

INFLUENCE OF SLURRY PROPERTIES AND SPRAY DRYING PARAMETER ON THE MORPHOLOGY OF SPRAY DRIED CARBONATED APATITE GRANULES

Fadzil Ayad Zakaria¹, K. Jamuna Thevi¹, Abdul Yazid Abdul Manaf¹, Kashfi Ismail¹,
Tatiana Montes Rodriguez² and Jose Fernando Mikan²

¹*Advanced Materials Research Centre, SIRIM Berhad, Lot 34, Jalan Hi-Tech 2/3,
Kulim Hi-tech Park, 09000 Kulim, Kedah, Malaysia*

²*Facultad de Medicina, Universidad Militar Nueva Granada,
Transversal 3, No 49-00, Bogota, Colombia*

ABSTRACT

In the preparation of ceramic powder for forming processes such as spray drying, homogeneous dispersion of powder in an aqueous medium is essential. The particle should not settle fast under the effect of gravity but remain in suspension to avoid inhomogeneities during forming. From this work the slurry properties with different percentage of solid content, dispersant and binder were studied and compared in terms of slurry viscosity and stability. It was observed that slurry at 70wt% solid content produced bigger and better segregated granules after spray drying than those at 40 wt% and 60 wt%. The control of compressor air pressure and inlet temperature was also studied on its effects to the morphology of the final product of the spray dried granules.

INTRODUCTION

Bioactive ceramics of various sizes and forms, for example block, granular, dense and porous forms are now fabricated commercially for orthopedic application. Bioactive ceramic blocks are used mainly for the vertebral replacement, reconstruction of iliac crest and filling the cavities left after excision of bone tumors and the granular forms are often used for filling interstices surrounding a block of defects with skeletal irregularities, such as those encountered during revision surgery for aseptically loosed hip prostheses [1]. Spherical bioceramic can also be utilized for coating purposes as spherical powders has better rheological properties than irregular powders and thus produce better coating for hip implants and chromatographic separation [2].

One of the techniques of preparing granular forms bioactive ceramic is by spray drying method. This ceramic shaping process requires the dispersion of the ceramic powder in an aqueous medium. These aqueous slurries has to fulfill several requirements such as the powders should not settle down fast under the effect of gravity and should be able to remain in suspension. As ceramic powder has the tendency to agglomerate, appropriate amount of dispersant is required where it will alter the powder surface properties to have repulsive forces making the particles remain separated in suspension [3, 4]. Spray

drying method is routinely used as a spray granulation from slurries to obtain powder with various morphologies, depending on operating parameters. They can be hollow, dense and are spherical most of the time, or sometimes with a donut shape [5]. The aim of this work is to focus on morphology of the spray dried carbonated apatite from the effect of slurries state of dispersion and the parameters of spray drying condition.

METHODOLOGY

Carbonated apatite precursor (pCAp) was prepared using technique based on previous work [6] with main elements constitute of calcium and phosphate with a molar ratio of 1.8. Chemical precursors from $\text{Ca}(\text{PO}_4)_2$ (Fluka) and CaCO_3 (Fluka) were mixed homogeneously together using ball mill. Duramax D3005 (Rohm and Haas) was used as a dispersant for slurry stabilization. Slurries with carbonated apatite solid content of 40, 60 and 70 wt% were prepared to determine the optimum conditions for slurry stability at high solids content. After the addition of dispersant and binder in the slurry, the slurries were mixed using mechanical stirrer for 24 hours. The binder used was water soluble poly ethylene glycol (PEG) at 5wt%. Slurry viscosity was determined using rotating spindle viscometer (Brookfield RVT DV-II). The slurry stability was evaluated by measuring the particle settling rate inside graduated test tubes. The height of the sediment inside the test tube was measured as shown in Equation 1 and Figure 1, where H_o is total slurry height and H_t is suspension height at time interval.

$$\text{Sediment height, SH (\%)} = \frac{H_o - H_t}{H_o} \times 100 \quad (1)$$

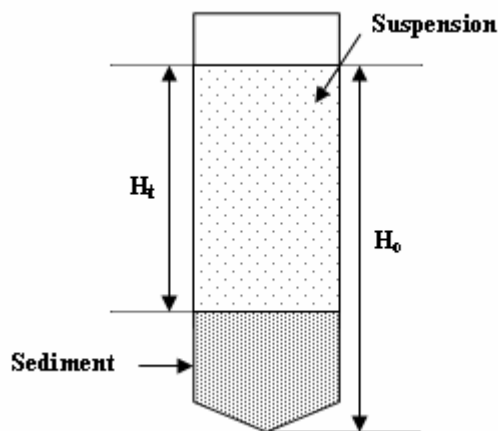


Figure 1: Slurry stability evaluation

The production of spray-dried granules took place in LabPlant SD-05. Pump flow rates used were at 350mL/h. The air-pressure and air inlet temperature were varied between 0.4 bar – 0.6 bar and 210°C – 250°C respectively. Morphology of the spray

dried granules was inspected using Scanning Electron Microscope (FESEM; Leo 1525, Germany).

RESULTS AND DISCUSSION

The morphology of the pCAp powder is shown in Figure 2. The particles are in a wide range, between 1 and 15 μm with surface area of 2.42 m^2/g . Mixture of coarse and fine powders has a better particle packing, thus producing specimen with the highest green density [7].

Dispersants or deflocculants are commonly added during dispersion to create chemically coated and charged particle surface, which mutually repel. Charge and repulsion decrease with the increase of interparticle spacing (IPS), so the maximum distance between particles is maintained. In the absence of repulsive forces, particle in suspension can approach each other and form loose bonds, increasing viscosity [8]. Therefore, stabilization of slurries of high solids content can be achieved with the addition of an appropriate dispersant which has the function to lower the viscosity of the slurry while ensuring the powder particles will not settle within a short period of time. Dispersants that are functioning both via an electrostatic and a stearic mechanism are called polyelectrolytes which usually consist of a hydrocarbon chain and a polar ionic part (COO^- , SO_3^-). Duramax D3005, which is an ammonium polyacrylate aqueous solution, was employed for the stabilization of slurries with 40, 60 and 70wt% solids content, and its concentration was varied between 0.035 to 0.44 wt% of active ingredient per dry carbonated apatite precursors powder. The pH of the slurries was around 9.5. The effect of dispersant concentration on viscosity is shown in Figure 3. Viscosity measurement of the slurries was recorded at rotational speed of 100 rpm using largest spindle (no.1). Slurries at low and intermediate solid content (40 and 60 wt% respectively) exhibit constant and low apparent viscosity (~ 7 and 20 mPas respectively), independent of dispersant concentration. At higher solid loading content (70 wt %), the apparent viscosity was dependant of the dispersant concentration. At a dispersant concentration of less than 0.11 wt% of dispersant active ingredient, the apparent viscosity was high and constant, ~ 100 mPas. However, the apparent viscosity dropped to 38 mPas when 0.14 wt% of dispersant active ingredient added. At this concentration, it can be considered as the optimum dispersant concentration point, where the addition of dispersant alters the powder surface properties effectively so that repulsive forces become higher than the attractive ones and the particles can remain separated in suspension [9]. At higher dispersant concentration, apparent viscosity significantly raised, revealing the ineffectiveness of adding dispersant at higher concentration.



Figure 2: SEM micrograph of carbonated apatite precursor powder

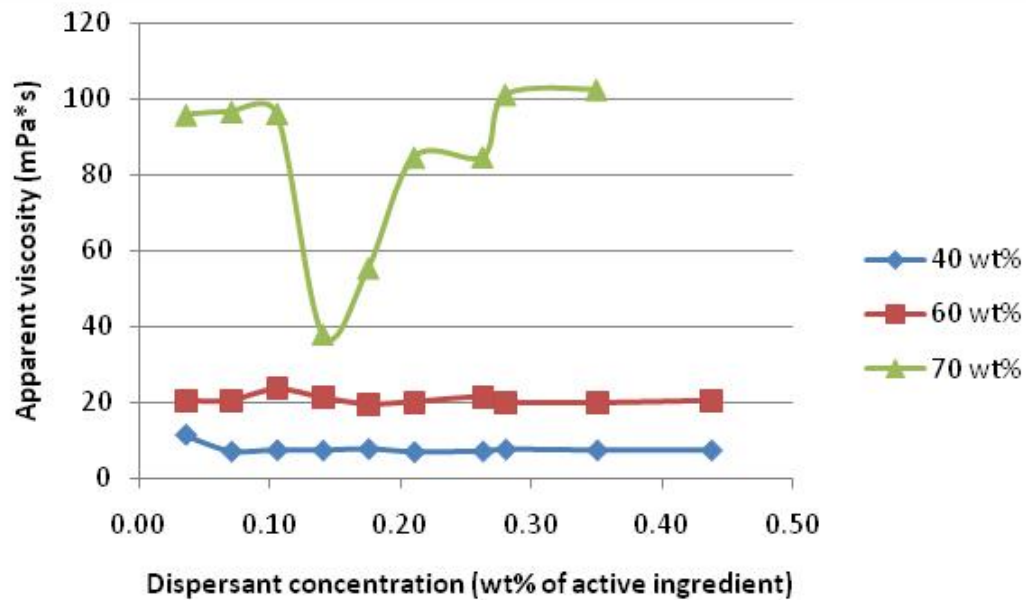


Figure 3: Effect of Duramax D3005 dispersant concentration on the apparent viscosity of CAP precursors at different weight percent of solid contents.

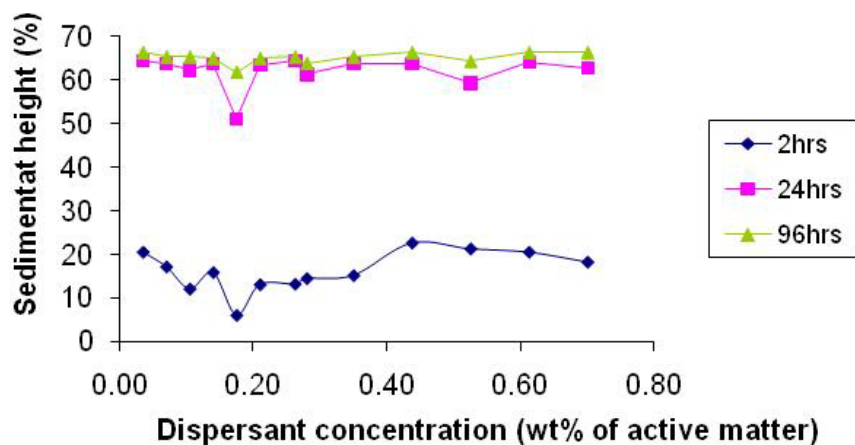


Figure 4: Settling time of CAP precursor powder at 40 wt% solid content

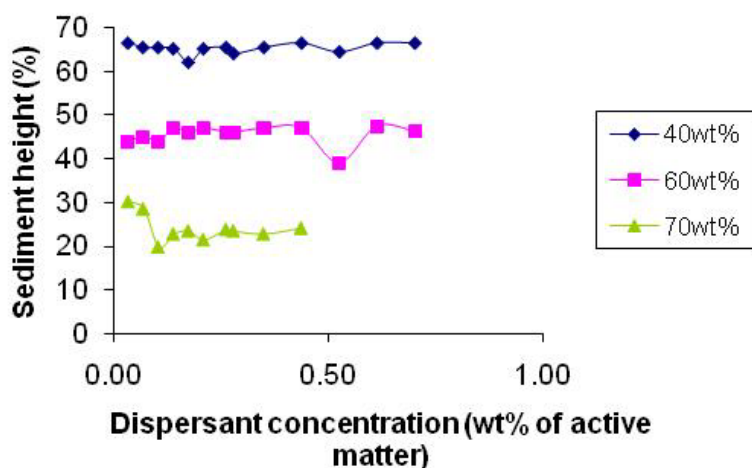


Figure 5: Settling height of CAP precursor powder after 96 hour sedimentation.

Slurry stability was evaluated by measuring the settling powder as a function of time and dispersant concentration. Lower sediment height suggests that the powder stays suspended in the slurry thus resulting in a more stable slurry system. The stability for slurries of 40 wt % solids content (Figure 4) is almost constant at dispersant concentration of less than 0.11 wt% active ingredient. A reduction in sedimentation height was observed at 0.14 wt% dispersion concentration before it increases again. The reduction in sedimentation height indicates stable slurry, where minimum settling was observed, thus can be chosen as the optimum dispersant concentration for the 40 wt% solids content. Different solids content requires different concentration of dispersant to obtain stable slurry. After 96 hours of settling duration (Figure 5), sediment height of slurry containing high solid content (70 wt %) has the lowest sedimentation (~20%)

while the intermediate solids content (60 wt %) and low solids content (40 wt %) showed higher settling ($\sim 42\%$ and $\sim 78\%$ respectively). The optimum Duramax D3005 concentration where minimum settling for 60 wt% and 70wt% of solids content occurred, were determined at 0.53 and 0.11 wt%.

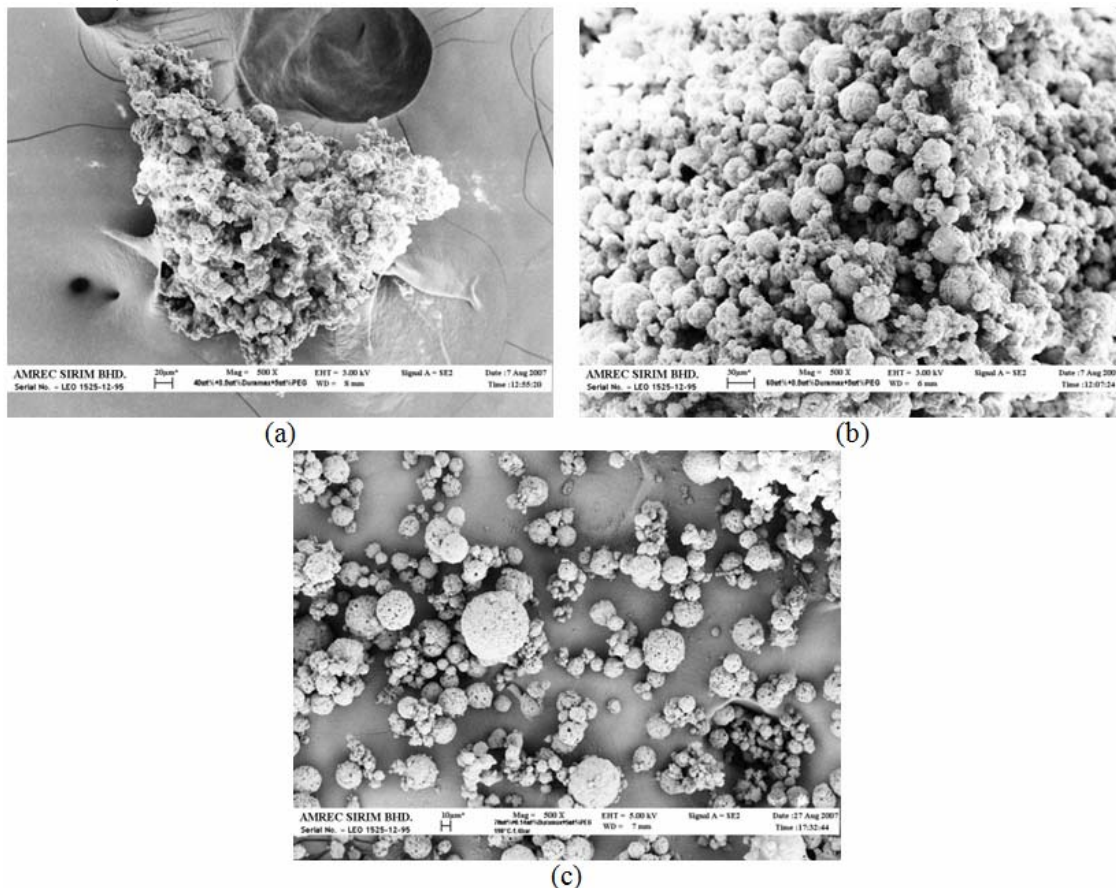


Figure 6: Morphology of granules prepared at (a) 40 wt% solid content, (b) 60 wt% solids content and (c) 70 wt% solid content

Finally, in order to test the potential of these stabilized slurries, the slurries were spray dried to produce spherical granules. The effect of solid content on spray drying was studied by comparing batches with slurries containing 40, 60 and 70 wt% solids content. The slurries were added with 5 wt% of polyethylene glycol binder and spray dried using Lab Plant SD05 equipment. Binder addition to the slurry is necessary for spray drying application where the formation of coherent spherical granules is required [10]. Spray dried granules produced with 40, 60 and 70 wt% solids content are shown in Figure 6. The combination of low solids content (40 wt %) and high inlet pressure (2.0 bar) produced small sized spherical granules, around $10\ \mu\text{m}$. The granules were clumped together as possibly owed to the amount of binder is too high in comparison to the solid content. An increase of the slurry solids content increased the size of granules. At 60 wt% solid content, the size improved to around $20\ \mu\text{m}$. However, the granules still attached to one another. The combination of binder at 5 wt% in to 70 wt% solid content improved the quality of the granules produced. Bigger granules up to the size of

50 μm were obtained and the granules did not attached together. Since it is clear that production of good quality granules requires high solid content, high solid content slurries was prepared and used for the spray drying parameters studies.

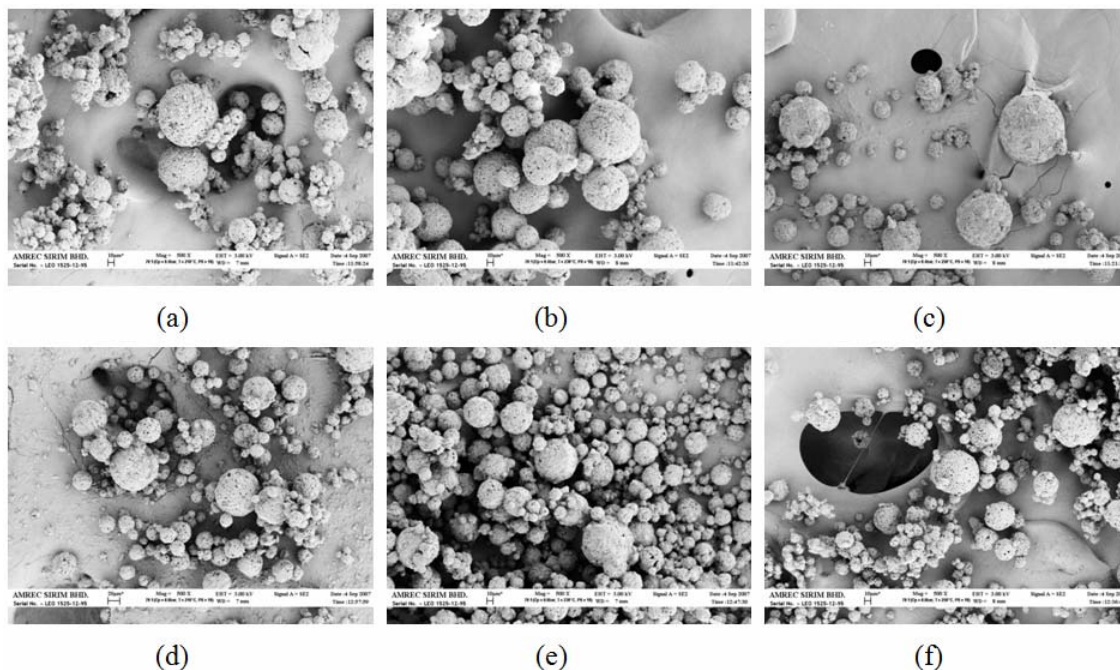


Figure 7: Morphology of spray dried granules at different compressive air pressure and inlet temperature. (a) 0.4 bar, 210°C, (b) 0.4 bar, 230°C, (c) 0.4 bar, 250°C, (d) 0.6 bar, 210°C, (e) 0.6 bar, 230°C and (f) 0.6 bar, 250°C

The spray dried parameters were manipulated based on compressive air pressure and inlet temperature as shown in Figure 7. In this analysis, the slurry was prepared using 70 wt% solid content, 0.14 wt% of active ingredient of Duramax D3005 dispersant and 1 wt% of PEG binder. At lower compressive air pressure, it was observed that the granule size obtain were bigger than those of higher pressure. At 0.4 bar, granule size obtained were up to $\pm 140\mu\text{m}$ and at 0.6 bar, the granule size were smaller, at up to $80\mu\text{m}$ only. This phenomenon occurs as in a pressure-nozzle, slurry accelerating through small channels achieves turbulence and breaks up into droplets. The droplets therefore, travelling in the chamber before drying up and being collected in the collection bottle. At a low pressure, the travel and warm up period of drying is longer, thus crust formation starts later in the drying process resulting in an increase in granule size [11]. The difference in the inlet temperature however was observed not to be significant enough to play a role in the size of the granules.

CONCLUSION

Carbonated apatite precursors granules were prepared by spray drying technique. The preparation of the slurries plays an important role for the production of the granules. Different dispersant concentration is needed for different amount of solids content to

achieve the lowest viscosity for easy processing of the slurries. When combined with binder and spray dried, the quality of the granules were also seen to change. The best granules were prepared at high solids content, 70 wt%, where the granules were spherical, not attached to one another and the size was bigger. The spray drying compressive air pressure is an important parameter to be controlled if bigger granules are desired where lower compressive air pressure would lead to generation of granules with bigger diameter.

ACKNOWLEDGMENT

The authors would like to thank industrial attachment students, Fahmi and Fazilah for their help in this study and also the financial support of Malaysian Ministry of Science, Technology and Innovation for the Science Fund 030302 SF0010 grant.

REFERENCES

- [1]. N. Ikeda, K. Kawanabe and T. Nakamura, Quantitative comparison of osteoconduction of porous, dense A-W glass ceramic and hydroxyapatite granules (effect of granule and pore sizes), *Biomaterials*, **20**, (1999), 1087 – 1095.
- [2]. A. Tsetsekou, C. Agrafiotis and A. Millias, Optimization of the rheological properties of alumina slurries for ceramic processing applications. Part I: Slip casting, *Journal of the European Ceramic Society*, **21** (2001) 363-373
- [3]. J. Reed (1995), Principles of ceramic processing (2nd Edition), John Wiley & Son Inc., New York, 363-373.
- [4]. Malaysia Patent Pending PI20042325.
- [5]. P. Roy, G. Bertrand and C. Coddet (2005), Spray drying and sintering of zirconia based hollow powders, *Powder Technology*, **157** 20-26.
- [6]. F.A. Zakaria, K. Jamuna Thevi, S.H. Abu-Bakar, Z. Hussin, S. Muhamad and J.F. Mikan-Venegas, Preparation of carbonated apatite and its evaluation. In Proceedings of the Materials & Processes for Medical Devices Conference, pages 43-48, Boston, Massachusetts, USA, November 2005.
- [7]. Hampton, J.H.D., Savage, S.B., and Drew, R.A.L., Experimental analysis and modeling of slip casting, *Journal of American Ceramic Society* **71** (12) (1988) 1040-1045
- [8]. J.E. Funk Jr., Understanding Ceramic Slips, Ceramic Industry, (June 2006)
- [9]. Horn, R.G., Surface forces and their action in ceramic material, *Journal of American Ceramic Society* **73** (5) (1990) 1117 – 1135.
- [10]. Tsetsekou, A., Agrafiotis, C., Leon, I. and Miliias, A., Optimization of the rheological properties of alumina slurries for ceramic processing applications. Part II: Spray drying, *Journal of the European Ceramic Society* **21** (2001) 493-506.
- [11]. X.Q. Cao, R. Vassen, S. Swartz, W. Jungen, F. Tietz and D. Stoever, Spray drying of ceramics for plasma spray coating, *Journal of the European Ceramic Society*, **20**, (2000) 2433-2439