

Original Article

Long-term effect of acidic pH on the surface microhardness of ProRoot mineral trioxide aggregate, Biodentine, and total fill root repair material putty

Koral Bayraktar, Fatima Betul Basturk, Dilek Turkaydin, Mahir Gunday

Department of Endodontics, Marmara University, Basibuyuk Saglik Yerleskesi, Istanbul, Turkey

ABSTRACT

Background: The purpose of this study was to compare the microhardness values of ProRoot mineral trioxide aggregate (MTA), Biodentine, and total fill root repair material (TF-RRM) Putty at varying pH and times.

Materials and Methods: In this laboratory experiment, materials were mixed and placed in cylinder blocks with internal dimensions of 6 mm × 4 mm. Ten samples of each material were soaked in buffered solutions of butyric acid with 4.4, 5.4, 6.4, and 7.4 pH values and stored at 37°C in 100% humidity. The samples were submitted to the microhardness test at the end of 1 week and then 1 month. Multivariate analysis of variance and Tukey honestly significant difference tests were carried out to compare the mean values at a significance level of $P < 0.05$.

Results: Low pH caused a significant decrease in the microhardness values of all samples. Surface microhardness increased with time ($P < 0.0001$). The microhardness values of Biodentine were significantly greater than those of ProRoot MTA and TF-RRM putty ($P < 0.0001$). The lowest microhardness values were recorded for TF-RRM putty groups regardless of the pH of the environment and the evaluation time.

Conclusion: An acidic environment impaired the surface microhardness of all root repair materials tested. Overall, the mean surface microhardness of TF-RRM Putty was lower than those of ProRoot MTA and Biodentine. Biodentine showed the greatest microhardness values at all pH values, regardless of the evaluation time.

Key Words: Hardness tests, inflammation, mineral trioxide aggregate, root canal filling materials, tricalcium silicate

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Address for correspondence:

Dr. Fatima Betul Basturk,
Department of Endodontics,
Marmara University,
Basibuyuk Saglik
Yerleskesi, 9/3 34854
Maltepe, Istanbul, Turkey.
E-mail: fatimabasturk@
gmail.com

INTRODUCTION

In many clinical applications, reparative materials are placed in contact with inflamed tissues and environments where it may be exposed to a low pH.^[1-3] It is possible that variations in the pH value of host tissues at the time of mineral trioxide aggregate (MTA) placement could affect its physical and chemical

properties.^[1] A low pH might affect setting reactions,^[1] adhesion,^[2] sealing ability,^[3] compressive strength,^[4] and solubility^[5] of MTA. Lee *et al.*^[1] reported that an acidic environment of pH 5 adversely affected both the physical properties and the hydration behavior

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of MTA. Namazikhah *et al.*^[6] found that the surface microhardness of MTA was impaired after soaking in butyric acid that was buffered to a pH of 4.4, 5.4, 6.4, or 7.4 during the setting process.

Even though MTA is the material of choice for root-end repair on the basis of biological principles, the cost and handling properties remain practical obstacles to its use.^[7] Thus, other bioactive endodontic cements such as Biodentine (Septodont, Saint Maur des Faussés, France) and total fill root repair material (TF-RRM) (FKG, La-Chaux-de-Fonds, Switzerland) have been introduced to the endodontic field to overcome these limitations.

Biodentine is recommended for use as a dentine substitute under resin composite restorations and an endodontic repair material because of its enhanced compressive strength,^[8] push-out bond strength,^[9] biocompatibility,^[10] bioactivity, and biomineralization properties.^[11]

TF-RRM, which is known as EndoSequence root repair material (RRM) (Brasseler, Savannah, GA, USA) in The United States and iRoot BP Plus RRM (Innovative Bioceramix, Vancouver, Canada) in Canada, is dispensed in premixed, ready-to-use injectable, or putty form. According to the manufacturer, the main compositions of both TF-RRM formulations are the same (calcium silicates, zirconium oxide, tantalum pentoxide, calcium phosphate monobasic, and filler agents), differing only in particle size. TF-RRM, especially putty, is marketed as a ready to use material with a minimum of waste.^[12] Unlike MTA, the radiopacifiers used in TF-RRM are tantalum and zirconium oxide instead of bismuth oxide, to overcome tooth discoloration.^[13]

With the increasing number of available bioactive endodontic materials, it is important to investigate their physical and mechanical performances to give insight for various clinical applications. It is likely that the exposure of bioactive endodontic cements to an acidic environment affects the superficial physical and chemical properties of these products, which play a critical role in their biological behaviors.^[13] However, there is limited research about the effect of acidic environment to the microhardness of TF-RRM. Thus, the purpose of this comparative study was to evaluate the surface microhardness of ProRoot MTA (Dentsply, Maillefer, Switzerland), Biodentine, and TF-RRM Putty, following exposure to a range of acidic environments during short-and long-term

hydration. The null hypothesis was that the surface microhardness values of tested materials would not be affected significantly when they were exposed to an acidic environment.

MATERIALS AND METHODS

Tooth colored ProRoot MTA (Dentsply, Maillefer, Switzerland), Biodentine (Septodont, Saint Maur des Faussés, France), and TF-RRM Putty (FKG, La-Chaux-de-Fonds, Switzerland) were investigated in this laboratory experiment. The instruments and the test materials were conditioned at 23°C ± 1°C in the laboratory for 1 h before use. ProRoot MTA and Biodentine were mixed according to the manufacturers' instructions. TF-RRM putty was in a ready to use form. All tested materials were transferred to polylactic acid cylindrical molds with internal dimensions of 4 mm ± 0.1 mm high and 6 mm ± 0.1 mm diameter, which were prepared using a three-dimensional-printing technique (3Dortgen, Istanbul, Turkey).

The methodology of previous studies was followed by Namazikhah *et al.*, Bolhari *et al.* and Wang *et al.*^[6,14,15] In our study, an attempt was made to mimic a clinical situation by exposing three different root repair materials (namely, ProRoot MTA, Biodentine and TFRRM-Putty) to butyric acid at pH values of 4.4, 5.4, 6.4, and 7.4.

Ten samples of each material were placed on pieces of gauze soaked in buffered solutions of butyric acid. To make sure that the pH of the experimental set-up was consistent throughout the experiment, the acid-soaked pieces of gauze were replenished every 24 h. All specimens were then covered by moist gauze and stored at 37°C in 100% humidity. By the end of 1 week, and then 1 month, the specimens were wet polished at room temperature using silicon carbide-based sandpapers of 600-grit and 1200-grit particle size (The MetaServ 250, Buehler, Germany) for microhardness testing.

The Vickers microhardness test of each specimen was performed using a Micro-Vickers Hardness Tester Model 401MVD (WolpertWilson, Wolpert Wilson Instruments, Aachen, Germany) and a square-based pyramid-shaped diamond indenter with a full load of 50 g load with a dwell time of 10 s which formed 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°. Four indentations were made on each specimen and an average was calculated. The Vickers microhardness value was displayed on the digital read-out of the microhardness tester. The results were recorded after a total of 1 week, then 1 month in buffered solutions of butyric acid.

Multivariate analysis of variance and Tukey honestly significant difference tests were carried out by NCSS (Number Cruncher Statistical System, 2007 Statistical Software, Utah, USA) to compare the mean values for surface microhardness at a significance level of $P < 0.05$.

RESULTS

The means and standard deviations of the surface microhardness of the experimental groups regarding the time of exposure are shown in Table 1.

There were significant differences between the groups ($P \leq 0.001$). Overall, the microhardness values of Biodentine were significantly greater than those of ProRoot MTA and TF-RRM Putty ($P \leq 0.0001$) at each time interval. The mean microhardness values of the pH 7.4 specimens were significantly greater than the pH 4.4 and 5.4 groups. The mean microhardness of the pH 5.4 samples was not significantly different from the pH 6.4 samples ($P = 0.144$). Regardless of the evaluation time, the pH of 4.4 specimens' microhardness values were the weakest of all the samples.

Table 1: The means and standard deviations of the surface microhardness of the experimental groups regarding the time of exposure

Material/pH	1 week (HV)	1 month (HV)	P
ProRoot MTA			
pH 4.4	36.21±4.66	39.7±5.44	0.0001
pH 5.4	44.7±2.82	50.6±4.06	0.0001
pH 6.4	51.64±4.78	57.7±4.92	0.0001
pH 7.4	58.62±3.46	66.3±5.42	0.0001
Biodentine			
pH 4.4	59.53±3.31	63±3.92	0.0001
pH 5.4	68.91±4.88	71.3±3.95	0.001
pH 6.4	72.4±3.69	74.7±3.5	0.0001
pH 7.4	77.09±4.07	79.8±3.97	0.077
TF-RRM Putty			
pH 4.4	30.47±1.26	37.9±1.2	0.0001
pH 5.4	34.16±3.94	41.1±3.54	0.0001
pH 6.4	37.81±4.34	43.4±4.58	0.0001
pH 7.4	45.15±4.12	48.8±3.94	0.0001

MTA: Mineral trioxide aggregate; TF-RRM: Total Fill Root Repair Material; HV: Vickers Hardness

The mean microhardness values for all tested materials after 1 month were significantly greater than those after 1 week ($P \leq 0.0001$) [Figure 1], with the exception being the Biodentine groups which were exposed to a pH value of 7.4. The difference was not significant for that group ($P > 0.05$). At 1 week, the microhardness values of ProRoot MTA were significantly greater than those of TF-RRM Putty at all pH values ($P \leq 0.0001$).

DISCUSSION

Acidic pH may affect the properties of dental materials, which are routinely placed in environments that may be inflamed.^[16] Inflammation in the pulpal and periapical region typically lowers the pH of the surrounding tissue to an acidic level.^[1,16] Furthermore, the acidic environment may be generated by bacteria and their by-products in the root canals. Consequently, the root repair materials may come in contact with inflammatory tissue when used for perforation repair or retrograde filling.

A low pH is an important factor that can cause local anesthesia failure,^[17] as well as a reduction in the microhardness of the root repair materials,^[15] which may, in turn, cause prolonged healing or treatment failure.

Hence, it is worthwhile to evaluate changes in the mechanical properties of the material after immersion in a physiologic solution with different pH values.^[18] The butyric acid, which is a by-product of anaerobic bacteria, was used in this study to simulate the clinical environmental conditions of a periradicular infection.^[6] We may conclude that the more acidic the solution, the more decrease in the microhardness of root repair materials after soaking in butyric acid that

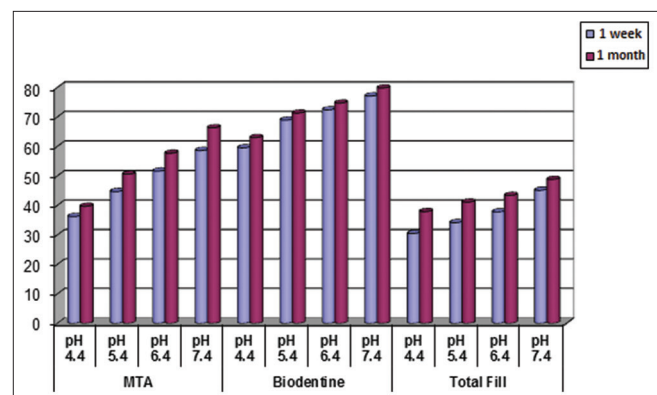


Figure 1: The schematic representation of surface microhardness values of all groups.

was buffered to a pH of 4.4, 5.4, 6.4, or 7.4 during the setting process. Therefore, our study rejected the null hypothesis that the acidic environment would not affect the surface microhardness of the selected root repair materials.

In our study, the mean Vickers surface microhardness values at pH 6.4 and 7.4 for each material were not statistically significant. Given that the mean pH of the pus is 6.68,^[16] the materials we tested would not significantly deteriorate in an environment with an average pH of pus. However, pH values lower than 5.4 resulted in significant changes in the microhardness values of bioactive endodontic materials. The ideal pH for MTA hydration is 7.00.^[19] To simulate an extreme clinical condition, the pH 4.4 condition was selected in our study.

Previous studies by Namazikhah *et al.* and Elnaghy^[6,20] showed similar microhardness variations at different pH levels, but with lower values than those in our study. A possible reason for this variation might be the differences in the evaluation time. Furthermore, Lee *et al.*^[1] compared the surface microhardness of MTA samples under various physiological environments. They found that an acidic environment of pH 5 adversely affected the surface microhardness values compared with pH 7. These results were in accordance with our findings. Because of the decrease in the microhardness of the specimens in a low pH environment, caution should be taken on repairing sites in contact with inflamed tissues or acidic chemicals in the pulp chamber. Lee *et al.*^[1] suggested that treating the inflammation with an alkaline medication, such as Ca(OH)₂, may neutralize the environmental pH before applying MTA on an inflamed area. It was also recommended to postpone acid-etching procedures for at least 96 h after mixing MTA.^[21]

Microhardness was used as an indicator on the overall strength and the setting reaction of the material. In instances of incomplete setting, physical properties of MTA might be adversely affected.^[1,22]

If a problem in the hydration process of the material occurs, it would reveal itself as a decrease in the microhardness values. In the present study, surface microhardness increased with the increase in the evaluation time to 1 month. Shie *et al.*^[18] reported that the strength of MTA significantly increased by an approximately two-fold factor after 7-days period compared with 0 day. They suggested that the

immersion-induced increase in mechanical strength might be attributable to the more complete hardening during immersion.^[18] Kayahan *et al.*^[21] also observed a trend for the compressive strength and surface microhardness of specimens to increase with time which corresponds with our findings.

One of the limitations of this study was that the specimens were polished prior to the microhardness testing to achieve a smoother surface for a more consistent measurement of the indentations.^[21] However, the polishing procedure removes the most superficial layer which was directly exposed to the acid environment.^[15] In our study, all specimens underwent the same polishing procedure. Therefore, the influence of polishing on the microhardness results can be expected to be consistent.

Regardless of the pH of the environment exposed, the mean surface microhardness of TF-RRM Putty was lower than those of ProRoot MTA and Biodentine. Particle size and shape distribution might improve calcium silicate-based materials' handling characteristics.^[23] However, while some of the properties may be improved, others may be even lost. The thickening agents and the setting time accelerator included in the composition of TF-RRM might interfere with the hydration reaction of the cement, especially at low pH values when the crystalline structures of the hydrated cement appeared less cohesive.^[1,24] This may be the reason for the decreased microhardness values. However, further research is required to confirm this hypothesis.

In the present study, Biodentine showed the greatest microhardness values at all pH values, regardless of the evaluation time. Even though the exact mechanism for the morphologic alterations is unknown, exposure to different pH values results in morphologic changes of the Biodentine in a manner that varied from the ProRoot MTA^[20] and TF-RRM Putty.

CONCLUSION

An acidic environment impaired the surface microhardness of all root repair materials tested. Surface microhardness increased with time. Therefore, the null hypothesis was rejected. However, Biodentine seems more appropriate for use when exposed to a low pH environment compared with ProRoot MTA and TF-RRM Putty.

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Conflict of interest

The authors declare that they have no conflict of interest related to this study.

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