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Basic Properties of Novel Bioactive Cement Based on Silica-Calcium Phosphate Composite and Carbonate Apatite

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Abstract. Silica-calcium phosphate composite (SCPC) and carbonate apatite (CO_3Ap) are resorbable bioactive materials with the ability to adapt to bone structure and to induce bone regeneration. Considering the similarity between bone and dental structure, where both are mainly composed of calcium deficient carbonate containing hydroxyapatite, we hypothesize that a SCPC-CO_3Ap bone cement might also be favorable for the regeneration of dentin and pulp tissue. Therefore, in the present study we report on the effect of composition and structure of SCPC-CO_3Ap cement on the morphology, setting and mechanical properties of the material. The novel bioceramics cement composed of vaterite, dicalcium phosphate anhydrous (DCPA) and SCPC. The powder cement ratio were divided into 5 groups with different percentage of SCPC. Set cement was examined by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and the mechanical strength was evaluated by diametral tensile strength. XRD patterns revealed that the apatite formation was formed after 72 hours, however the intensity of apatite varied based on the SCPC content. The DTS evaluation indicated that group 3 has the highest mechanical strength compared to others. This was supported by SEM analysis of set cement showing more compact surface microstructure of group 2 and 3 compared to other different ratio and control group. The novel bioceramics cement was successfully made using vaterite, DCPA and SCPC. This new cement is currently being investigated for dental application to induce dentinogenesis.

Introduction

Dental pulp is the inner part of a tooth surrounded by mineralized tissue called dentin which protects the pulp from external threat such as thermal shock and bacterial invasion. The pulp is a loose connective tissue with various cells including fibroblast, odontoblast, immune cells, undifferentiated mesenchymal cells, sensory nerves and blood vessels.[1] A healthy dental pulp is important for sensory innervation, nutrition, development of the tooth and production of reparative dentin when dentin is broken or the pulp is injured. In cases with heavily broken tooth due to caries exposure or dental trauma, the vitality of the tooth is jeopardized leading to inflammation of the pulp tissue that can eventually leads to pulp necrosis and inflammation of the periapical area.

Treatment for injured dental pulp in order to maintain its vitality is called pulp capping treatment, by placing a material on the injured/exposed pulp or dentin-pulp interface to induce a dentinal bridge formation prior to filling the tooth with permanent dental restoration. For several decades, the golden standard for pulp capping agent is calcium hydroxide, where abundant number of studies have proven its efficiency in achieving its goal to save the vitality of the pulp. However, the material has some drawbacks as well, calcium hydroxide are very soluble and has no adhesive capability to the dentin structure thus provides poor sealing properties.[2]

Dentin as a protective layer of the pulp consist about 30% water and 70% inorganic substances (hydroxyapatite). Considering the similarities of bone structure to dentin, we proposed

the used of silica-calcium phosphate composite (SCPC) and carbonate apatite (CO_3Ap) that have been proven to be resorbable bioactive materials with the ability to adapt to bone structure and to induce bone regeneration[3-9] to be used as pulp capping materials. The used of these bioceramics will hopefully induced the regeneration of dentin (dentinogenesis).

Materials and Methods

Preparation of CO_3Ap and Silica-Calcium Phosphate Composite Powder. The CO_3Ap powder composed of vaterite (Yabashi Industries Co., Ltd, Ohgaki, Japan) and dicalcium phosphate anhydrous (DCPA) (J.T. Baker Chemical Co., NJ, USA). The particle size of vaterite powder has average of approximately 0.7 μm. The commercially DCPA powder was reduced to 0.4 μm by grinding DCPA powder in a planetary ball mill (Fritsch 8 6560, Idar-Oberstein, Germany) with 95% ethanol for 1 hour and drying for 3 hours. The SCPC containing 40.68% CaO, 20.34% P_2O_5, 19.49% Na_2O, and 19.49% SiO_2 (in mol %) was prepared using a powder metallurgy technique. The powders were mixed in polyethylene bottles over a roller for 24 h, then treated by calcination at 800°C (Thermolyne 30400, Barnstead International, Dubuque, IA) for 1 h, and then ground to the size-average of 90 μm.[10]

Preparation of Samples. The CO_3Ap and SCPC powder were mixed homogeneously to obtain cement powder. The cement powder divided into 5 groups which were group 1 (60% DCPA : 40% vaterite : 0% SCPC) as a control group, group 2 (60% DCPA : 10% vaterite : 30% SCPC), group 3 (60% DCPA : 20% vaterite : 20% SCPC), group 4 (60% DCPA : 30% vaterite : 10% SCPC), and group 5 (60% DCPA : 0% vaterite : 40% SCPC). 1 mol/L of disodium hydrogen phosphate (Na_2HPO_4; pH 8.2) was used as the cement liquid. Powder phase and liquid phase were mixed with spatula at a liquid to powder (L/P) ratios of 0.5. The paste was put into Teflon mold (6 mm in diameter × 3 mm in height). Both ends of the mold was covered with a glass slides then clamped. The molds were placed inside plastic container with distilled water to maintain 100% relative humidity. The plastic container then placed into an incubator and kept at 37°C for 72 h. The samples were removed from the mold after completion of treatment times and immersed in the 99% ethanol for 3 minutes then dried in the oven at 80°C for 3 h.

Characterization of samples. X-ray diffraction was used to identify the crystalline phases of the samples by crushed into powder then characterized by mean of X-ray diffraction (XRD: D8 Advance, Bruker AXS GmbH., Karlsruhe, Germany).

Mechanical strength measurements. The mechanical strength of samples was examined in terms of diametral tensile strength (DTS). The paste was packed into a split Teflon mold (6 mm in diameter × 3 mm in height). The mold is placed by storing in an incubator within 24 hours at 37°C and 100% relative humidity. The samples were crushed using a universal testing machine (LRX Plus; Llyod Instruments, Ltd., West Sussex, UK) at a crosshead speed of 1 mm/min. DTS values were taken as average of at least 10 samples.

Morphological observation. Microstructure evaluation of the fractured surface of the samples was performed by scanning electron microscope (SEM: S-3400N, Hitachi High-Technologies, Tokyo, Japan) at 15 kV of accelerating voltage after gold sputters coating.

Results and Discussion

Key to the success of pulp capping treatment is the continuity of pulp vitality as indicated by normal pulp response to stimuli, the absent of symptoms or sign of inflammation and the formation of reparative dentin on the injury site.[1,2]

Engineering the mechanical properties and biological performance of pulp capping material are essential for successful pulp capping. The material should be able to adhere to dentin and the restorative material placed above it, resist mastication force, have good handling properties and reasonable setting time to be used in clinical situation. Moreover, the pulp capping material should stimulate the regeneration of dentin by stimulation of cell proliferation, be biocompatible to other cells in the site and in some cases able to release bioactive molecule needed for dentinogenesis.[1,2,11]

Cement consists of calcium carbonate ($CaCO_3$) and anhydrous dicalcium phosphate mixed with Na_2HPO_4 aqueous solution resulted in a formation of CO_3Ap in physiological conditions.[6] Previous study on rat tibia defect using CO_3Ap showed that the cement could set even in the presence of blood or body fluid. This is an important feature considering bleeding is a major problem in exposed pulps, less soluble material is preferable to avoid washing out of material before the material had any effect on the tissue. CO_3Ap is one of the major inorganic substances in dentin. Therefore, the formation of CO_3Ap from this new cement and the release of silica and phosphate from SCPC could enhance the formation of reparative dentin.

Figure 1 showed the XRD patterns of the apatite formation that was formed after 72 hours treatment. The XRD pattern of group 1 as a control group revealed that the apatite formation could be achieved after 72 hours, meanwhile group 2, 3, 4, and 5 showed that the intensity of apatite was low depending on the SCPC content. In other words, when amount of SCPC increased, the apatite formation decreased.

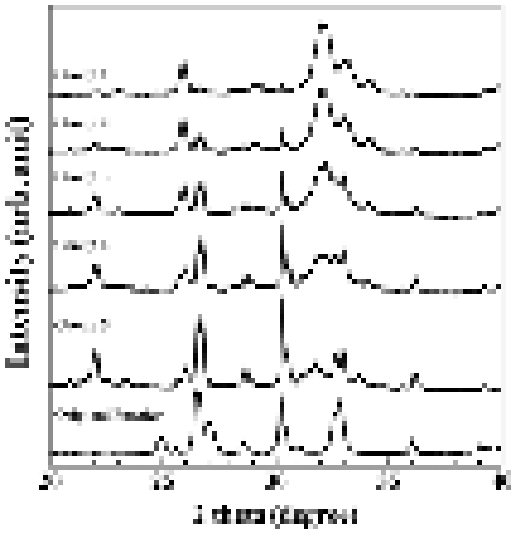

Fig. 1 XRD patterns of samples after 72 hours treatment. Original powder (60% DCPA: 40% vaterite) was listed as reference.

Figure 2 summarizes the DTS evaluation values of the set cement after kept at 37°C, 100% relative humidity for 72 h. The DTS values were: 2.06 ± 0.32 MPa (group 1); 5.17 ± 0.53 MPa (group 2); 5.64 ± 0.73 MPa (group 3); 3.97 ± 0.71 MPa (group 4); and 4.01 ± 0.32 MPa (group 5). The highest DTS values was for group 3, however there was no statistically significant difference between group 3 and group 2. The high mechanical strength for cement samples in group 2 and 3 is associated with the high contents of SCPC component in the two materials. The bioactive silicate functional groups of SCPC appeared to bind the powdered components in the cement and contribute to formation of areas with more dense structure as seen in the SEM analyses (Figs. 4b and 4c).

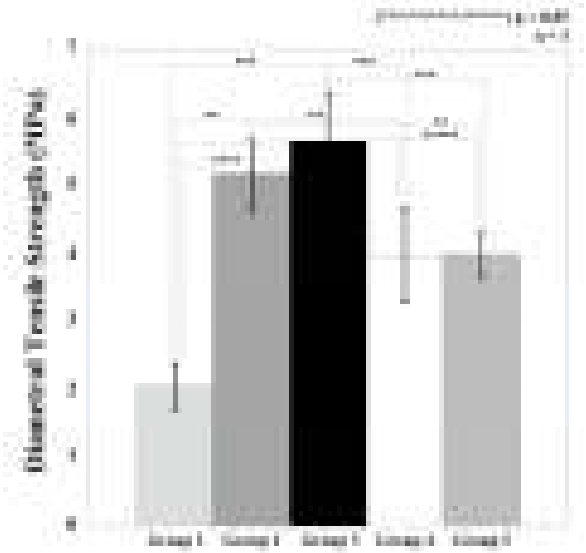

Fig. 2 Mechanical strength evaluation in the term of diametral tensile strength after treated 72 hours. At least 3 samples were measured for DTS.

Figure 3 and 4 demonstrate the surface morphology and cross section microstructure of samples before and after the DTS evaluation. SEM analysis of set cement showing more compact surface microstructure of group 2 and 3 compared to other different ratio and control group. When vaterite and DCPA were exposed to 1 mol/L Na_2HPO_4 solution, they dissolve and supply the Ca^{2+}, CO_3^{2-} and PO_4^{3-}. However, the SCPC was not dissolved completely, they dissolve later after the aqueous solution supersaturated with respect to CO_3Ap. The CO_3Ap crystal would be precipitated.

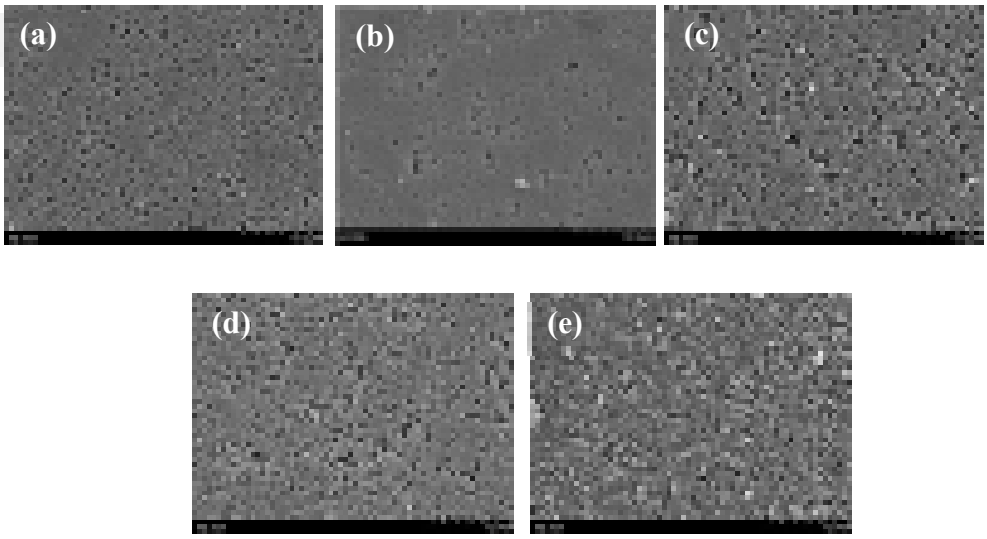

Fig. 3 Morphology of the surface samples before DTS evaluation. (a) group 1; (b) group 2; (c) group 3; (d) group 4; and (e) group 5.

In general, the formation of new apatite crystals in cement samples of group 1, 2, 3, and 4 created a more dense surface than that of samples in group 5. In the absence of vaterite component in the cement, the low apatite formation is explained by the lack of sufficient Ca^{2+} ions.

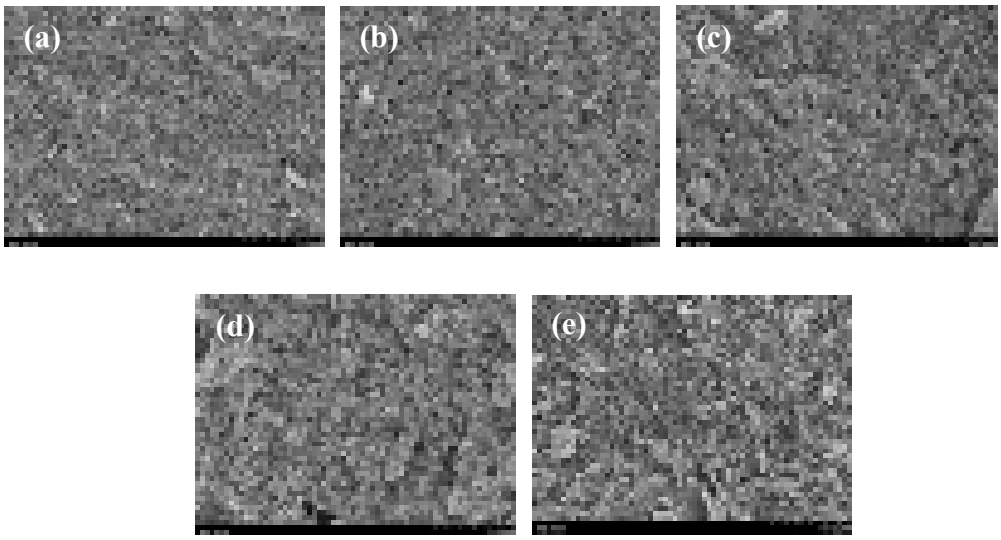

Fig. 4 Morphology of the cross-section samples after DTS evaluation. (a) group 1; (b) group 2; (c) group 3; (d) group 4; and (e) group 5.

Conclusion

The novel bioceramics cement was successfully made using vaterite, DCPA and SCPC. The presence of SCPC and vaterite had a synergistic effect on the mechanical properties of the cement. The Si-OH functional groups of SCPC appeared to facilitate binding the calcium phosphate components together to create a relatively more dense structure. The pool of Ca^{2+} ions provided by vaterite facilitates the reaction with the silicate surface of SCPC. The new cement is currently being investigated for dental application to induce dentinogenesis.

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