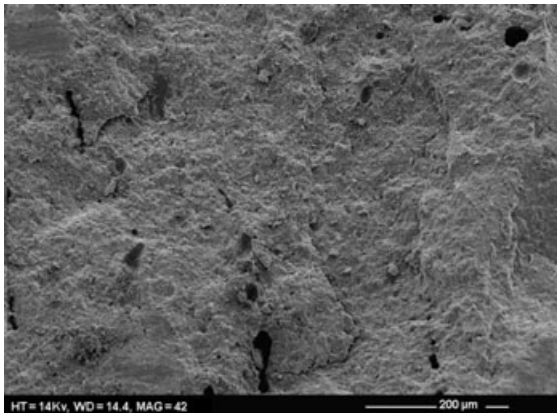

Figure 7 Scanning electron microscopy image of a specimen exposed to pH 7.4. Superficial gel form structure of hydrated cement can be seen (original magnification ×42).

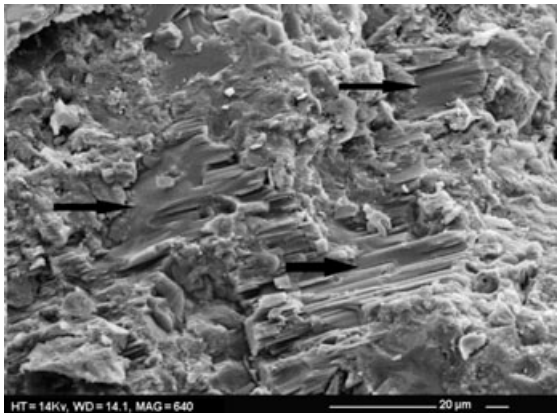

Figure 8 Scanning electron microscopy image of a specimen exposed to pH 7.4. Colloidal gel form structure of hydrated cement that cover crystalline structure can be seen (original magnification ×640).

of the surrounding environment at a high level (pH 11–12). Duarte *et al.* (2003) confirmed that MTA released calcium ions as a result of hydration of calcium oxide, the main component of MTA and Portland cement. Torabinejad *et al.* (1995) reported the pH value of MTA to be between 10.5 and 12.9. The biological properties of MTA, e.g. the ability to induce changes in cellular activity of osteoblasts, have been attributed to its alkalinity (Koh *et al.* 1997).

Santos *et al.* (2005) noted that the pH of samples increased to a peak of 10.39 within the first 24 h after mixing followed by a decrease to 7.72 within 360 h.

It is recommended that MTA be allowed to set untouched for 72 h or longer to decrease the chance of MTA displacement (Song *et al.* 2006, Vanderweele *et al.* 2006). In the present study, the samples were kept in humid situation for 4 days to allow optimum setting.

Within the human body under normal physiologic conditions, any minor change in pH is controlled by the carbonic acid-bicarbonate buffer system and the other pH regulatory systems active in connective tissue (Wray 1988); periodontal tissue is no exception (Azuma 2006). However, in certain clinical applications, MTA is placed in an environment where inflammation may

be present and the surface of the unset material will be exposed to a low pH environment, e.g. when used as a root filling material, as an apical barrier in teeth with open apices or for repair of root canal perforations (Malamed 1997, Torabinejad & Chivian 1999).

Placement of MTA in an inflamed low pH environment may influence its physical and chemical properties. Lee *et al.* (2004) studied the effect of pH on the hydration process of MTA. They immersed and stored MTA samples in solutions of pH 5, 7 and 7.4 for 7 days and reported that their microhardness at low pH was reduced. However, immersion of the material in acid does not simulate clinical conditions as most often only one surface of the MTA will be exposed to an acidic environment. Furthermore, in situations where the initiating and perpetuating factors of an inflammatory process are removed by appropriate treatment, it is possible that the pH of the environment returns to normal in a shorter time period than the 7 days used by Lee *et al.* (2004). Finally, various types of acid have dissimilar effects on the physical and chemical characteristics of Portland cement (Taylor 1997) and might also have different effects on MTA. The type of acid used by Lee *et al.* (2004) was not stated.

Lota *et al.* (2000) demonstrated that considerable changes in the microstructure of hydrated cement occurred in the presence of polyacrylic acid when compared with a control paste. Rai *et al.* (2004) reported that hydration of Portland cement was considerably retarded when malic acid was added. In the presence of tartaric acid, the silicate hydration-phase of Portland cement was retarded strongly (Rai *et al.* 2006). In contrast, Singh *et al.* (1986a) revealed that lactic acid accelerated the hydration of Portland cement by increasing the crystalline character of calcium hydroxide resulting in advanced growth of the hydration products. Different concentrations of citric acid have been shown to have dissimilar effects on Portland cement (Singh *et al.* 1986b). Singh *et al.* (1986b) indicated that 0.1% citric acid accelerated the hydration process of Portland cement whereas concentrations >0.1% retarded hydration. In the present study butyric acid, a by-product of anaerobic bacterial metabolism (Zeikus 1980, Barker 1981, Tonetti *et al.* 1991) was used to simulate the clinical conditions of periradicular infections.

The microhardness of a material is not a measure of a single property. It is influenced substantially by other fundamental properties of the material such as yield strength, tensile strength, modulus of elasticity (Bentz 2007) and crystal structure stability (Gilman 1997). Thus, it can be used as an indicator of the setting process and the overall strength or resistance to deformation when compared with baseline information. It can also indicate the effect of various setting conditions on the overall strength of a material (Blake 1985).

There are two universal types of microhardness test, Vickers and Knoop. The main difference is attributed to the shape of the diamond indenter. The shape of the Vickers diamond indenter is a square pyramid whereas the shape of the Knoop diamond indenter is an elongated pyramid shape. Gong *et al.* (2002), when measuring the silicon nitride ceramic samples, showed that Knoop hardness values were generally lower than the corresponding values for Vickers hardness. However, there is a strong correlation between these two values that may be related to elastic recovery occurring at the indentation.

Measurement of the Vickers microhardness formed the basis of the present investigation. In addition, in an attempt to evaluate the effect of pH on MTA microstructure, a SEM evaluation was also carried out.

Danesh *et al.* (2006) reported that the Vickers microhardness of MTA was 39.99. Lee *et al.* (2004) noted that the microhardness of MTA using the Knoop scale was 51.20. The results of the present study indicated that the Vickers microhardness of MTA was significantly affected by low pH environments. At pH 7.4, the surface microhardness of MTA was 53.19 with the Vickers scale. This value decreased significantly following exposure to pH 6.4, 5.4 and 4.4. This finding is in accordance with Lee *et al.* (2004) who reported that weaker specimens resulted from immersion and storage in a low pH environment. It has been reported that on occasion MTA fails to set, requiring replacement at a further appointment (Shabahang *et al.* 1999, Torabinejad & Chivian 1999, Shabahang & Torabinejad 2000). One reason for this lack of hydration might be the acidic pH of inflamed tissue in contact with the material, including the presence of various acids secreted by bacteria in an infected site (Seltzer & Naidorf 1985, Lardner 2001, Costa Junior *et al.* 2003).

The results reported by Lee *et al.* (2004) and the present study support the observation that MTA does not harden as well in a low pH environment. Moreover, in the SEM analysis, a greater degree of porosity was seen in samples that were exposed to the low pH environments, although it was not possible to grade precisely and objectively the degree of porosity within the context of the SEM examination.

Roy *et al.* (2001) compared the sealing ability of different root-end filling materials whilst exposed to acidic pH. In their study, MTA was placed on a matrix of Calcium Phosphate Cement (CPC) that was claimed to release water and thus have the potential to enhance the hydration of MTA. They reported that the sealing ability of Super EBA, MTA and MTA with CPC matrix was not affected by low pH.

Conclusion

Under the conditions of this study, surface hardness of MTA was impaired in an acidic environment. In terms of the internal microstructure, there were no distinct morphological differences between groups. However, a trend was observed that the more acidic the solution, the more extensive the porosity of the specimens.

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