Real-time Monitoring of Hardening of Nanosilica Sol containing DCPA Cements in an ESEM

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Statement of Purpose: Recently, we developed a microwave assisted approach to produce calcium phosphate, especially dicalcium phosphate anhydrous (DCPA) based cement compositions (MW-DCPA). Our technique can eliminate exothermicity and pH related problems during setting of the regular DCPA cement and can improve compressive strength significantly. Addition of nanosilica sol can further improve the mechanical performance of such cements. This study aims at investigating the mechanism of hardening of compositions containing the nanosilica sol in real-time by using an Environmental Scanning Electron Microscope fitted with Energy Dispersive X-ray analysis (ESEM-EDX). It is expected that the results will elucidate the mechanisms for the setting of this cement. The ESEM has the capability to examine electrically insulating specimens under various temperature, pressure, and humidity conditions [1]. This helps in monitoring the development of microstructure in real-time without any need for conventional sample preparation protocol of sputter coating, drying, or chemical fixation [2].

Methods: An Environmental Scanning Electron Microscope (ESEM, FEI Quanta 3D FEG Dual Beam Electron Microscope) equipped with a Gaseous Secondary Electron Detector (GSED) was used to image the process. The raw DCPA (Dicalcium Phosphate Anhydrous, Monetite) powder is made first, before the addition of the nanosilica sol. The DCPA cement powder is synthesized from a calcium hydroxide component, setting solution, and de-ionized water (DI). Subsequently, the microwave procedure takes place and nanosilica sol is added as the final powder setting solution. Cement samples are analyzed at 6 minutes after sample preparation and every 1 minute 40 seconds till the estimated final setting time of 30 minutes. The samples were ground but were not coated for this analysis. Humidity and temperature are controlled by the ESEM in order to watch the setting process while limiting outside factors.

Results: Results show that an initial hydrated calcium silicate gel is present. It is suggested that the attraction forces are related to acid-base interparticle bonding of salt bonding by acidic cations and silanol-dissociated silanol bonds resulting in a homogeneous self-setting paste. The self-setting properties of cements and the progressive hydration reaction of the calcium and silica particles react with water and form a nanoporous amorphous gel on the cement particles while calcium hydroxide ($Ca(OH)_2$), portlandite) nucleates and grows in the available voids and pore spaces. Our cement production process produces DCPA cement with 18MPa of strength and 45-60MPa of strength when combined with nanosilica. The hydration of DCPA with nanosilica sol has been shown to take place in wet conditions. During the first few minutes a gel is seen forming as granular precipitates and a nanosilica sol binds particles together. Setting can be watched occurring in as little as 20 minutes in real time. The control of the environment allows for the setting process to proceed at different rates under different conditions as seen in Figure 1 and 2. The addition of nanosilica has also been show to close cracks in samples surface and bind particles together with higher attraction forces.

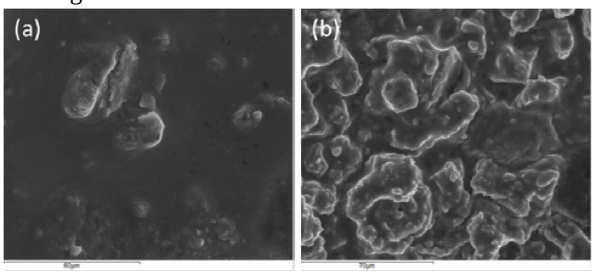

Figure 1. Same Area of DCPA+SiO_2 47.4%RH 25.4 C a) 6:00min Left b) 19:20min Right

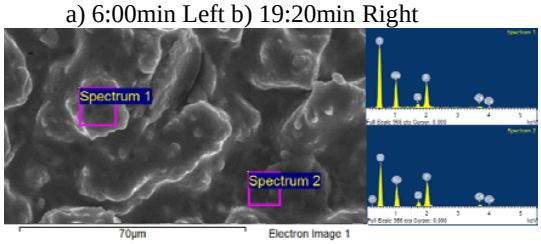

Figure 2. Two Regions and Their Makeups DCPA+SiO_2– EDS Data 17:40 Minutes Setting 47.4% RH 25.4 °C

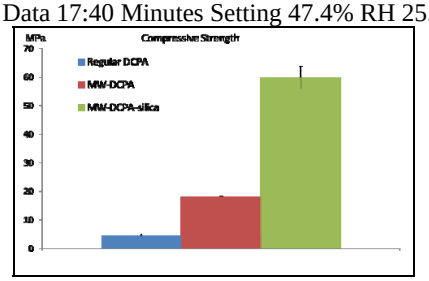

Figure 3. Compressive Strength of Regular DCPA, MW-DCPA and MW-DCPA-Silica

Conclusions: The setting of a microwave assisted DCPA containing nanosilica sol has been investigated and outlined for studying the setting morphological evolution. The benefits of adding nanosilica has been seen in many applications such as biological and construction cements. These benefits can be translated into the same desirable mechanical properties for the creation of bioactive bone cement.

References:

1. Franz, N. J Mater Sci 2006; 41.14 4561-4567.
2. Danilatos, G. Microscopy Research and Technique 25. John Wiley & Sons, Inc. 2005; 354-361.