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Preparation of Biodegradable Porous Calcium Metaphosphate Granules as Bone Filler by Starch Consolidation

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Abstract. Porous calcium metaphosphate granules for bone fillers were prepared by starch consolidation with baking powder and surfactant. Paste for foaming was prepared by the mixing of calcium metaphosphate powder and water with the various amount of starch (10~20㎛ size), where solid contents 30%, 45%, 60% of the paste. In order to obtain the optimum micro/macro porous structure, the appropriate contents of baking powder and surfactant at a fixed content of starch were examined. In order to examine the content of baking powder on pore morphology, the baking powder was added 60, 180, and 300 wt% of the paste at fixed content of starch. And then, in order to investigate the effect of surfactant on porous structure, surfactant was added 0.035, 0.1, and 0.16 wt% of paste weight at fixed content of starch and baking powder. Foaming was conducted using microwave method, and foamed samples were sintered at 900 °C. The sintered porous blocks with starch only showed uneven and closed macro pores without any micro pores. However, the sintered porous blocks with starch, baking powder, and surfactant showed homogeneous micro and macro porous structures ranging 20~60, and 300~1000 ㎛ in pore size, respectively. The porosity was increased with the increase of surfactant up to about 70 %.

Introduction

Calcium phosphate ceramics especially such as hydroxyapatite (HA) and β-Tricalcium phosphate have been extensively studied and clinically used as bone substitute materials due to their similar chemical composition to bone [1, 2]. Recently, Calcium phosphate granules as a bone filler have been used in dentistry or orthopedics to regenerate damaged or diseased bone, in the form of dense or partially porous structure. Currently, attention to bone fillers with porous network geometry is growing because the increase of their specific surface area and the better provision of nutrients through the interconnected pores by circulation of body fluid may improve bone cell apposition [3, 4]. It was reported by Herbert et. al. that if pore size of bone substitute is lager 100 ㎛, bone and blood vessel enable to grow into the pores, and if more than 200㎛, osteoconduction could be achieve effectively [5]. Starch consolidation method has been tried for development of macroporous HA due to rigid porous structure available without powder compaction, capability of shaping micro and macro porous geometry with small amount of liquid, easy formation of homogenous pore distribution, and lower cost for product [6, 7]. The biodegradable property of calcium phosphates can be also combined with these advantages by starch consolidation.

Calcium metaphosphate (CMP) has been introduced as a new bone substitute material and a candidate for scaffold in tissue engineering because of its biocompatibility, osteoconductivity, and biodegradable property [8, 9]. In this study, porous calcium metaphosphate granules with micro and macro pores for bone fillers were prepared by starch consolidation with foaming agents such as baking powder and surfactant.

Materials and Methods

Calcium phosphate monobasic, $Ca(H_2PO_4)\cdot H_2O$ [Duksan chemical Co., Korea] was calcined above 700 °C to obtain CMP powder, followed by crushing and grinding below 75㎛ in particle size. After ball milling of CMP powders in ethyl alcohol with zirconia balls for 24 hours and sedimentation for 5 hours, the slurry was dried in a vacuum evaporator, then fine particles with sub-micron size were obtained. The paste formulation for each experimental condition shows in table 1. Microwave irradiation was used for foaming. For the foaming paste, the ratio of calcium metaphosphate to distilled water was fixed with 30:70 in volume percent. In order to examine the effect of starch on the pore characteristics, the 30, 45, and 60 wt% starches were added into the paste, respectively. After find the optimum starch content for porous structure, baking powder as foaming agent was added into the paste with the optimum content of starch. The content of baking powder was 60, 180, and 300 wt% of the paste. In order to investigate the effect of surfactant on porous structure, the various content of surfactant was added to the paste, which was consisted of optimum contents of starch and baking powder. The content of surfactant was 0.035, 0.1, and 0.16 % of the paste weight. The prepared specimens were heat-treated up to 900 °C with a multi-step heating schedule because of different decomposition behavior of additives; (1) heating up to 240 °C at a rate of 1 °C/min and holding for 30 minutes at 240 °C, (2) heating up to 400 °C at 0.5 °C/min, and holding for 1 hour at 400 °C, (3) heating up to 900 °C and holding for 1 hour, and then, (4) furnace cooling to room temperature. Surface morphology and pore size of porous sintered body were examined by SEM (Hitachi-4200, Hitachi Co., Japan). Apparent bulk porosity for the specimens was determined by measurement of weight and volume.

Table 1. Experimental formulation of additives for foaming

No.		Starch (wt%)	Baking powder (wt%)	surfactant (wt%)
	1	30	-	-
A	2	45	-	-
	3	60	-	-
	4	60	60	-
B	5	60	180	-
	6	60	300	-
	7	60	180	0.035
C	8	60	180	0.1
	9	60	180	0.16

* The content of each additive is based on weight percent to CMP powder.

Results and Discussion

All CMP pastes with starch showed good thixotropy and shear-thinning behavior. The viscosity of pastes was increased with the increase of starch content. Fig. 1 shows surface morphology of CMP foamed with starch content. The porous structure of CMP was obtained and the porosity increased from 48.5 to 66.7 % with increasing starch content. The pore size was varied from 1 to 1.5 mm with increasing starch content. Although the size of starch was about 20 ㎛, the tendency of the agglomeration of starch particles of starch was growing with starch content. The pore size thus increased with starch content. However, there are no micro pores with the addition of starch. In addition, most of macro pores were not interconnected each other and pore distribution was not homogeneous, either. In fig 2, the addition of baking powder into the paste with 60 wt% of starch was generated micro pores throughout the sample with closed macro pores. This result indicates that

baking powder is very effective to make homogeneous micro pores, but average porosity (38.2~46.7 %) was less than that with starch only. In order to improve foaming property of CMP paste, various amount of alcoholic and olefinic surfactant was added into the CMP paste with 60 wt% starch and 180 wt% of baking powder. As shown in fig. 3, the surface morphology of porous CMP with surfactant represented relatively homogeneous micro and macro pore distribution compared to the results of the above two types of samples. Micro pore size was approximately 40~50 ㎛ and macro pore size ranged from about 500 ㎛ (0.035 and 0.1 wt% surfactant) to nearly 1 mm (0.16 wt% surfactant). In samples with 0.16 wt% surfactant, the interconnection between micro and/or macro pores was appeared with the thinning of bulk skeletal and relatively weak mechanical strength. From these results, it was found that the baking powder influenced the micro pore formation and the surfactant made the stable macro pores homogeneously. In high magnification (fig. 5), it could be confirmed that micro and macro pores were homogeneously and evenly distributed well.

Conclusion

Micro and macro porous CMP fillers were prepared by starch consolidation with baking powder and surfactant. It was found that baking powder in CMP paste was effective in micro pore formation and surfactant in macro pores. In our preliminary study, the foaming of CMP paste by microwave method was more effective than by dry oven, in terms of the pore characteristics. It is believed that the porous CMP prepared by starch consolidation may be used as bone fillers with improved osseointegration and colonization by natural bone due to the biodegradation property of CMP with time.

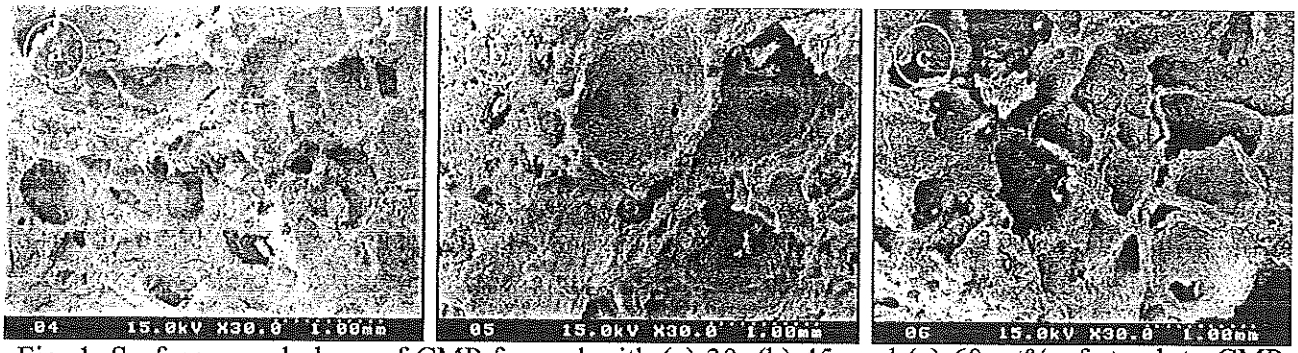

Fig. 1. Surface morphology of CMP foamed with (a) 30, (b) 45, and (c) 60 wt% of starch to CMP powder weight after sintering at 900 °C.

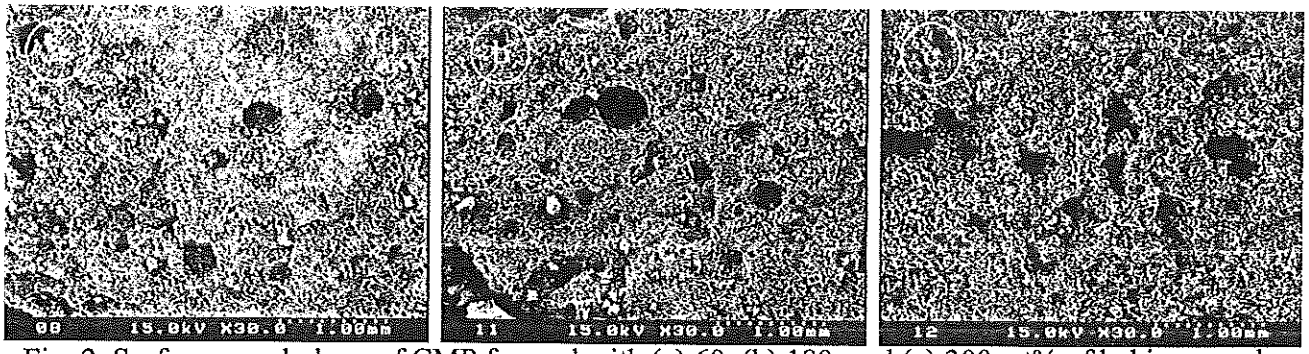

Fig. 2. Surface morphology of CMP foamed with (a) 60, (b) 180, and (c) 300 wt% of baking powder to CMP powder weight at the constant content of starch (60 wt%) after sintering at 900 °C.

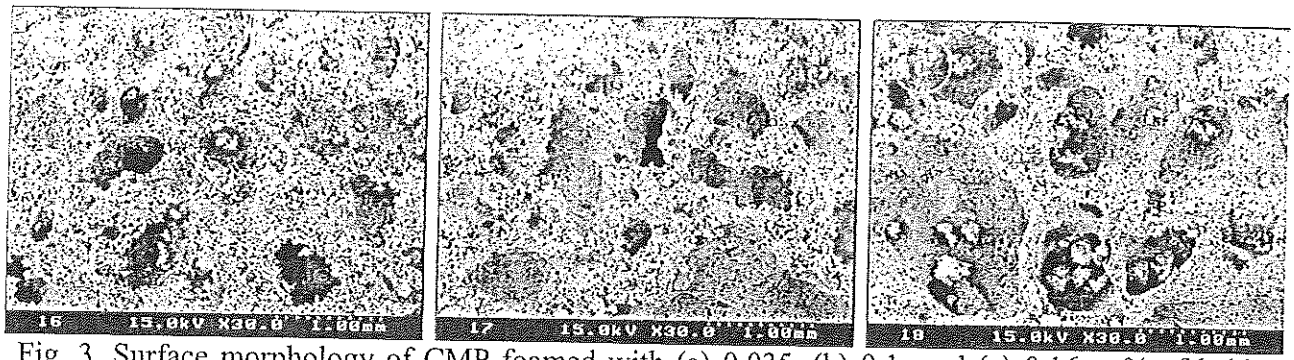

Fig. 3. Surface morphology of CMP foamed with (a) 0.035, (b) 0.1, and (c) 0.16 wt% of baking powder to CMP powder weight at the constant contents of starch and baking powder (60 wt%, 180 wt%), respectively, after sintering at 900 °C.

Table 2. Porosity of specimens with content of each additive.

Amount of Additives	A: Starch only (%)			B: Baking powder with constant content of starch (60 wt%)			C: surfactant with constant content of starch (60 wt%) and baking powder (180 wt%)		
	30	45	60	60	180	300	0.035	0.1	0.16
Porosity (%)	48.5	57.3	66.7	38.2	41.5	46.7	56.8	64.5	72.5

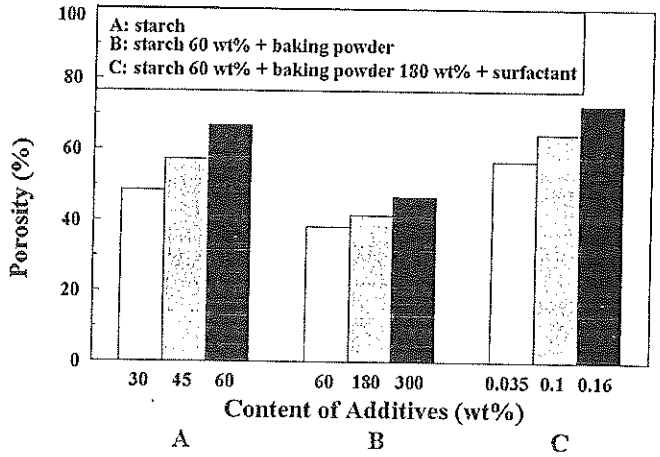

Fig. 4. Porosity of specimens with content and type of additives.

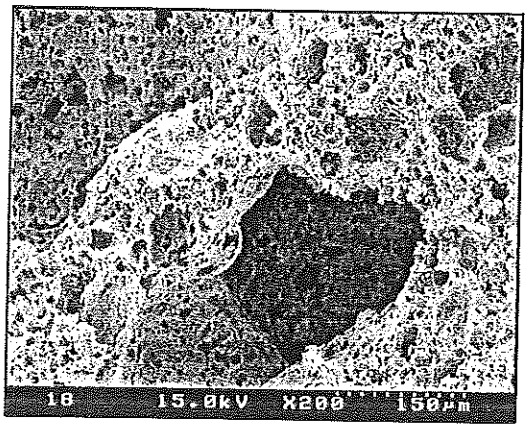

Fig. 5. Higher magnification of sample # 9 in table 1 (×200).

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