Effect of Additives on Mineral Trioxide Aggregate Setting Reaction Product Formation

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Abstract

Introduction: Mineral trioxide aggregate (MTA) sets via hydration of calcium silicates to yield calcium silicate hydrates and calcium hydroxide ($Ca[OH]_2$). However, a drawback of MTA is its long setting time. Therefore, many additives have been suggested to reduce the setting time. The effect those additives have on setting reaction product formation has been ignored. The objective was to examine the effect additives have on MTA's setting time and setting reaction using differential scanning calorimetry (DSC). **Methods:** MTA powder was prepared with distilled water (control), phosphate buffered saline, 5% calcium chloride ($CaCl_2$), 3% sodium hypochlorite (NaOCl), or lidocaine in a 3:1 mixture and placed in crucibles for DSC evaluation. The setting exothermic reactions were evaluated at 37°C for 8 hours to determine the setting time. Separate samples were stored and evaluated using dynamic DSC scans (37°C → 640°C at10°C/min) at 1 day, 1 week, 1 month, and 3 months (n = 9/group/time). Dynamic DSC quantifies the reaction product formed from the amount of heat required to decompose it. Thermographic peaks were integrated to determine enthalpy, which was analyzed with analysis of variance/Tukey test (α = 0.05). **Results:** Isothermal DSC identified 2 main exothermal peaks occurring at 44 ± 12 and 343 ± 57 minutes for the control. Only the $CaCl_2$ additive was an accelerant, which was observed by a greater exothermic peak at 101 ± 11 minutes, indicating a decreased setting time. The dynamic DSC scans produced an endothermic peak around 450°C–550°C attributed to Ca(OH)2 decomposition. The use of a few additives (NaOCl and lidocaine) resulted in significantly less $Ca(OH)_2$ product formation. **Conclusions:** DSC was used to discriminate calcium hydroxide formation in MTA mixed with various additives and showed NaOCl and lidocaine are detrimental to MTA reaction product formation, whereas $CaCl_2$ accelerated the reaction. *(J Endod 2015;41:88–91)*

Key Words

Calcium hydroxide, differential scanning calorimetry, mineral trioxide aggregate, setting reaction, setting time

Mineral trioxide aggregate (MTA) was introduced to dentistry as a repair material for lateral root perforations (1). Since that time, MTA has been used in many dental applications, with this influx of applications attributed to MTA's biocompatibility and sealing ability (2, 3). Although these favorable properties remain MTA's strong suit, its long setting time has warranted improvements. MTA sets through an exothermic reaction, requiring hydration of its powder to produce the cement paste that matures over time (4). The setting of MTA is best understood through examining the hydration reactions of its main constituent, Portland cement, in which the most important reactions are tricalcium silicate and dicalcium silicate reacting with water to produce calcium silicate hydrates (C-S-H) and calcium hydroxide ($Ca[OH]_2$) (5–7). Once MTA is fully hydrated, the $Ca(OH)_2$ reaction product comprises approximately 10%–15% of the set cement (7, 8). The setting time of MTA has been documented to be 165 minutes (9), 45–140 minutes for the initial and final setting (10), 40–140 minutes for the initial and final setting (11), 50 minutes (12), 151 minutes (13), and 220–250 minutes (14). Traditionally, resistance to penetration in the form of Gillmore and Vicat needles has been used to assess the setting time of cements. Although these methods are inexpensive and easy to use, they are somewhat subjective and perhaps reflect the variation in reported setting times. More importantly, they provide little direct information to the underlying chemical processes responsible for the setting of the cement.

Alternatively, differential scanning calorimetry (DSC) may be used to study the setting of MTA by measuring the heat evolved (ie, the exothermic heat) during the early stages as well as by monitoring the reaction products that formed via their decomposition upon heating (7). It is through this testing methodology that more objective data on MTA's setting may be acquired. When reacted MTA is heated, it is possible to calculate the quantity of product formed from the quantity of heat required to decompose it. Decomposition of C-S-H occurs via dehydration at around 115°–125°C, whereas $Ca(OH)_2$ decomposes to CaO (and H_2O) via dehydroxylation at around 440°–580°C (5, 6). Other reactants and products may also decompose at certain temperatures, but in Portland cement the degree of hydration is indicated by the quantity of $Ca(OH)_2$ formed (6).

To improve MTA's setting time, many investigations have described MTA preparations with various additives (12–25). Commendably, many of these studies also examined if the additives had effects on various physical properties. Although they indicated further studies were required, 1 study cautiously recommended using either 5% calcium chloride ($CaCl_2$) or sodium hypochlorite (NaOCl) gel in place of water when mixing MTA to be used in single-visit endodontic procedures (12).

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However, although maintenance or improvement in physical properties of MTA with additives is important, the effect those additives have on setting reaction product formation has been ignored. One should recognize that the bioactivity of MTA is attributed to hydration of the powder causing Ca^{+2} dissolution and diffusion, reaction product formation (C-S-H and $Ca[OH]_2$), and further reactions resulting in apatite formation (3, 26, 27). It is conceivable that any changes to the setting reaction and reaction product formation may impact the formation of this bioactive layer. With this in mind, the objective of this study was to examine the effect additives have on MTA's setting time and setting reaction using DSC.

Materials and Methods

In a 3:1 (powder:liquid) mixture, MTA powder (ProRoot White; Dentsply Tulsa Dental, Johnson City, TN) was prepared with distilled water (control), phosphate buffered saline (PBS; Fisher Scientific, Pittsburgh, PA), 5% $CaCl_2$ (Fisher Scientific [prepared as a solution by dissolving $CaCl_2$ in distilled water at a 5% concentration]), 3% NaOCl (ChlorCid V; Ultradent Products, South Jordan, UT), or lidocaine (2% Xylocaine Dental with epinephrine 1:100,000; Novocol Pharmaceutical, Cambridge, Ontario, Canada). The 3:1 (powder:liquid) mixture was applied to all preparations to standardize proportions. The mixtures were transferred to preweighed 40-μL aluminum crucibles (Mettler-Toledo, Columbus, OH) and weighed in an analytical balance with the amount of mixture in each calculated. Each mixture group was tested at the following time points: immediately after, 1 day, 1 week, 1 month, and 3 months (n = 9/mixture group/time); individual specimens were only tested once. With the exception of the immediate specimens, the groups were stored in an incubator at 37°C with 100% humidity until their prescribed time of analysis (1 day, 1 week, and so on).

Each crucible of the immediate specimens was fitted with a lid to prevent water evaporation and placed in the DSC (Model 822e, Mettler-Toledo) for an isothermal scan at 37°C for 8 hours to analyze any exothermic peaks associated with setting. As a reference during measuring, an empty 40-μL aluminum crucible was used. After the 8-hour isothermal scan, this immediate specimen was weighed again, and the lid was pierced to allow for equilibration of pressure and release of volatile products upon heating (ie, water evaporation). The crucible was placed back on the DSC sensor for analysis by a dynamic scan from 37°C → 640°C at 10°C/min. (Because the dynamic scan was at the 8-hour mark in the immediate specimens, it is later termed "8 hour" for data comparison.) For the remaining groups, at their designated time frames, the test samples were weighed and fitted with a pierced lid before the same dynamic DSC evaluation (37°C → 640°C). As mentioned previously, the dynamic thermal scan is used to quantify reaction product formation via the enthalpy (J/g) associated with their decomposition upon heating. All resulting DSC thermograms were evaluated by the DSC manufacturer's software (STARe, Mettler-Toledo). Both the time of setting of exothermic peak(s) and enthalpy associated with $Ca(OH)_2$ decomposition computed via integration of the endothermic peak were determined from the respective isothermal and dynamic thermograms. $Ca(OH)_2$ decomposition enthalpy was statistically analyzed with 2-way analysis of variance with the mixture group and time as factors with a post hoc Tukey studentized range (honest significant difference) test when indicated at α = 0.05 (SAS, Cary, NC).

Results

The isothermal DSC evaluations resulted in thermograms with exothermic peaks identified across an 8-hour period at 37°C. The time, number, and height/area of exothermic peaks associated with setting varied across additive mixture groups. The control, PBS, and lidocaine groups exhibited 2 exothermic peaks averaging 44 ± 12 minutes, 49 ± 20 minutes, and 36 ± 8 minutes for the first, less intense peak and a second peak averaging 343 ± 57 minutes, 355 ± 43 minutes, and 316 ± 58 minutes, respectively. The NaOCl group's thermograms showed an average peak of 49 ± 16 minutes, with 2 instances showing an additional peak at 317 and 343 minutes. The $CaCl_2$ group had only 1 exothermic peak occurring on average at 101 ± 11 minutes (Fig. 1).

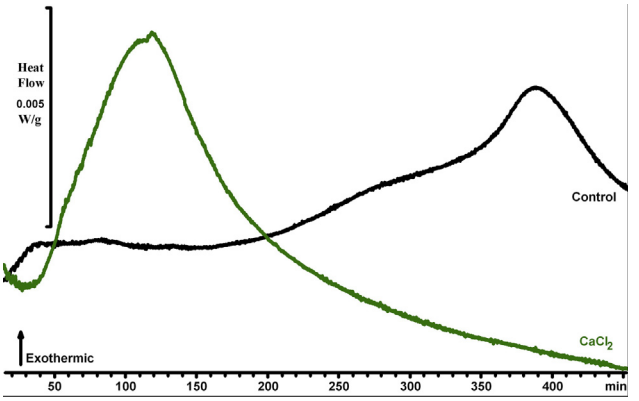

Figure 1. Comparison of exothermic setting peaks during isothermal DSC.

For the DSC thermograms resulting from the dynamic scan, endothermic peaks were identified across a temperature range of 37°C → 640°C. Figure 2 displays thermograms among the groups at 1 week. A comparison of thermograms across additives showed qualitative differences for NaOCl in which more endothermic peaks were present in a distinct pattern across all time frames, specifically from 160°C–340°C. For all groups and time frames, an endothermic peak appeared between 100°C and 150°C associated with the liberation of water and dehydration of the C-S-H reaction product (5–7). However, it should be noted that ettringite produced from the tricalcium aluminate component of MTA powder also dehydrates around 120°–130°C (5, 6) and may be obscured by the much more abundant C-S-H dehydration. For the 8-hour and 1-day group, an endothermic peak was identified around 160°–200°C because of the dehydration of gypsum (5–7) (not visible in the 1-week thermogram in

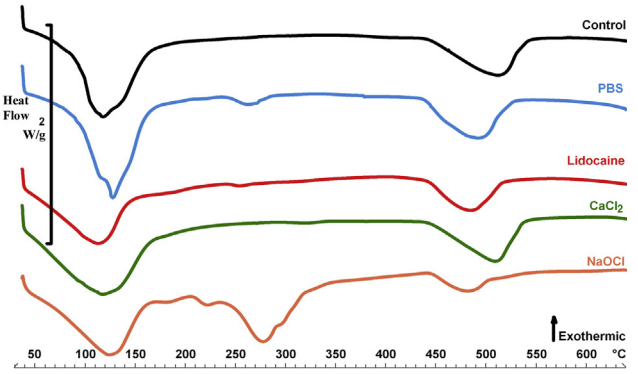

Figure 2. Comparative DSC thermograms of MTA mixed with different additives 1 week after mixing. The endothermic peaks around 100°C–150°C and 450°C–550°C are associated with the liberation of water/dehydration of calcium silicate hydrates and dehydroxylation of calcium hydroxide reaction products, respectively.