# Preparation of Calcium Phosphate Paste

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## ABSTRACTS

Calcium phosphate paste (CPP) were prepared by mixing between calcium sodium potassium phosphate, $Ca_2NaK\ (PO_4)_2$ (CSPP) and monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2.H_2O$ (MCPM). CSPP were obtained by reaction between calcium hydrogen phosphate ($CaHPO_4$), potassium carbonate ($K_2CO_3$) and sodium carbonate ($Na_2CO_3$) in solid state sintering process followed by quenching in air at 1000°C. The paste was aging in simulated body fluid (SBF) for 0.5, 1, 3, 6, 12, 24hr, 3, 7 and 14 days. The morphological investigation indicated the perfect apatite crystal were first growth at 3 days in SBF. The obvious growth of apatite crystal was shown 7 and 14 days indicating the prediction of paste would have rapid reaction with bone after implantation. Mechanical strength of CPP were increase from 0.2 to 1.4MPa at 0.5 and 24hr respectively which indicated the paste completely set to hardened after 24 hrs.

## INTRODUCTION

Hydroxyapatite(HA), $Ca_{10}(PO_4)_6OH_2$ form is used in hard tissue repair because of its chemical and crystallographic similarity to the carbonated apatite in teeth and bones. Stochiometry hydroxyapatite was reported having a very slow resorbable rate and remain in the form of that ceramic materials after fracture bone completely heal thus would lead to the mechanical defect to new born growth(1). Calcium phosphate phase self harden, to form HA in the form of calcium deficient (CDHA), $Ca_9(HPO_4)_5OH$.This form having higher resorbable rate. A major disadvantage of the current orthopedics implant materials is that they exist in a hardened form required the surgeon to fit the surgical site around the implant or to carve the graft to desire shape. The CPP powder can be mixed with water to form the thick paste that can sculpted during surgery to conform to the defects in hard tissues and then to set in situ to form CDHA. The calcium phosphate pastes are used as bone graft in the form of cementous which requires to bone deficits that arise from bone diseases or fracture. Paste can be injectable or non-injectable. It is also to be used together with other implant or directly to fracture part figure.

The aims of present study was to prepare the calcium phosphate paste and study the apatite crystal form in the simulated body solutions as bonding ability. The bone bonding ability is evaluated by examining ability of apatite to form on its surface in simulated body solutions. The essential requirement for an artificial material to bond to living bone is the formation of bonelike apatite on its surface when implanted in the living body and that this in vivo formation can be reproduced in a simulated body fluid (2). The examination of apatite formation on material in SBF is useful for prediction the in vivo bioactivity of a material, and the number of animals used in and the duration of animal can be reduce remarkably by using this method.

## MATERIALS AND METHODS

*Preparation of calcium sodium potassium phosphate, $Ca_2\ NaK\ (PO_4)_2$ (CSPP)*

CSPP were prepared by mixing between 40.96g of calcium hydrogen phosphate ($CaHPO_4$), 10.40g of potassium carbonate ($K_2CO_3$) and 7.98g of sodium carbonate ($Na_2CO_3$). The mixing process was taken in rotary mixer for 24 hours to form homogenous mixed. The homogenous mixed powder were undergo sintering process as solid state reaction at 1200°C for to 12 hours and the quenched in air to produce

CSPP powder. The quenched powder was then mill using planetary mono mill at speed 300rpm with 15 balls for 30 minutes to get fine powder.

*Preparation of calcium phosphate powder.*

Calcium phosphate powder were prepared by mixing between 7.63g of CSPP and 2.73g monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2.H_2O$ (MCPM) during milling process. The mixing was milled using planetary mono mill at speed 300rpm with 15 balls for 30 minutes to get the calcium phosphate paste powder.

*Preparation of calcium phosphate paste.*

5g of calcium phosphate paste powder were mixed with 3.4ml of distilled water to produce the paste of calcium phosphate. The paste was press in to 6 x 12mm of cylindrical PTFE mould and then immersed in ringers' solution for 3 days to enhance the hardening process. The paste was demould after 3 days in ringers' and then continue immersing in SBF. SBF solution was replaced every 3 days to get fresh ion. Samples were taken out from the solution and performed the mechanical testing for the period of 0.5, 1, 3, 6, 12, 24 and 48hrs. The crushed samples then washed for 1 hour in acetone to stop the reaction kinetic.

*Preparation of Simulated Body Fluid Solution*

1000 ml of SBF was prepared by dissolving of 9 reagent in distilled water in sequence as detailed in table 1. HCL were use to control the pH within 7.4 when temperature reached 36.7 °C. SBF solution were then the store in refrigerator to avoid the precipatation

Table 1: Reagent for SBF preparation

| No | Reagent | Amount (g) |
|---|---|---|
| 1 | NaCl | 7.996 |
| 2 | $NaHCO_3$ | 0.350 |
| 3 | KCl | 0.224 |
| 4 | $K_2HPO_4.3H_2O$ | 0.228 |
| 5 | $MgCl_2.6H_2O$ | 0.305 |
| 6 | 1M HCL | 37.5ml |
| 7 | $CaCl_2$ | 0.278 |
| 8 | $Na_2SO_4$ | 0.074 |
| 9 | $(CH_2OH)_2CNH_2$ | 6.057 |

*Characterization*

The mechanical properties studies were performed using Instron 8874 with 1kN load transducer and fitted with spherical setting to maximize the distribution of load during compression test on to specimen surface. The test was carried out at $1mm.min^{-1}$ of cross head velocity (3) until 40% of load reduce. The specimens were test in compression mode aided by Merlin software. Microstructure of the surface of cross section specimen was examined using a scanning electron microscopy.

## Result and Discussion

Figure 1 shows the compressive strength with a change of aging time in SBF solution. The mechanical strength of specimen was recorded between 0.5 to 48hrs. This mechanical strength indicate the harden sequence of this calcium phosphate paste, and also ultimate strength of the calcium phosphate paste. The initial setting time was seeing begin at 4 hours and the hardening process took place after 8 hours up to 24 hours The mechanical stress was about 0.2 MPa during 0.5hr curing in SBF and increase steadily to 0.3 to 0.4 MPa for 2 and 4 hours respectively. During the hardening process paste mechanical stress was found to increase from up to 1.3 from 0.5 MPa indicated completed harden after 24hrs which was no significant change in strength shown until 48hrs. The calcium phosphate paste which was prepared using CSPP and MCPM produce slightly higher in setting time compare to paste produce which other calcium phosphate. The setting and hardening properties of calcium phosphate paste are due to the progressive dissolution of the CSPP phase and the formation of an entangled network of calcium deficient hydroxyapatite (CDHA) crystal and the hydration process of MCPM. The hydration property of calcium phosphate paste contributed by the combination of physical and mechanical process. To produce the better setting time;depending on site requirement, the physical factor such as reduction in crystal size and increase the porosity would lead to factor of hydration (4).

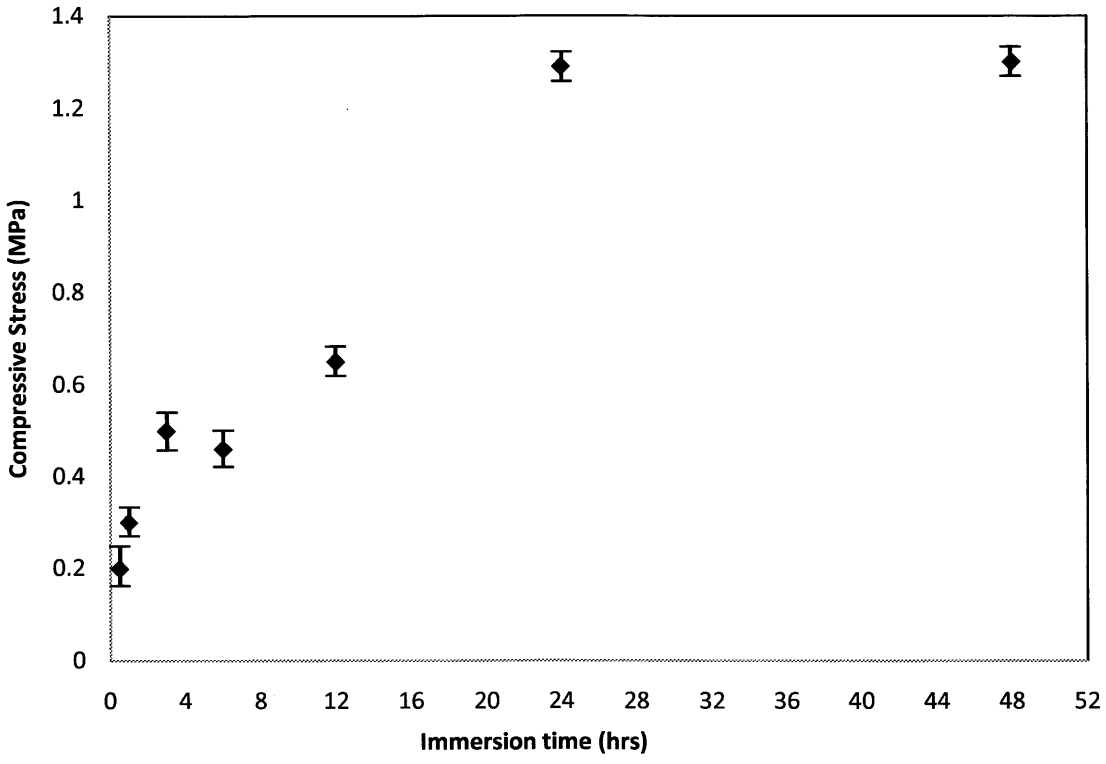


Figure 1 show the mechanical strength of calcium phosphate paste during hardening process curing in SBF until 48 hours

Figure 2 shows SEM micrograph of the morphological behavior of paste during the hardening process. The specimen was soaked in the SBF solution from 0.5hr to 14 days to investigate the growth of apatite crystal. From the micrograph, the specimens indicate no apatite layer form in the surface at 0.5 to 24hrs (figure 2a).The apatite crystals indicate to grow at 24hrs after curing in SBF and were first growth in perfect crystal at 3 days curing (figure 2c) and continue to form the apatite crystal layer inside the specimen and became more compact (figure 2d). In the preparation of calcium phosphate paste, the in vitro aging(immersion in SBF solution) play important role in predicting the ability to new bone bonding to the developed material. The perfect crystal was growth at 3 days in SBF solution indication the reaction between the new bone and materials begin at this stage in term of growing a new bone. The result described this material able to have apatite form on its surface in SBF will has apatite produced on its surface in the living body. This relationship holds as long as the material does not contain a component that induces toxic or antibody reaction.

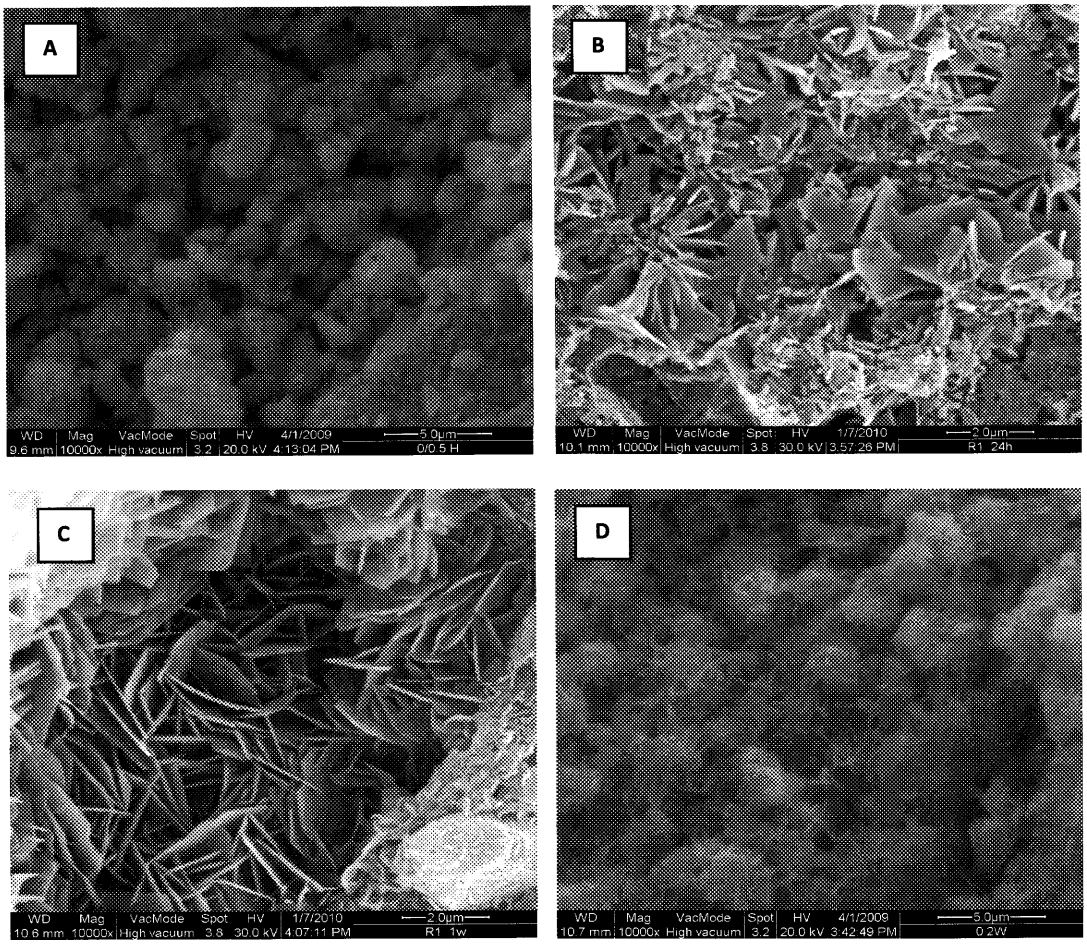


Figure 2; SEM micrograph shows the morphology of apatite crystal grow in calcium phosphate paste for (a) 0.5 hr, (b) 3 days, (c) 7 days and (d) 14 days.

## CONCLUSION

Calcium phosphate paste or cement can produce from the various calcium phosphates; in this work calcium phosphate paste was prepared by mixing between CSPP and MCPM. The prepared paste was produce slightly take slightly longer time to harden this suitable for certain requirement during surgery

which sometimes need slow hardened process. The apatite crystal growth on the surface indicated the in vivo compatibility of material and can be considered for application in bone replacement surgery.

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