

## Inorganic Phosphate Wet Foams Stabilization to Porous Ceramics by Direct Foaming

ASHISH POKHREL, DONG NAM SEO, GAE HYUNG CHO and IK JIN KIM\*

Institute for Processing and Application of Inorganic Materials, Department of Advanced Materials Science and Engineering, Hanseo University 360, Daegok-ri, Haemimyun, Seosan-City, Chungnam 356-706, Republic of Korea

\*Corresponding author: E-mail: [ijkim@hanseo.ac.kr](mailto:ijkim@hanseo.ac.kr)

(Received: 17 October 2012;

Accepted: 19 August 2013)

AJC-13933

The optimization of inorganic hydroxyl foams with an admixture of calcium phosphates was done using an *in situ* particle-surface modifier through the process of direct foaming. The purpose of the study was to observe the behaviour of the hydroxyl apatite wet foams using admixtures in order to form highly stable wet foams to porous ceramics. Porous ceramics were formed utilizing a simple process, understanding the changes in the stability. The resulting microstructures occurred by adjusting the particle-amphiphile concentration and different ratios of additional additives in the initial suspension. The influence of different parameters were satisfactorily described in terms of balance between the stabilizer and controlling parameters as viscosity, contact angle, bubble size and porosity. Stabilized wet foams were formed, sintering at 1200 °C for 2 h gave micro porous ceramics with porosity of more than 65 %.

**Key Words:** Hydroxyapatite, Wet foams, Foam Stability, Viscosity, Bubble size and Porosity.

### INTRODUCTION

The inorganic matrix of cortical bone consists of a porous structure with an interconnected porosity of nearly 65 % so, for bone in growth to occur readily into a porous ceramic bone substitute material, which mimics the natural bone structure, the typical size must be greater than 100  $\mu\text{m}$ <sup>1,2</sup>. So, the ideal bone substitute is a material that will form a secure bond with the tissues by allowing and even encouraging, new cells to grow and penetrate. One way to achieve this is to use a new material that is osteophilic and porous, so that new tissue and ultimately new bone, can be induced to grow into the pores and help prevent loosening and movement of the implant.

Hydroxyapatite (HA) is a naturally occurring mineral form of calcium apatite with the formula  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , but is usually written as  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  to denote that the crystal unit cell comprises two entities. Hydroxyapatite is the hydroxyl end member of the complex apatite group. Ceramics used for the repair and reconstruction of diseased or damaged parts regarding the musculo-skeletal system are termed as bio-ceramics. Various industrial uses for bio-ceramics and scaffolds have led to its mass production in different ways with regards to the medical purpose, of which the recently invented process of particle stabilization described<sup>3-5</sup>. They provided a simple and low cost way for the production of bioceramics by wet foam. These foams later sintered or self-settled to give porous bioceramics with various outstanding properties. The pore size,

shape and volume fraction of such ceramics control both their strength and the ability of the newly regenerated bone to receive nutrients and discharge waste products through unconstrained vessels<sup>6</sup>. Advantages of using foams instead of bulk material are their relative light weight and (if the foam is solidified) a comparative toughness in respect to dense materials. Especially in biomedical applications an open porous material exhibits further advantage: in comparison to dense substrates, cells can migrate into the three dimensional matrix and vascularization of the bone graft material is possible. This is especially important for temporary grafts, which will be replaced by the growing bone after some month or years.

In this work, we described the process of the bio-ceramics by the simple and versatile method. Two calcium phosphate (CaP) materials known to be hydroxyapatite and calcium phosphate were chosen as they are closely related to inorganic phase of bone and offer different resorption properties. Furthermore, these materials can be combined with each other or with further CaP materials showing stronger dissolution abilities to obtain tailored resorption rates. Wet foams produced by this method are ultra-stable against drainage, Ostwald ripening and bubble coarsening, which after drying and sintering a (closed or open) porous microstructure is obtained.

### EXPERIMENTAL

High-purity hydroxyapatite powder was from Sigma-Aldrich, United Kingdom and calcium phosphate powder also

from Sigma-Aldrich, Germany. Deionized water, hydrochloric acid (35 % Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China) were also used.

**Suspension preparation:** Suspensions were prepared using propyl gallate as an amphiphile by the stepwise addition of hydroxyapatite powder to an aqueous mixture of 0.01 M NaOH. Different weight % of propyl gallate was dissolved keeping the water required at less and added to the hydroxyapatite suspension. Suspensions' solid loadings and pH were initially fixed as 15 vol % and 9.9, respectively. Homogenization was carried out by a general homogenizer with the fixed rpm for some hours. The propyl gallate (PG) was adjusted to the required concentration in the final suspension and the suspension was mixed with the other calcium phosphate suspension prepared, which was unmodified and was in different solid loadings. They were added exactly before foaming under slight stirring in order to avoid local particle agglomeration. Finally, pH was set to 9.9 and the solid contents were fixed to 15/30 vol % (hydroxyapatite/calcium phosphate) in the suspensions at the ratio of 1:1. In other experiments, suspensions under various pH and different ratios of the compositions were also tested.

**Contact angle and surface tension:** The suspensions' contact angles and surface tensions were measured by the pendant drop method (KSV Instruments Ltd., Helsinki, Finland). Suspensions were prepared by the addition of propyl gallate to give solid loadings of 15/30 vol % (hydroxyapatite/calcium phosphate) of the mixtures. Drop volume was varied between 5 and 10  $\mu\text{L}$  depending on the suspension's contact angle and surface tension.

**Foaming, drying and sintering:** Foaming of 150 mL suspensions was carried out using a household mixer (Super Mix, France, 150 watt) at full power for 10-15 min. Foams' bubble size distributions were evaluated by optical microscopy in transmission mode (Somtech Vision, South Korea) with a connected digital camera. Bubbles' sizes were measured using linear intercepts. Their average sizes were determined from the analyses of particular areas. Wet samples were shaped into cylinders by hand and subsequently dried in air at 20-25  $^{\circ}\text{C}$  for 24-48 h. The dried foams were sintered in an electric furnace (muffle furnace) at 1200  $^{\circ}\text{C}$  for 2 h. The heating rate was 1  $^{\circ}\text{C}/\text{min}$  and the cooling rate was 3  $^{\circ}\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

**Zeta potential:** Zeta potential is the physical property exhibited by any particle in suspension. It can be used to optimize the formulations of suspensions and emulsions, which are the basics of colloid science. The particles in dispersion may adhere to one another and form aggregates, which may separate by sedimentation, which in scientific terms is called as flocculation or coagulation. This property can be explained through colloidal stability and DVLO theory, which has already been explained by Studart *et al.*<sup>7</sup>

As shown in Fig. 1, we found out the IEP of the inorganic particles and took into account the initial charge carried by the particles in different pH modifications<sup>8</sup>. We administered the pH of the hydroxyapatite suspension at 9-10 that had the

higher energy (mV) in their surface according to their zeta potential measurements.

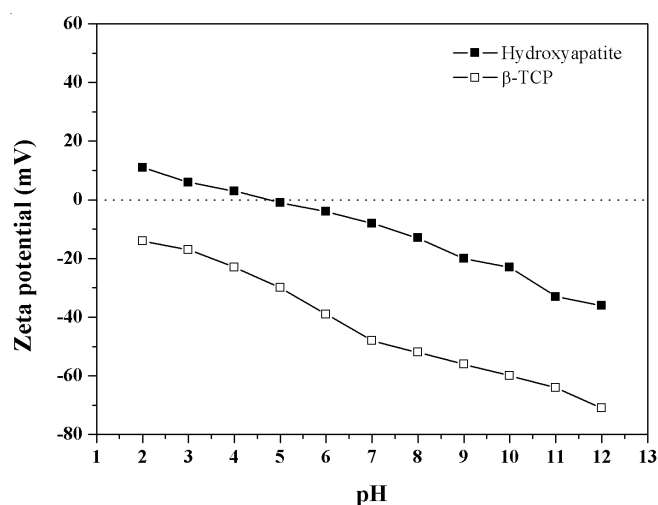


Fig. 1. Zeta potential of hydroxyapatite and  $\beta$ -TCP 0.2 vol % of solutions in water with respect to pH

**Viscosity and bubble size:** The microstructures of wet foams can be tailored by the concentration of not only the particles but also the influence of amphiphiles used for stabilizing the particles<sup>9,10</sup>. It was also determined by varying the solids content in the hydroxyapatite suspension containing particles at different propyl gallate concentrations. The screening of the particle's surface charge upon addition of amphiphile lead to the increase in the suspension viscosity (Fig. 2), which is because of the surface charge screening leading to the diffused layer around the particle surface not being sufficiently thick enough to overcome the attractive van der Waals force between the particles. Besides van der Waal's attraction, hydrophobic attractive forces might also play a role on the viscosity increase observed<sup>4</sup>.

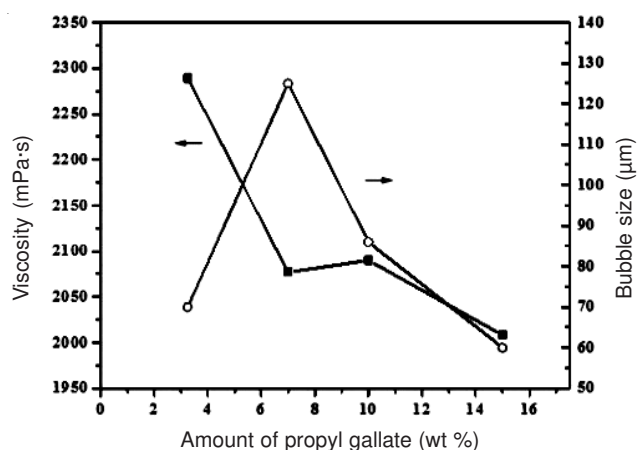


Fig. 2. Viscosity and bubble size with respect to propyl gallate concentration in suspension at the ratio of 1:1

Fig. 2 also shows a non-linear change in the behaviour of the hydroxyapatite suspension with different amounts of the amphiphiles concentration used to stabilize the particles. It showed a drastic decrease in the viscosity of the suspension, which on further increasing the amphiphiles showed gradual decrease. This can be due to the achievement of the critical

concentration of the amphiphiles, leading to the uncommon bubble size formation, whereby larger bubbles were formed on a slight increase of the amphiphiles and gradually decreased on further increasing, which was as expected. Change in the viscosity related to the amount of amphiphiles in the suspension had a direct effect in the bubble size of the wet foams. As it is directly related to the porosity and density of the ceramics formed. We decided to add additives in the initial suspension to achieve the targeted results of an average of 50-100  $\mu\text{m}$  bubbles. As shown in Fig. 3, the additives in the form of calcium phosphates were added to the initial suspension in a 1:1 ratio of different solid concentration. There was a linear increase and decrease in the stabilization and bubble size of the foamed foam. After the increase of the concentration of additives to 30 vol % and adding in the same ratio to the starting hydroxyapatite suspension, the viscosity showed little decrement and had higher propagation of air and uniform distribution of bubbles. After an increment in the volume of the additive added to the initial suspension there was sudden increase of viscosity as shown in the figure. It also led to the increase in average bubble size due to non-uniform distribution of bubbles. This was a result of less penetration of the air during frothing. The sintered ceramics produced with the composition of 15/30 vol % suspensions at the ratio of 1:1, gave a linear shrinkage of just 10 % and stable bio-ceramics yielding higher mechanical strength.

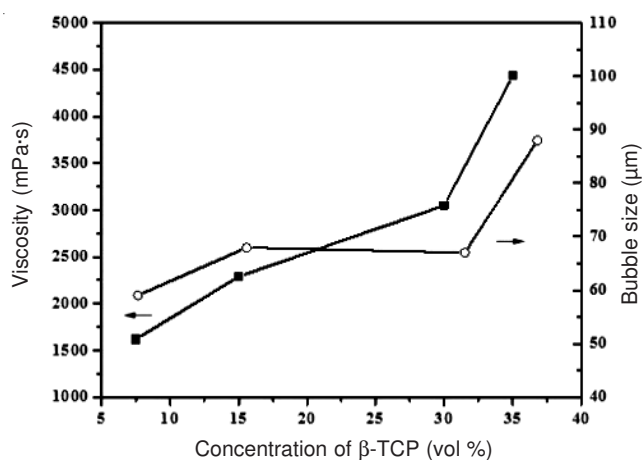


Fig. 3. Viscosity and bubble size, with respect to additives concentration in the suspension at a constant propyl gallate concentration

**Contact angle and surface tension:** Here we discuss the comparative analysis of the degree of hydrophobization in the same ratio of the same solid content regarding the two bio related ceramic powders with the change in the propyl gallate concentration and the difference in the concentration of additives. As already proved, the suspension surface tension and contact angle have a direct effect on the stability of the wet foams and well-tailored microstructures<sup>5,11</sup>. Fig. 4 shows that contact angle decreases with the increase in the concentration of the amphiphiles thus increasing the surface tension of the initial suspension. This leads to the formation of unstable wet foam, which showed either no foaming or higher degree of drainage with a low percentage of stability. With these observed values for the critical concentration of the amphiphiles *via*

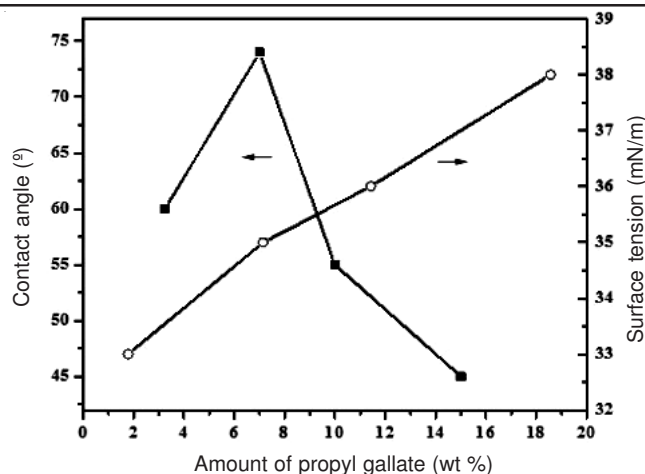


Fig. 4. Contact angle and surface tension with respect to propyl gallate at 1:1 ratio of additive

Fig. 4, we added the additives in different concentrations and observed the change in the contact angle and surface tension of the suspension. Results shown in Fig. 5 give the exact values for the stabilization of foam in the air-water interface. The change in the additive and increasing the amount of additives lead to the increase in the contact angle and relatively less surface tension compared to the data's regarding the difference in the propyl gallate concentration and thus can be proved by the given theory of stabilization<sup>12</sup>. Further, as the change in the particle hydrophobicity occurs upon adsorption of the propyl gallate, the initial suspension reduces the surface tension of the suspension and gives higher contact angles leading to the stabilization of the wet foams. The higher contact angle at the amphiphile concentration of 7 wt % to the amount of hydroxyapatite had less stability but higher strength observed by the general force given by hand. Taking into account the observations from different concentrations of the amphiphiles and keeping its concentration constant, we changed the volume of the additives and observed its effect in the surface tension of the colloidal suspension. Fig. 4 showed that the higher contact angles at the concentration of 15/30 vol % in the same ratio giving higher stable foams as it was also well accomplished with less surface tension. The standard of 3.25 wt % to the amount of the hydroxyapatite in the suspension was taken as it showed the higher stable foams.

The concentration of the additives and the initial suspensions showed the gradual increase in the contact angle and consequently the decrease in the surface tension, which can be seen in the Fig. 5. These conditions were proved to be efficient for the higher degree of partial hydrophobization of the particles in previous scientific researches<sup>13</sup>. Further increment in the concentration of the additives lead to changes in the viscosity of the initial suspension, which leads to many destabilization mechanisms explained before in our literature. The sintered ceramics at 15/30 vol % of the hydroxyapatite/ $\beta$ TCP at the ration of 1:1 and 15/35 of the same components gave stable crack free porous ceramics, which had smaller differences in the microstructure and yielded higher mechanical strength.

**Microstructures:** After all these tailoring and controlling measures, we sintered the wet foams for the comparative analysis of the pure calcium phosphate and pure hydroxyl apatite foams.

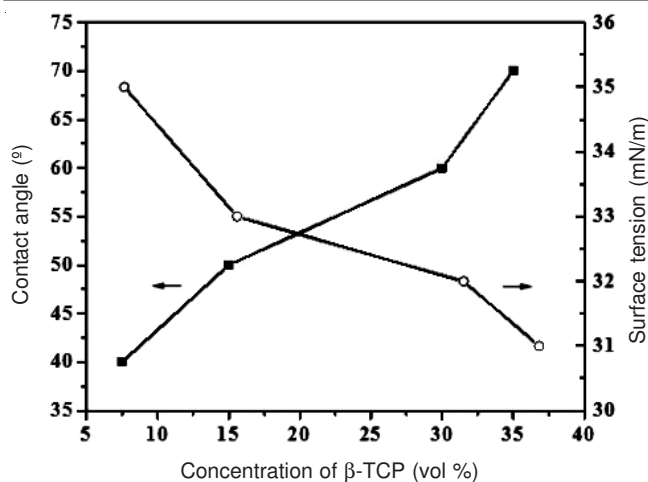


Fig. 5. Contact angle and surface tension with respect to additives concentration in the suspension at constant propyl gallate but different ratio of additives

The results can be seen, the difference in the bubble size of the pure  $\beta$ -TCP suspension with large inter bubble differentiation whereas the pure hydroxyapatite suspension hydrophobized with propyl gallate gave comparatively smaller bubble size with uniform distribution. However, according to the controlling parameters explained throughout the literature in Figs. 2-5 both the wet foams as well as sintered structure were considered unstable thus we changed the composition of the initial suspension. The microstructures were tailored by adding the additive as the mixture of the modified hydroxyapatite and non-modified  $\beta$ -TCP suspension in the ratio of 1:1. This showed the uniform distribution of bubbles with minimal intracellular distances. The sintered structure showed smaller pores and the formed structure showed higher mechanical strength due to its homogenous distribution. To overcome the results, we adjusted the volumetric composition as already defined in the literature; the microstructures were achieved as shown below in Fig. 6 the structures in Fig. 6(a and a<sup>1</sup>) and Fig. 6(b and b<sup>1</sup>) show the uniform pore distribution with an average pore size of less than 100  $\mu\text{m}$ . The average inter-cellular differences were 1-5  $\mu\text{m}$  and were uniform for whole structures. The sintered ceramics also showed a linear shrinkage of less than 10 % with higher mechanical strength. Conclusively, to confirm our results, best sample was repeated with the same procedures but with an increased sintering temperature, the microstructures were seen as shown in Fig. 6(c) and (c<sup>1</sup>) giving glassy phase of CaP, as hydroxyapatite has lower melting point.

### Conclusion

Porous bioceramics were formed by sintering the stable wet foams formed through the process of direct foaming mixing the mixture of the partially hydrophobized and non-hydrophobized suspensions. The produced ceramics had a

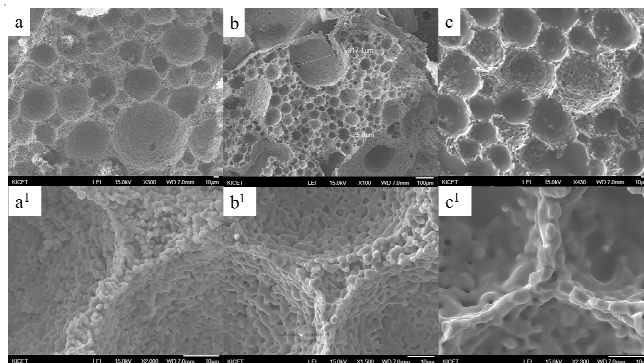


Fig. 6. Microstructures (a) and a<sup>1</sup>) (15 vol % H.A + 30 Vol %  $\beta$ -TCP at the ratio of 1:1), (b) and b<sup>1</sup>) (15 vol % H.A + 35 Vol %  $\beta$ -TCP at the ratio of 1:1), at 1200 pC and (c) and c<sup>1</sup>) (15 vol % H.A + 30 Vol %  $\beta$ -TCP at the ratio of 1:1 at 1300 pC)

porosity of more than 65 % and had higher mechanical strength. The influence of different parameters were satisfactorily described in terms of balance between stabilizer and controlling parameters as viscosity, contact angle and bubble size. The formed porous bioceramics after its bio-compatibility test can be used as scaffolds and also a base for tissue culture during tissue engineering and also other multifunctions.

### ACKNOWLEDGEMENTS

This research was financially supported by the Ministry of Education, Science Technology (MEST), the National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation and Hanseo University.

### REFERENCES

- Larry L. Hench, *J. Am. Ceram. Soc.*, **74**, 1487 (1991).
- B.P. Binks, *Curr. Opin. Colloid Interf. Sci.*, 721 (2002).
- A.R. Studart, U.T. Gonzenbach, I. Akartuna, E. Tervoort and L.J. Gauckler, *J. Mater. Chem.*, 3283 (2007).
- I. Akartuna, A.R. Studart, E. Tervoort and L.J. Gauckler, *Adv. Mater.*, **20**, 4714 (2008).
- A. Pokhrel, J.G. Park, W. Zhao and I.J. Kim, *J. Ceram. Process. Res.*, **13**, 420 (2012).
- R.M. Pilliar, M.J. Filiaggi, J.D. Wells, M.D. Grynypas and R.A. Kandel, *Biomaterials*, **22**, 963 (2001).
- A.R. Studart, U.T. Gonzenbach, E. Tervoort and L.J. Gauckler, *J. Am. Ceram. Soc.*, **89**, 1771 (2006).
- A. Pokhrel, J.G. Park, W. Zhao and I.J. Kim, *J. Ceram. Process. Res.*, **13**, 420 (2012).
- A. Pokhrel, J.G. Park, J.S. Nam, D.S. Cheong and I.J. Kim, *J. Korean Ceram. Soc.*, **48**, 463 (2011).
- N.O. Engin and A.C. Tas, *J. Am. Ceram. Soc.*, **83**, 1581 (2000).
- E. Saiz, L. Menendez, P. Miranda, K. Gryn and A.P. Tomsia, *Mater. Sci. Eng.*, **C27**, 546 (2007).
- U.T. Gonzenbach, A.R. Studart, E. Tervoort and L.J. Gauckler, *J. Am. Ceram. Soc.*, **90**, 19 (2007).
- H.-S. Ryu, H.-J. Youn, K.S. Hong, B.-S. Chang, C.-K. Lee and S.-S. Chung, *Biomaterials*, **23**, 909 (2002).