Particle Size Changes in Unsealed Mineral Trioxide Aggregate Powder

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Abstract

Introduction: Mineral trioxide aggregate (MTA) is commonly supplied in 1-g packages of powder that are used by some clinicians across several treatments against the manufacturer's instructions. ProRoot MTA cannot be resealed after opening, whereas MTA Angelus has a resealable lid. This study assessed changes in particle size distribution once the packaging had been opened. **Methods:** Fresh ProRoot MTA and MTA Angelus powder were analyzed by using laser diffraction and scanning electron microscopy and compared with powder from packages that had been opened once and kept in storage for 2 years. The ProRoot packet was folded over, whereas the MTA Angelus jar had the lid twisted back to its original position. **Results:** After 2 years, ProRoot MTA powder showed a 6-fold increase in particle size (lower 10% from 1.13 to 4.37 μm, median particle size from 1.99 to 12.87 μm, and upper 10% from 4.30 to 34.67 μm), with an accompanying 50-fold change in particle surface area. MTA Angelus showed only a 2-fold increase in particle size (4.15 to 8.32 μm, 12.72 to 23.79 μm, and 42.66 to 47.91 μm, respectively) and a 2-fold change in particle size surface area. **Conclusions:** MTA reacts with atmospheric moisture, causing an increase in particle size that may adversely affect the properties and shelf life of the material. Smaller particles have a greater predisposition to absorb moisture. Single-use systems are advised. *(J Endod 2014;40:423–426)*

Key Words

Laser diffraction, mineral trioxide aggregate, particle size, pre-hydration, single-use applications

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Mineral trioxide aggregate (MTA) is an important endodontic material with multiple uses (1–3). The MTA patent describes its ideal composition as 1 part bismuth oxide and 4 parts Portland cement (4). The latter component is hygroscopic and can absorb atmospheric moisture. ProRoot MTA (MTA-P) (Dentsply Maillefer, Ballaigues, Switzerland) is supplied in 1-g packets, with the instructions "1 gram-1 treatment." Therefore, the packet should not be opened until its use, and any powder not dispensed for the patient should not be reused. Nevertheless, a search of the term *MTA Uses* on a popular Internet discussion forum, "Dentaltown," revealed numerous postings from clinicians who are using MTA-P packets for multiple applications to lower the cost per application. The high cost influences its clinical use. A recent survey has shown that if cost was not an issue, some 85% of pediatric dentists and endodontists would use it over formocresol (5). Furthermore, cost has limited the uptake of MTA by educational institutions (6, 7).

Whereas opened packets of MTA-P cannot easily be resealed, the container for white MTA Angelus (MTA-A) (Angelus Soluções Odontológicas, Londrina, Brazil) has a resealable lid. The packaging is marked with the international standard symbol for "Do not reuse, Single use only, Use only once" (8, 9); however, it is marketed as providing 7 applications for 1 gram (10).

The existing literature does not address whether multiple use of MTA from the same container affects its properties. It can be expected that because MTA powder is hygroscopic, when it is left exposed to atmospheric moisture, it will react in a similar way as MTA powder mixed with water (1). The particles will begin to hydrate and agglomerate with neighboring particles into larger structures. Therefore, MTA powder that has had significant exposure to moisture should show an increased particle size. A larger particle would have a lower surface area than that of the particles from which it was formed and thus be less reactive, which could have implications for setting time, compressive strength, and alkalinity.

Although the thermodynamic process involved in cement hydration is not completely understood (11), a simplified mathematical model to understand the relationship between particle size and the degree of hydration is the following: (12)

$$\alpha(r) = 1 - \left(1 - \left(\frac{kt}{r}\right)\right)^3 \qquad \text{(Equation 1)}$$

Alpha (α) is the degree of hydration, t is the time, k is the rate constant, and r is the radius of the particle. From this formula, there is an exponential increase in the degree of hydration as the particle size is reduced. This also suggests any differences in particle size distribution between MTA-P and MTA-A may also alter the degree of hydration.

Studies on the particle size distribution of MTA are few (13–15). The patent for white MTA describes the Portland cement component as having 90% of the particles finer than 25 μm, 50% of the particles finer than 9 μm, and 10% of the particles finer than 3 μm (16). Bismuth oxide powder is supplied in various particle size distributions, and the patent does not discuss the resultant particle size distribution once bismuth oxide has been added. Scanning electron microscopic (SEM) examination of MTA indicates that particles range from <1 μm to as large as 50 μm (17, 18).

The distribution of MTA particle size has been determined by using a flow particle analyzer; however, this method cannot accurately measure particles that are less than 1.5 μm or greater than 40 μm (17, 18). An alternative method for assessing particle size distribution is laser diffraction, which measures the size of particles

TABLE 1. Particle Size Distribution of MTA

Cement type	D10 (10% of particles are below this size) (μm)	D50 (median particle size) (μm)	D90 (90% of particles are below this size) (μm)
MTA-P freshly opened	1.13	1.99	4.30
MTA-P aged 2 y	4.37	12.87	34.67
MTA-A freshly opened	4.15	12.72	42.66
MTA-A aged 2 y	8.32	23.79	47.91
Latex 0.8 μm	0.69	0.77	0.86
Latex 1 μm	0.81	0.91	1.03
Latex 3 μm	2.73	2.88	3.06
Latex 5 μm	4.66	5.59	8.18
Latex 20 μm	15.22	18.55	21.05

through the scattering of the laser beam through a dispersed particulate sample. The MicroPlus analyzer (Malvern Instruments, Worcestershire, UK) can accurately measure particles from 0.05–550 μm and is widely used in the cement industry for quality control of Portland cement (19).

This study was undertaken to evaluate changes in the particle size of MTA over time that result from atmospheric exposure during storage. It sets the groundwork for future work to explore concerns with MTA properties when taken from multiple-use containers.

Materials and Methods

This study replicated the methods of an investigation of fly ash, an industrial cementitious product similar to MTA (20, 21). For laser diffraction analysis, the refractive index used for MTA was 1.842, which was calculated as a weighted average from the refractive index of 20% bismuth oxide and 80% Portland cement.

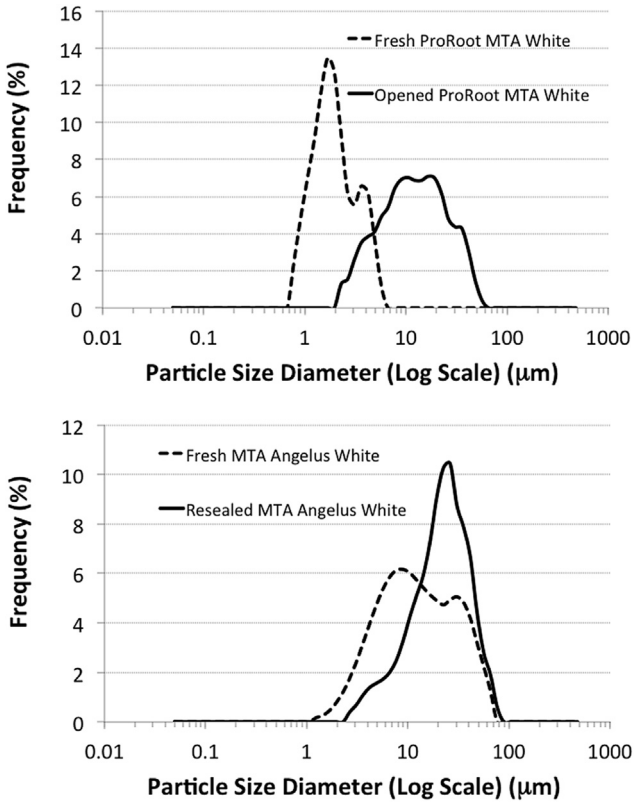

Figure 1. Particle size distribution of MTA-P and MTA-A when fresh and 2 years after having the packaging opened.

A packet of MTA-P (lot 09001921) was opened, folded on itself, and kept within closed boxed packaging for 2 years under normal room conditions, and another unopened packet of the same lot served as the control. A jar of MTA-A (lot 12862) was opened once, reclosed, and then kept for 2 years. For comparison, an unopened jar of fresh material (lot 21381) was tested soon after receipt from the supplier. The manufacturer's instructions for MTA-P suggest storing MTA between 10°C and 25°C. All containers were kept at room temperature in a cabinet away from sunlight, in accordance with the manufacturer's instructions for storage, for a period of 2 years. This duration was based on the expiration date being 3 years from manufacture (S. Freeman, personal communication). The study was performed in Brisbane, a city with a subtropical climate, with a mean maximum temperature of 25.3°C and a mean minimum temperature of 15.5°C (22).

One gram of each MTA sample was placed into 1 L distilled water within a Malvern MicroPlus analyzer, with analysis taking 4 seconds. The water dispersant was under continuous ultrasonic agitation to prevent agglomerated cement sinking to the bottom of the beaker and to prevent reagglomeration. The water was supplemented with 1 g/L sodium hexametaphosphate (Calgon) to prevent the MTA powder floating on the surface of the water and also to prevent hydration of the cement during the analysis. The period from placing the powder into the dispersant until analysis was less than 10 seconds. Spherical latex beads of 5 known sizes (0.8–20 μm) (lot #011899; ProSciTech Pty Ltd, Kirwan, Australia) served as controls for instrument calibration. Particle area was estimated by using spherical and cubic particle models with mean particle size as the diameter.

Samples of fresh and 2-year-aged MTA-P were examined by using SEM with backscatter imaging. Powder was sprinkled onto carbon tape and left uncoated. Images were taken at 15.0 kV with final magnification of $\times$1200 under low vacuum conditions by using an FEI 200 SEM (Quanta, Hillsboro, OR).

Results

Results from laser diffraction analysis are presented in Table 1 and Figure 1. MTA-P underwent a 6.5-fold increase in median particle size from 1.99 to 12.87 μm, whereas MTA-A showed a 2-fold increase in its D10 and D50, although its D90 remain relatively unchanged.

In terms of particle surface area, for MTA-P the increase in particle size from fresh to aged product was from 15.2 to 725.4 square microns, a 47.7-fold change in available surface area. For MTA-A, the surface area change was from 936.5 to 1882.6 square microns, a 2-fold change. When particles were modeled as being perfectly cubic, the surface area reduction was 6.9-fold for MTA-P and 1.4-fold for MTA-A.

Backscattered SEM images of MTA revealed the agglomeration of particles (Fig. 2). In these images, bismuth oxide appears as bright white particles (approximately 1–4 μm), which corresponds to the first modal peak of 3–4 μm seen in the particle size distribution for MTA-P.