Published in final edited form as:
J Endod. 2012 August ; 38(8): 1126–1129. doi:10.1016/j.joen.2012.04.013.

Characterization of the Mineral Trioxide Aggregate–Resin Modified Glass Ionomer Cement Interface in Different Setting Conditions

Ashraf A. Eid, BDS, MSc[*], **Takashi Komabayashi, DDS, MDentSc, PhD**[†], **Etsuko Watanabe, DDS, PhD**[*], **Takanobu Shiraishi, PhD**[*], and **Ikuya Watanabe, DDS, PhD**[*]

[*]Department of Dental and Biomedical Material Sciences, Graduate School of Biomedical Sciences, Nagasaki University, Nagasaki, Japan

[†]Department of Endodontics, Texas A&M Health Science Center Baylor College of Density, Dallas, Texas

Abstract

Introduction—Mineral trioxide aggregate (MTA) has been used successfully for perforation repair, vital pulpotomies, and direct pulp capping. However, little is known about the interactions between MTA and glass ionomer cement (GIC) in final restorations. In this study, 2 null hypotheses were tested: (1) GIC placement time does not affect the MTA-GIC structural interface and hardness and (2) moisture does not affect the MTA-GIC structural interface and hardness.

Methods—Fifty cylinders were half filled with MTA and divided into 5 groups. The other half was filled with resin-modified GIC either immediately after MTA placement or after 1 or 7 days of temporization in the presence or absence of a wet cotton pellet. The specimens were then sectioned, carbon coated, and examined using a scanning electron microscope and an electron probe micro-analyzer (SEM-EPMA) for interfacial adaptation, gap formation, and elemental analysis. The Vickers hardness numbers of the interfacial MTA were recorded 24 hours after GIC placement and 8 days after MTA placement and analyzed using the analysis of variance test.

Results—Hardness testing 24 hours after GIC placement revealed a significant increase in hardness with an increase of temporization time but not with a change of moisture conditions ($P < .05$). Hardness testing 8 days after MTA placement indicated no significant differences among groups. SEM-EPMA showed interfacial adaptation to improve with temporization time and moisture. Observed changes were limited to the outermost layer of MTA. The 2 null hypotheses were not rejected.

Conclusions—GIC can be applied over freshly mixed MTA with minimal effects on the MTA, which seemed to decrease with time.

Keywords

Elemental analysis; EPMA; GIC; mineral trioxide aggregate; MTA; SEM

Mineral trioxide aggregate (MTA) is a cement composed of tricalcium silicate, di-calcium silicate, tricalcium aluminate, calcium sulfate, bismuth oxide, and small amounts of other

Address requests for reprints to Dr Ashraf A. Eid, Nagasaki University Graduate School of Biomedical Sciences, Department of Dental and Biomedical Material Sciences, Nagasaki, 852-8523 Japan. ashraf.abulfotooh@gmail.com.

The authors deny any conflicts of interest related to this study.

mineral oxides that modify its chemical and physical properties (1). It was first used to seal off all pathways of communication between the root canal system and the external surface of the tooth (2). It is now widely used as a root-end filling material (1, 3), in vital pulp therapy including direct pulp capping and pulpotomy of immature teeth (apexogenesis) (4, 5), and as an apical barrier in immature teeth with necrotic pulps (apexification) (6). Lately, it has been successfully used in regenerative endodontic procedures in immature teeth with apical periodontitis (7, 8).

The advantages of MTA include high biocompatibility, radiopacity that is slightly greater than that of dentin, low solubility, and high alkalinity (pH = 12.5) that may impart some antimicrobial properties (9). The main disadvantages of MTA are its difficult manipulation and long setting time (10, 11). After the MTA powder is mixed with sterile water to make a thick creamy mix, it takes an average of 3 to 4 hours for the material to form a solid barrier (12). However, complete setting of MTA may take up to 21 days (13). The hydrophilic nature of MTA makes it an ideal material for different endodontic applications in which contact with blood, body fluids, and moisture is inevitable, but it complicates the same-visit application of the final adhesive restoration, which requires a relatively dry field. Consequently, the application of the restoration usually requires a separate appointment after MTA has reached its initial setting stage.

The current literature contains few studies on glass ionomer cement (GIC)-MTA interactions. GIC was found to bond to MTA (14), although bond strength values seem comparatively inferior to that of resin composites (15). Placing GIC after 45 minutes, 4 hours, or 3 days of MTA placement did not affect the setting of MTA (16) or GIC (17). Nevertheless, placing GIC over freshly mixed MTA caused excessive interfacial cracking and void formation compared with calcium hydroxide paste (18). To our knowledge, a comparison between immediate and delayed placement of GIC over MTA in different setting conditions and the effect of that on the MTA-GIC structural interface and hardness was never attempted.

Therefore, the aim of the present study was to investigate the effect of MTA setting conditions and GIC placement time on the hardness and structural interface of the 2 materials. Two null hypotheses were tested: (1) GIC placement time does not affect the MTA-GIC structural interface and hardness and (2) moisture does not affect the MTA-GIC structural interface and hardness.

Materials and Methods

MTA (ProRoot MTA; Dentsply, Tulsa, OK) was mixed with sterile water according to the manufacturer's instructions. Fifty transparent plastic cylinders (4-mm diameter, 7-mm long) were half filled with the mixture, and the surface of MTA was smoothed using a plastic plunger. The bases of all cylinders were in contact with sterile gauze wetted with distilled water to simulate natural setting conditions (tissue side). The specimens were then randomly divided into 5 equal groups ($n = 10$), and the other half of the cylinders were filled with resin-modified GIC (Fuji II LC; GC Corporation, Tokyo, Japan) and cured for 20 seconds using a curing light (L.E. Demetron 1; Kerr Corp, Danbury, CT) as follows: group IMM: GIC was applied and cured immediately after MTA placement; group 1Dw: GIC was applied and cured after MTA was allowed to set for 24 hours in a wet condition (covered with a wet cotton pellet) and temporary filling was added (IRM; Dentsply De-Trey, Konstanz, Germany); group 1Dd: same as group 1Dw but in a dry condition (with no cotton pellet); group 7Dw: GIC was applied and cured after MTA was allowed to set for 7 days in a wet condition; group 7Dd: same as group 7Dw but in a dry condition. In the wet condition groups, IRM and cotton pellets were removed using a sharp excavator without touching the

MTA surface. It was neither rinsed nor polished afterward. A gentle stream of air was used to remove excess moisture from the MTA surface before GIC placement. In the dry condition groups, IRM was applied on the outermost part of the plastic cylinders with no direct contact with the MTA surface. IRM was later removed using a sharp excavator, and any debris was gently blown using an air syringe. All the specimens were stored in an incubator at 95% humidity and 37°C during the entire procedure.

Specimen Preparation

The MTA-GIC specimens were embedded in transparent epoxy resin (SpeciFix-20; Struers, Ballerup, Denmark). The hardened epoxy resin blocks were sectioned perpendicularly to the MTA-GIC interface using a low-speed saw and polished with silicon carbide papers (500–2,000 grit) followed by a 0.3-μm alumina suspension on a rotary polishing cloth. The polished sections were then covered with a thin layer of carbon using a carbon coater (JEE-400 Vacuum Evaporator; JEOL Ltd, Tokyo, Japan).

Microstructural Analysis of the Interface

An electron probe microanalyzer (EPMA-1600e; Shimadzu, Kyoto, Japan) with a built-in scanning electron microscope (SEM) was used to analyze the MTA-GIC interface. Using the SEM, the following points were investigated on every specimen by 2 blinded observers: the adaptation of the 2 materials at the interface, the intrinsic crack pattern and propagation, the separation of the 2 materials and location, the presence or absence of the intermediate layer, and the distinctive morphologic features in MTA and GIC. The EPMA mapping analysis mode with preset settings (15-kV current, 1-μm beam size, and 1-μA sample current) was used to detect the elemental distribution of bismuth, fluorine, silicon, and calcium along the MTA-GIC interface. The area designated for the mapping analysis was 512 × 512 μm.

Hardness Testing

Vickers hardness testing was performed on half of the specimens in each group 24 hours after GIC placement and on the rest of the specimens 8 days after MTA placement using a hardness testing machine (MVK-H1; Akashi Co, Tokyo, Japan) with a 50 gram-force load and a 5-second dwell time. Ten measurements were made for each sample on the MTA side 100 μm away from the interface. The data were statistically analyzed using analysis of variance to investigate if there were significant differences among the groups. If analysis of variance showed significant differences, a post hoc pair-wise comparison was made using the Tukey test. The level of statistical significance was set at $\alpha = 0.05$.

Results

Microstructural Analysis of the Interface

The SEM showed that all the groups underwent adhesive separation and gap formation at the interface. Cohesive separation in MTA was also found in all groups, but it was observed more often in the dry condition groups (1Dd and 7Dd) compared with the wet condition groups (1Dw and 7Dw). Isolated island-like structures at the interface consisting of both materials were obvious in group IMM (Fig. 1*A*), with numerous voids and cracks evident at the interface. All groups exhibited vertical and horizontal cracks in GIC that interconnected with each other in the internal voids within the GIC. The changes observed were limited to the outermost interfacial layer of the MTA, and neither the deeper layers of MTA nor the GIC itself seemed affected. As for the EPMA elemental analysis, calcium appeared to be evenly dispersed as densely packed fine particles predominantly on the MTA side. In the wet condition groups, the growth of calcium crystals was evident at the interface, which appeared to increase in size with time. This observation was not made in the dry condition

groups (Fig. 1*C* and *D*). Silicon was observed on both sides; on the GIC side, it was evenly distributed in small particles, whereas on the MTA side it took the form of large, widely dispersed clusters. Bismuth appeared as widely spaced, relatively large particles or aggregations of particles on the MTA side only. Fluorine was present as densely packed small particles exclusively on the GIC side. Because calcium and silicon were found in both materials, their migration could not be mapped. The bismuth migration to the GIC side was not detected in any of the specimens tested, whereas the migration of fluorine to the MTA side was detected in 1 group 1Dw specimen (Fig. 1*B*).

Hardness Testing

The mean and standard deviations for MTA hardness are summarized in Table 1. Hardness testing after 24 hours of GIC placement showed significant differences in hardness ($P < .001$) with increased temporization time (IMM < 1Dw < 7Dw and 1Dd < 7Dd) but not with the moisture condition (1Dw vs 1Dd and 7Dw vs 7Dd). Hardness testing after 7 days of GIC placement showed no significant differences among all the groups ($P = .92$). Nevertheless, there seemed to be a tendency toward higher hardness values ($P = .059$) in the wet condition groups compared with the dry condition groups (1Dw vs 1Dd and 7Dw vs 7Dd).

Discussion

One of the most notable drawbacks of MTA is its prolonged maturation process that often continues past the manufacturer's stated setting time of 3 to 4 hours (19). Earlier studies reported that the resistance to dislodgment (20, 21), push-out bond strength (13, 22), microbial leakage, and hardness of MTA were all affected over time. Consequently, the placement time of the final adhesive restoration on MTA is of clinical interest. This study did not reject the first null hypothesis. The results showed that even though there were significant differences in MTA hardness values among the groups tested 24 hours after GIC placement, the differences were not significant 8 days after MTA placement. This difference indicates that changes in the MTA hardness were transient, and the time of GIC placement did not influence the setting reaction of MTA. These observations agree with earlier reports using laser Raman spectroscopy and stereomicroscopy (16, 17) and also indicate that the changes may be attributed to the slow setting reaction of MTA rather than the interaction with GIC. The interfacial adaptation of MTA seemed to improve with the increased temporization time, which may be because of the high affinity of GIC to uptake the hydration water necessary for MTA setting (18). This fact might explain the high incidence of interfacial porosity and cracking observed in the IMM group. Nevertheless, adhesive separation and gap formation at the interface were commonly found in all groups. One reason for this phenomenon is the setting contraction of resin-modified GIC, which is comparable to the contraction of resin composites (23). Another reason is the vacuum-related dehydration shrinkage of GIC required for SEM-EPMA procedures, a factor that is not related to the setting reaction of either material (24).

The second null hypothesis was also not rejected because there were no significant differences in hardness between the wet and dry condition groups. However, wet condition groups tended to have higher hardness values. In the literature, there are mixed results regarding the effect of moisture on the properties of MTA, which may be caused by the lack of consistency in the definition of the dry condition among researchers (13, 20, 25). A possible explanation for the current results is that MTA can acquire the water necessary for maturation from the tissue moisture or even through the root without the need of a wet cotton pellet (26, 27). Another factor might be the relatively small sample size because the P value between the 2 moisture conditions was 0.059. The cohesive separation on the MTA side of the dry condition groups may be related to the incomplete setting of interfacial MTA in the dry condition groups. This was also observed earlier and was attributed to the water

withdrawal from the MTA into the GIC (18). However, this incomplete setting did not seem to significantly affect the hardness of these groups. A notable observation was the formation of calcium salt crystals at the interface in the wet condition groups (Fig. 1*C*). This can be attributed to the normal maturation process of MTA in the presence of sufficient moisture as described in previous studies (28, 29), a fact that might explain its absence in the dry condition groups. It was also reported earlier that the presence of calcium salts at the MTA-GIC interface was a result of the interaction of the negatively charged carboxylate anion ($RCOO^-$) in the polyacrylic acid with the calcium in the MTA (16). It is not clear at this point if the presence of these crystals at the interface would affect the clinical performance of MTA or GIC, but this was beyond the scope of this study.

In cases in which direct contact of MTA with the final restoration is inevitable, such as pulpotomy for both primary and immature permanent teeth and perforation repair, it is recommended by the manufacturer to perform a 2-visit procedure to place the final restoration (30). In the first visit, a wet cotton pellet is applied over the MTA, and the tooth is temporized. In the second visit, the cotton pellet is removed, and the permanent restoration applied after the MTA has sufficiently hardened. It would be clinically beneficial for patients and dentists alike if the final adhesive restoration can be placed over MTA during the same visit. This way the cost and chairside time of the procedure will decrease significantly. Based on the current results, both null hypotheses were not rejected. The effect of GIC placement over MTA after different time intervals and setting conditions was transient. The GIC and deeper layers of MTA did not seem to be affected. Further research is required to assess the long-term clinical outcome of these interfacial reactions. In conclusion, resin-modified GIC can be successfully applied on freshly mixed MTA in a single visit with no expected adverse reactions between the 2 materials.

Acknowledgments

The authors would like to thank Ms Jeanne Santa Cruz (Texas A&M Health Science Center Baylor College of Density) for the critical editing of this paper. The authors also thank Dr Chul Ahn and Ms Liyue Tong (UT Southwestern Medical Center) for their statistical consultation.

Supported in part by NIH UL1 RR024982.

References

1. Torabinejad M, Watson TF, Pitt Ford TR. Sealing ability of a mineral trioxide aggregate when used as a root end filling material. J Endod. 1993; 19:591–5. [PubMed: 8151252]
2. Lee SJ, Monsef M, Torabinejad M. Sealing ability of a mineral trioxide aggregate for repair of lateral root perforations. J Endod. 1993; 19:541–4. [PubMed: 8151240]
3. Torabinejad M, Hong CU, Lee SJ, Monsef M, Pitt Ford TR. Investigation of mineral trioxide aggregate for root-end filling in dogs. J Endod. 1995; 21:603–8. [PubMed: 8596081]
4. Ford TR, Torabinejad M, Abedi HR, Bakland LK, Kariyawasam SP. Using mineral trioxide aggregate as a pulp-capping material. J Am Dent Assoc. 1996; 127:1491–4. [PubMed: 8908918]
5. Torabinejad M, Chivian N. Clinical applications of mineral trioxide aggregate. J Endod. 1999; 25:197–205. [PubMed: 10321187]
6. Shabahang S, Torabinejad M. Treatment of teeth with open apices using mineral trioxide aggregate. Pract Periodontics Aesthet Dent. 2000; 12:315–20. [PubMed: 11404920]
7. Banchs F, Trope M. Revascularization of immature permanent teeth with apical periodontitis: new treatment protocol? J Endod. 2004; 30:196–200. [PubMed: 15085044]
8. Reynolds K, Johnson JD, Cohenca N. Pulp revascularization of necrotic bilateral bicuspids using a modified novel technique to eliminate potential coronal discolouration: a case report. Int Endod J. 2009; 42:84–92. [PubMed: 19125982]

9. Parirokh M, Torabinejad M. Mineral trioxide aggregate: a comprehensive literature review—part I: chemical, physical, and antibacterial properties. J Endod. 2010; 36:16–27. [PubMed: 20003930]
10. Kogan P, He J, Glickman GN, Watanabe I. The effects of various additives on setting properties of MTA. J Endod. 2006; 32:569–72. [PubMed: 16728254]
11. Parirokh M, Torabinejad M. Mineral trioxide aggregate: a comprehensive literature review–part III: clinical applications, drawbacks, and mechanism of action. J Endod. 2010; 36:400–13. [PubMed: 20171353]
12. Torabinejad M, Hong CU, McDonald F, Pitt Ford TR. Physical and chemical properties of a new root-end filling material. J Endod. 1995; 21:349–53. [PubMed: 7499973]
13. Gancedo-Caravia L, Garcia-Barbero E. Influence of humidity and setting time on the push-out strength of mineral trioxide aggregate obturations. J Endod. 2006; 32:894–6. [PubMed: 16934637]
14. Yesilyurt C, Yildirim T, Tasdemir T, Kusgoz A. Shear bond strength of conventional glass ionomer cements bound to mineral trioxide aggregate. J Endod. 2009; 35:1381–3. [PubMed: 19801234]
15. Bayrak S, Tunc ES, Saroglu I, Egilmez T. Shear bond strengths of different adhesive systems to white mineral trioxide aggregate. Dent Mater J. 2009; 28:62–7. [PubMed: 19280969]
16. Nandini S, Ballal S, Kandaswamy D. Influence of glass-ionomer cement on the interface and setting reaction of mineral trioxide aggregate when used as a furcal repair material using laser Raman spectroscopic analysis. J Endod. 2007; 33:167–72. [PubMed: 17258638]
17. Ballal S, Venkateshbabu N, Nandini S, Kandaswamy D. An in vitro study to assess the setting and surface crazing of conventional glass ionomer cement when layered over partially set mineral trioxide aggregate. J Endod. 2008; 34:478–80. [PubMed: 18358902]
18. Camilleri J. Scanning electron microscopic evaluation of the material interface of adjacent layers of dental materials. Dent Mater. 2011; 27:870–8. [PubMed: 21565396]
19. Roberts HW, Toth JM, Berzins DW, Charlton DG. Mineral trioxide aggregate material use in endodontic treatment: a review of the literature. Dent Mater. 2008; 24:149–64. [PubMed: 17586038]
20. Sluyk SR, Moon PC, Hartwell GR. Evaluation of setting properties and retention characteristics of mineral trioxide aggregate when used as a furcation perforation repair material. J Endod. 1998; 24:768–71. [PubMed: 9855831]
21. Hashem AA, Wanees Amin SA. The effect of acidity on dislodgment resistance of mineral trioxide aggregate and bioaggregate in furcation perforations: an in vitro comparative study. J Endod. 2012; 38:245–9. [PubMed: 22244646]
22. Vanderweele RA, Schwartz SA, Beeson TJ. Effect of blood contamination on retention characteristics of MTA when mixed with different liquids. J Endod. 2006; 32:421–4. [PubMed: 16631840]
23. Attin T, Buchalla W, Kielbassa AM, Helwig E. Curing shrinkage and volumetric changes of resin-modified glass ionomer restorative materials. Dent Mater. 1995; 11:359–62. [PubMed: 8595836]
24. Yiu CK, Tay FR, King NM, Pashley DH, Carvalho RM, Carrilho MR. Interaction of resin-modified glass-ionomer cements with moist dentine. J Dent. 2004; 32:521–30. [PubMed: 15304297]
25. Walker MP, Diliberto A, Lee C. Effect of setting conditions on mineral trioxide aggregate flexural strength. J Endod. 2006; 32:334–6. [PubMed: 16554206]
26. Budig CG, Eleazer PD. In vitro comparison of the setting of dry ProRoot MTA by moisture absorbed through the root. J Endod. 2008; 34:712–4. [PubMed: 18498896]
27. Pelliccioni GA, Vellani CP, Gatto MR, Gandolfi MG, Marchetti C, Prati C. Proroot mineral trioxide aggregate cement used as a retrograde filling without addition of water: an in vitro evaluation of its microleakage. J Endod. 2007; 33:1082–5. [PubMed: 17931938]
28. Lee YL, Lee BS, Lin FH, Yun Lin A, Lan WH, Lin CP. Effects of physiological environments on the hydration behavior of mineral trioxide aggregate. Biomaterials. 2004; 25:787–93. [PubMed: 14609667]
29. Han L, Okiji T, Okawa S. Morphological and chemical analysis of different precipitates on mineral trioxide aggregate immersed in different fluids. Dent Mater J. 2010; 29:512–7. [PubMed: 20823620]

30. [Accessed February 1, 2012] ProRoot MTA (Mineral Trioxide Aggregate) root canal repair material direction for use. Available at: http://www.tulsadentalspecialties.com/Libraries/Tab_Content_-_Accessories/MTA_DFU_rev_8-8-03.sflb.ashx

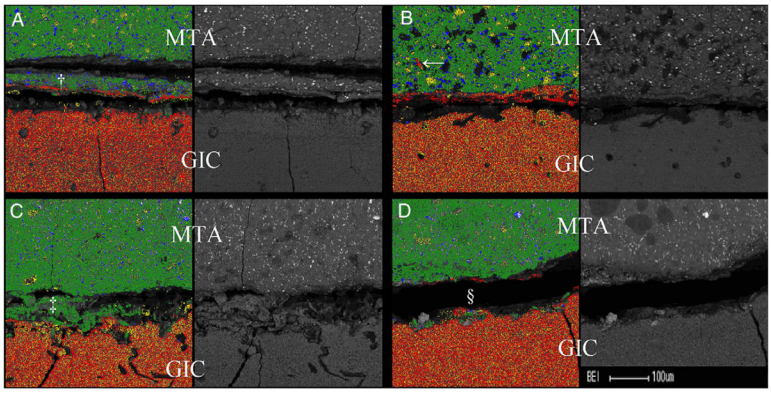

Figure 1.

Representative EPMA mapping analysis images with their matching scanning electron microscopic micrographs. (*A*) Cohesive separation noted on both sides resulting in an island-like intermediate layer formed of both materials (†) in group IMM. (*B*) Evidence of fluorine migration toward the MTA side (*arrow*) in group 1Dw. (*C*) Calcium salt crystals (‡) growing to occlude the MTA-GIC interfacial gap in group 7Dw. (*D*) Excessive gap formation (§) with a mostly adhesive separation pattern in group 7Dd. (Color legend for EPMA images: green: calcium; blue: bismuth, red: fluorine; yellow: silicon.)

TABLE 1

The Mean Vickers Hardness Values of MTA at the Interface

	IMM	1Dw	1Dd	7Dw	7Dd
Mean VHN ± SD 24 h after GIC placement	18.7^{a} ± 7.3	42.0^{b} ± 10.7	47.3^{b} ± 13.9	67.4^{c} ± 15.9	60.1^{c} ± 18.6
Mean VHN ± SD 8 days after MTA placement	59.7^{c} ± 11.5	64.1^{c} ± 12.3	56.0^{c} ± 14.6	67.4^{c} ± 15.9	60.1^{c} ± 18.6

SD, standard deviation; VHN, Vickers hardness numbers.

Groups identified by different superscript letters were significantly different at $P < .05$.