STRENGTH DISTRIBUTIONS OF SINTERED HYDROXYAPATITE NANOPARTICLES

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ABSTRACT

In the past two decades, calcium phosphates, and especially hydroxyapatite (HA), have been used as bone substitutes, and the mechanical strength is one of the most important properties in this application. The flexural strength of an HA object depends on the nature of the HA powder, specimen preparation, flex test geometry and experimental conditions. HA was prepared by two methods, namely: wet and hydrothermal. The fundamental difference between these methods lies in the method of mixing the reactants and the reaction temperature. The obtained powders were pressed into pellets at 150 MPa and tested for flexural strength using a ring-on-disc method. The two-parameter Weibull and normal distributions were used to characterize the observed flexural strengths. Results were correlated with scanning microscope observations of fracture surfaces of the polished broken discs. The two-parameter Weibull distribution was found to be superior for the samples made with HA from the hydrothermal method. For the samples from the wet method, the normal distribution was equally suitable. The reason for this difference was sought by examining the discs for surface flaws.

1 INTRODUCTION

Fabrication of dense hydroxyapatite (HA) ceramics with practical fracture resistance is feasible if the HA is very pure and the particles feature optimum shape and size distribution (e.g., Jarcho et al. [1]). While fine-grained HA ceramics close to the theoretical density can be made upon sintering such powders at moderate temperatures, there are often many strength-limiting microstructural heterogeneities. Thus, it is of great importance to understand the variables that lead to flaws. Starting with the synthesis of the HA itself, we find that there are several widely practiced methods, including solid-state reaction, wet precipitation and hydrothermal synthesis. While all of these methods give the correct chemical structure, they also all produce agglomerates, either during reaction or drying. Such agglomerates, featuring low-density assemblies of particles, can persist during powder consolidation. Apparently, the irregular morphology of these agglomerates causes poor packing, which can result in uneven grain growth during sintering. These microstructural heterogeneities decrease the flexural strength of the sintered HA. For both dense and porous brittle materials, linear elastic mechanics shows that the fracture strength is determined by the presence and nature of flaws, which act as stress concentrators in the solid. The fracture stress is then limited to the stress value required to propagate the critical flaw located at the cavity surface (e.g., Pernot et al. [2]).

In this and related work, we attempt to examine these hypotheses by relating the agglomerate morphology to the density the green compacts, the density and surface morphology of sintered parts, and finally the flexural strength of the part.

2 MATERIALS AND METHODS

HA was synthesized using the two methods as described elsewhere (Kothapalli et al., [3,4]). Briefly, HA was prepared using the wet method at different reactant concentrations (0.5, 1.0 and 2.0 g/dL) and reaction temperatures between 25-100^{o}C. Likewise, using the hydrothermal method,

HA was synthesized using reaction temperatures between 25-250°C and aging times between 2-10 h. The hydrothermal reaction was carried out in a stirred autoclave held at fixed temperature. Each of the recovered HA samples was pressed uniaxially at 150 MPa for 1 min into 12-mm-diameter pellets, and sintered at 1200°C for 1 h. Nine pellets were made from each sample. Tables 1 and 2 show the preparation conditions of the samples used in the present study.

Table 1. Preparation conditions of the samples for wet method synthesis.

Sample ID	Concentration, g/dL	Temperature, ^{o}C
0.5-25	0.5	25
0.5-70		70
0.5-100		100
1.0-25	1.0	25
1.0-70		70
1.0-100		100
2.0-25	2.0	25
2.0-70		70
2.0-100		100

Table 2. Preparation conditions of the samples for hydrothermal method synthesis.

Reaction temperature, °C	Codes for aging times of		
	2 h	5 h	10 h
25	25-2	25-5	25-10
70	70-2	70-5	70-10
100	100-2	100-5	100-10
130	130-2	130-5	130-10
170	170-2	170-5	170-10
200	200-2	200-5	200-10
250	250-2	250-5	-

The flexural strength of the sintered pellets was tested according to ASTM F394–78, which is basically a ring-on-ring flex test of the disk [5]. The biaxial flexural strength was evaluated using the equation

$$S = -0.2387\, P\, (x\text{-}y)/d^2 \qquad (1)$$

where P is the load causing fracture, d is the pellet thickness at fracture origin and x, y are the parameters which takes into account the radius of loading (inner) ring, the radius of the pellet and the radius of support (outer) ring. Figure 1 is a scale drawing of the geometry.

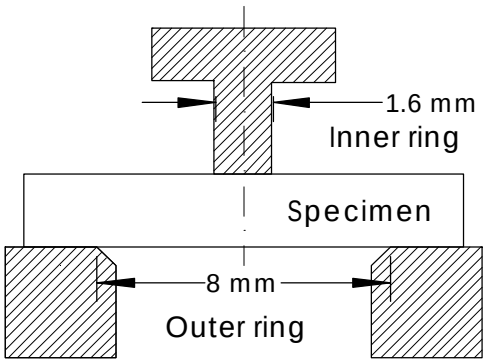

Figure 1. Test geometry according to ASTM F394-78.

The observed distribution of strengths were compared with two-parameter Weibull and normal distribution functions and the resulting distribution parameters were correlated with the characteristic crack size observed on the surfaces of fractured discs. The two-parameter Weibull probability density $p(x)$ is given by

$$p(x) = (b/a^b)\, x^{b-1} \exp[-(x/a)^b] \tag{2}$$

where b is the shape parameter and a is the scale parameter.

The surface morphology of the fractured sintered specimens was studied by environmental scanning electron microscopy (ESEM). The sintered pellets were polished using various grades of silicon carbide papers (grade 400-1200), while 1.0-μm diamond paste was used for the final polishing. The pellets were then coated with a gold film to reduce charging.

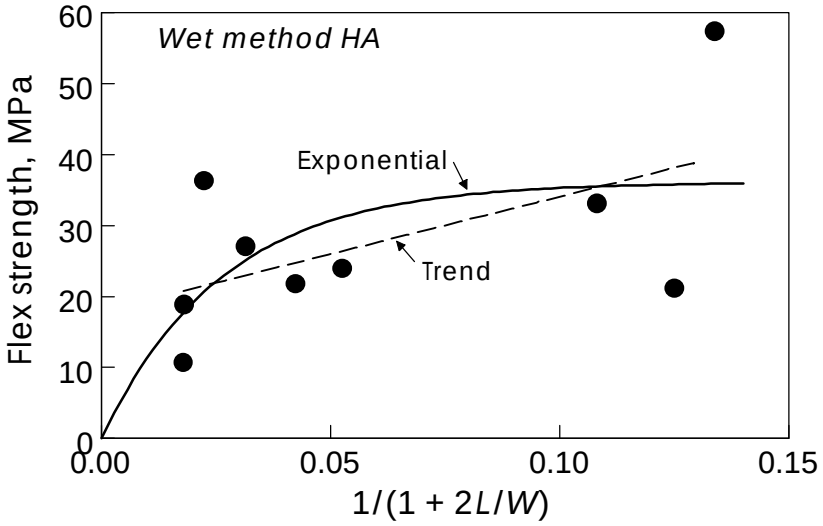

Figure 2. Correlation flexural strength and inverse stress amplification factor of pellets pressed with HA synthesized by the wet method.

3 RESULTS AND DISCUSSION

Two-parameter Weibull analysis of biaxial flexural strength data for wet-method HA gave Weibull scale parameters between 11.2-70.3 MPa and shape parameters in the range 1.81-8.46. These results are compiled in Table 3, along with the total probability for each sample's results relative to the normal distribution. As is evident, the Weibull distribution does not represent the failure stress distribution any better than the normal distribution (mean range 10.3-57.6 MPa and standard deviation range 2.11-36.5 MPa) for the samples synthesized by wet method. For the HA prepared by the hydrothermal method, Weibull analysis gave scale parameters between 21.2-74.7 MPa, and shape parameters in the range 1.8-5.8, while the normal distribution analysis gave average strength values in the range 18.8-64.6 MPa and standard deviations from 8.3 to 22 MPa. In contrast to the wet method, the Weibull analysis gave higher likelihood and thus was deemed a more accurate description of the distribution of strength values.

The scatter in the strength properties of materials is often described using Weibull statistics because of its "weakest link" origin [6]. The weakest link in the case of the HA ceramic disks would be the largest flaw in the bottom surface of the disk under the inner ring of the test fixtures.

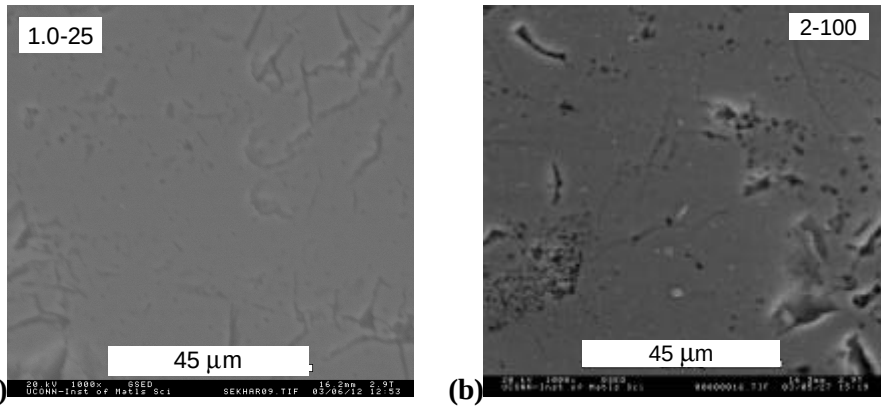

Figure 3. ESEM images of the crack surfaces for some representative samples. (a) 1.0-25 showing a smooth surface; (b) 2.0-100 showing large cracks.

Table 3. Weibull and normal analysis of flexural strength data for wet method.

	Weibull analysis		Normal analysis		
sample code[a]	a, MPa	b	$\bar{y}$,MPa	s, MPa	Probability ratio, Weibull/Normal
0.5-25	20.9	3.72	19.0	5.28	0.68
0.5-70	25.0	2.50	21.2	9.86	0.56
0.5-100	30.0	2.06	24.6	13.7	2.8
1.0-25	23.1	8.46	21.8	3.31	1.3
1.0-70	36.7	3.92	33.0	10.8	1.4
1.0-100	28.8	6.79	27.0	4.10	0.48
2.0-25	39.5	5.11	36.3	8.75	1.2
2.0-70	70.3	1.82	57.6	36.5	3.2
2.0-100	11.2	5.30	10.3	2.11	0.67

[a] Concentration, g/L – Temperature, °C

Earlier work by the authors showed that the biaxial flexural strengths of the pellets depend on the preparation conditions of HA, their microstructural characterization and crack size on the pellet's surface. Figure 2 shows the correlation between crack size and flexural strength of pellets pressed with HA from wet method. Linear regression analysis revealed a weak positive slope (9.6% chance of error by rejecting the hypothesis of zero slope), which is consistent with the inverse relationship between crack size and flexural strength following the classic theory for stress amplification due to cracks (e.g., Young and Budynas [7]). The exponential relationship shown has the expected limits of finite strength for cracks of low aspect ratio, and zero strength for cracks of high aspect ratio; thus it is probably the best descriptor, in view of the limited data, of the expected strengths. Figure 3 displays representative ESEM images of the cracks on the polished surface of the disc. As can be readily seen, the cracks in the 2.0-100 sample are far larger that those in the 1.0-25, which is accord with their respective a's of 23.1 and 11.2 MPa.

Table 4. Weibull and normal analysis of flexural strength data for hydrothermal method.

	Weibull analysis		Normal analysis		
Sample code	a, MPa	b	$\bar{y}$, MPa	s, MPa	Probability ratio, Weibull/Normal
25-2	31.2	3.50	28.1	9	1.0
70-2	49.0	2.13	41.2	22.2	2.3
100-2	43.3	2.50	38.4	16.5	1.7
130-2	36.9	2.63	32.7	13.9	1.6
170-2	58.7	3.11	52.5	18.8	1.1
200-2	64.9	5.07	59.4	15.6	1.5
250-2	38.2	2.95	34.1	12.8	1.1
25-5	45.9	5.56	42.2	10.1	1.5
70-5	21.2	2.67	18.8	8.25	1.3
100-5	44.6	5.42	40.9	10.7	1.6
130-5	74.8	2.83	64.6	27.5	1.2
170-5	50.4	2.95	43.9	17.8	1.2
200-5	38.0	3.90	34.4	10.8	1.1
250-5	24.3	1.80	19.6	12.7	4.0
25-10	37.5	5.83	34.7	7.15	1.0
70-10	38.5	1.81	31.0	19.4	2.2
100-10	37.8	3.78	34.0	10.9	1.2
130-10	58.4	5.20	53.5	13.1	1.3
170-10	41.8	4.15	37.9	10.8	1.0
200-10	33.9	4.14	30.7	9.42	1.3

[a] Temperature, °C – Aging time, h

4 CONCLUSIONS

The two-parameter Weibull probability density function was found to be superior to the normal distribution for describing the flexural strengths of bioceramic HA synthesized under various reaction conditions using the hydrothermal method. For the samples derived from the wet method, the normal distribution was equally suitable. As the crack size in the sample increased, the flexural strength appeared to decrease, although high scatter in the results prevented an exact description of this relationship.

5 REFERENCES

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