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Mechanical properties of sintered hydroxyapatite and tricalcium phosphate ceramic

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The ultimate values for compressive strength, Young's modulus, and toughness of cylindrical specimens of unitary aspect ratios and uniform grain-size distributions were extrapolated for hydroxyapatite (HAP) to 70 MPa, 9.2 GPa, and 0.36 J cm^{-3}, and for tricalcium phosphate (TCP), to 315 MPa, 21 GPa, and 2.34 J cm^{-3}. For total volume porosities of 50%, the corresponding values were determined: for HAP, 9.3 MPa, 1.2 GPa, 0.042 J cm^{-3}, for TCP, 13 MPa, 1.6 GP, 0.077 J cm^{-3}. Porosities of HAP specimens ranged from 3%–50%; TCP from 10%–70%. Two pore-size distributions were employed. Exponential dependencies of the mechanical properties were found upon porosity ($p < 0.0001$). No differences in measured mechanical properties, as determined in compression, could be attributed to pore size. The superiority of TCP increases with density and suggests that a larger or more selective pore-size distribution could be effectively employed in TCP biological implants. This work also suggests the dominant role of secondary calcium phosphates in increasing compressive strengths. © *1999 Kluwer Academic Publishers*

1. Introduction

Synthetic calcium phosphates have been used clinically to repair bone defects for over 10 years. Initially, two sintered materials were offered: porous tricalcium phosphate ceramic (TCP) and dense hydroxyapatite (HAP). Porous TCP is permeated with cells and tissue and subsequently resorbs *in vivo*. It functions as a conductive, sacrificial scaffold for new bone development when placed in hard tissue [1, 2]. Dense HAP, also very biocompatible, functions as a permanent space filler without ingrowth [3]. Subsequently porous, unsintered HAP has been prepared by the hydrothermal exchange of phosphate for carbonate in certain calcarious coral species [4]. A clinician selects porous ceramics if the new bone is expected to mature and remodel and if a more physiological repair is desired. If the newly formed bone is not expected to remain, then dense HAP is generally implanted.

The limiting disadvantages of these synthetic materials as biomaterials are often the deficient mechanical properties characteristic of ceramics. As a class, bulk calcium phosphates are not to be used in sites that experience significant body-weight bearing loads. The primary indications for bulk calcium phosphates have been in granular form for filling defects or for mixing with ground or morselized bone to extend bone graft. Although bone bonds so tightly to calcium phosphates that laboratory-induced failure does not preferentially force separation of the bone/ceramic interface [5, 6], the permanent existence of a mechanically inferior material in bone premanently weakens the defect site. The presence of a large amount, or large pieces, of HAP may also adversely affect vascularity.

Clinical applications of these materials might be expanded by exploiting or improving appropriate mechanical properties. This investigation determined some mechanical properties of a series of porous calcium phosphate ceramics sintered at a temperature known to maintain integrity of the desired principal phase. Additionally, grain-size distributions remained constant for each ceramic and did not confound the determination of compressive strengths. Because extensive literature reports of the compressive strength of HAP now span nearly a decade, these published data are compared with a large number of specimens in the current study.

2. Materials and methods

2.1. Preparation of porous calcium phosphates

Hydroxyapatite was prepared by a modification of the precipitation method of Hayek and Newesely [7], tricalcium phosphate was supplied (Miter, Inc., formerly of Columbus, OH). Pores of two size distributions were induced by blending dried powders with varying percentages of a sized, sacrificial porogenic material and compacting the mixtures into cylinders (nominally 17–22 mm diameter, 17–22 mm high) at 69–350 MPa prior to sintering. HAP specimens were sintered at 1100 °C.

All cylinders were machined to 10 mm diameters, except 15 TCP specimens which were turned to 15 mm. The faces were made parallel and heights reduced to present cylindrical prisms for mechanical testing having an aspect ratio near unity. Machining was accomplished without lubricant at 555 r.p.m. using an uncoated carbide-tipped tooling insert for non-metals (Kennametal NPR51 K68, Raleigh, NC). All specimens were cleaned ultrasonically in alcohol (2 × 10 min) and oven-dried at 105 °C prior to testing.

2.2. X-ray diffraction

A Philips electronic polycrystalline diffractometer PW1316/90 wide-range goniometer with an XRG 3100 generator and DMS-41 data measuring system, theta compensating slit, and graphite diffracted beam crystal monochromator equipped with a copper target (35 kV, 20 mA), nickel filter, and scintillation detector, was used to record diffractograms at a resolution of 2° 2θ min^{-1}. Counts and assignments are given in Tables I and II.

2.3. Fourier transform–infrared analysis

Fourier transform–infrared (FT–IR) spectra were recorded in potassium bromide in the diffuse reflectance mode at a resolution of a 4 μm after accumulating 64 scans on a Rio-Rad Digilab FTS-7 spectrophotometer (Bio-Rad, Cambridge, MA). Spectra are presented in Figs 1 and 2.

2.4. Mechanical testing

Samples were tested in compression on an Instron 4505 static, screw-driven testing machine fitted with

TABLE I XRD data for hydroxyapatite

hkl	2θ (deg)	I/I_0	Counts[a]
110	16.80	2.6	33
101	18.86	1.2	16
200	21.75	5.1	66
111	22.85	4.6	60
201	25.30	2.0	26
002	25.85	33.5	433
102	28.10	9.2	119
210	28.90	15.4	199
211	31.75	100.0	1293
112	32.15	55.1	712
300	32.85	69.5	898
202	34.06	25.9	335
301	35.40	5.5	71
212	39.15	6.4	83
310	39.75	23.6	305
221	40.40	2.3	30
103	40.75	0.6	8
311	41.95	7.2	93
302	42.65	0.2	2
113	43.80	6.0	77
400	44.30	1.6	21

[a]Counts background corrected.

TABLE II XRD data for tricalcium phosphate

hkl	2θ (deg)	I/I_0	Counts[a]
110	16.90	14.1	133
113	18.35	1.1	10
202	20.10	3.7	35
108	21.30	1.1	10
204	21.75	9.7	91
1.0.10	25.70	21.5	203
211	26.10	3.8	36
212	26.40	7.6	72
214	27.70	53.5	504
0.0.12	28.60	1.3	12
300	29.55	14.2	134
2010	30.95	100.0	942
218	32.35	22.9	216
306	32.90	7.5	71
1.1.12	33.40	7.3	69
220	39.25	79.6	750
223	35.00	9.8	92
2.1.10	35.50	11.9	112
311	35.80	4.0	38
226	37.25	10.1	95
135	37.75	5.7	54
1.0.16	39.75	13.4	126
404	40.95	14.1	133
3.0.12	41.55	11.1	105
2.0.16	43.45	8.9	84
322	43.80	6.4	60
408	44.40	10.5	99

[a]Counts background corrected.

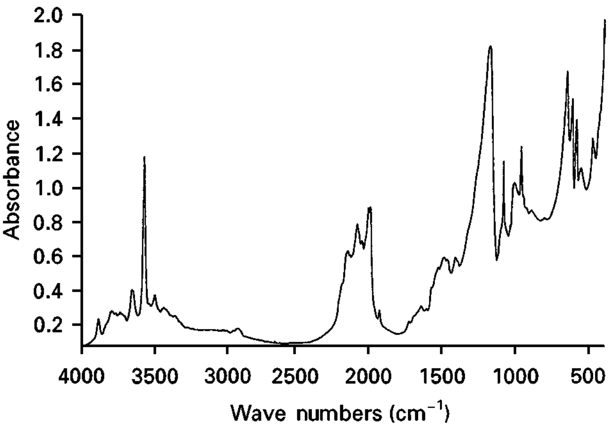

Figure 1 FT–IR spectrum of hydroxyapatite.

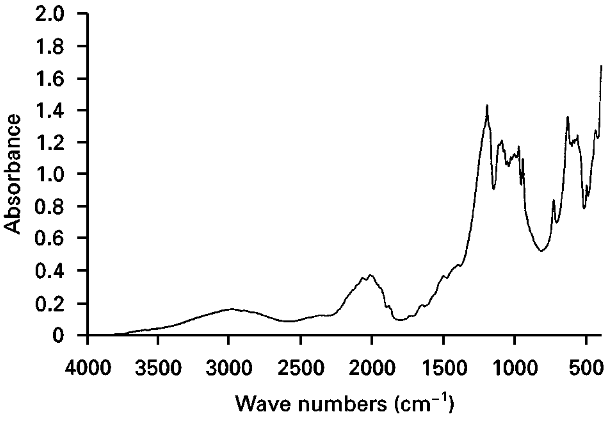

Figure 2 FT–IR spectrum of tricalcuim phosphate.

a 10 kN load cell using a crosshead speed of 12.70 mm min^{-1} (Instron Corporation, Scanton, MA). The 100 kN load cell was required for the most dense specimens. Load–displacement data were acquired 50 times per sec and with the Instron Series IX automated testing software package, version 5.21. Specimen failure was detected in the load threshold mode with a load level of 1.5 kN, or 10 kN with the 100 kN load cell. Young's modulus of electricity was determined automatically from a least-squares fit from the steepest portion of the load–displacement curve. Stress and energy were determined at the first peak, the point of initial failure, and toughness by normalizing energy to specimen volume.

2.5. Grain-size determination

Mean grain size was calculated from the full-width at half-maximum peak height after regressing the grain size, D, of known standards, as determined by scanning electron microscopic measurements, on to $(D \cos \theta)^{-1}$. All data pairs contributing to the diffraction profile were utilized after correcting the intensities for background.

2.6. Pore-size distribution

Average pore sizes were determined with an image analyzer (Osteoplan System II, Kontron, Eching, Germany) from thin sections of ceramic (approximately 1 cm diameter, 20 ± 5 μm thick), embedded in polymethylmethacrylate and ground (Exakt Cutting-Grinding System, Hamburg, Germany). Fifty fields were examined at 200 diameters for each specimen.

2.7. Statistical evaluation

Data analysis was performed using general linear modeling procedures (SAS Institute, Inc, Cary, NC).

3. Results

Stress, modulus, and toughness were regressed on to porosity to fit Equation 1

$$\ln(y) = a + bx \qquad (1)$$

where y is the measured value of the mechanical property of interest, a and b are regression coefficients, and x is the porosity expressed as the complement of the ratio of the observed and theoretical densities. Ultimate values for HAP specimens extrapolated to full density are 70 MPa, 9.2 GPa, and 0.36 J cm^{-3} for compressive strength, Young's modulus, and toughness respectively, and for TCP, 315 MPa, 21.0 GPa, and 2.3 J cm^{-3}. Properties at 50% of the theoretical densities and the 95% confidence intervals are presented in Table III. Theoretical densities were obtained from crystallographic studies: HAP, 3.156 g cm^{-3} [8, 9]; TCP, 3.067 g cm^{-3} [10]. Scatter plots are presented in Figs 3–8 with 95% confidence intervals. In all cases the probability of obtaining correlation coefficients, r, at least as large as those obtained from Table III, from a random sample population in which the x, y pairs are not exponentially correlated, is less than 0.0001.

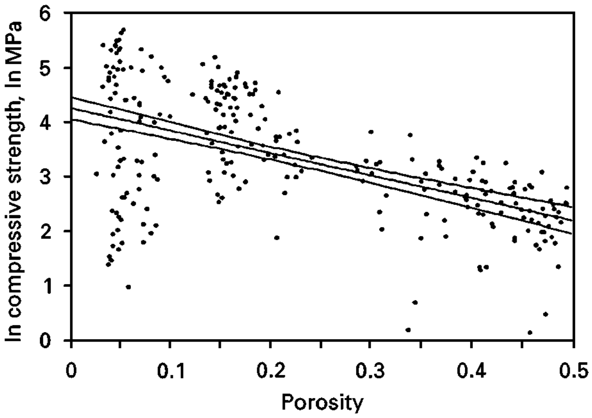

Figure 3 Compressive strength versus porosity for HAP.

TABLE III Summary of regression analyses. Extended calculations are for convenience to the reader and do not necessarily imply statistical significance.

	a (S.E.)	b (S.E.)	r^2	n	Res MS[a]	Ultimate value (95% C.I.)	Value at 50% porosity (95% C.I.)
HAP							
Compressive strength (MPa)	4.2421 (0.1050)	− 4.0219 (0.3874)	0.2970	257	0.9334	69.6 (56.6, 85.4)	9.31 (8.75, 9.91)
Modulus (MPa)	9.1298 (0.0478)	− 4.0216 (0.1764)	0.6709	257	0.1935	9226 (8401, 10132)	1235 (1201, 1271)
Toughness (J cm^{-3})	− 1.0305 (0.1569)	− 4.2762 (0.5750)	0.1811	252	2.0422	0.3568 (0.2624, 0.4853)	0.0406 (0.0383, 0.0462)
TCP							
Compresive strength (MPa)	5.7540 (0.0694)	− 6.4034 (0.1723)	0.8410	263	0.3262	315 (275, 361)	12.8 (12.4, 13.3)
Modulus (MPa)	9.9508 (0.0523)	− 5.1839 (0.1301)	0.8584	264	0.1860	20970 (18926, 23235)	1570 (1528, 1613)
Toughness (J cm^{-3})	0.8510 (0.1028)	− 6.8205 (0.2550)	0.7334	262	0.7133	2.342 (1.915, 2.865)	0.0774 (0.0734, 0.0816)

[a] Residual mean square.

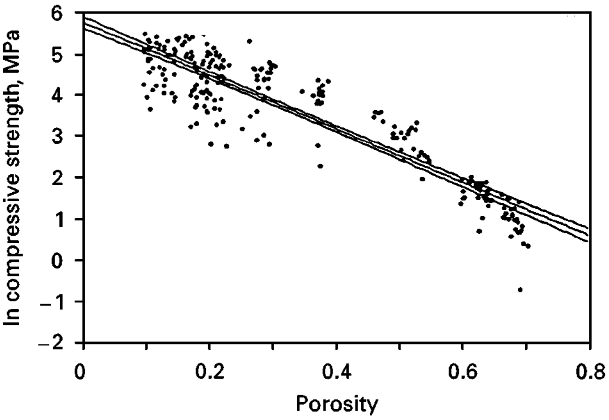

Figure 4 Compressive strength versus porosity for TCP.

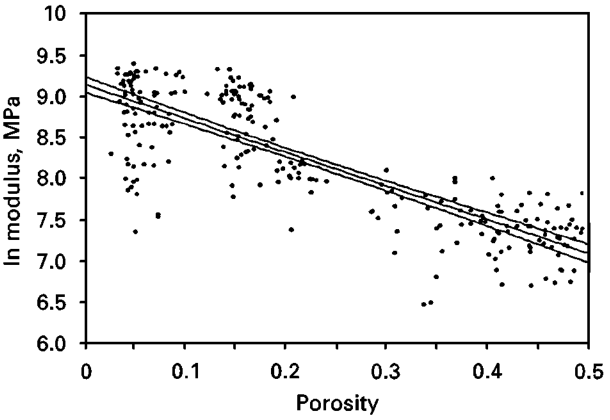

Figure 5 Modulus of elasticity versus porosity for HAP.

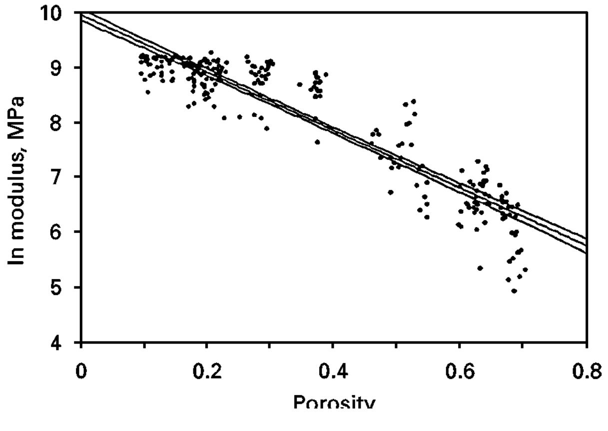

Figure 6 Modulus of elasticity versus porosity for TCP; $y = 9.9508382 - 5.1838976\,x$.

Pore sizes were estimated from 14 samples. The means for the small pore samples ranged from approximately 70–110 μm for HAP, 100–130 μm for TCP. The means for larger pores spanned 160–180 μm for HAP for 90–190 μm for TCP. The standard deviation was estimated as 16–19 μm. There was some suggestion that mean pore size increased with porosity. The mean grain size was 1.9 μm.

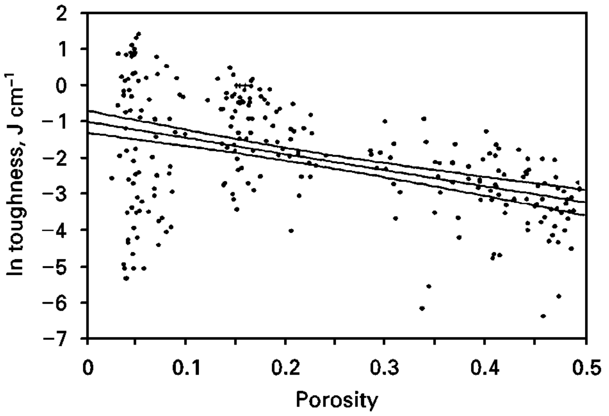

Figure 7 Toughness versus porosity for HAP.

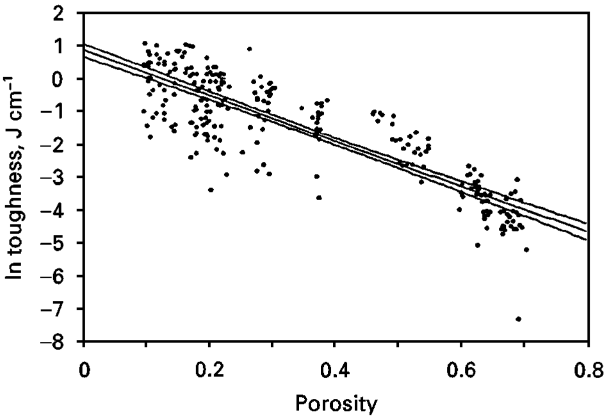

Figure 8 Toughness versus porosity for TCP.

4. Discussion

Initial examination of the data reveals the superiority of the compressive strength, modulus of elasticity, and toughness of porous tricalcium phosphate ceramic over hydroxyapatite in the range of porosities studied. For specimens of 50% total volume porosity TCP has a 1.4-, 1.3-, and 1.8-fold advantage in these respective properties. As densities increase to theoretical values, the relative improvements increase to 4.5, 2.3, and 6.6 to favor TCP over HAP for mechanical considerations.

Hydroxyapatite fails in a shear mode whereas tricalcium phosphate fails in tension as judged by the morphology of test specimen remnants. HAP cylinders shatter to form rectangular prisms with long faces parallel to the destructive force plane. TCP cones adhere to the platens of the test fixture [11].

4.1. Compressive strength of hydroxyapatite

Previously published compressive strengths for dense HAP range from approximately 138 MPa [12] to 798 MPa [13] and 917 MPa [14]. Intermediate values of 685 MPa [15], 537 MPa [16] and 420 MPa [17] might be extrapolated from porous samples ranging from 35%–70%, from 3%–19%, and from 2%–50% porosity, respectively. Ranges in strength expected from uncertainties in experimental error and specimen flaws are exaggerated by differing sintering conditions and synthesis routes. The reported values were obtained from hydroxyapatite prepared by sintering gelatinous precipitates or by sintering commercially available, non-stoichiometric "hydroxyapatite" or "tricalcium phosphate" powders. A variety of sintering times, temperatures, and atmospheres were employed. Some workers selectively report the highest compressive strength from the best sample. Inappropriate aspect ratios and small specimen dimensions that inflate stresses were sometimes used. In some cases porosity was induced by varying sintering temperatures or times without due consideration of the effect of grain size on compressive strength. In general, the literature can be better understood by grouping data by sintering conditions and synthesis route.

Firstly, infrared spectral data confirm loss of OH and decomposition to orthophosphates for precipitated hydroxyapatite after extended heating in air for 20 h at 1150 °C [18] even though an apatitic X-ray diffraction pattern can remain after heating to 1230 °C [19] and 1250 °C [20]. Upon heating to 1450 °C tricalcium phosphate ($Ca_3P_2O_8$) and tetracalcium phosphate ($Ca_4P_2O_9$), appear [18]. Hydrothermally prepared HAP dehydroxylates and decomposes to some extent after atmospheric pyrolysis for 3 h at 1000 °C [21]. Peelen *et al.* [15] confirmed the decomposition of commercial. HAP above 1100 °C by thermogravimetric analysis. Thus, mechanical properties reported on materials heated at conditions beyond these restraints are suspect because of the presence of secondary phases.

Secondly, the use of commercially available powders introduces impurities, such as magnesium, that may substitute for calcium and stabilize undesired calcium phosphate compounds [10, 22]. Commercial calcium phosphate is prepared by allowing lime to react chemically with a technical grade of phosphoric acid. Although this material, commonly referenced as hydroxyapatite and otherwise sold as tricalcium phosphate, is often used in food, pharmaceutical, and personal-care products, it is by no means reagent quality. Chemical analyses have been reported by four groups [13, 15, 22, 23].

In particular, the low stress of 138 MPa from Rao and Boehm [12] was obtained by pooling mechanical testing data from precipitated hydroxyapatite (11 specimens) and fluorapatite (20 specimens) sintered at 900–1200 °C for 0.5–4 h. As only one-third of these specimens were HAP, we remain uncertain about the ultimate compressive strength obtained from this work.

The highest value of 917 MPa ± 15%(138 MPa) was obtained by Jarcho *et al.* [14] on 25 precipitated HAP specimens sintered for 1 h at 1100 °C. The grain size was 0.3 μm. Test specimens were small and of inadequate aspect ratios (4.6 mm diameter × 2.0 mm high) and aspect ratio (0.43) [24, 25].

Subsequent work by de With *et al.* [13], who reported the compressive strength of dense HAP as 798 ± 56 (7.0%) MPa ($n = 8$), may not fully support the other high value upon closer inspection. These bluish colored samples were prepared by sintering isostatically pressed (100 MPa) commercial powder, a non-stoichiometric mixture, in a moist oxygen atmosphere for 6 h at temperatures from 1100–1250 °C. The compressive strength of only the most dense sample (5 mm diameter × 15 mm, aspect ratio 3.0), presumably sintered at 1250 °C, was reported. The grain size was slightly less than 4 μm.

de With *et al.* [13] acknowledge the presence of magnesium and sodium at levels exceeding 0.1 wt% in the starting material and the existence of secondary calcium phosphate phases by X-ray diffraction in samples heated at and above 1150 °C. Compositional variance is used to explain the 40% reduction in activation energy for grain growth (34 versus 56 kcal mol^{-1}) [14]. It is quite possible that substituents and/or spatial rearrangements of the crystal lattice also altered mechanical strength.

The works of Peelen *et al.* [15] and Akao *et al.* [16] provide intermediate values for ultimate compressive strength. They did not attempt to characterize fully dense materials, but controlled porosity with sintering temperature (1100 °C–1300 °C and 1150°C–1300°C respectively). The first group compacted commercially available powder with a constant amount of hydrogen peroxide, the latter precipitated powder with no porogenic material. The relative ranges of porosities vary between the studies as expected: 40%–70% and 3%–19%. Compressive strengths ranging from 30–160 MPa were obtained in the former study using the more porous samples; 308–509 MPa were reported for the denser materials.

Peelen *et al.* [15] compressed adequately sized specimens of proper aspect ratio (1 cm diameter × 1–1.5 cm high) as apparently did Akao *et al.* [16] (5 × 5 mm cross-section × 10 mm length). Additionally, Akao *et al.* [16] reported average grain sizes between 1 and 3 μm, slightly less than reported by de With *et al.* [13]. These grain sizes are higher than those reported by Jarcho *et al.* [14] due to elevated sintering temperatures and extended sintering times. As Peelen *et al.* [15] and Akao *et al.* [16] sintered HAP above 1100 °C, it is likely the proposed elevation in compressive strength from decomposition products is attenuated by larger grains [26].

Data tabulated by Akao *et al.* [16] (four points) and the five points plotted by Peelen *et al.* [15] are fit to logarithmic expressions with high correlation ($r^2 = 0.9$ and 0.95, respectively). The combination of all 9 data points from both studies closely approximates the expected logarithmic relationship ($r^2 = 0.98$) as shown in Equation 2

$$\ln(\sigma_c) = 6.40 - 3.90P \tag{2}$$

over a wide range of porosities. The ultimate compressive strength of hydroxyapatite from these combined data is 602 MPa. Such consistency obtained from materials of different synthetic routes suggests that the effect of secondary calcium phosphate phases formed by excessive sintering dominates the effect of elemental impurities within starting materials. Unfortunately, the effect of varying grain size cannot be separated in this model.

A more thorough study, perhaps, by Driessen *et al.* [17] tends to confirm this middle figure of 600 MPa for ultimate compressive strength, but raw data are not available for detailed analysis. Commercial powders of characterized impurity were mixed with varying concentrations of hydrogen peroxide, sintered in wet oxygen from 800–1300 °C for 6 h, and machined into cylinders (4 mm diameters × 6 mm high) for compressive testing. Six samples up to 50% porosity were obtained. Compressive strength was regressed logarithmically on to porosity. The coefficient of the porosity variable was reported as -4.6, but the precise ultimate compressive strength was not given. It appeared to approximate 420 MPa as read from their Fig. 3. (The coefficient obtained from the previously discussed combined data of Akao *et al.* [16] and Peelen *et al.* [15] was -3.9; that from the current study, -4.0). Denissen and de Groot report compressive strengths of sintered HAP to be 390–430 MPa for dense samples also sintered in wet oxygen, but their experimental conditions may not be as clearly defined [23].

More recent studies of Juang and Hon [27] and Wen *et al.* [28] indicate the significance of compositional purity on compressive strength. Juang and Hon increased the compressive strength of precipitated HAP by admixing alumina prior to densification and sintering from 1200–1450 °C. In optimizing alumina content and sintering temperature they note that alumina drives the decomposition of HAP by consuming a degradation product. The increase in compressive strength from 440 MPa (97% dense) to 813 MPa is attributed to a little decomposition of HAP. Wen *et al.* characterized precipitated HAP sintered at 1050–1200 °C containing 15% and 35% TCP. The highest compressive strength of 280 MPa was obtained from samples of 5%–9% open porosity containing 15% TCP. In both these studies, compressive strengths increased with small amounts of TCP and decreased with larger amounts.

Martin and Brown [11] prepared calcium-deficient hydroxyapatite and carbonate-containing apatite by alternative methods at low temperature to develop bone-treating modalities in a clinical setting. They also note compositional variations on compressive strengths, but no reduction in strength due to formation at lower temperature. They state their value of 174 MPa for the compressive strength of calcium-deficient HAP is consistent with literature reports for sintered HAP of comparable porosities. Their carbonate-containing apatite exhibited reduced mechanical properties. Carbonate content has also been cited as a factor in influencing mechanical properties as suggested by Toriyama *et al.* [29] in their work with apatites prepared by mechanochemical processes.

The present study has the advantage of inducing and controlling porosity with a porogenic material without the confounding effects of changes in grain size. Additionally, sufficiently low sintering temperatures and short sintering times reduce the formation of secondary phases and dehydroxylation. As extrapolated from 257 specimens of 50%–97% crystallographic density, the ultimate compressive strength of hydroxyapatite sintered at a temperature to maintain phase purity is 70 MPa in the current study. The 95% confidence interval 57–86 MPa. Although this is outside the broad, and tenuous, 140–920 MPa range published by others, it is clear that decomposition products exert strong effects, especially in the studies of Juang and Hon [27], Wen *et al.* [28] and Peelen *et al.* [15] and Akao *et al.* [16], in increasing compressive strength. Reports from limited numbers of specimens should not be given extreme weight, especially if the dimensions or purity of the test specimens are inadequate.

4.2. Compressive strength of tricalcium phosphate ceramic

Little has been reported in the English literature concerning the mechanical properties of beta-tricalcium phosphate. Driessen *et al.* [17] compared the compressive and tensile strengths of beta-tricalcium phosphate (commonly, but inappropriately, called beta-whitlockite) [30] and hydroxyapatite, and Jarcho *et al.* [31] briefly summarized the fracture strength, compressive strength, modulus of elasticity, and Knoop hardness for the dense material.

Just as Driessen *et al.* [17] did not report many raw data concerning HAP, so it is with TCP. The range of total volume porosities studied was approximately 2%–50%. The coefficient of the porosity variable in their exponential equation was -6.2 (current study, -6.4), indicating that the compressive strength of TCP is more sensitive to changes in porosity than HAP (-4.6; current study, -4.0). The ultimate compressive strength of TCP read from their graph approximates 750 MPa, almost 80% more than the ultimate compressive strength they present for HAP (420 MPa, graphically). The value of 530 ± 60 MPa is reported for the most dense sample (98%), but the better estimate of the ultimate compressive strength, the *y*-intercept, should be reported from the regression analysis. They prefer to state that the compressive strengths of these ceramics are equivalent, 600 ± 200 MPa, but it is doubtful that these values can be appropriately averaged, and statistical tests were not reported to confirm whether differences exist.

No raw data accompanied the report of Jarcho *et al.* [31]. The report of experimental details indicates that polished cylinders of inappropriate size (4.6 mm diameter × 1.6 mm high, aspect ratio 0.35) were employed. The composition of 100% "β-whitlockite" was determined by X-ray diffraction. The relative density and grain size of this test sample sintered at 1100 °C for 1 h followed by a 4 h soak at 900 °C were 98% and 0.3 μm, respectively. The average compressive strength was determined as 68.7 MPa ± 89 MPa (13%) for 17 specimens.

The compressive strength of 50% porous tricalcium phosphate ceramic calculated from the regression analysis of the present study is 12.8 MPa. The 95% confidence interval is 12.4–13.3 MPa [32]. This is approximately 40% of the result of Driessen *et al.* [17] of 33.8 MPa obtained graphically as summarized in Equation 3

$$\ln \sigma_c = 6.62\text{–}6.2P \qquad (3)$$

The error bar presented on their graph, presumably a standard deviation for an unreported number of specimens, spans 5 MPa at a relative density of 50%.

The ultimate compressive strength of tricalcium phosphate extrapolated from 263 specimens of 10%–70% porosity in the current study is 315 MPa; the range of the 95% confidence interval is 275–361 MPa. While this value is approximately one-half those cited, the literature is not so strong here.

4.3. Young's modulus of elasticity of hydroxyapatite

As there are three groups of ultimate stress values reported for synthetic hydroxyapatites, so there are three groups of modulus values. However, there is not a full correspondence. Moduli range from approximately 10 GPa [23] to 35 GPa [14] and then to 117 GPa [13] depending upon method of synthesis and sintering conditions. The present data conclude a modulus of 9.2 GPa (95% confidence interval from 8.4–10.1 GPa from 257 specimens).

De With *et al.* [13] tabulated some estimates of Young's modulus for HAP determined by at least three techniques. Four of the five literature values they cite range from 108–117 GPa . Their determination is 117 GPa based upon pulse-echo techniques which employ measurements of specimen density and longitudinal and shear-wave velocities. The high value for modulus correlates with their high value for compressive strength; and perhaps for the same reason, namely the presence of decomposition products of HAP and secondary phases generated during excessive sintering cycles. The slightly lower estimate of the modulus by Akao *et al.* [16] (95 GPa, determined graphically from data in their Tables I and II) accompanies their reduced stress value (537 MPa, extrapolated); and the products of lower modulus by Denissen and de Groot [23] (5–13 GPa) correspond to a range of intermediate to low compressive strengths (430–130 MPa). Although the absolute modulus of elasticity values for these latter materials appear somewhat inconsistent with the others cited, some correlation is suggested between stress and modulus for the ceramics synthesized by this group. The material used in the current study is also of low modulus and low compressive strength (9.2 GPa, 70 MPa). The relationship between purity and modulus has been developed by the models of Voigt and Reuss [33] and has been applied to compressed, unsintered mixtures of commercially available HAP and dicalcium phosphate dihydrate [34].

Although an anecdotal relationship between compressive strength and modulus is acknowledged in the ceramics industry (Dörre [35]), this may not provide a full account for all the data currently available. Jarcho *et al.* [14] reported a high compressive strength, 917 MPa, on a purer material, but they determined the modulus in tension to be only 34.5 GPa on an unspecified sample. Akao *et al.* [36] seemed to confirm this modulus, initially, by reporting 30.4 GPa in compression. However, using data in the subsequent, fuller report [16] the ultimate modulus of elasticity is calculated as 95.1 GPa from the following equation obtained by regressing ln modulus on to porosity ($r^2 = 0.94$, $n = 4$)

$$\ln(E) = 4.56 - 3.97P \qquad (4)$$

These determinations of moduli were made on HAP prepared by three different methods and thus, materials of varying purity would be expected: de With *et al.* [13] sintered commercial powder, Jarcho *et al.* [14] sintered precipitated HAP at 1100 °C, thereby reducing decomposition, and Akao *et al.* [16] sintered precipitated HAP up to 1300 °C which would cause the formation of secondary phases although they report none detected by X-ray diffraction. The gain size of these materials also varied: approximately 1.7–3.9 μm for de With *et al.*'s material, unreported by Jarcho *et al.* but presumably 0.15–0.7, 1–3 for Akao *et al.*'s and 1.9 for the current study. Based upon experiences with aluminum oxide ceramics, it is unlikely that variances in grain sizes of HAP will effect Young's modulus of elasticity [37].

The proposed explanation for the range of observed mechanical properties follows (see Table IV). The presence of dehydroxylated HAP and other decomposition products tends to increase the compressive strength and modulus (de With *et al.* [13]). Compresive strength and modulus diminish as purity increases (Akao *et al.* [16]). Purer HAP has a low compressive strength (present study and that suggested by Rao and Boehm [12]) and modulus. Perhaps the unusually high compressive strength datum of Jarcho *et al.* [14] may be associated with reduced grain size in a manner known to occur with aluminum oxide [26]. The reported modulus of Jarcho *et al.* [14] remains an anomaly. Selective reporting of data, improper specimen dimensions, omission of pertinent characterization data or experimental detail, and the absence of modulus values by Peelen *et al.* [15] and Rao and Boehm [12] make this hypothesis difficult to confirm. However, it is consistent with observation and with known theories.

4.4. Young's modulus of elasticity of tricalcium phosphate

The ultimate modulus for TCP determined in this study is 21.0 GPa. The 95% confidence interval spans 18.9–23.2 GPa as determined from 264 specimens. This compares with 33 GPa obtained in tension as reported by Jarcho *et al.* [31], but insufficient data in the cited work precludes adequate confirmation.

4.5. Toughness of hydroxyapatite and tricalcium phosphate

The work performed to crush a test specimen in compression can be estimated by integrating the area under the force–displacement curve. This specimen-related property becomes a material property by dividing the energy to failure by specimen volume. Because of the brittle nature of these ceramics and their intended use as implant materials, the point of failure in the current study was chosen as the first peak in the load–displacement curve. This would be the

TABLE IV Summary of mechanical test data for hydroxyapatite

Referernce	Stress (MPa)[a]	Modulus (GPa)	D, (μm)	Synthetic route
Jarcho *et al.* [14]	920	35	0.2–0.7	Precipitated, sintered at 1100 °C
de With *et al.* [13]	800	117	2–4	Sintered commercial powder to 1250 °C
Akao *et al.* [16]	540[b]	95[b]	1–3	Precipitated, sintered to 1300 °C
Peelen *et al.* [15]	30–160[c]			Sintered commercial powder to 1300 °C
Akao and Peelen	600			
Juang and Hon [27]	440		2–9	Precepitated, sintered to 1450 °C
Denissen and de Groot [23]	430	11–13		Precipitated, sintered to unspecified temperature in wet oxygen
Driessen *et al.* [17]	420			Sintered commercial powder to 1300 °C in wet oxygen
Dennisen and de Groot [23]	130–410	5–13		Commercial powder hot pressed to 900 °C or sintered to unspecified temperature in wet oxygen
Wen *et al.* [28]	280[d]			Precipitated, sintered to 1200 °C
Martin and Brown [11]	174[c,e]	6[c,e]		Low-temperature calcium-deficient HA
Rao and Boehm [12]	140		≈ 2	Precipitated, sintered to 1200 °C
Present work	70	9	1.9	Precipitated, sintered at 1100 °C

[a] Ultimate stress or maximum stress from the most dense specimen, unless noted

[b] Extrapolated from published report (see text).

[c] From porous specimens

[d] From porous specimens with 15% TCP

[e] Calcium-deficient

point at which sufficient damage would jeopardize continued function if this function where dependent upon the maintenance of implant integrity. Using 262 data pairs, the ultimate toughness of TCP is extrapolated to 2.34 J cm^{-3} (95% confidence interval 1.91–2.86 J cm^{-3}), for HAP, 0.357 (0.262–0.486) J cm^{-3}. For comparably sized implants of 50% porosity, the work to break a tricalcium phosphate ceramic specimen is 1.8 times greater than to break hydroxyapatite, 6.6 times greater at full density. Apparently this is the first report of this property for these synthetic calcium phosphate ceramics.

5. Conclusion

If minimum values of compressive strength, Young's modulus of elasticity, or toughness can be specified for a clinical application of bulk ceramic material, it can be seen by inspection of Figs 3–8 that much greater porosities of TCP can be used than in pure HAP implants, without compromising the safety of the device. At the current level of understanding, this would permit greater tissue penetration, firmer fixation, and faster resorption of the scaffolding material to enhance physiological repair of a bone defect site. The results of the current study are consistent with literature reports and suggest that the strength of HAP can be increased by elevating sintering temperatures of effect the formation of stabilizing decomposition products.

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