Chemical characteristics of mineral trioxide aggregate and its hydration reaction

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MINERAL TRIOXIDE AGGREGATE (MTA) was developed in early 1990s and has been successfully used for root perforation repair, root end filling, and one-visit apexification. MTA is composed mainly of tricalcium silicate and dicalcium silicate. When MTA is hydrated, calcium silicate hydrate (CSH) and calcium hydroxide is formed. Formed calcium hydroxide interacts with the phosphate ion in body fluid and form amorphous calcium phosphate (ACP) which finally transforms into calcium deficient hydroxyapatite (CDHA). These mineral precipitate were reported to form the MTA-dentin interfacial layer which enhances the sealing ability of MTA. Clinically, the use of zinc oxide eugenol (ZOE) based materials may retard the setting of MTA. Also, the use of acids or contact with excessive blood should be avoided before complete set of MTA, because these conditions could adversely affect the hydration reaction of MTA. Further studies on the chemical nature of MTA hydration reaction are needed. (Restor Dent Endod 2012;37(4):188-193)

Key words: Calcium hydroxide; Calcium silicate hydrate; Dicalcium silicate; Hydration; Mineral trioxide aggregate; Tricalcium silicate

Introduction

MINERAL TRIOXIDE AGGREGATE (MTA) was developed in early 1990s by Torabinejad and Dentsply Tulsa Dental (ProRoot MTA, Dentsply Tulsa Dental, Johnson City, TN, USA). MTA was originally developed for perforation repair and root end filling.1,2 And due to its clinical success, MTA has expanded its uses to one-visit apexification, pulp capping, and so on.3,4 Since its introduction to endodontics, MTA has shown great clinical success due to its good sealing ability and biocompatibility.5-7 Among many advantages of MTA, main and unique advantage is that the setting of MTA is not adversely affected by presence of water. Indeed, MTA needs water in its setting reaction, thus it is considered hydrophilic and water tolerant. Considering that the traditional root perforation repair materials such as composite resin and glass ionomer are sensitive to the existence of water, water tolerance of MTA is believed to be its unique advantage which results in clinical success. However, until now, the setting reaction and the reaction product of hydrated MTA has not been fully investigated and clearly understood, although the setting mechanism and hydration products of MTA have significant effects on the chemical and physical properties of MTA. Thus, the aim of this article is to review the chemical characteristics and the hydration reaction of MTA.

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Materials and Methods

Pubmed search was used in preparation of this article. The keywords used for search of the articles were ‘mineral trioxide aggregate + hydration’ and ‘mineral trioxide aggregate + interface’. Some articles which were hand-searched regarding these key words were also included. Articles written in language other than English were excluded.

Chemical constitutions of MTA

United States (US) patent #5415547 and #5769638 exclaims that the principal component of grey ProRoot MTA is Portland cement.7 Other US patents regarding the white ProRoot MTA (US patent #20030159618, #2004226478, #20050263036) showed that the chemical ingredients of white aggregate is not identical to that of grey MTA.

MTA is composed of complex compounds. Main constituents of MTA are tricalcium silicate and dicalcium silicate.8-10 In addition, MTA contains relatively small amount of tricalcium aluminate and tetracalcium aluminoferete. To increase radiopacity, bismuth oxide was added in MTA. It was well known in cement chemistry, that tricalcium silicate and dicalcium silicate are made from lime (CaO) and silica (SiO2).11,12 These and some other raw materials such as aluminum oxide (Al2O3), magnesium oxide (MgO) and ferric oxide (Fe2O3) are heated in clinker to form four phases of tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferete. Among these, tricalcium aluminate was known to reduce the setting time of MTA.13 Thus, lime, silica, aluminum oxide, ferric oxide, and bismuth trioxide are the main oxides that constitute MTA. Asagary et al. also confirmed that the grey and white MTA are composed mainly of lime (CaO), silica (SiO2) and bismuth oxide (Bi2O3).1 They also reported that white MTA contained significantly lesser amount of aluminum oxide (Al2O3), magnesium oxide (MgO) and ferric oxide (Fe2O3) than grey MTA.7

Heavy metal contents in MTA

It has been widely known that MTA and Portland cement are very similar in their chemical compositions.14,15 In this regard, there have been studies which compared the constituting elements of MTA and Portland cement. In 2007, Chang and Bae reported that MTA and Portland cement have similar elemental compositions.16 Chang et al. also demonstrated that MTA and Portland are composed of similar oxides and phases.17 However, there are still differences between Portland cement and MTA in heavy metal contents.18 In a previous study of Chang et al., which used mixture of hydrochloric acid and nitric acid (‘aqua-regia’) for leaching various heavy metals from MTA and Portland cement, it was known that MTA contained significantly less arsenic, lead, chromium than Portland cement.19 From this study, it was recognized that the purity of MTA and Portland cement is not comparable. White MTA contains much less iron than grey MTA.20 However, white MTA still contains considerable amount of iron which could be a possible cause of tooth discoloration.20 The cause and effect relationship between tooth discoloration and iron contents of MTA needs further investigation. The other study carried out by the same author also showed that ProRoot MTA is free of lead and hexavalent chromium which were known to be calcinogen.21 Another study of Schembri et al. also reported that MTA contained lesser amount of arsenic than Portland cement.22 Matsunage et al. proclaimed that ProRoot MTA is safe material in terms of heavy metal contents.23 Considering these reports, clinical use of ProRoot MTA appears to be safe in terms of its heavy metal contents.19,21

Hydration product of MTA

Hydration reaction of MTA was reported to be similar to that of Portland cement. The setting reaction of MTA and Portland cement is a complex process. At first, the particles of tricalcium silicate react with water. In this process, the periphery of the tricalcium silicate powder is melted and form calcium silicate hydrate.24 Calcium silicate hydrate is known to be composed of calcium and silicon which were derived from MTA and hydroxyl ion which is supplied from mixing liquid. ProRoot MTA contains bismuth oxide as a radiopacifier. In this reason, in the setting reaction of ProRoot MTA, it was reported that bismuth is incorporated into calcium silicate hydrate and to form calcium-silicate-bismuth-hydrate, which is similar to calcium silicate hydrate.25

Another hydration reaction occurs between tricalcium aluminate and water. This reaction results in ettringite in the presence of gypsum, and eventually yield monosulfate once the gypsum was depleted.29 However, this reaction product is reported to be produced in quite smaller quantities than calcium silicate hydrate gels because the quantities of tricalcium aluminate contained in MTA is much smaller than tricalcium silicate.

Previous study reported that calcium silicate hydrate is a solid gel which shows amorphous appearance. As the setting process continues, the amounts of formed calcium silicate hydrate increases and occupy the voids between the particles. The presence of calcium silicate hydrate gel in hydration process of MTA has been reported in many previous reports.24-29

The other product which is formed as a result of setting reaction of MTA is calcium hydroxide. Calcium hydroxide is known to be formed as a result of the hydration reaction of MTA.8 Calcium hydroxide explains the high pH of MTA. And it was postulated that the formation of calcium hydroxide
attributed the hard tissue forming ability of MTA. As the setting reaction further progresses, the formed calcium hydroxide reacts with calcium sulfate to form ettringite.\cite{30} Calcium hydroxide also reacts with phosphate ion to form amorphous calcium phosphate which eventually yields hydroxyapatite.\cite{31}-\cite{33} In other words, as the MTA matures in phosphate containing body fluids, the calcium deficient hydroxyapatite (CDHA) is formed at the surface of MTA. CDHA is composed of calcium released from MTA, phosphate ion and hydroxyl ion which are contained in body fluids. Previous studies reported that the type and the morphology of CDHA formed in Dentin-MTA interfaces were various and tended to be dependent on pH, Ca/P ratio, and the type of solution in which the MTA-dentin interface is exposed.\cite{34}

**Effect of pH on hydration reaction of MTA**

It was reported that physical and chemical properties of MTA are adversely affected in a low-pH environment.\cite{35} It was also reported that the quality of crystals which is a reaction product of hydrated MTA was poor in acidic pH compared to alkaline pH.\cite{35} Another study recommended that the acid-etching of ProRoot MTA should be delayed until 96 hours after MTA placement to avoid the harmful effect of acid etching on MTA surface.\cite{35} Regarding the alkaline environment, there is a report that calcium hydroxide induced alkalinity increased porosity and unhydrated microstructure of MTA.\cite{34} Generally, there is no consensus on whether the calcium hydroxide affects the sealability of MTA.\cite{37,38} In this sense, further studies on the effect of calcium hydroxide on hydration reaction of MTA is necessary.

**Interface between MTA and dentin**

Although the superior sealing ability of MTA was well documented and reported, there has been relatively scarce study on the morphology of MTA-dentin interface.\cite{39,40} Recently, Reyes-Carmona studied and reported the interfacial layer formed between MTA and dentin.\cite{41,42} Reyes-carmona et al. and Dreger et al. reported that this interfacial layer was formed as a result of biomineralization and some tag-like structures were formed in this process.\cite{40,41} These were the pioneering reports that the tag-like structures was formed in MTA-dentin interface. Bird et al. also reported that the interfacial layer made of hydroxyapatite was formed between MTA and dentin.\cite{39} Based on these studies, it could be postulated that the superior sealing ability of MTA could be partly attributed to the formation of tag-like structures in MTA-dentin interface. It was interesting that MTA produced more MTA tag-like structures than Portland cement.\cite{40} It was also interesting finding that hydrated MTA immersed in phosphate buffered saline (PBS) produced more mineral precipitation than those immersed in distilled water.\cite{43} These tag-like structures are believed to be the result of ionic dissolution of MTA which resulted in growth and nucleation of the apatite layer.\cite{44,45} Dreger et al. reported that the calcium ions released from the cements diffused through the dentinal tubules and reacted with phosphate ions in the tissue fluids, and yield calcium phosphate.\cite{40} And eventually, this calcium phosphate incorporated other ions and matured into carbonated apatite (CDHA).\cite{40} This phenomenon suggested the possibility that the precipitated minerals formed the mineralized layer between MTA and dentin which yielded chemical bonding between MTA and dentin.\cite{33} Han and Okiji demonstrated that dentin which was in contact with MTA uptook Ca and Si from this calcium silicate based materials.\cite{46} They reported that the Ca and Si uptake of dentin caused chemical and structural modification of it, which might result in higher acid resistance and physical strength (Figure 1).

![Figure 1. Scanning Electron Microscope (SEM) image which shows the formation of tag-like structures in Ortho MTA-dentin interface and in dentinal tubules. (a) in Ortho MTA-dentin interface (X1,000); (b) in dentinal tubules (X1,000). Courtesy of Dr. Joon-Sang Yoo.](http://dx.doi.org/10.5395/rde.2012.37.4.188)
Interaction between MTA and adjacent filling materials

In the procedures of perforation repair, MTA is placed and the other restorative materials such as glass ionomer (GI) cement or intermediate restorative material tend to be overlaid on top of it. However, the reports regarding the interaction between MTA and these filling materials are scarce. Camilleri reported that MTA interacted with adjacent restorative materials which resulted in elemental migration between MTA and other restorative materials. They also suggested that the zinc oxide eugenol (ZOE)-based cements should not be used adjacent to MTA because zinc causes retardation of cement hydration and increases porosity. They also reported that the placement of GI material on partially set MTA resulted in weakening of GI because it lost water to MTA during the hydration reaction of MTA.

Effects of blood or serum contact of MTA during hydration

Generally, it was known that MTA was very tolerable to the presence of blood or serum in its setting reaction. However, recently, studies were published regarding the effect of blood or serum contamination of MTA during hydration reaction. At first, in 2008, Tingey et al. reported that the surface of MTA set in water and fetal bovine serum (FBS) showed difference. According to their report, MTA set in the presence of water showed marked crystalline structures mostly assumed to be calcium product. However, the surface of MTA set at the presence of FBS showed globular appearance rather than crystalline one. Nekoofar et al. also reported that MTA which was set at the presence of fresh whole blood showed decreased compressive strength and the surface of the blood contaminated MTA showed absence of acicular crystalline structure formation. This result means that the blood contamination of unset MTA adversely affects the setting reaction and mechanical strength of MTA. The detrimental effect of serum incorporation in the hydration reaction of MTA was clearly shown by Kim et al. This study markedly demonstrated that the MTA samples exposed to FBS in their setting reaction did not harden properly. All of these studies speculate that some protein components in serum or whole blood prevent the complete hydration and complete setting of MTA. However, mechanism of this phenomenon needs to be verified in future studies.

Conclusions

MTA is mainly composed of tricalcium silicate and dicalcium silicate. MTA and Portland cement are similar in their chemical composition, however, MTA contains lower amounts of heavy metals than Portland cement. The hydration reaction of MTA mainly produces calcium silicate hydrate and calcium hydroxide. Calcium hydroxide could form CDHA in contact with body fluids. Calcium silicate hydrate, calcium hydroxide and CDHA forms the interfacial layers between MTA and dentin which results in good sealing ability of MTA. The use of ZOE-based materials may retard the setting of MTA. Also, the use of acidic primer or contact with excessive blood should be avoided before complete set of MTA, because these conditions could adversely affect the hydration reaction of MTA.

Conflict of Interest: No potential conflict of interest relevant to this article was reported.

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