

# Selective Laser Sintering of Bioceramic Materials for Implants

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## ABSTRACT

Selective Laser Sintering (SLS) process is employed for fabrication of bioceramics for orthopedic implants. Hydroxyapatite and Calcium Phosphate ceramics are coated with polymer as a intermediate binder by using a spray drier. Polymer coated materials are SLS processed to make green parts, which are infiltrated and fired to remove the polymer. SLS processed green parts of hydroxyapatite have low density due to the small particle size with large specific surface area. This paper discusses the possibilities and problems in free-form fabrication of bioceramic.

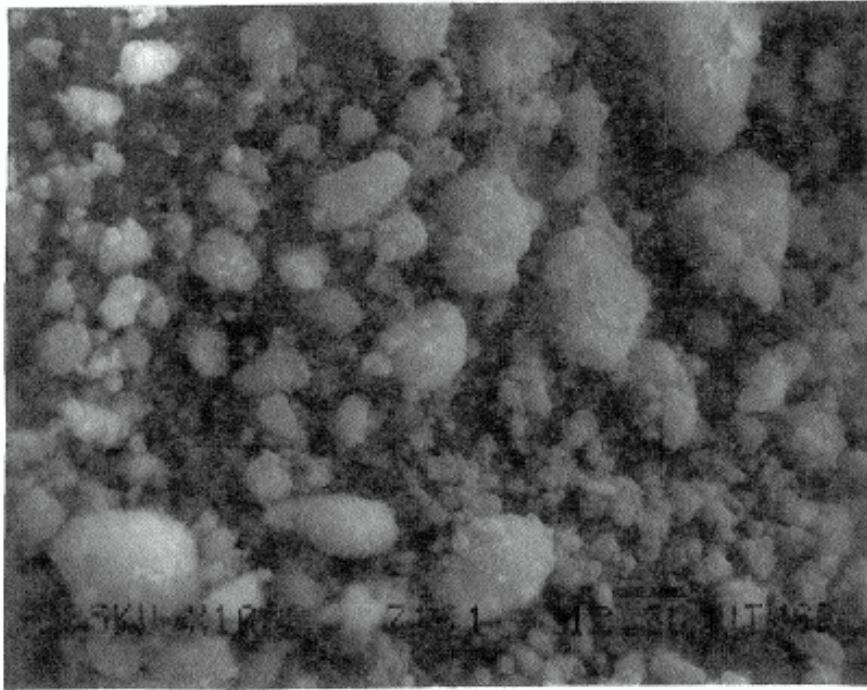
## INTRODUCTION

Many attempts have been made to find material that will assist in the regeneration of bone defects and injuries. Calcium phosphate ceramics, particularly hydroxyapatite(HA),  $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ , has received special attention as potential bone implant material because of its biocompatibility with the tissue and its compositional similarities to human bone and tooth. Many studies and methods, from powder compaction sintering to hot isostatic pressing, have been reported for the fabrication of HA. However, sintered HA materials by conventional techniques are as weak as sea coral even at high compacting pressure, because HA decomposes at temperatures lower than the required temperature for sintering.

Selective Laser Sintering (SLS) processes for preparing ceramic green parts with polymer as intermediate binder and post processing with the aid of ceramic cement have been discussed in detail in literature [1]. One advantage of SLS process for fabrication of bioceramic is the accurate construction of a complete facsimile bone structure from the geometric information obtained from either patient computed tomographic (CT) data or a computer Aided Design (CAD) software package[2]. Another advantage is the ability to controlling pore structure for biogenesis through control of polymer content.

## MATERIALS and METHODS

HA, obtained from Monsanto Inc. as Tricalcium Phosphate, TCP, was used as starting material. HA powders are very cohesive and consist of very porous agglomerates with mean particle size of 1 to 2  $\mu\text{m}$  and bulk density of less than 0.4  $\text{g}/\text{cm}^3$  [3]. The surface area determined by Mercury intrusion analysis is about 60  $\text{m}^2/\text{g}$ , suggesting very small particles. Stoichiometric HA contains constitutional water in the form of  $\text{OH}^-$  ions. This water can be driven off at 1200 °C. Figure 1 shows the microstructure of finely divided HA powders.



**Fig.1 : Scanning Electron Micrograph of HA (X1000)**

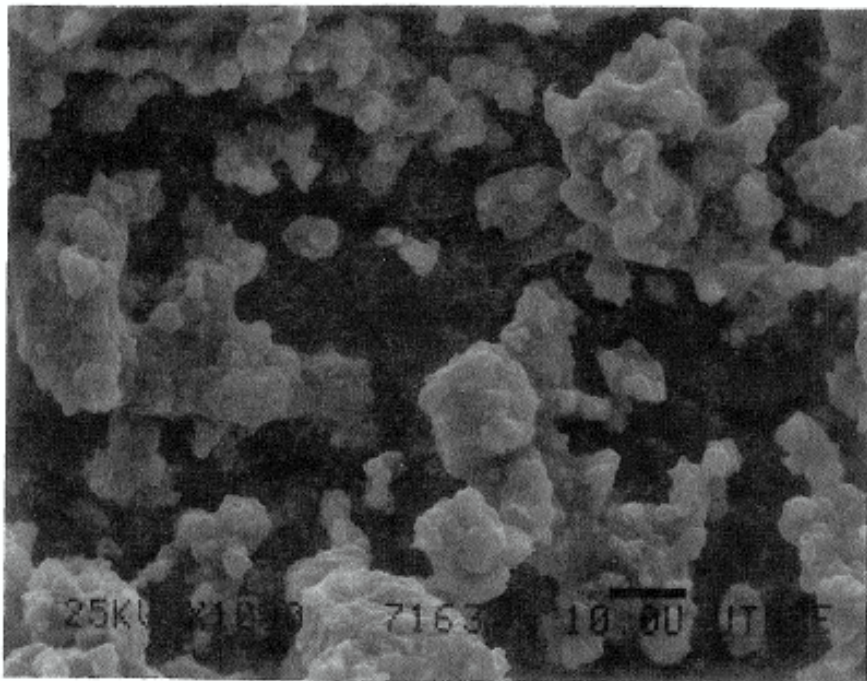
Two intermediate polymeric binders, UCAR 430 Acrylic Polymer Latex (obtained from Union Carbide Corporation) and PMMA emulsion copolymer, designed to depolymerize completely to gaseous product when heated above 400°C were investigated. Inorganic ceramic cement, Cerama Bind™ 542 was obtained from Aremco Products Inc. This inorganic cement is an alumino-phosphate material that can react to form phosphate bonded HA material.

Polymer was deposited on the HA powder by spray drying a slurry of the powder with polymer emulsion in "Pulvis Mini Spray" drier. To determine the required amount of polymer binder, the coated powder was heated in air to 150 °C to fuse the polymer. Afterwards, the powder was cooled and qualitatively examined. More than 20 % (45 vol.%) of UCAR 430 was required to produce a cake that barely permit handling. While PMMA copolymer coated materials showed better properties at 20 % coating, cakes could still be easily crumbled. These problems were attributed to the high surface area of the finely divided HA powder.

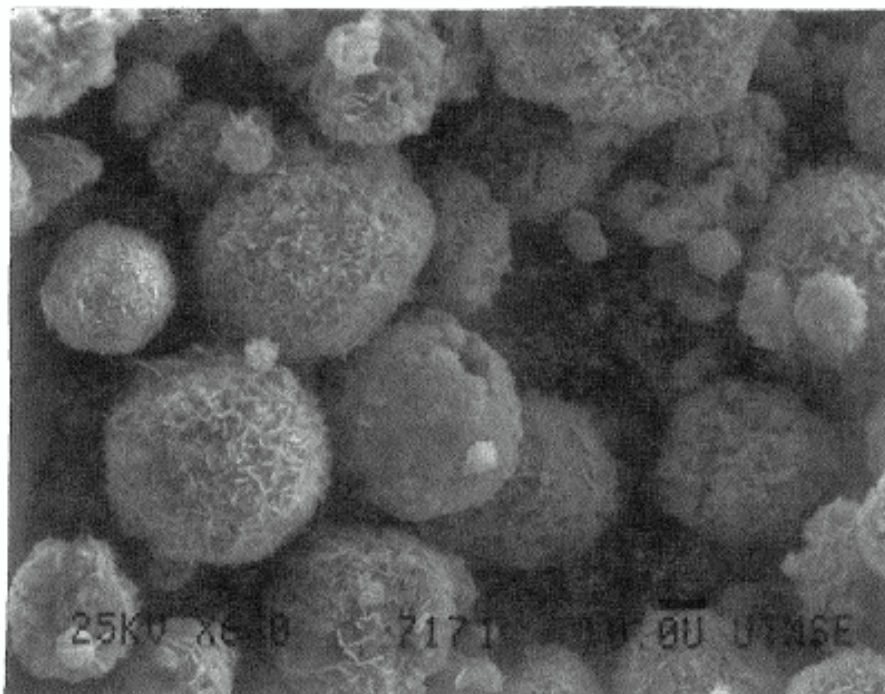
In an attempt to modify surface area, 50 g HA was reacted with 100 ml of 5 M ortho-phosphoric acid( $H_3PO_4$ ), and heated to 150 °C to form a cake. The cake was then ground back to finely divided powder by a Szegvari attritor system, type 1HSA. The morphology of the reacted HA powder is shown in Figure 2. The powder was spray dried and examined as before. The oven sintered cake showed much improved strengths, enough to permit rough handling, with the 14% (30 vol.%) of PMMA copolymer.

Based on the oven tests, we scaled up the coating of reacted HA powders with the 14 % of PMMA copolymer by using an Anhydro Laboratory Spray Drier #1 [4]. The operating conditions are as follows:

Solid content	: 45 wt.%
Inlet temperature	: 175 °C
Outlet temperature	: 110 °C
Atomizer speed	: 30,000 rpm



**Fig 2 : S.E.M. of 5 M reacted HA ( X 1000 )**



**Fig 3 : S.E.M. of a polymer coated powder (X800)**

Figure 3 shows the Scanning Electron Micrograph of a polymer coated powders. Spray dried powders are SLS processed using an University of Texas SLS machine. The operating conditions are presented in Table 1.

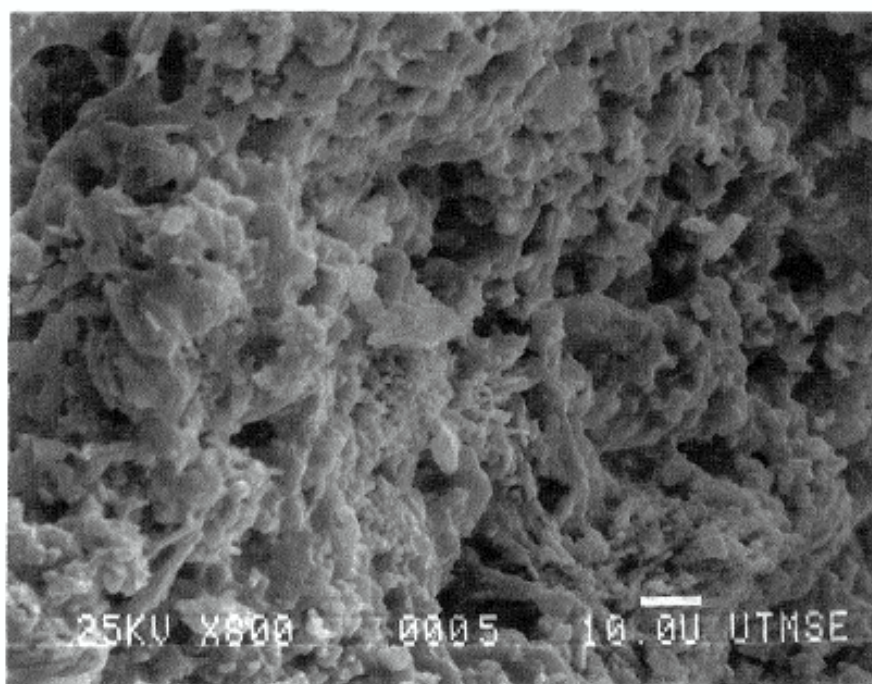
**Table 1 :** Operating condition of SLS machine

Power ( W )	Bed Temp.(°C)	Layer Thickness	Scan Space (mil)	Scan Speed (inch\sec)
5	120	8 mil	5	15

SLS processed parts were infiltrated with the phosphoric acid based inorganic cement. High surface tension was observed on infiltration which prevented effective penetration by the cement. Diluted methanol and Witcolate D51-51 surfactant (Witco Corporation) were used to reduce the surface tension. Infiltrated green parts were dried for 5 days in ambient condition. Upon drying, the parts were cured in the oven at 200 °C raised at 50 °C/hr. As a final step, green parts were fired up to 700 °C in the furnace for 2 hours to burn off the polymer.

## RESULTS AND CONCLUSIONS

Oven tests and some preliminary SLS work(not discussed) showed that parts made with polymer coated non-reacted HA, could not achieve acceptable green strengths. Low bulk density due to very large specific surface area caused by very small particle sizes and large porosity is believed to be the reason for this behavior.



**Fig 4:Scanning Electron Micrograph of sintered Surface (X800)**

While HA in its pure form has bulk density of less than  $0.4 \text{ g/cm}^3$ , HA reacted with 5 M phosphoric acid shows increased density over  $0.7 \text{ g/cm}^3$ . SLS processed part made of reacted HA has sufficient strengths for rough handling as oven tests of sintered cakes predicted. The strengths of post-processed bioceramic parts have shown even more promise and are currently being evaluated.

While the SLS processed parts have promising strengths with sufficient pores, biological and mechanical limitations are still prevalent in bioceramics. The implant material should be not only strong enough to be compatible with its use, but also biologically acceptable. The material's porosity should be suitable for bone tissue growth to fix the prosthesis with connecting bones. Fig 4. shows a fractured surface of a part that was post processed and fired. Clearly, there is considerable porosity, and we believe that this interconnected porosity should be sufficient for ingrowth of fibulious tissue. The strengths of these porous structures are currently being evaluated. We believe that the strengths will be sufficient for low-load bearing implants.

## REFERENCES

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