

# Comparative Study Regarding the pH Influence on Surface Microhardness of Two Reparative Materials Used in Endodontic Treatment in Prosthetic Purpose

LIANA AMINOV<sup>1</sup>, MARIA VATAMAN<sup>1</sup>, MADALINA MOCANU<sup>3</sup>, CRISTINA ELENA IANCU<sup>4</sup>, ANISIA IULIANA ALEXA<sup>5</sup>,  
DANA CRISTIANA MAXIM<sup>2\*</sup>, LAURA ELISABETA CHECHERITA<sup>1\*</sup>

<sup>1</sup> University of Medicine and Pharmacy „Gr. T. Popa” Iasi, Department of Odontology-Periodontology and Fixed Prosthesis, 16 Universitatii Str., 700115, Iasi, Romania

<sup>2</sup> University of Medicine and Pharmacy „Gr. T. Popa” Iasi, Department of Surgical Sciences, 16 Universitatii Str., 700115, Iasi, Romania

<sup>3</sup> University of Medicine and Pharmacy „Gr. T. Popa” Iasi, Department of Normal and pathological Physiology, 16 Universitatii Str., 700115, Iasi, Romania

<sup>4</sup> University of Medicine and Pharmacy „Gr. T. Popa” Iasi, Department of Pharmacognosy, 16 Universitatii Str., 700115, Iasi, Romania

<sup>5</sup> University of Medicine and Pharmacy „Gr. T. Popa” Iasi, Department of Hystology, 16 Universitatii Str., 700115, Iasi, Romania

*The irrigation solutions used in endodontic therapy have different pH values and different chemical properties that have sometimes been found to adversely affect the physical and chemical characteristics of repairing materials. These materials are used mainly in areas of inflamed tissue, with a lower pH. The aim of the study was to evaluate the changes in the hardness of two reparative dental materials depending on pH variations and to determine which of the additives they are combined with gives them greater stability to pH variations. The changes in surface microhardness (Vickers microhardness) of two repairing materials: Grey MTA (Dentsply Tulsa Dental, USA) and BioAggregate (Innovative BioCeramix Inc., Vancouver), mixed with four different vehicles (distilled water, physiological saline, lidocaine and calcium chloride), subsequently subject to different environmental pH value, were assessed. The analysis of the average surface hardness showed a significant increase in hardness at high pH (pH = 7) and higher values for BioAggregate as compared with MTA. Ph variations of the environment in which biomaterials are setting reduce their microhardness and surface resistance, and this was more significant when the two materials were combined with lidocaine and distilled water.*

*Keywords: endodontic treatments, reparative systems, biomaterials, surface microhardness, low pH, stomatognathic system homeostasis*

During endodontic therapy, irrigating solutions are used in different concentrations and for different time periods, depending on several factors, such as: lesion diagnosis, associated symptoms, stages of treatment, presence of allergies and possibility of ensuring a good isolation. To remove the organic material, microorganisms and their toxins, many types of irrigating solutions have been proposed, which, together with the mechanical action of instruments can achieve a satisfactory debridement and antiseptics of root canals. [1-3].

MTA is a tricalcium mineral complex and is considered to be a potentially ideal material for perforation repair, retrograde fillings, apexifications and vital pulp therapy [4, 5]. When MTA is dissolved in water, calcium ions are released and precipitate with silica gel which solidify in less than 4 h, reaching a high resistance to compression [6].

Following final irrigation with a chemical solution, part of the irrigant may remain within the canal area, thus affecting the properties of MTA. Witherspoon et al. [7] evaluated the effect of EDTA and BioPure MTAD on the rough surface of MTA and found that BioPure MTAD increases its roughness. Yan et al. [8] evaluated the effects of Na hypochlorite (5.25%), CHX (2%) and Glyde File Prep on in vitro bond strengths of MTA-dentin and suggested that Glyde File Prep may adversely affect them.

MTA contains 50% to 75% (by weight) of calcium oxide and 15% -25% silicon dioxide. Adding water, the cement hydrates and forms a silicate hydrate gel. The physico-

chemical basis of MTA is attributed to the production of hydroxyapatite when the calcium ions removed by MTA come in contact with tissue fluid. This release of calcium ions promotes an alkaline pH. Therefore, MTA was used to repair root perforations, as apical filling material, for pulp capping, and pulpotomy procedures [9]. In addition, given its sealing ability, it has been suggested as an apical sealant in the treatment of open apex teeth and pulp necrosis [10].

The hydration rate is characteristic to the cement setting process [11-13], when sufficient water intake is required. Besides the positive aspects of its use, the MTA also has some drawbacks, such as the relatively long setting time, which favours its disintegration and dislodgement. Its granular consistency makes it difficult to insert in cavities [14]. In many clinical applications, MTA is placed in an environment that is inflamed and has a low pH [15]. Torabinejad et al. [16] demonstrated that initially MTA has a pH of 10.2, which increases 3 h after mixing to 12.5. Variations in pH values of host tissue response are likely in the case of pre-existing pathological conditions, which affect its physical and chemical properties. Homeostasis specific stomatognathic system is achieved by its morphological and functional balance between the components through specific mechanisms [17]. Recently, several studies were conducted to improve the physical and chemical properties of MTA, new additives usable in patients are studied to solve the clinical deficiencies [18]. Thus, MTA combined with other common additives may increase its compressive strength [19].

\* email: checherita.laura@gmail.ro; danamaxim@yahoo.com

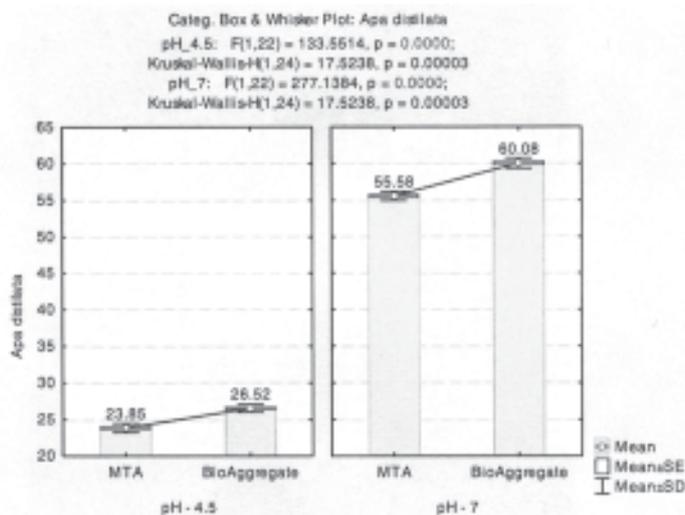


Fig. 1. Statistical indicators of microhardness (distilled water) in relation with the used biomaterial and pH value

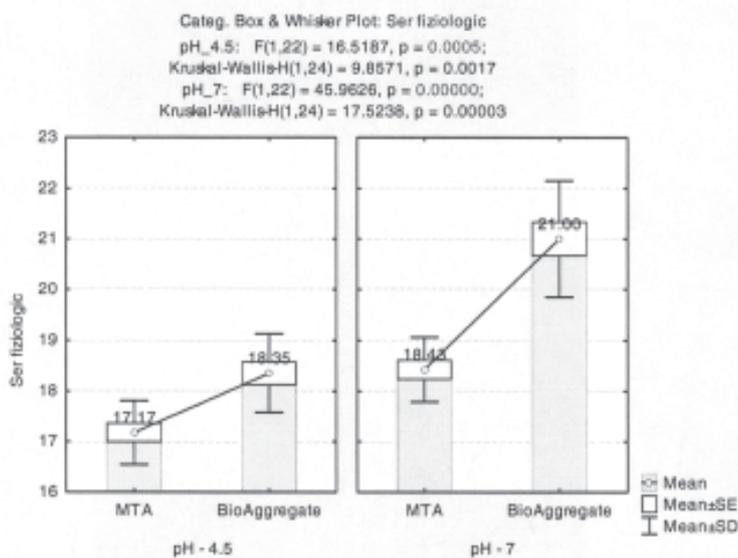


Fig. 2. Statistical indicators of microhardness (saline solution) in relation with the used biomaterial and pH value

DiaRoot BioAggregate, another root repair material, is a biocompatible pure white powder containing ceramic nano-particle. Upon mixing DiaRoot with BioA-liquid, the hydrophilic BioAggregate powder forms a hermetic seal inside the root canal. It is also characterized by antibacterial effectiveness and ease of material manipulations. The liquid-BioA-liquid (1 vial x 0.38mL) is the exact amount required for 1.0g powder. Excess Liquid BioA may affect setting time and material properties.

The literature indicates that humidity affects various physical properties of MTA such as sealing ability, hardening time and elasticity [20, 21]. Various previous papers concluded that the sealing ability of MTA in an aqueous environment may be compromised in the first 72 h due to the increased solubility of the material [22].

The aim of this study was the comparative evaluation of changes in surface microhardness (Vickers microhardness) of two root repair materials: Grey MTA (Dentsply Tulsa Dental, USA) and BioAggregate (Innovative BioCeramix Inc., Vancouver, Canada) mixed with 4 different vehicles (distilled water, physiological saline, lidocaine, and calcium chloride) and subsequently subject to different pH values of the setting environment.

### Experimental part

Microhardness testing procedure involves a series of easy tasks using a diamond indenter to make an indentation that is measured and converted to a hardness value. It is very useful for testing a wide range of materials, as long as the test samples are carefully prepared. Usually

loads are very light, ranging from a few grams to one or several kilograms. Methods for hardness testing are used for metals, ceramics, composites, various cements - almost any material.

As vehicles for each of the two study materials we chose: distilled water (the original liquid with which the two materials are mixed according to the instructions), an anesthetic commonly used in practice (lidocaine), saline solution, and calcium chloride 2% ( $\text{CaCl}_2$ ), available in the dental office. The materials were mixed according to manufacturer's instructions. Each MTA sample was mixed with the recommended amount of water and the same amount of saline solution, lidocaine and  $\text{CaCl}_2$ . Mixed materials were weighed and placed in polycarbonate tubes with inner diameter of 6 mm and a height of 5 mm.

The samples were divided into 2 groups: GR1 (MTA) and GR2 (BioAggregate), eight specimens of each liquid mixing vehicle being obtained under each group (a total of 32 samples per group). Specimens were then subject to a constant vertical force using an amalgam condenser with inner diameter similar to that of the polycarbonate tubes. A wet cotton pellet was placed both over the openings of MTA and BioAggregate containing polycarbonate tubes to ensure a moist environment, and the specimens were stored at room temperature ( $30^\circ\text{C}$ ), covered, for three days. Each of the eight specimens of each liquid vehicle were divided into two: in four samples a pellet soaked in acetic acid  $\text{pH} = 4.5$  and in the remaining four samples a pellet soaked in neutral aqueous solution,  $\text{pH} = 7$  were placed at the bottom of the tube. One vial was used as control.

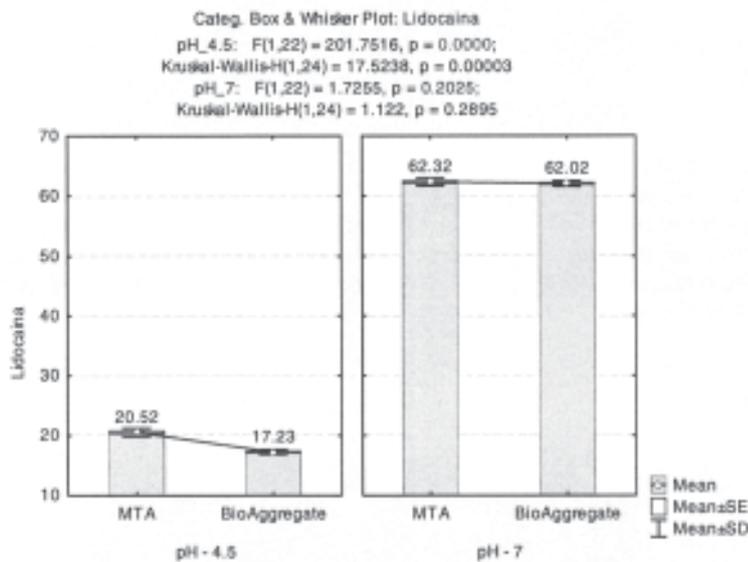


Fig. 3. Statistical indicators of microhardness (lidocaine) in relation with the used biomaterial and pH value

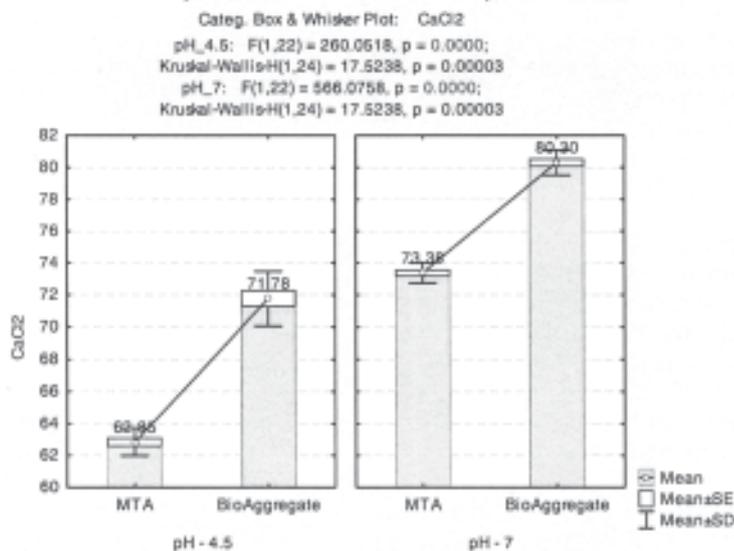


Fig. 4. Statistical indicators of microhardness (calcium chloride) in relation with the used biomaterial and pH value

After 3 days, the samples were removed from vials. The surface exposed to acid of each specimen was then wet polished at room temperature using minimum hand pressure and silicon carbide sand paper of different particle size (Standard ANSI grit 600, 800 and 1200) to obtain a surface smooth and facilitate testing. Then, the polished specimens were gently washed under light pressure distilled water to remove surface debris and then gently air dried.

Vickers microhardness of each specimen was measured using the hardness tester EmcoTEST M1C 010-D model with sample holder 6-fold and a square based diamond with a with a full load of 50 g for 5 s at room temperature, which produced quadrangle depressions with two equal orthogonal diagonals. Then, Vickers microhardness was read and recorded for each specimen. The results were processed by means of a system using heavy-load XY coordinates/tables with integral highest-precision highly-focused optical encoders. Data were processed using C.A.M.S. Testing Sysem/Newage C.A.M.S with automatic data storage system. For statistical analysis, One-Way ANOVA and Tukey Post-Hoc analyzed the differences between experimental groups after the calculation of mean  $\pm$  standard deviation [22].

## Results and discussions

The mean microhardness values obtained in each group with their standard deviation at 95% confidence intervals are shown in tables 1 and 2 and graphically in figures 1 - 4. The highest value among all groups and

subgroups was recorded in the CaCl<sub>2</sub> group at pH = 7. A lower mean was obtained in the saline group. The difference between the means was analyzed by One-Way ANOVA and showed that the difference between the means was statistically significant at pH = 7 and 4.5.

Correlational analysis showed a slightly higher increase of microhardness value for BioAggregate when compared with MTA ( $r = 0.99$  vs.  $R = 0.98$ ). Also the results showed a significant correlation between pH and microhardness values when distilled water was used as additive.

Correlational analysis demonstrated a greater increase of microhardness value for BioAggregate when compared with the increase recorded for MTA ( $r = 0.80$  vs.  $R = 0.67$ ). Also, the results demonstrated a significant correlation between pH and microhardness values when saline solution was used as additive.

Correlational analysis showed a slightly higher increase of microhardness value for BioAggregate compared with the increase recorded for MTA ( $r = 0.99$  vs.  $R = 0.98$ ). Also, the results demonstrated a significant correlation between pH and microhardness values when lidocaine was used as additive.

Correlational analysis demonstrated a higher increase of microhardness value for MTA as compared with BioAggregate ( $r = 0.97$  vs.  $R = 0.95$ ). Also, the results demonstrated a significant correlation between pH and microhardness values when CaCl<sub>2</sub> was used as additive.

Analysis of the mean surface hardness values of the two materials used as repair materials in endodontics prepared by mixing with various additives showed a

Table 1  
MEAN VALUES OBTAINED FOR MTA (MPa)

Additives	Surface microhardness (Mpa)	MTA
	pH = 4,5 Mean ± Standard deviation	pH = 7 Mean ± Standard deviation
Distilled water	23.85±0.61	55.58±0.62
Saline solution	17.17±0.63	18.43±0.64
Lidocaine	20.52±0.70	62.33±0.64
Calcium chloride	62.85±0.88	73.38±0.63

Table 2  
MEAN VALUES OBTAINED FOR BIOAGGREGATE ( BA ) (MPa)

Additives	Surface microhardness (MPa)	BioAggregate
	pH = 4.5 Mean ± Standard deviation	pH = 7 Mean ± Standard deviation
Distilled water	26.52±0.52	60.08±0.70
Saline solution	18.35±0.78	21.00±1.15
Lidocaine	17.23±0.40	62.02±0.47
Calcium chloride	71.78±1.70	80.30±0.79

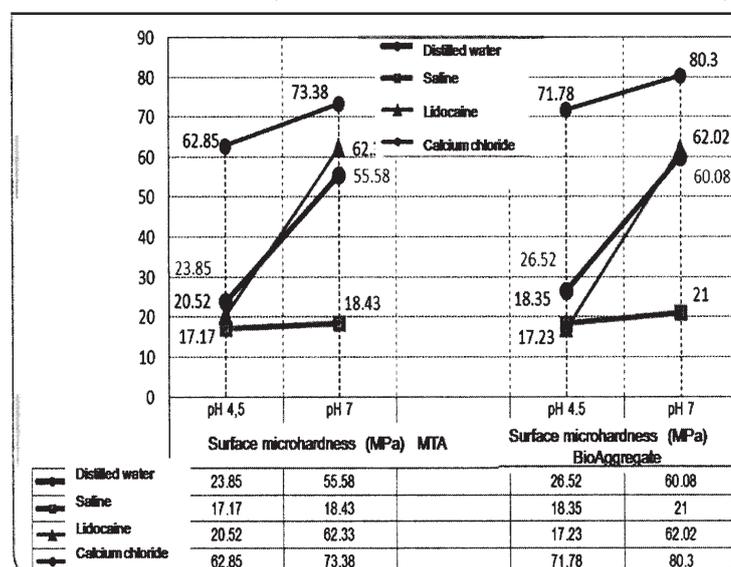


Fig.5. Mean values for MTA and BioAggregate ( BA ) (MPa)

significant increase in hardness in case of high pH (pH = 7) and also higher values for BioAggregate as compared with MTA (fig. 5)

Endodontic therapy includes the use of some irrigating solution with different pH values and chemical properties that have sometimes been found to adversely affect the physical and chemical properties of the used materials. In addition, the studied materials are mainly used in areas of inflamed tissue, that is of lower pH. For these reasons we aimed at evaluating the changes in the hardness of materials in relation with pH variations, and which of the additives they are mixed with give them greater stability to pH variations. MTA in combination with CaCl<sub>2</sub> was used because this solution can release calcium ions and was confirmed not to be toxic to human cells in vitro [17].

It was also noticed that a CaCl<sub>2</sub> concentration higher than 2% affects the cement, increasing the risk of setting contraction and decreasing the final strength. At pH 4,5, MTA in combination with saline solution was not completely set even after the three days of the experiment and had the lowest Vickers microhardness value. In conclusion, surface hardness of both MTA and BioAggregate mixed with 2% CaCl<sub>2</sub> was found not to be significantly affected by an acid environment, the differences between them being minimal.

## Conclusions

Low pH adversely affects the physical properties of both MTA and BioAggregate, decreasing their surface hardness. According to this study it can be concluded that pH changes in the environment in which these biomaterials set reduce surface strength and microhardness, and this decrease is more significant when the two materials are mixed with lidocaine and distilled water.

By combining the two powder types with 2% CaCl<sub>2</sub> there was a significant increase in surface hardness in both cases and an increased strength to environmental pH lowering, the parameter investigated in this study, Vickers microhardness, remaining almost unchanged.

## References

1. BUI, T.B., BAUMGARTNER, J.C., MITCHELL, J.C., J. Endod., **34**, 2008, p. 181.
2. DE-DEUS, G., SOARES, J., LEAL, F., LUNA, A.S., FIDEL, S., J. Endod., **34**, 2008, p. 459.
3. BARBIZAM, J.V.B., FARINIUK, L.F., MARCHESAN, M.A., PECORA, J.D., J. Endod., **28**, 2002, p. 365.
4. HOLDEN, D.T., SCHWARTZ, S.A., KIRKPATRICK, T.C., SCHINDLER, W.G., J. Endod., **34**, 2008, p. 812.
5. SONMEZ, D., SARI, S., CETINBAS, T.A., J. Endod., **34**, 2008, p. 950.
6. PACE, R., GIULIANI, V., PAGAVINO, G., J. Endod. **34**, 2008, p. 1130.

7. WITHERSPOON, D.E., SMALL, J.C., REGAN, J.D., NUNN, M., J. Endod., **34**, 2008, p. 1171.
8. YAN, P., PENG, B., FAN, B., FAN, M., BIAZ, Z., J. Endod., **32**, 2006, p. 58.
9. NEKOOFAR, M.H., ADUSEI, G., SHEYKHREZAE, M.S., HAYES, S.J., BRYANT, S.T., DUMMER, P.M., Int. Endod. J., **40**, 2007, p. 453.
10. SHABAHANG, S., TORABINEJAD, M., Pract. Periodontics Aesthet. Dent., **12**, 2000, p. 315.
11. LEE, Y.L., LEE, B.S., LIN, F.H., YUN LIN, A., LAN, W.H., Biomaterials, **25**, 2004, p. 787.
12. BORTUN, C.M., CERNESCU, A., ARDELEAN, L., HANGANU, L.C., Mat. Plast., **49**, no. 1, 2012, p. 5.
13. HANGANU, S.C., ARMENCIA, A.O., GRIGORAS, S., HANGANU, L.C., VIZUREANU, P., Mat. Plast., **47**, no. 3, 2010, p. 375.
14. MOHAN, N., MISHRA, L., RAVISHANKER, C., SUBBA, V., Int. J. of Dental Science, **8**, (2), 2010, p. 112.
15. WALKER, M.P., DILIBERTO, A., LEE, C., J. Endod., **32**, 2006, p.334.
16. TORABINEJAD, M., CHIVIAN, N., J. Endod., **25**, 1999, p.197.
17. CHECHERITA, L., FORNA, N.C., STAMATIN, O., COBZARU, R, LEON, M.M., CIOLOCA, D., Rev. Chim. (Bucharest), **64**, (10), 2013, p. 1172.
18. SARKAR, N.K., CAICEDO, R., RITWIK, P., MOISEYEVA, R., KAWASHIMA, I., J. Endod., **31**, 2005, p. 97.
19. JUMANCA, D., GALUSCAN, A., PODARIU, A.C., ARDELEAN, L., RUSU, L.C., Rev. Chim. (Bucharest), **63**, , no. 8, 2012, p. 783.
20. ROMINU, R.O., NEGRUTIU, M., RUSU, L.C., ARDELEAN, L; TUDOR, A., Rev. Chim. (Bucharest), **63**, no. 3, 2012, p.265
21. HANGANU, S.C., ARMENCIA, A.O., MURARIU, A.M., GRIGORAS, S., HANGANU, L.C., Mat. Plast., **50**, no. 2, 2013, p. 119.
22. CERNAT, R.I., MOCANU, R.D., POPA, E., SANDU, I., OLARIU, R.I., ARSERNE, C., Rev. Chim. (Bucharest), **61**, no. 11, 2010, p. 1130

---

Manuscript received: 19.12.2013