



# Synthesis of a mineral trioxide aggregate by spray-pyrolysis

Jeong-Cheol Lee, Seung-Hoon Um, Sang-Hoon Rhee\*

Department of Dental Biomaterials Science, Dental Research Institute and BK21 Plus, School of Dentistry, Seoul National University, Daehakro 101, Jongno, Seoul 110-749, Korea

Received 26 August 2015; received in revised form 2 October 2015; accepted 5 October 2015  
Available online 18 October 2015

## Abstract

A mineral trioxide aggregate (MTA) was newly synthesized by spray-pyrolysis following a sol–gel reaction. The precursor solution of MTA was prepared by condensation following a hydrolysis reaction between  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{SO}_4$  under nitric acid. The MTA powder was then synthesized with the precursor solution at 1500 °C at a carrier gas flow rate of 10 L/min after producing droplets by ultrasonic spray generator. The particle shape was spherical, with little clusters of smaller particles on the large particles, and their average size was about 0.8 μm. The phase analysis of the MTA powder by X-ray diffraction showed that it was composed of  $\text{Ca}_3\text{SiO}_5$ ,  $\text{Ca}_2\text{SiO}_4$ , and  $\text{Ca}_3\text{Al}_2\text{O}_6$  with a small amount of CaO and amorphous phases. The electron probe microanalysis showed that Ca, Si, Al, and S were distributed homogeneously within the particles. The final setting time measured by modified Vicat under 95% relative humidity was about 14 min. The early stage of setting was mainly led by the rapid formation of fiber-like calcium–silicate–hydrates (C–S–H) gels and  $\text{Ca}(\text{OH})_2$  crystals due to the rapid dissolution of calcium silicates. The late stage of setting was dominated by the formation of large columnar-structured  $\text{Ca}(\text{OH})_2$  crystals and  $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$  crystals with the continuous formation of fiber-like C–S–H gels. The compressive strengths were about 10 MPa after 1 h and 68 MPa after 7 d of setting. These results showed that an MTA powder with a high compressive strength and fast setting rate could be synthesized by spray-pyrolysis following a sol–gel reaction.

© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** MTA; Spray-pyrolysis; Sol–gel reaction; Final setting time; Compressive strength

## 1. Introduction

A mineral trioxide aggregate (MTA) is a mixture of a refined Portland cement, which contains large amounts of tricalcium silicate, dicalcium silicate, tricalcium aluminate, and small amounts of gypsum and tetracalcium aluminoferrite [1–3] with bismuth oxide as a radiopacifier. Trace amounts of silicon dioxide, calcium oxide, magnesium oxide, potassium sulfate, and sodium sulfate are also found in MTAs [1–3].

MTAs have been used for pulp capping, pulpotomy, apexogenesis, apical barrier formation in teeth with open apices, repair of root perforations, and as a root canal filling material [4] because they are nontoxic, noncarcinogenic, nongenotoxic, biocompatible with the host tissues, insoluble in tissue fluids, and dimensionally stable [5,6].

The setting of MTA begins with the hydration of the constituent elements such as tricalcium silicate, dicalcium silicate, and tricalcium aluminate. When calcium silicate (tricalcium silicate and dicalcium silicate) powders react with water, the hydrolysis occurs, and then columnar-structured calcium hydroxide crystals and flake- or fiber-like (dependent on the Ca/Si mole ratio) calcium–silicate–hydrate (C–S–H) gel form, grow, interlock together, and finally harden. Meanwhile, when the tricalcium aluminate reacts with water, this instantly produces hexagonal-shaped tricalcium aluminate hexahydrate crystals and also sets the MTA [7]. The reaction between tricalcium aluminate and water is so fast that it is difficult to obtain sufficient handling time. Thus, gypsum is used to retard this reaction by producing  $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_{32} \cdot 6\text{H}_2\text{O}$  (ettringite) through reaction with sulfur and tricalcium aluminate; [8–10] ettringite prevents the hydrolysis reaction of tricalcium aluminate by enclosing the surface of the tricalcium aluminate. This reaction continues until the sulfate in the MTA

\*Corresponding author. Tel.: +82 2 740 8696; fax: +82 2 740 8694.  
E-mail address: [rhee1213@snu.ac.kr](mailto:rhee1213@snu.ac.kr) (S.-H. Rhee).

is fully consumed by repeated iterations of the partial breakage of the ettringite layer through the expansion and re-formation of ettringite [7]. Thus, the initial setting progresses mainly due to the hydration of two calcium silicates, which produce fiber-like C–S–H gels and columnar-structured calcium hydroxide crystals, because the ettringite crystals retard the hydration reaction of tricalcium aluminate. However, the late stage of setting is primarily influenced by the hydration of tricalcium aluminate, which produces hexagonal-shaped tricalcium aluminate hexahydrate crystals.

The MTAs are synthesized through the same method as the one produce Portland cement; it is prepared through powder mixing, sintering at high temperature, quenching, crushing, and then grinding processes [7]. Quenching is a critical procedure to achieve the proper chemical characteristics of a MTA, but it is a dangerous and difficult process to carry out in a laboratory. The successive crushing and grinding processes of the product are time-consuming, require high energy, and have a high probability of contamination by the grinding media. Thus, it is desirable to simplify the synthetic procedure and improve purity control for biomedical applications.

In addition, the problems of the MTAs synthesized by the current process are their slow setting rate and granular consistency, which originate from their high crystallinity and large particle sizes with irregular shapes. A long setting time is inconvenient for the patient, and a coarse granular consistency impedes the even delivery of the mixture to very tiny root canal spaces and makes it hard to compact adequately. Thus, small and spherical MTA particles with low crystallinity are desirable to achieve a fast setting rate, easier handling properties, and high compressive strength.

In this study, the spray-pyrolysis method, which provides a relatively easy way to control the stoichiometry of an MTA, and to yield high purity and high reproducibility, was newly applied to synthesize small spherical particles with a narrow powder size distribution, elemental homogeneity in the particles, low crystallinity, and a substantial amorphous phase in the MTA, all of which provoked a fast setting rate, and easy handling. After the synthesis of the MTA powder, its shape, phase, setting characteristics, and compressive strength as a function of setting time were evaluated.

## 2. Materials and methods

### 2.1. Synthesis of an MTA powder by spray-pyrolysis following a sol–gel reaction

An MTA powder was synthesized by spray-pyrolysis following a sol–gel reaction. A  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(NH}_4)_2\text{SO}_3$  gel solution was prepared by the hydrolysis and condensation of calcium nitrate tetrahydrate (Aldrich), tetraethyl orthosilicate (Aldrich), aluminum nitrate nonahydrate (Aldrich), diammonium sulfate (Aldrich), and nitric acid (Aldrich) at 70 °C for 1 h under an Ar atmosphere. Their molar ratios were 1:0.31:0.05:0.04:0.16, respectively.

The tetraethyl orthosilicate, deionized water, and ethanol (1:20:10 in molar ratio) were mixed in a two-necked round

bottom flask, which was connected with a condenser, at 70 °C for 0.5 h under Ar atmosphere. Subsequently, the calcium nitrate tetrahydrate, aluminum nitrate nonahydrate, and diammonium sulfate were added sequentially into the tetraethyl orthosilicate solution and then mixed further for 1 h. Finally, the hydrolysis and condensation reaction of the solution was carried out for 0.5 h at 70 °C under Ar atmosphere after adding concentrated nitric acid (70 wt%, Aldrich). The precursor solution maintained its sol state even after the process of sol–gel reaction because large amount of deionized water and ethanol was added, which prevented the gelation.

The  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-(NH}_4)_2\text{SO}_3$  gel solution was then made into small droplets using an ultrasonic spray generator (1.7 MHz, 18 vibrators, Donglim, Korea) fed into an alumina reaction tube (120 cm in length and 5 cm in diameter) at 1500 °C with a carrier gas (air) flow rate of 10 L/min maintained by a compressor. The droplets passed through the alumina reaction tube, were converted to solid particles by heat, and passed through the front part of the exhaust line, which was maintained at 0 °C by a cooling pipe using a chiller (RBC-11, Jeio Tech, Korea). The resulting powder was then collected in a Teflon<sup>®</sup> filter placed in the rear part of the exhaust line of the reactor, which was kept at around 100 °C to avoid water condensation. Hereafter, the synthesized MTA was referred to as the nMTA (new MTA) distinguished from the currently used MTA.

For the setting test, the nMTA powder was mixed with deionized water on glass slabs and loosely compacted using a plugger into custom made split Delron molds that were 6 mm in height and 4 mm in diameter [11]. The water-to-cement mixing ratio was 1:3 (in wt%). The molds were occluded on one end with a microscope glass slide, wrapped with a damp gauze sponge, and allowed to set for various time intervals at 37 °C in a 95% humidity chamber [11]. The setting tests of the nMTA and the mixture of nMTA and bismuth oxide was also carried out according to the same procedures described above except for the pre-mixing process between the nMTA and bismuth oxide (Aldrich) powders; the nMTA and bismuth oxide were mixed with the ratio of 4:1 (in wt%) using agate mortar and pestle for 0.5 h [12].

### 2.2. Characterizations

All microstructures were observed by a field emission scanning electron microscope (FE-SEM; S-4700, Hitachi, Japan). The shortest diagonal of each particle was considered to represent its particle diameter, and 1510 particles were observed for the analysis. The relative frequency was plotted as a function of particle diameter. The crystal phases of the specimens before and after different periods of setting time were evaluated using an X-ray diffractometer (XRD; D8 Discover, Bruker, Germany). The elemental distributions of calcium, silicon, aluminum, and sulfur in the powder were analyzed with an electron probe microanalyzer (EPMA; JXA-8500 F, JEOL, Japan). The accelerating voltage was set to 15 kV and the probe current was set to 20 nA using a focused

Download English Version:

<https://daneshyari.com/en/article/1458913>

Download Persian Version:

<https://daneshyari.com/article/1458913>

[Daneshyari.com](https://daneshyari.com)