



## Effect of Adding Nano Size Silica on Setting Time and Porosity of Mineral Trioxide Aggregate

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### ABSTRACT

**Introduction:** The aim of this study was to evaluate the effect of addition of nano-silica (SiO<sub>2</sub>) to mineral trioxide aggregate (MTA) on its setting time and porosity. **Methods and Materials:** The concentration 8% of nano-silica were prepared and added to the MTA powder. After mixing with water the setting time and porosity were evaluated and compared with pure MTA. Statistical analysis was performed using the *t*-test. The level of significance was set at 0.001. **Results:** The mean setting time of MTA+8% nano-silica (9.8±0.78) was significantly lower than MTA (23.3±2.16) (*P*<0.001). Also the mean porosity by imbibition method in MTA+8% nano-silica (23.49±0.48) was significantly higher than MTA (15.69±2.10) (*P*<0.001). There was no significant difference in mean porosity by scanning electron microscope (SEM) method in MTA+8% nano-silica (31.26±10.73) and MTA (32.74±5.26) (*P*>0.001). **Conclusion:** This *in vitro* study showed us an addition of 8% of nano-silica to MTA reduced the setting time. Although evaluation by imbibition test showed increasing of porosity in nano-silica MTA compared with pure MTA.

**Keywords:** Mineral Trioxide Aggregate; Nano-silica; Porosity; Setting Time

### Introduction

Although mineral trioxide aggregate (MTA) was initially used as a root-end filling material [1], it then widely used in all fields of endodontics [2]. Before that time restorative materials used in endodontics, did not have ideal properties [3]. Recently MTA has been used for pulp capping, apexogenesis, pulpotomy, repair of root perforations, apical barrier formation in teeth with open apices, and as a root canal filling material. MTA has also been considered as a bioactive material [4-7] that is hard tissue conductive, hard tissue inductive, and biocompatible [8].

Composition of MTA consists of tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>, C<sub>3</sub>S), dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>), tricalcium aluminates (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, C<sub>3</sub>A) and tetracalcium aluminoferrite. Moreover, bismuth oxide is added for radiopacity and a little amounts of mineral oxides such as SiO<sub>2</sub>, CaO, MgO, K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. In

other words, MTA is made of refined Portland cement [9, 10].

When mixed with water, MTA forms a colloidal gel that solidifies into a hard structure also in the presence of moisture. MTA is a bioactive material able to form apatite on its surface when in presence of phosphate [11, 12]. MTA also releases some of its components in phosphate-buffered saline, which promotes a bio mineralization process [13].

Previous studies have shown that MTA has better sealing ability and biocompatibility *versus* traditional dental materials [1, 14, 15]. However, the long setting time (3-4 h) is one of the major defects of this material [8, 9]. As a result, the studies on change in MTA in order to decrease setting time, with same mechanical properties, is underway. Several studies have evaluated and suggested different strategies to improve the properties of MTA. One strategy is to incorporate ingredients, such as disodium hydrogen phosphate, into MTA to decrease its setting time [16].

The amorphous or glassy silica (SiO<sub>2</sub>), which is the major component of a pozzolan, reacts with calcium hydroxide to form front calcium silicate hydration. The rate of the pozzolanic reaction is proportional to the amount of surface area available for the reaction. Therefore, it is plausible to add nano-silica (NS) particles to make high-performance concrete. [17]

In recent years, increasingly NS is noticed as a mineral compound for cements. Nanoscale silica reacts with calcium hydroxide crystals, which are in the interfacial transition zone (ITZ) between hardened cement paste and aggregates, and create calcium silicate hydrate (C-S-H) gel [18]. NS particles also can act as nucleus to bond strongly with cement hydrates [19].

The results of studies with scanning electron microscope (SEM) showed that NS behaves as filler and activator to improve microstructure and promote pozzolanic reaction [17].

The pozzolanic reaction is the chemical reaction that occurs in Portland cement containing pozzolans. At the basis of the pozzolanic reaction stands a simple acid-base reaction between calcium hydroxide, also known as portlandite, or (Ca(OH)<sub>2</sub>), and silicic acid (H<sub>4</sub>SiO<sub>4</sub> or Si(OH)<sub>4</sub>) [20].

The aim of this study was to compare initial setting time (the initial setting time of the cement was considered as the time between the onset of mixture and the moment when the marks of light needles could not be observed on the cement surface [21]) and porosity of MTA+ NS with those of pure MTA.

**Table 1.** Setting time of MTA and MTA+NS Mixed with Water

Group	Setting time [Mean(SD)]
MTA	23.3(2.16)
MTA+NS	9.8(0.78)

**Table 2.** Porosity (by SEM method) of MTA and MTA+NS Mixed with Water

Group	Porosity [Mean(SD)]
MTA	32.74(5.26)
MTA+NS	31.26(10.73)

**Table 3.** Porosity (by imbibition method) of MTA and MTA+NS Mixed with Water

Group	Porosity [Mean(SD)]
MTA	15.69(2.10)
MTA+NS	23.49(0.48)

## Materials and Methods

In this *in vitro* study, 8% NS (Huaxuan, China) was added to the MTA powder using Ball Mill machine (Noah, Guangdong, China). Materials were divided into the following groups: group 1 (control): MTA (Angelus, Londrina, PR, Brazil), group 2: MTA+NS. According to manufacturer's instruction for MTA, a 3:1 (w/w) powder to liquid ratio was used for all samples.

### Setting time

Materials were mixed and placed in 20 brass molds (5 mm in diameter and 5 mm in height). After mixing, all samples were placed in an incubator at 37°C and 95% relative humidity. A flat-end indenter with 1.0 mm diameter was used with a 400-g load and carefully lowered vertically to the surface of materials. These stages were repeated at 60-sec interval. The setting time was recorded when the needle failed to make a mark on the surface of materials [20].

### Porosity (Imbibition method)

Four specimens from each group were set at 37°C and 95% relative humidity. After 70% setting of samples, each sample was unmolded, dried with filter paper, and weighed (initial mass- m<sub>1</sub>). Then each specimen was immersed in 20 mL distilled water at 37°C. After 24 h, additional water was removed, and the saturated mass was recorded (m<sub>2</sub>). Weight measurement process was repeated 3 times for each sample to the nearest 0.001 g [22]. The percentage of porosity for each sample was calculated using the following formula: %porosity=[(m<sub>2</sub>/m<sub>1</sub>)-1]×100 [23].

### Porosity: Scanning electron microscopy (SEM)

Three specimens from each group were evaluated under the field emission scanning electron microscopy (FESEM) (Tescan, Mira3) under 1.07k× magnification mode to analyze elemental distribution.

### Statistical analysis

Statistical analysis was performed using the *t*- test. The level of significance was set at 0.001.

## Results

The mean setting times of MTA+NS (9.8±0.78min) was significantly shorter than pure MTA (23.3±2.16 min) (*P*<0.001) (Table 1). There was no significant difference between MTA+NS (31.26±10.73) and pure MTA (32.74±5.26) in the mean of porosity by SEM method (*P*>0.001) (Table 2); but the mean of porosity for MTA+NS group (23.49±0.48) was significantly higher than MTA group (15.69±2.10) by imbibition method (*P*<0.001) (Table 3). SEM method showed that the microstructure of the MTA+NS particles is denser and more homogeneous than of the pure MTA (Figure 1).

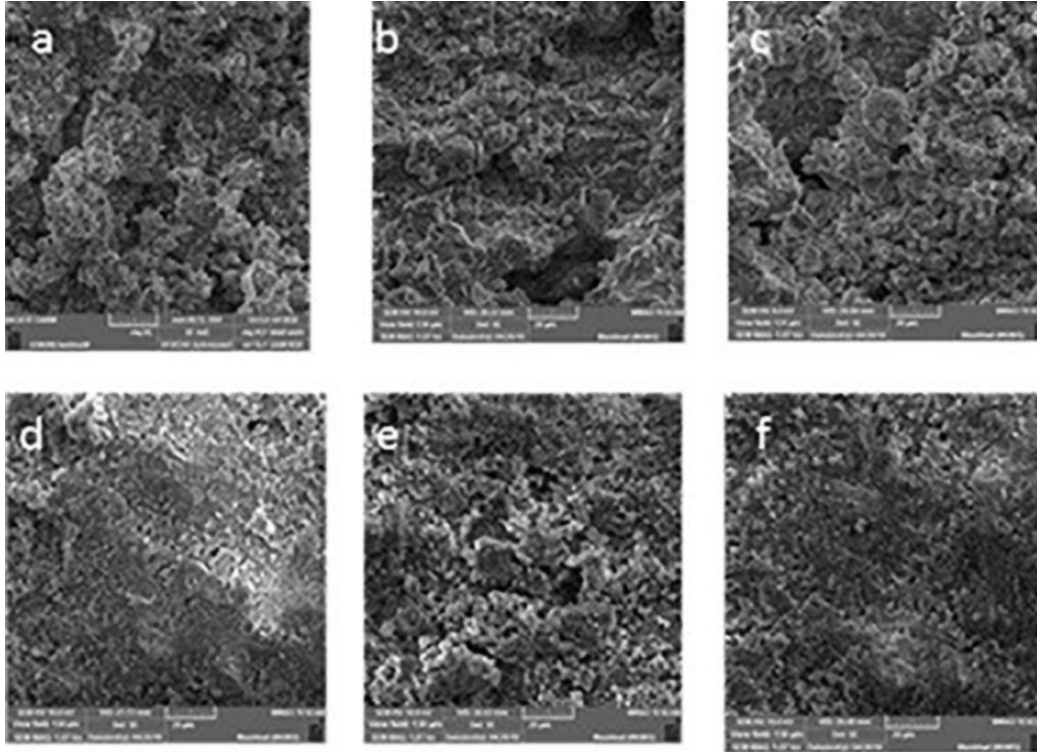


Figure 1. These pictures show; A, B, C) MTA group; D, E, F) MTA+NS group with 1.07k× magnification by SEM

## Discussion

The purpose of this study was to evaluate the effect of adding NS to MTA on the setting time and porosity. MTA is primarily composed of type 1 Portland cement and bismuth oxide (4:1 ratio). Previous studies have shown that Portland cement has similar physical properties and behaviors in comparison with MTA [24-26]. The results of our study showed that microscopic structure in MTA+NS group was denser and more homogeneous than pure MTA. Also, there was no significant difference between MTA+NS and pure MTA group in mean porosity by SEM method; but the mean porosity of MTA+NS group was significantly higher than pure MTA by imbibition method.

Despite its different benefits, MTA has some defects such as long setting time. Many studies have been made to overcome these drawbacks by adding materials into its structure; however, adding or removing different materials to overcome these shortcomings can affect adversely MTA's properties. Thus, producing new compositions of MTA needs to comprehensive studies [27].

The purpose of this study was to evaluate effect of addition of NS to MTA on setting time and porosity. Short-setting time of MTA prevents washout of MTA plugs. Previous studies have been made to decrease setting time of MTA by adding some additives such as  $\text{CaCl}_2$ , polymers, plasticizers or other materials [28, 29].

Although, some additives increase toxicity, decrease physical properties or jeopardize bioactivity [1].

The aim of the usage of ultra-fine additives like NS, is improving the properties of plastic and hardened cement. Micro- and nano-scaled silica particles have a filler effect; it means filling up the spaces between the cement particles. Also, nano-silica particle has a pozzolanic reactivity [16].

Recent researches have been reported that Portland cement has similar physical characteristics and behaviors to MTA [17, 18]. Most of added elements have a similar effect in Portland cement and MTA [12].

Black *et al.* [30] showed that because of seeding effect (By placing a seed or solution of seeds in a drop which is saturated to the "Metastable Zone" one can use the seeds to grow larger single crystals) [30], the hydration of tricalcium silicate ( $\text{C}_3\text{S}$ ) can be accelerated by addition of nanoscaled silica or calcium silicate hydrate (C-S-H) particles [30]. It is expected that acceleration of hydration can affect physical properties in cements. Black *et al.* [31] showed that  $\text{Ca}_3\text{Al}_2\text{O}_6$  accelerate the hydration process and improve short-term compressive strength of  $\text{Ca}_3\text{SiO}_5/\text{Ca}_3\text{Al}_2\text{O}_6$  composites versus pure  $\text{Ca}_3\text{SiO}_5$ .

In our study, addition of nano silica particles to MTA decreased setting time but porosity by imbibition method increased. So it will be helpful to do porosity test in longer periods

of time. As mentioned in the study by Marciano [31], some properties of MTA powder mixed with 80% distilled water and 20% propylene glycol (PG) was studied versus MTA mixed only with distilled water. MTA+PG group showed higher final setting time and high porosity at 1 day of hydration but porosity reduced between 1 and 28 days for MTA+PG [31].

In the previous studies, the effect of different additives such as sodium fluoride, strontium chloride, hydroxyapatite, and tricalcium phosphate in Gandolfi's study [22], and distilled water, phosphate buffered saline, 5% calcium chloride ( $\text{CaCl}_2$ ), 3% sodium hypochlorite ( $\text{NaOCl}$ ), or lidocaine in Zapf's study to MTA on the final setting time were investigated [32]. Result in Gandolfi's study [22] showed that final setting time of all experimental cements was faster than MTA. But results of Zapf's [32] study showed that only  $\text{CaCl}_2$  act as an accelerator.

Some studies investigated influence of adding NS to cement. The result of these studies showed that addition of NS decrease porosity and pores sizes [33, 34], also suggested it would be beneficial to investigate MTA+ NS+SF composition [34].

Moreover, there have been some studies about MTA surface porosity, the results showed that there was no significant difference between Nano MTA and MTA [35, 36].

According to the results of this study, addition of NS to MTA caused a decrease in porosity and final setting time. However, all of the abovementioned results should be compared in standard settings. Result of imbibition test is the opposite of some recent results. At the end it would be suggested to repeat this pilot test in more samples and longer periods of time.

Introducing new compositions of MTA needs further investigations. It is important to note that changes in the physical and/or chemical components of MTA can adversely affect other properties such as biocompatibility. Finally, every new formulation has to be tested *in vitro* as well as *in vivo* conditions before their applications in humans.

## Conclusion

The addition of 8% nano- $\text{SiO}_2$  to MTA accelerated the hydration process, reduced the setting time, and had adverse effect on the porosity of MTA (by imbibition method).

Introducing new compositions of MTA needs further investigations. It is important to note that changes in the physical and/or chemical components of MTA can adversely affect other properties such as biocompatibility. Finally, every new formulation has to be tested *in vitro* as well as *in vivo* conditions before their applications in humans.

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## References

1. Lee J, Kim H-J, Chen T, Lee K, Kim K-S, Glotzer SC, Kim J, Kotov NA. Control of energy transfer to CdTe nanowires via conjugated polymer orientation. *J Phys Chem C P*. 2008;113(1):109-16.
2. Pariookh M, Torabinejad M. Mineral trioxide aggregate: a comprehensive literature review-part I: chemical, physical, and antibacterial properties. *J Endod*. 2010;36(1):16-27.
3. Torabinejad M, Ford T. Root end filling materials: a review. *Dent Traumatol*. 1996;12(4):161-78.
4. Enkel B, Dupas C, Armengol V, Akpe Adou J, Bosco J, Daculsi G, Jean A, Laboux O, LeGeros RZ, Weiss P. Bioactive materials in endodontics. Expert review of medical devices. 2008;5(4):475-94.
5. Zand V, Lotfi M, Aghbali A, Mesgariabasi M, Janani M, Mokhtari H, Tehranchi P, Pakdel SM. Tissue Reaction and Biocompatibility of Implanted Mineral Trioxide Aggregate with Silver Nanoparticles in a Rat Model. *Iran Endod J*. 2016;11(1):13-6.
6. Zizka R, Ctvrtlik R, Tomastik J, Facevicova K, Gregor L, Sedy J. In Vitro Mechanical Properties of Mineral Trioxide Aggregate in Moist and Dry Intracanal Environments. *Iran Endod J*. 2018;13(1):20-4.
7. Samiei M, Aghazadeh M, Lotfi M, Shakoei S, Aghazadeh Z, Vahid Pakdel SM. Antimicrobial Efficacy of Mineral Trioxide Aggregate with and without Silver Nanoparticles. *Iran Endod J*. 2013;8(4):166-70.
8. Pariookh M, Torabinejad M. Mineral trioxide aggregate: a comprehensive literature review-part III: clinical applications, drawbacks, and mechanism of action. *J Endod*. 2010;36(3):400-13.
9. Roberts HW, Toth JM, Berzins DW, Charlton DG. Mineral trioxide aggregate material use in endodontic treatment: a review of the literature. *Dent Mater*. 2008;24(2):149-64.
10. Borges AH, Guedes OA, Volpato LER, Siebert Filho G, Borba AM, Zina O, Piva E, Estrela C. Physicochemical properties of MTA and Portland Cement after addition of aloe vera. *Iran Endod J*. 2017;12(3):312.
11. Gandolfi MG, Van Landuyt K, Taddei P, Modena E, Van Meerbeek B, Prati C. Environmental scanning electron microscopy connected with energy dispersive x-ray analysis and Raman techniques to study ProRoot mineral trioxide aggregate and calcium silicate cements in wet conditions and in real time. *J Endod*. 2010;36(5):851-7.

12. Gandolfi MG, Iacono F, Agee K, Siboni F, Tay F, Pashley DH, Prati C. Setting time and expansion in different soaking media of experimental accelerated calcium-silicate cements and ProRoot MTA. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod.* 2009;108(6):e39-e45.
13. Reyes-Carmona JF, Felipe MS, Felipe WT. Biomineralization ability and interaction of mineral trioxide aggregate and white portland cement with dentin in a phosphate-containing fluid. *J Endod.* 2009;35(5):731-6.
14. Koh ET, McDonald F, Ford TRP, Torabinejad M. Cellular response to mineral trioxide aggregate. *J Endod.* 1998;24(8):543-7.
15. Osorio RM, Hefti A, Vertucci FJ, Shawley AL. Cytotoxicity of endodontic materials. *J Endod.* 1998;24(2):91-6.
16. Samiei M, Shahi S, Ghasemi N, Dastmalchi S, Bargahi N, Asgari S. Effect of Different Additives on Genotoxicity of Mineral Trioxide Aggregate. *Iran Endod J.* 2018;13(1):37.
17. Björnström J, Martinelli A, Matic A, Börjesson L, Panas I. Accelerating effects of colloidal nano-silica for beneficial calcium-silicate-hydrate formation in cement. *Chemical Physics Letters.* 2004;392(1-3):242-8.
18. Chen R, Ye Q. Research on the comparison of properties of hardend cement paste between Nano-SiO<sub>2</sub> and silica fume added concrete. *Concr Res.* 2002;1:7-10.
19. Wang B, Wang L, Lai F. Freezing resistance of HPC with nano-SiO<sub>2</sub>. *Journal of Wuhan University of Technology-Mater. Sci. Ed.* 2008;23(1):85-8.
20. Akbari M, Zebarjad SM, Nategh B, Rouhani A. Effect of nano silica on setting time and physical properties of mineral trioxide aggregate. *J Endod.* 2013;39(11):1448-51.
21. Bortoluzzi EA, Broon NJ, Bramante CM, Felipe WT, Tanomaru Filho M, Esberard RM. The influence of calcium chloride on the setting time, solubility, disintegration, and pH of mineral trioxide aggregate and white Portland cement with a radiopacifier. *J Endod.* 2009;35(4):550-4.
22. Gandolfi MG, Siboni F, Primus CM, Prati C. Ion release, porosity, solubility, and bioactivity of MTA Plus tricalcium silicate. *J Endod.* 2014;40(10):1632-7.
23. Cutajar A, Mallia B, Abela S, Camilleri J. Replacement of radiopacifier in mineral trioxide aggregate; characterization and determination of physical properties. *Dent Mater.* 2011;27(9):879-91.
24. Islam I, Chng HK, Yap AU. Comparison of the physical and mechanical properties of MTA and portland cement. *J Endod.* 2006;32(3):193-7.
25. Islam I, Chng HK, Yap AU. X-ray diffraction analysis of mineral trioxide aggregate and Portland cement. *Int Endod J.* 2006;39(3):220-5.
26. Ribeiro DA, Duarte MA, Matsumoto MA, Marques ME, Salvadori DM. Biocompatibility in vitro tests of mineral trioxide aggregate and regular and white Portland cements. *J Endod.* 2005;31(8):605-7.
27. Saghiri M, Asgar K, Lotfi M, Garcia-Godoy F. Nanomodification of mineral trioxide aggregate for enhanced physicochemical properties. *Int Endod J.* 2012;45(11):979-88.
28. Guerreiro-Tanomaru JM, Vazquez-Garcia FA, Bosso-Martelo R, Bernardi MI, Faria G, Tanomaru MF. Effect of addition of nano-hydroxyapatite on physico-chemical and antibiofilm properties of calcium silicate cements. *J Appl Oral Sci.* 2016;24(3):204-10.
29. Bosso-Martelo R, Guerreiro-Tanomaru JM, Viapiana R, Berbert FL, Duarte MA, Tanomaru-Filho M. Physicochemical properties of calcium silicate cements associated with microparticulate and nanoparticulate radiopacifiers. *Clin Oral Investig.* 2016;20(1):83-90.
30. Black L, Breen C, Yarwood J, Deng C-S, Phipps J, Maitland G. Hydration of tricalcium aluminate (C<sub>3</sub>A) in the presence and absence of gypsum-studied by Raman spectroscopy and X-ray diffraction. *J Mater Chem.* 2006;16(13):1263-72.
31. Marciano MA, Guimarães BM, Amoroso-Silva P, Camilleri J, Duarte MAH. Physical and chemical properties and subcutaneous implantation of mineral trioxide aggregate mixed with propylene glycol. *J Endod.* 2016;42(3):474-9.
32. Zapf AM, Chedella SC, Berzins DW. Effect of additives on mineral trioxide aggregate setting reaction product formation. *J Endod.* 2015;41(1):88-91.
33. Lin K, Chang WC, Lin D, Luo H, Tsai M. Effects of nano-SiO<sub>2</sub> and different ash particle sizes on sludge ash-cement mortar. *J Environ Manage.* 2008;88(4):708-14.
34. Senff L, Hotza D, Repette W, Ferreira V, Labrincha J. Influence of added nanosilica and/or silica fume on fresh and hardened properties of mortars and cement pastes. *Advances in Applied Ceramics.* 2009;108(7):418-28.
35. Saghiri MA, Asgar K, Lotfi M, Garcia-Godoy F. Nanomodification of mineral trioxide aggregate for enhanced physicochemical properties. *Int Endod J.* 2012;45(11):979-88.
36. Cutajar A, Mallia B, Abela S, Camilleri J. Replacement of radiopacifier in mineral trioxide aggregate; characterization and determination of physical properties. *Dent Mater.* 2011;27(9):879-91.

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