

Mechanical properties of natural hydroxyapatite using low cold compaction pressure: Effect of sintering temperature

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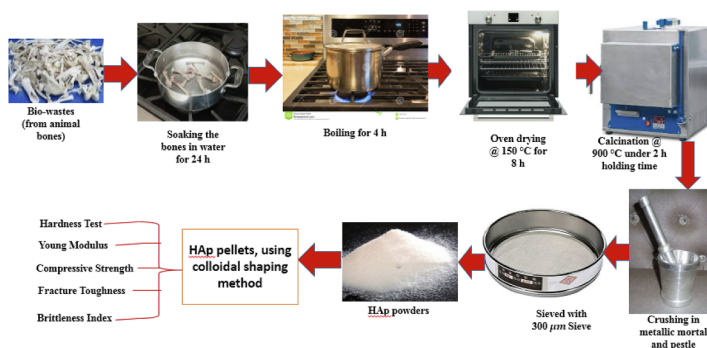
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HIGHLIGHTS

- Non-separated animal bones which is characteristic of abattoir dumping sites was used as precursors for HAp synthesis.
- A facile method which eliminates intensive energy application to synthesize high grade HAp is presented.
- The influence of the pore shapes of synthesized samples on mechanical properties was demonstrated.
- HAp compacts differ on their mechanical properties under different conditions.
- The study suggests a wide range of mechanical properties that can fulfil different clinical necessities.

GRAPHICAL ABSTRACT



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ABSTRACT

This study describes the effect of sintering temperature on the microstructural, calcium/phosphorus (Ca/P) ion ratios and mechanical properties of non-separated biowastes processed hydroxyapatite (HAp) prepared through a low cold compaction protocol. The HAp was produced by a sintering temperature of 900 °C. Furthermore, HAp sintered at 900 °C was subjected to sintering temperatures of 1000 and 1100 °C. The structural and morphological evolution of the fabricated biomaterials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with electron dispersive X-ray analysis (EDX) respectively. Uniaxial compaction using a pressure of 500 pa was used to produce rectangular shaped pellets to investigate the influence of sintering temperature on the mechanical properties of the produced pellets. From XRD analysis, it was found that hydroxyapatite derived from the biowastes showed good thermal stability and did not exhibit phase instability with traces of other calcium phosphates. The SEM micrographs showed microporous structure of the biomaterials and an increase in temperature reduced the porosity and enhanced the mechanical properties. It was also noticed that the trend of transformation of the average shape of pores was from strongly flattened to round at higher sintering temperatures. Electron dispersive X-ray analysis (EDX) revealed that the atomic Ca/P ratios of the as-sintered HAp specimens ranged from 1.58 to 1.79 for sintering temperatures of 900–1100 °C. The synthesized hydroxyapatite powder showed inclusion of the fluorapatite phase at sintering temperature of 1000 °C with a

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reduction in the crystallite size. For both scenarios (sintering temperature and compaction pressure), a consistent trend in mechanical properties (microhardness, fracture toughness and Young's modulus) is noticed at every point of measurement except for compressive strength. The reduction in compressive strength when compaction pressure was applied could be as a result of the stress induced in the HAp powders during compaction which may have made it more susceptible to cracks. The hardness value obtained for the synthesized hydroxyapatite pellets is in the range of that of actual human femoral cortical bone.

1. Introduction

Some studies have identified abattoirs as sources of pollution because they are known for generating mostly non-separated organic solid and liquid wastes [1,2]. These biowastes (animal bones) spills are a source of environmental hazards through the contamination of air and also surface and ground waters. Therefore, efforts to valorise these biowastes are a good approach to mitigating these problems. Producing biomaterials from these biowastes has proven to be a useful approach and it has been reported that natural biomaterials have better mechanical properties during long term evolutions [3–10]. Therefore investigations of microstructural evolutions are very important in developing materials with superior mechanical properties [6–11].

A well-known biomaterial, hydroxyapatite (HAp), is a calcium phosphate and recognized to be osteoconductive and bioactive due to its very close similarity to the natural bone mineral [12]. In recent works, HAp has been derived from both natural (mostly biowastes) and synthetic sources by using several processing routes [13–17]. A lot of works has been devoted to the development of HAp from natural sources like fish bones [18,19], porcine bones [20], eggshells [15,21] and seashells [22,23]. The most popular method to synthesize HAp is sintering. Stea and co-workers [57] reported that HAp subjected to sintering process forms very coherent bonds with bone tissues [57]. HAp synthesis techniques have been developed over decades and can be sub categorized into: sintering in conventional muffle furnaces, microwave sintering and the spark plasma method. Recently, Beaufils and co-workers [69] used a template-assisted electro-deposition method to demonstrate that HAp nanowires production with a well-controlled morphology, size and high aspect ratio can be synthesized with improved biological and mechanical properties.

The gradient of mechanical properties for sintered HAp varies in compression and tension [58–60]. Sintering of HA bioceramics employed for implant-coating or bone fillers affects the porosity, grain size, densification, calcium/phosphorus (Ca/P) ratio and can alter the mechanical properties of the resulting bioceramics [67,68]. It has also been reported that the mechanical properties of HAp is correlated with the grain sizes and the bonding between the grains, and the pore shapes [66]. The sintering temperature is a major factor which influences all of the mentioned parameters [61–63]. Microstructural properties can be influenced by thermal gradients during sintering. Lower sintering temperatures can be adopted to ensure better bioactivity for HAp scaffolds and higher sintering temperature regimes and dwell times can be useful in enhancing mechanical properties [64]. It has been suggested that improvement in mechanical properties of HAp can be improved when there is minimal grain growth during sintering [68]. In as much as the mechanical integrity is important, porosity of scaffolds is a critical factor as well. This is because porosity affects the exchange of nutrients, metabolic wastes etc. during cell culture [65].

Essentially, the main drawbacks of HAp over the years are its low biodegradability and mechanical integrity [12,24–26]. The investigation of the mechanical reliability of HAp, for instance, comparable to natural cortical bone has persisted. In addition, mechanical properties of HAp considering the effects of sintering temperature are still wide open to explore the optimized applications of HAp. There have been efforts to establish the relationship between porosity and mechanical properties of sintered hydroxyapatite. However, to the best of our knowledge, the shapes of pores have received little or no attention or in some cases have

been considered ideally spherical. Essentially, microstructures of HAp are formed by a cluster of defects which have varying shapes, sizes and porosity.

Hence, besides the focus on producing low-cost clinical grade hydroxyapatite, we report the effect of sintering temperature on the phase purity, microstructural evolution which emphasizes shapes of pores, and mechanical properties of HAp derived from non-separated biowastes. The mechanical characterization by measurements of microhardness, compressive strength, Young's modulus and fracture toughness of the HAp pellets with the addition of very low compaction pressure were evaluated.

2. Materials and methods

2.1. Materials

Waste non-separated animal bones were collected from an Abattoir in Zaria, Nigeria, and were used as a source to produce HAp. Tap water was used throughout the process. Atomic Absorption Spectrometry (AAS) was used to probe the concentration of heavy metals which could have effects on the purity of synthesized HAp in the tap water sample. It was observed that the concentration in parts per million (ppm) of heavy metals such as Copper (Cu), Iron (Fe) and Zinc (Zn) were in negligible amounts. This is line with the assertion that concentrations of trace heavy metal ions in tap water are usually very low [82].

2.2. Synthesis of HAp powder

The collected raw animal bones were properly cleaned by using large amount of tap water to make it free from impurities. To deproteinize, the cleaned bone samples were boiled for 3 h and again washed with tap water severally and dried at 150 °C for 8 h. The resultant powders were calcined under atmospheric condition using an electric furnace at 900 °C at a ramp rate of 5 °C/min with 2 h of soaking time and allowed to furnace cool. The resulting samples were subjected to diffraction analysis and the sample heated at 900 °C showed high crystallinity of 86.15% and pure phase (without impurities) and was subjected to further sintering process (see sub section 2.3).

2.3. Sintering of HAp

The sample subjected to thermal treatment at 900 °C was crushed with a ceramic mortar and pestle and sieved through a 300 µm mesh sieve to obtain a fine powder prior to characterization. Sintering temperatures, 1000 and 1100 °C were chosen to sinter the powdery samples for 2 h at the heating rate of 5 °C/min. The sintered powdery samples including the initial samples sintered to 900 °C, were labelled as HA-900 (900 °C), HA-1000 (1000 °C), HA-1100 (1100 °C) and the as received raw animal bones (RB). These notations will be used in all discussion in this study.

2.4. XRD analysis

To investigate the phase composition of the raw and synthesized powders, X-ray powder diffraction (XRD) patterns were collected on a Rigaku Miniflex diffractometer operating a copper tube ($\lambda = 1.5418 \text{ \AA}$) generated at a voltage of 40 kV and a current of 30 mA. The goniometer

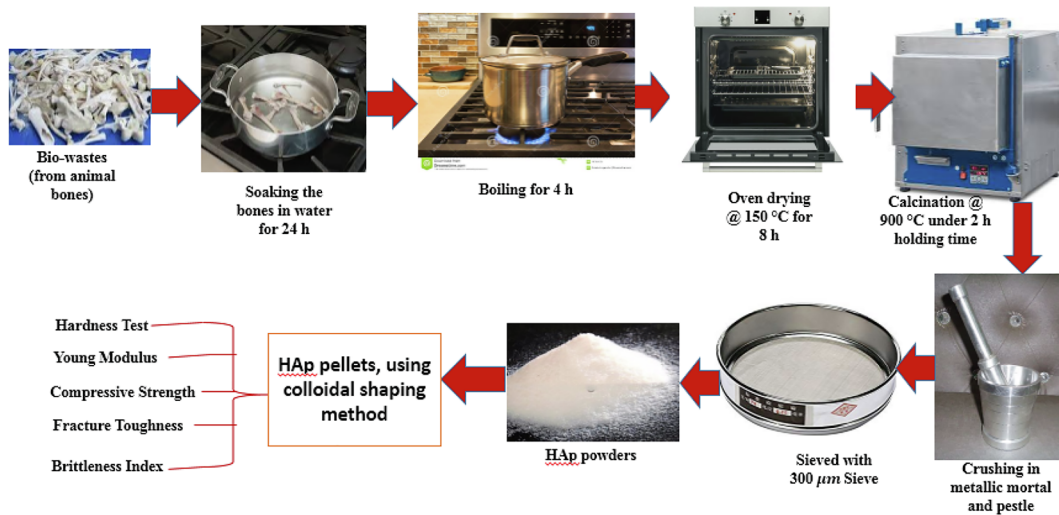


Fig. 1. Schematic of the synthesis, sintering processes and mechanical properties evaluation of the HAp bio-ceramic.

was set at a scan rate of $0.033^\circ/\text{s}$ over a 2θ range of $20\text{--}80^\circ$

The crystallinity of the powders was estimated using equation (1) [27]:

$$x_c = 100 \times \frac{I_{300} - V_{112/300}}{I_{300}} \quad (1)$$

Where I_{300} represents the intensity of (300) diffraction peak, $V_{112/300}$ represents the reflection of the hollow between (112) and (300) diffraction peaks of HAp. The lattice parameters were calculated using equation (2):

$$\frac{1}{d^2} = \frac{4}{3} \left[\frac{h^2 + k^2 + hk}{a^2} \right] + \frac{l^2}{c^2} \quad (2)$$

Where 'd' is the inter-planar distance, (hkl) are the lattice planes, 'a' and 'c' are the lattice parameters. The broadening of the diffraction peaks can be related to the crystallite size which has the tendency to be equal or smaller to the grain size using Scherrer's equation [28]. The (002) and (310) HA peaks were selected for the evaluation of Bragg line broadening [29,30].

2.5. SEM analysis

The microstructure of the samples was studied on an ultra-high vacuum and high resolution scanning electron microscope (SEM) operated at 5 kV. The samples were prepared by gold sputtering the surface of the samples using a low deposition rate. Each gold sputtered sample was viewed at 15,000 X.

2.6. Porosity measurements

The porosity of the sintered samples was determined using equation (3):

$$\text{Porosity (\%)} = \left(1 - \frac{\text{Weight of HAp}}{\text{Volume of HAp} \times \text{Density of HAp}} \right) \times 100 \quad (3)$$

3.16 g/cm^3 was used as the typical density of HAp [77–79].

2.7. Hydroxyapatite pellets preparation

The as-prepared HAp powders were uni-axially compacted at a pressure of 500 Pa into square shaped pellets ($25 \text{ mm} \times 25 \text{ mm} \times 25 \text{ mm}$) for hardness and compressive tests. The sintering of the pellets was conducted in air atmosphere at 900, 1000

and 1100°C for 2 h in an electric furnace at a heating and cooling rate of $5^\circ\text{C}/\text{min}$ and allowed to furnace cool.

2.8. Mechanical properties evaluation

2.8.1. Hardness testing

The micro hardness (Hv) of the sintered samples was determined via the Vickers indentation with a micro hardness tester (HV-1000). The pellets were subjected to an applied load of 300 g for a dwell time of 10 s. A total of 5 indentations were made and the resulting hardness values were averaged. The physical quality of the indenter and the accuracy of the applied load as defined clearly in Ref. [31] were controlled to ensure reliability of results.

2.8.2. Compressive strength evaluation

The compressive modulus of the prepared pellets was performed using a universal testing machine (UTM), equipped with a 5 kN load cell.

2.8.3. Fracture toughness testing

The fracture toughness, K_{IC} , was calculated from hardness test parameters [32] according to equation (4):

$$K_{IC} = 0.016 \left(\frac{E}{H_v} \right)^{0.5} \frac{P}{C^{1.5}} \quad (4)$$

Where: Hv = micro hardness value.

E = Young modulus,
P = applied load,
C = is the crack length.

2.8.4. Young modulus evaluation

The Young modulus was obtained using the expression:

Young Modulus (E) = Stress/Strain = Yield Strength/Strain.

Yield strength was obtained from the relationship between the hardness values according to Ref. [32] as:

$$HV = 3\sigma_y, \text{ implying that } \sigma_y = HV/3 \quad (5)$$

Strain was obtained from the compressive test parameters i.e. compressive strain = change in length/original length. The applied load, P is the applied load used in the micro hardness test. The length of the crack from the indentation corner (l) and the indentation diagonal (2a) were obtained from micro hardness test analysis.

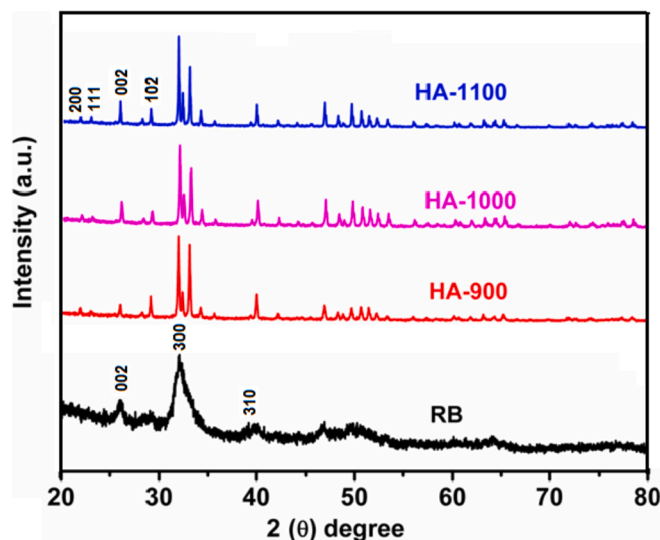


Fig. 2. X-ray diffraction signatures of as-received samples (RB) and sintered samples at 900, 1000 and 1100 °C. All reflections belong to the HAp phase.

2.8.5. Brittleness index

The brittleness index which is a ratio of hardness (resistance to plastic deformation) and fracture toughness (resistance to crack propagation) was calculated by using equation (6) [70]:

$$B = H/K_{Ic} \quad (6)$$

The preparation, sintering, and mechanical properties evaluation process of the HAp bio-ceramic is illustrated schematically in Fig. 1.

3. Results and discussion

3.1. XRD patterns of samples

The XRD patterns of the as-received powders (RB) show major reflections corresponding to HAp and fewer reflections of hydrated calcium sulphates as shown in Fig. 2. The low and broad reflections observed for RB can be ascribed to the low crystallinity of the HAp phase in the samples. After heat treatment (sintering at temperatures from 900 to 1100 °C for 2 h), the hydrated reflections are not visible, and the crystallinity of the HAp phases in the samples were more evident as depicted by the increasing sharp and narrow reflections signalling the effect of sintering on the transformation of hydrates to pure HAp and can be indexed as hexagonal hydroxyapatite which is in close agreement with standard values for HAp (Joint Committee on Powder Diffraction Standards, Card #09-0432).

It is evident from Fig. 2 that at the sintering regimes (900–1100 °C), a single phase of HAp was observed without reflections of other calcium phosphate groups such as β -TCP and α -TCP which agrees with study carried out by Ref. [25]. The broad reflection noticed for raw HAp can be attributed to the inclusion of amorphous phases and dislocations which exists between crystallite boundaries in the powders [33]. Some related studies have found that biphasic HAp starts to become visible at sintering temperature above 1000 °C [34–37] which is attributed to the decomposition of HAp at this temperature. The results obtained in this study signify that at the highest sintering temperature of investigation (1100 °C), the HAp remained in its pure phase without decomposing as only the apatite peaks are observed. A possible explanation for the thermal stability of HAp obtained at the sintering regimes in this study can be ascribed to the restricted kinetics of diffusion inherent within the apatite particles during sintering. These findings suggests that the conventional sintering method described in this study can be replicated to obtain pure HAp of high crystallinity.

Table 1

Cell parameters of HAp derived from bio waste bones at different calcination temperatures.

Calcination temperature (°C)	Sample Code	Average crystallite size (nm)	Crystallinity	c/a ratio
–	RB	7.7	86.65	0.71
900	HA-900	99	86.15	0.52
1000	HA-1000	92.3	89.14	0.53
1100	HA-1100	111.1	75.06	0.73

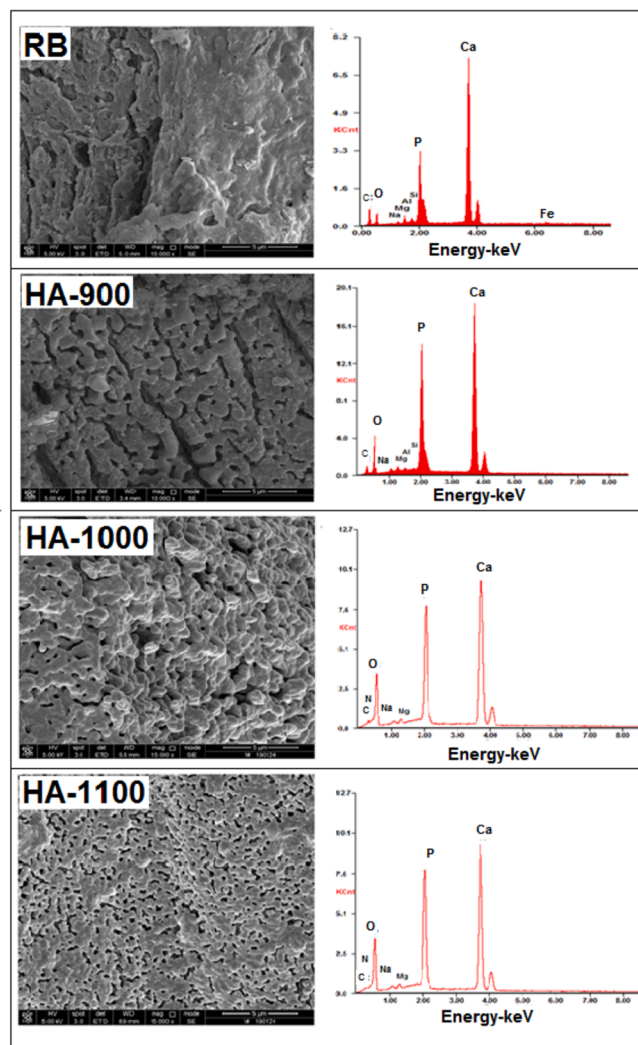


Fig. 3. SEM/EDX micrographs of RB, HA-900, HA-1000, HA-1100.

Table 1 shows the crystallinity, crystallite size and cell parameters of sintered powders which were estimated from the X-ray diffraction data. Variations in the crystallinity of the samples can be ascribed to disparities in molecular arrangement during heat treatment. However, considerable crystallinity was recorded for all the samples. As far as the crystallite sizes are concerned, an inverse relationship as compared to the crystallinity of samples was observed. Normally, crystallite size is independent of crystallinity and a very small crystallite size can cause the broadening of the XRD peaks as observed on the XRD patterns (see Fig. 1). Values of the lattice parameters ratio (c/a) was close to values obtained in earlier work carried out elsewhere [38].

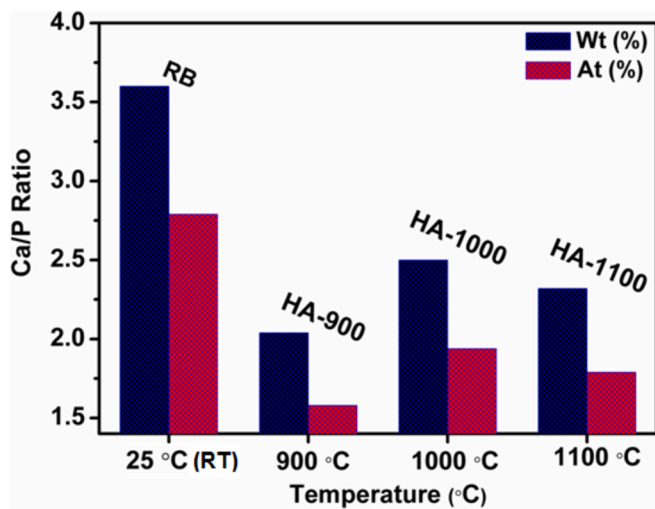


Fig. 4. Average Ca/P ratios for RB, HA-900, HA-1000, HA-1100. RT-Room Temperature.

3.2. SEM/EDX analysis

The SEM images and EDX spectra of the sintered and as-received samples are presented in Fig. 3. The variations in morphology before and after heat treatment such as the formation of slightly hollow surfaces noticeable on the microstructure of RB, particles which are discrete in nature and the densely packed smooth surface can be ascribed to the removal of organic residues over the waste animal bones during sintering which was also described in a study carried out elsewhere [39]. The sintered samples (HA-900, 1000, 1100) show grain structures which are distinct in nature with obvious grain boundaries evident in the morphology. The inter connectivity between the grain structure becomes closer to each other which typically defines the initiation of a defined crystalline grain structure of hydroxyapatite [40–43]. Hence the sample sintered at 1100 °C (HA-1100) produced a denser and smoother surface with various grain structures and boundaries. The distributions of pores are quite visible and somewhat homogenous throughout the sintered sample matrix with an increase in sintering temperature accompanying a reduction in porosity. In addition, uniformity in pores was observed for HA-1100 sample which has the potential of providing a better platform for soft tissue enhancement and proliferation of cells when used in orthopaedic applications [44]. The elemental composition of the sintered HAp was investigated by EDX analysis. The sintered samples composed primarily of the three elemental constituents of HAp—calcium (Ca), phosphorus (P) and oxygen (O) with traces of minor elements such as magnesium (Mg), sodium (Na) and potassium (K).

Essentially, the elemental composition of the samples has huge similarities to the chemical composition of natural bone as reported by Ref. [72]. Average values of Ca/p ratios of sintered samples are presented in Fig. 4. From the figure, calculated Ca/P ratios for sample HA-900 were 2.04 and 1.58 for weight and atomic percentages respectively. Generally, the atomic Ca/P ratios of the as-sintered HAp specimens ranged from 1.58 to 1.79 for sintering temperatures of 900–1100 °C. Comparatively, the atomic Ca/P ratio (1.58) of HA-900 was the closest to stoichiometric Ca/P ratio of hydroxyapatite (1.67) amongst all the HAp samples investigated in this study. The obtained Ca/P ratios of HAp obtained from this work has deviations from the theoretical value for pure stoichiometric HAp of 1.67. One of the most critical factors which could be responsible for the deviation of Ca/P ratios from stoichiometry is the sintering temperature which affects the type and composition of calcium based compounds which would appear in the resultant HAp bioceramic. Another possible explanation ascribed to the deviation is that ions such as Ca^{2+} , PO_4^{3-} and OH^- are known to facilitate the exchange of ions and their intensity may differ as a result of

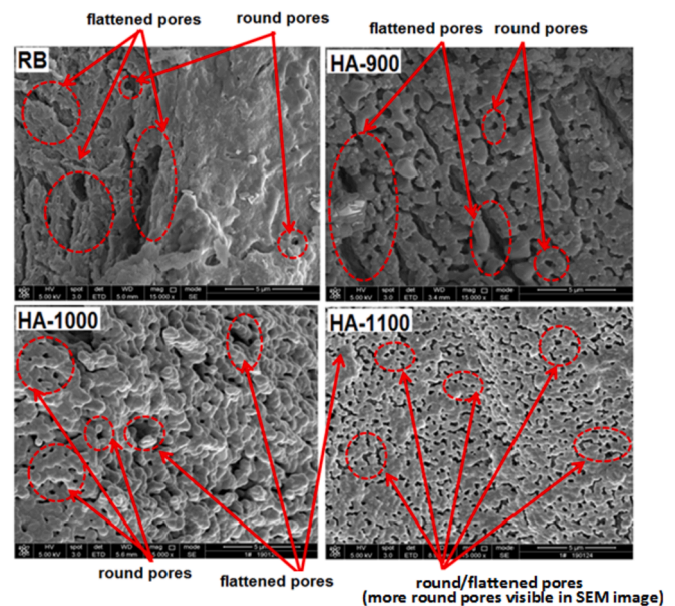


Fig. 5. Average pore shapes (flattened and round) visible in microstructure for RB, HA-900, HA-1000, HA-1100.

Table 2

Variations in porosity of raw and synthesized hydroxyapatite at different sintering temperatures.

Samples Notation	%P ₁	%P ₂	%P ₃	%P ₄	%P ₅	%P _{avg}	SD
RB	59.8	61.6	60.5	59.7	59.5	60.2	0.76
HA-900	51.7	51.8	51.6	51.7	51.7	51.7	0.06
HA-1000	49.5	49.2	49.3	49.7	49.6	49.5	0.18
HA-1100	46.7	46.8	47.0	46.9	46.9	46.9	0.10

% P₁₋₅ = Percentage porosities of the 4 samples.

SD = Standard Deviation.

the nutritional conditions of the source of raw animal bones. Again, the presence of defective HAp which are expressed as $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_{2-x}$ can reduce the Ca/P ratio [80].

Despite the deviation of the Ca/P ratio from that of stoichiometric HAp, particularly for HA-1000, all the samples exhibited characteristics of HAp phase from XRD results (see Fig. 2). Generally, it has been reported that HAp biomaterials with a Ca/P ratio close to stoichiometric theoretical value of 1.67 have huge potentials to promote osteoinductivity for bone healing in substitution and regeneration applications [71]. All the sintered samples have atomic Ca/P ratios of 1.58, 1.94 and 1.79 for HA-900, HA-1000 and HA-1100 respectively. This means that HA-900 is a calcium deficient hydroxyapatite (CDHA) which is highly soluble and as a consequence appears to be of greater biological interest because of its tendency to exhibit better osteoinductive support for bone healing [73–76].

3.3. Microstructural information on average pore shapes and calculated porosity for biomedical applications

It is observed that with increasing sintering temperature the average pore geometry transformed from flattened to round orientations (see Fig. 5: The pores are indicated by red arrows). It is possible that the strength of material with a round orientation leads to increased mechanical strength since the stress concentration near the pores is minimized. This assertion is in line with study of Bohner [71] who inferred that oblate (flattened) pore shapes influences the strength of biomaterials. In general, all the samples sintered exhibited a typical bone morphology comprising solid and porous regions. As the sintering

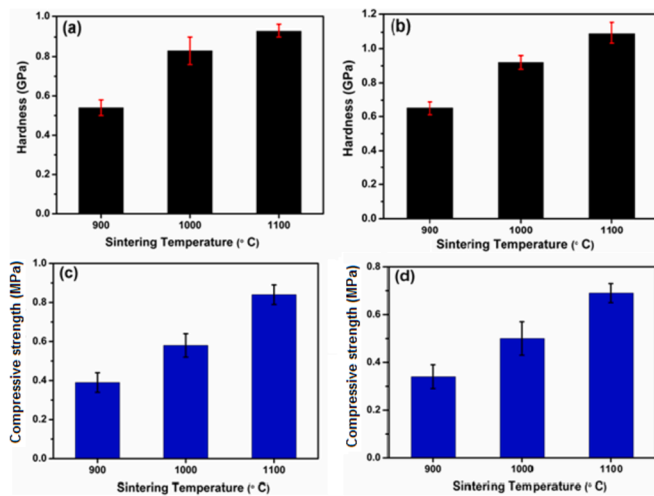


Fig. 6. Hardness and compressive strength values of pellets at different sintering temperature (a) Hardness with no compaction pressure; (b) Hardness with 500 pa compaction pressure (c) Compressive strength with no compaction pressure (d) Compressive strength with 500 pa compaction pressure.

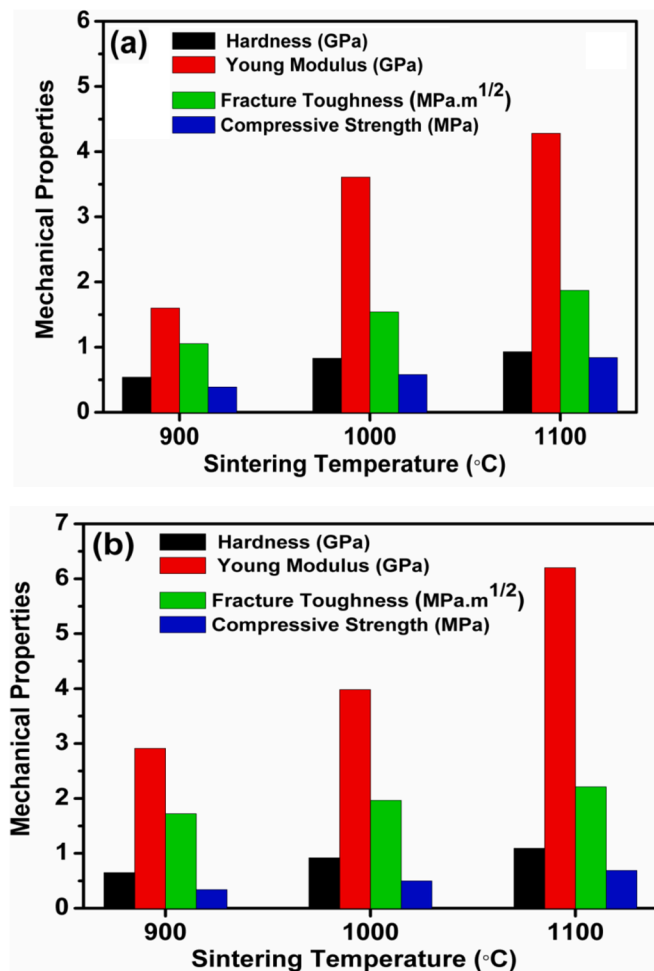


Fig. 7. (a) Mechanical properties of pellets at different sintering temperature with no compaction pressure; (b) Mechanical properties of pellets at different sintering temperature with 500 pa compaction pressure.

temperature was increased, the morphological features were denser. It is also noteworthy to state that more round pores are visible in SEM image of HA-1100 which suggests its improved mechanical properties.

Table 2 reveals the variations in porosity for RB and sintered samples (HA- 900, 1000 and 1100). It was revealed that the porosity of sintered samples was reduced with increasing sintering temperature as compared to the raw sample (RB). The porosity of the samples in this study varied from $46.9 \pm 0.10\%$ to $60.2 \pm 0.76\%$. It has been previously reported that porosities in the range of 40–90% encouraged osteointegration on the implant surface and enhanced adhesion of implants with bone [81]. Therefore the calculated porosities as observed in Table 1 reveal the suitability of the samples for biomedical applications. It was noticed that at higher sintering temperatures, the mechanical characteristics of the composites were enhanced which can be ascribed to reduction in the porosity of the samples. It is therefore safe to say that densification during sintering and reductions in porosity (Table 1) were the primary mechanisms for the enhancement of mechanical properties observed in this study (see sub-section 3.4).

3.4. Mechanical properties evaluation

A comparison of mechanical properties for the HAp pellets with and without compaction pressure for the experimental measurement of the mechanical properties (hardness and compressive strength) has been made and is illustrated in Fig. 6(a)–(d) with their corresponding error bars. For both scenarios, a consistent trend of improved mechanical properties is noticed at every point of measurement (sintering and compaction pressure) except for compressive strength, for instance, 0.69 and 0.84 MPa at 1100 °C with and without compaction pressure respectively. The reduction in compressive strength when compaction pressure was applied could be as a result of the stress induced in the HAp powders during compaction which may have made it more susceptible to cracks.

Fig. 7(a) and (b) shows composite plots of the mechanical properties which include experimental measurements (hardness and compressive strength) and calculated values (Young modulus and fracture toughness). Hardness, Young modulus, and fracture toughness all increase with sintering temperature. At the highest sintering temperature (1100 °C), where denser and uniformity in pores with more round pore geometry were observed (see subsection 3.2 and 3.3), the values of hardness, Young modulus and fracture toughness are as follows: 0.93 and 1.09 GPa; 4.28 and 6.20 GPa; and 1.87, 2.21 MPa m^{1/2} at no pressure and 500 pa compaction pressure respectively. The hardness, fracture toughness, Young modulus and compressive strength values at all points of measurement (compaction pressure and sintering temperature) for our synthesized HAp were in the range of values obtained by several researchers [32,45–54]. Vickers micro hardness values at every point of measurement are larger than that of the human femoral cortical bone. To buttress this, recently, a study carried out by Ref. [83] revealed that the micro-hardness of cortical bones of humans aged between 46 and 99 years fall with the range of 300–600 MPa while the range of micro-hardness obtained in this study was between 930 and 1090 MPa which suggest a range of clinical applications for the synthesized HAp in this study. Usually, the cortical bone is 10–15% harder than the cancellous bone adjacent in orientation. This variation can be ascribed to the calcium composition of the two types of bones [55]. The hardness values improved with compaction pressure. These hardness values obtained in this study are similar to data obtained by Ref. [56] for hydroxyapatite under cold compaction conditions and in line with results obtained by Ref. [32] under similar sintering temperature regimes, which substantiates our correlation of the improvement of mechanical properties with packed microstructures and increased sintering temperature.

A secondary mechanism for the observed trends in mechanical properties can be ascribed to the crystal structure of HAp. Usually, hydrogen ions (H⁺) of hydroxyapatite are arranged in atomic spaces

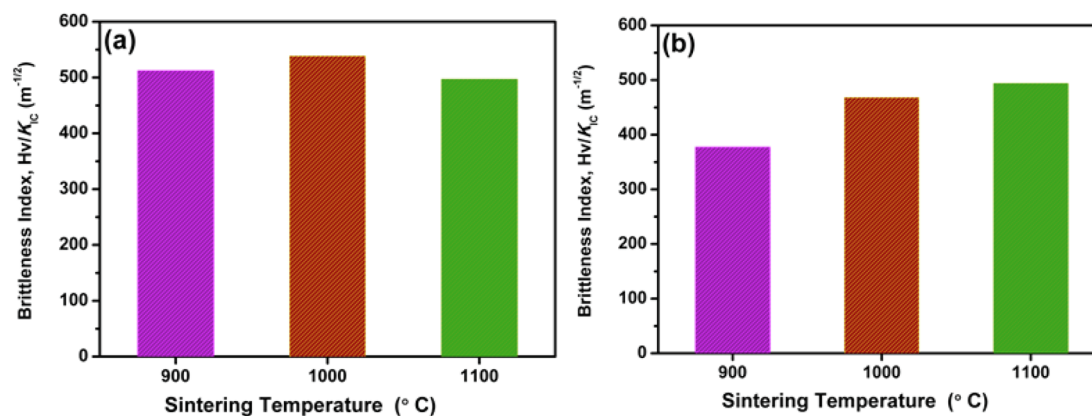


Fig. 8. Brittleness Index of pellets at different sintering temperature (a) no compaction pressure; (b) with 500 pa compaction pressure.

which are around the oxygen ions (O_2^-), forming hydroxyl (OH^-) groups which confers some level of disorder to the crystal structure of HAp. In the situation where some fluorapatite phase is found in the structure at increased sintering temperature as noticed for HA-1000 from X-ray diffraction data with JCPDS card number 34-0010, the OH^- groups are partially substituted by the fluoride (F^-) ions. The hitherto inherent hydrogen ions of the OH^- groups are not closely attached to the neighboring F^- ions by reason of the strong affinity of F^- to oxygen atoms resulting in a well-ordered apatite structure, which enhances the mechanical properties of the HAp pellets. In addition, when an amount of F^- ions replaces OH^- groups in the HA structure, the crystallite size decreases (see Table 1), thus, the mechanical properties improve. It is not clear why the crystallite size of HA-1100 increased and values of enhanced mechanical properties were noticed.

The brittleness index, Hv/K_{IC} as shown in Fig. 8 (a) and (b) suggests resistance of the pellets to crack propagation. The strong correlation observed between the brittleness index and Vickers hardness infers that pellets with higher hardness values are the most sensitive to fracture. Comparatively, HA-1000 sample at no compaction (Fig. 8(a)) and HA-1100 sample with compaction pressure (Fig. 8(b)) have higher tendencies to crack more readily when subjected to stress fields.

Generally, the trend observed for the mechanical property evaluation can be ascribed to the morphological transformations during increasing sintering temperatures. At higher sintering temperatures, there is more reactivity between particles of HAp powders due to higher grain coalescence. Considering the reactivity of powders at lower sintering temperature and the effect in mechanical properties enhancement, it can be inferred that there is enhanced surface area which serves as a catalyst for the sintering operation but simultaneously, the inherent van der Waal forces has the tendency to slow down packing of the HAp powder, thereby reducing the density of the compacts and consequently mechanical properties.

4. Conclusions

The present study has demonstrated the viability of producing porous HAp from non-separated biowastes through heat treatment and the following conclusions can be drawn:

1. During the sintering regimes (900–1100 °C), a single phase of HAp was observed without reflections of other calcium phosphate groups such as β -TCP and α -TCP
2. The synthesized hydroxyapatite powder showed thermal stability and the inclusion of the fluoroapatite phase during sintering temperature at 1000 °C which possibly reduced the crystallite size of HA-1000
3. From the microstructure of synthesized samples, it is observed that with increasing temperature the average pore geometry transformed

from flattened to round orientations which lead to increased mechanical strength since the stress concentration near the round pores is minimized.

4. The experimental data revealed that the hardness values of the synthesized hydroxyapatite are in the range of that of actual human femoral cortical bone.
5. The reduction in compressive strength for the produce HAp pellets when compaction pressure was applied could be as a result of the stress induced in the HAp powders during compaction which may have made it more susceptible to cracks.
6. The low cold compaction pressure (500 pa) which was applied during pelletizing of HAp powders improved the densification process and the mechanical properties of HAp samples.

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