HIGHER STRENGTH POROUS CALCIUM POLYPHOSPHATE MADE BY CONVENTIONAL SINTERING

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INTRODUCTION

Biodegradable porous calcium polyphosphate (CPP) for use as a bone substitute in high load-bearing sites must have adequate strength without sacrificing the open-pored structure required for bone ingrowth. Our previous studies[1] demonstrated significantly higher compressive strengths for samples made by additive manufacturing (AM) compared with conventional sintering (CS). The present study aimed to determine if modified CS processing could give the same beneficial results and to further understand the reason for the effect. To do so, two variants of CS samples, one group made as previously reported and a second group made using a modified process suggested by the previous studies on AM samples were studied. The reason for the difference between CS and AM samples as proposed elsewhere appeared to be related to differences in sinter-neck sizes[2]. Porous CPP constructs are formed using a 2-step sinter annealing process[3]and it was proposed that the larger sinter necks associated with the 35 volume % porous AM samples were associated with a higher step-1 sinter temperature required to form these samples. Differences in initial powder packing density (45 vs.55 % for AM and CS samples respectively) and/or surface energy change of CPP due to processing[2] were believed responsible.

EXPERIMENTAL METHODS AND RESULTS

Conventionally-sintered (CS) porous CPP structures are normally made by packing amorphous CPP powders in crucibles for the step-1 sinter anneal (585°C, 1 hr). (A step-2 anneal at 950°C follows to yield the final porous structure[2]). Formation of the AM samples involved addition of 10 wt % polyvinyl alcohol (PVA) plus a solvent to dissolve the PVA that then acted as a binder during the layer-by-layer particle build-up of the 'green' CPP construct. The 'green' samples were annealed at 400°C for 2 hours in order to burn out the organic binder and solvent. After this, the AM, like the CS samples, are subjected to the 2-step sintering process. To reach the same porosity of 35 volume % after sintering, step-1 sintering temperatures of 585 and 628°C had to be used for CS and AM samples respectively. In the present study, one wt % PVA in particle form was mixed with CPP powder prior to packing in crucibles. This 'modified' CS sample was given the same step-1 sinter temperature as the AM samples (i.e. 628°C, 1 hr) followed by the 950°C, 1 hr anneal. 'Modified' CS samples were compared with 'normal' CS samples (Table 1).

Table 1 Mechanical strengths and (packing and sintered) densities for CPP under different protocols

	CS-CPP		CS-CPP+ 1 (wt)% PVA		AM-CPP[2]
	585°C	628°C	585°C	628°C	628°C
Packing Density (%)	49.2	49.2	47.8	47.8	40.4
Sintered Density (%)	65.1	90.5	53.2	69.6	63.6
Bending Strength (MPa)	15.17	n/a	n/a	21.14	21.78

Physical characterizations ('green' density, volume % porosity and visual and structural appearance after sintering), and 3-point bending tests of CS samples were undertaken.

The packing densities of the two types of CS samples are shown in Table 1. However, using a 585°C Step-1 anneal for both sample types resulted in lower % density and lower strength for the

CPP + PVA samples. Using a Step-1 sinter anneal of 628°C resulted in the desired density (approximately) and higher strength for the CPP+PVA samples. According to glass sintering theory[4], a lower packing density should result in lower sintered density for fixed sintering conditions. This was considered to be a possible cause for the difference noted for CS compared with AM-made samples[2]. However, in view of the very small difference in packing density for the CS samples with and without 1 wt% PVA addition (47.8 vs. 49.2% density), another factor was considered responsible, namely a decrease in CPP surface energy due to carbon residue remaining after the PVA burn-out anneal. The observed darkened appearance of the 'modified' samples after this treatment supports this hypothesis. A surface modification resulting in lower surface energy would reduce the driving force for sintering thereby requiring a higher temperature Step-1 anneal to achieve a desired sample density. In the present study, a 628°C treatment of the CPP+PVA samples resulted in a final volume % porosity ≈ 31%, a slight overshoot of the 35 volume % goal. During sintering of the amorphous (or partially amorphous) CPP, sinter neck formation and growth occurs primarily by a viscous flow transport mechanism. The higher step-1 sinter temperature results in more extensive viscous flow (since viscosity is inversely related to temperature) resulting in the larger sinter necks and higher strengths. Comparisons of sinter necks for the two types of CS-made CPP samples, one using a 585°C step-1 anneal and the other a 628°C temperature, as well as an AM-made sample can be seen in Fig. 1.

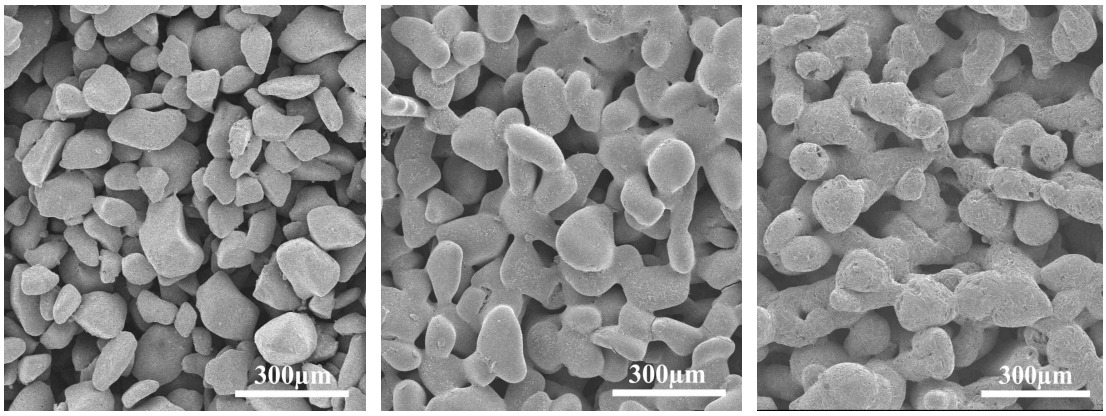

Figure 1 SEM images show the sinter-necks of CS (left), modified CS (middle) and AM-made (right) CPP

CONCLUSION

The higher mechanical strengths of CPP+1 wt% PVA samples is related to the use of a higher Step-1 sinter anneal which is hypothesized as being needed because of a modified surface and reduced surface energy of the CPP particles following the PVA burn-out anneal. Further studies to determine surface energy directly are suggested to test this hypothesis. The finding of a significant effect of just 1 wt% addition of PVA suggests an attractive route for preparation of higher strength CPP samples by conventional sintering methods.

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ACKNOWLEDGEMENTS

This study was funded by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Dept. of the Army – US Army Medical Research Acquisition Activity (USAMRAA)