Journal of the Formosan Medical Association (2017) 116, 424–431

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.jfma-online.com

ORIGINAL ARTICLE

Hydration behaviors of calcium silicate-based biomaterials

Yuan-Ling Lee [a,b], Wen-Hsi Wang [c], Feng-Huie Lin [c], Chun-Pin Lin [a,b,d,*]

[a] *Graduate Institute of Clinical Dentistry, School of Dentistry, National Taiwan University Hospital, National Taiwan University, Taipei, Taiwan*
[b] *Department of Dentistry, National Taiwan University Hospital, National Taiwan University, Taipei, Taiwan*
[c] *Institute of Biomedical Engineering, College of Medicine, National Taiwan University, Taipei, Taiwan*
[d] *School of Dentistry, China Medical University and China Medical University Hospital, Taichung, Taiwan, ROC*

Received 6 July 2016; received in revised form 16 July 2016; accepted 20 July 2016

KEYWORDS
calcium silicate;
calcium silicate hydrate;
hydration;
mineral trioxide aggregate

Background/purpose: Calcium silicate (CS)-based biomaterials, such as mineral trioxide aggregate (MTA), have become the most popular and convincing material used in restorative endodontic treatments. However, the commercially available CS-based biomaterials all contain different minor additives, which may affect their hydration behaviors and material properties. The purpose of this study was to evaluate the hydration behavior of CS-based biomaterials with/without minor additives.
Methods: A novel CS-based biomaterial with a simplified composition, without mineral oxides as minor additives, was produced. The characteristics of this biomaterial during hydration were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectrometry. The hydration behaviors of commercially available gray and white MTAs with mineral oxide as minor additives were also evaluated for reference.
Results: For all three test materials, the XRD analysis revealed similar diffraction patterns after hydration, but MTAs presented a significant decrease in the intensities of Bi_2O_3-related peaks. SEM results demonstrated similar porous microstructures with some hexagonal and facetted crystals on the outer surfaces. In addition, compared to CS with a simplified composition, the FTIR plot indicated that hydrated MTAs with mineral oxides were better for the polymerization of calcium silicate hydrate (CSH), presenting Si–O band shifting to higher wave numbers, and contained more water crystals within CSH, presenting sharper bands for O–H bending.

Conflicts of interest: The authors have no conflicts of interest relevant to this article.

* Corresponding author.School of Dentistry, China Medical University and China Medical University Hospital, No. 91, Hsueh-Shih Road, Taichung 40402, Taiwan, ROC.
E-mail address: pinlin@ntu.edu.tw (C.-P. Lin).

http://dx.doi.org/10.1016/j.jfma.2016.07.009

Conclusion: Mineral oxides might not result in significant changes in the crystal phases or microstructures during the hydration of CS-based biomaterials, but these compounds affected the hydration behavior at the molecular level.

Introduction

Mineral trioxide aggregate (MTA) is a type of mineral cement developed for restorative endodontic applications.[1] Its excellent sealing ability, good biocompatibility, and induction of hard-tissue regeneration have been supported by many *in vitro* and *in vivo* studies.[2–5] Recent studies have shown that an apatite-like layer forms on the surface of MTA when hydrated in simulated body fluids or phosphate-buffered saline, demonstrating the surface bioactivity of MTA.[6,7] Therefore, MTA has become the most popular and convincing material used in restorative endodontic treatments, including root perforation repair, retrograde filling, apical plug application, and vital pulp therapy. However, MTA requires a long setting time, potentially leading to future complications or even treatment failures. Recently, there have been several attempts to decrease the setting time of MTA using different additives,[8,9] such as Na_2CO_3 and Na_2HPO_4, without understanding the hydration behaviors of MTA.

The original commercially available MTA, approved by the Food and Drug Administration in 1997, is gray (GMTA) in color and primarily comprises tricalcium silicate (C_3S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), and bismuth oxide (Bi_2O_3). Subsequently, for aesthetic considerations, the GMTA form was modified after adding fluxing agent to remove the colored ingredients, generating a white MTA (WMTA), which was introduced to the market. In addition, the two commercially available MTAs also contain small amounts of additives, such as gypsum ($CaSO_4 \cdot 2H_2O$), MgO, SO_3, Na_2O_3, and K_2O.[10,11] In the cement industry, these minor additives are typically added to adjust the physical properties of Portland cements through effects on the cement hydration. However, the precise mechanism of how these minor additives affect the cement properties during hydration remains unclear.

In this study, to retain the desirable properties of MTAs, a novel calcium silicate (CS) with a simplified composition, containing only C_3S/C_2S, C_3A, and C_4AF, was developed. Because CS has the same major components as commercially available MTAs, except a small amount of minor additives, it would be a good reference material to investigate the hydration mechanism of CS-based biomaterials. The purpose of this study is to evaluate the hydration behaviors of CS-based biomaterials, including CS and the two commercially available MTAs.

Materials and methods

Material preparation

The main components of CS, including Ca_3SiO_5 (C_3S), $Ca_3Al_2O_6$ (C_3A), and $Ca_4Al_2Fe_2O_{10}$ (C_4AF), were prepared by sintering. The raw materials of each component were mixed in a ball mill individually and the substrates with molar ratios were mixed based on the chemical formula of the products. The mixed substrates were subsequently heated to 1400°C for C_3S preparation, 1300°C for C_3A preparation, and 1350°C for C_4AF preparation. The materials were incubated for 2 hours and subsequently quenched in air, followed by milling into powder. The crystal phases of the produced C_3S, C_3A, and C_4AF powders were confirmed through X-ray diffraction (XRD). Based on the ingredients of Type III high-early strength Portland cement, CS was produced after mixing C_3S, C_3A, and C_4AF at a weight ratio of 8:1:1 to mimic commercially available MTAs without minor additives.

Commercially available GMTA (ProRoot MTA; DENTSPLY Tulsa Dental, Johnson City, TN, USA) and WMTA (ProRoot MTA; DENTSPLY Tulsa Dental) were also used for further evaluation in this study.

Microstructure observation

The samples were prepared after mixing the CS powders with distilled water at a weight-to-volume ratio of 2:1, while both MTAs were mixed with distilled water in a weight-to-volume ratio of 3:1, according to the manufacturer's instructions. Subsequently, the mixture was compressed and condensed into a mold. The samples were stored in distilled water at 37°C for 7 days and then removed and air dried overnight at room temperature. The samples were sputter coated with gold using a sputter coater (BIO-RED SC 502; Fisons, Ipswich, UK) and the microstructure of the test materials, including the outer structure (surface structure) and the inner structure (fractured surface), was examined using a scanning electron microscope (SEM; Topcon ABT-60, Tokyo, Japan).

Transformation of hydrated products

The samples were hydrated at 37°C and 100% humidity for 7 days, followed by milling into powder for further evaluations. The crystalline phases of the prepared samples were examined through powder XRD using a Rigaku X-ray powder