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Hydroxyapatite ceramics prepared from two natural sources by direct thermal conversion: From material processing to mechanical measurements

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ABSTRACT

In this study, hydroxyapatite (HAp) was extracted from catfish bones (CB) and non-separated animal bones (NB). The bioceramic samples were prepared by a facile synthesis route and the representative scaffolds were prepared by cold compaction and sintered at 900 °C, 1000 °C and 1100 °C. To evaluate the properties of the produced HAp, X-ray diffraction (XRD) and Fourier Transform Spectroscopy (FT-IR) analyses were carried out. The evaluation of the hardness of the representative bio-derived scaffolds was experimentally conducted while the fracture toughness and brittleness index were obtained by calculation using the hardness test parameters. The experimental data showed that as temperature increased up to 1000 °C for CB, there was a consequential increase in hardness, while for NB, hardness values reduced throughout the sintering regimes. These gradients in mechanical measurements are ascribed to phase changes during heat treatment.

1. Introduction

A host of materials have been successfully used in bone treatment applications and of all of these materials, hydroxyapatite based bioceramics have generated huge interest due to their high compatibility with the human bone [1,2]. To put in context, any proper bone substituent has to mimic the structural features of the natural bone, hence, must have adequate mechanical properties which supports the osteo-regeneration process. Hydroxyapatite (HAp) can be prepared through different methods, for instance, hydrolysis, chemical co-precipitation, and solution-gelation methods. Alternatively, HAp can be prepared through the extraction from biological sources (e.g. marine shells, fish bones, eggshells, etc.) [3–6]. HAp produced from natural sources has been reported to be advantageous as compared to synthetically produced HAp [7,8]. In advancing the density of HAp, hot-pressing has shown experimentally that densification can be achieved within a lower temperature regime than when pressureless sintering is adopted [9]. However, in order to enhance homogeneity in densification with associated uniformity in microstructure with fewer pores, cold isostatic pressing method for hydroxyapatite powders will suffice by virtue of its isotropic pressure [10–12]. In addition, by reason of the poor mechanical integrity of pure hydroxyapatite, low compaction pressure can be used to obtain superior mechanical strength as reported by [13–15].

In this paper, the comparison of the properties of HAp produced from catfish and animal bones (biogenic sources) is reported. The powders were cold-isostatically pressed with a low pressure (1 MPa) and sintered at 900 °C, 1000 °C and 1100 °C.

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2. Materials and methods

2.1. Preparation of HAp

The two biogenic sources were used as precursors for hydroxyapatite production and prepared according to a protocol described by Akpan et al. [14]. The prepared HAp powders sieved through a 300 μm mesh were compacted with a pressure of 1 MPa in the form of circular disc (25 × 10 mm) to form scaffolds for hardness test and compression test. The thermal treatment of the powders was conducted at temperatures of 900, 1000 and 1100 °C for 2 h in a furnace. The sintered powdery samples for HAp sourced from the non-separated animal bones and catfish bones were labelled as NB-900, NB-1000, NB-1100 and CB-900, CB-1000, CB-1100 according to the temperatures of heat treatment, respectively.

2.2. XRD analysis

To elucidate the phases present and to index the diffraction peaks in the produced HAp, X-ray diffraction analysis using a Rigaku Miniflex Diffractometer was carried out after sintering the HAp. The identification of the phases was followed up by comparing the XRD data to standards using the cards 9-0432 which corresponds to the hexagonal HAp structure.

2.3. FT-IR analysis

To evaluate the surface chemistry of the produced HAp, Fourier transform infrared analysis was conducted in the transmission mode from 4000 to 400 cm^{-1}.

2.4. Mechanical testing

Microhardness measurements of the samples were conducted on the fabricated discs via the Vickers indentation with an applied load of 300 g and a resident time of 10 s. The fracture toughness and brittleness index of the samples were calculated using the expressions as adopted by Obada et al. [13]. The fracture toughness was obtained using Eq. (1) (a and l were obtained during hardness testing):

$$K_{Ic} = 0.203(c/a)^{-1.5} H_v(a)^{0.5} \quad (1)$$

where,

a = half diagonal length (mm)
l = crack length (mm)
2c = 2(a + l) (mm)
Hv = Hardness value

The brittleness index was obtained using Eq. 2 [26]:

$$B = H/K_{1c} \quad (2)$$

3. Results and discussion

3.1. XRD analysis

The XRD analysis of the produced HAp powders produced from the two biogenic sources is as shown in Fig. 1. The XRD signatures revealed reflections within the 2θ range from 20 to 60° which corresponds to stoichiometric HAp (JCPDS 9-432). The XRD patterns of NB and CB at different sintering temperatures show the most intense reflections corresponding to (002), (211), (112), (300), and (310) planes. All reflections are characteristics of the standard data and are in agreement with Heidari et al. [16,17]. The appearance of the new reflections in the XRD patterns for NB and CB-derived HAp in different heat regimes can be ascribed to TCP phases [18,19] which may be formed due to the degradation of the HAp phase to traces of tetra-calcium phosphate (TTCP). It should be noted that this phase is biocompatible [10].

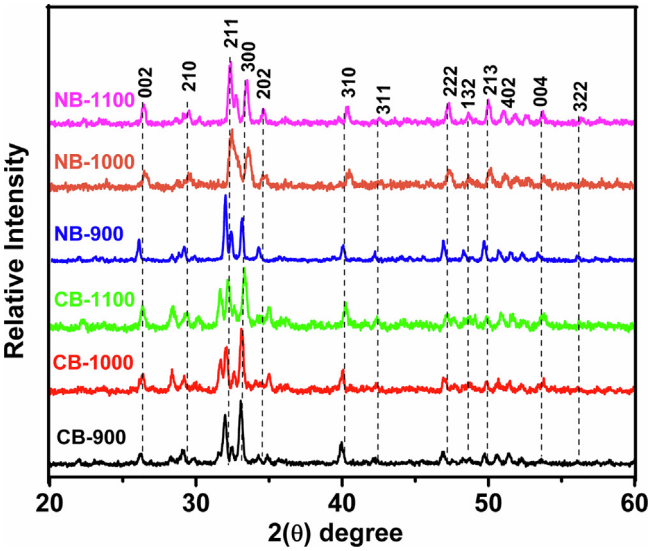

Fig. 1. XRD patterns of the synthesized HAp.

3.2. FT-IR analysis

The FTIR spectra of all samples have very close similarities with the result of natural sources-derived HAp as reported by Bahrololoom et al. and Abifarin et al. [20,25]. The broad H_2O band which was observed can be ascribed to *v3* and *v1* stretching modes of the H_2O molecules. The band at 1459.85 cm^{-1} are ascribed to CO_3^{2-} ions [21], while bands noticed at 2365 cm^{-1} is related to CO_2 (air) [20] (Fig. 2).

3.3. Mechanical measurements evaluation

The mechanical characteristics of the produced HAp are as shown in Figs. 3–5. Fig. 3 shows the gradient in hardness with increasing sintering temperature. For CB-derived HAp, there was

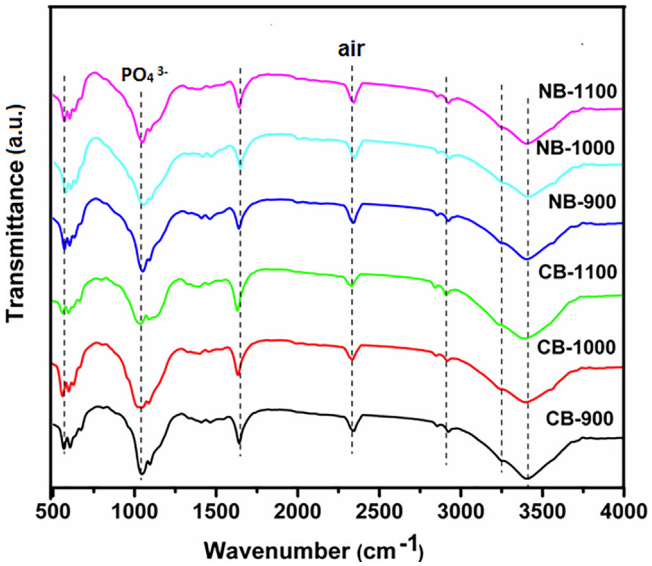

Fig. 2. FT-IR spectra of the synthesized HAp.

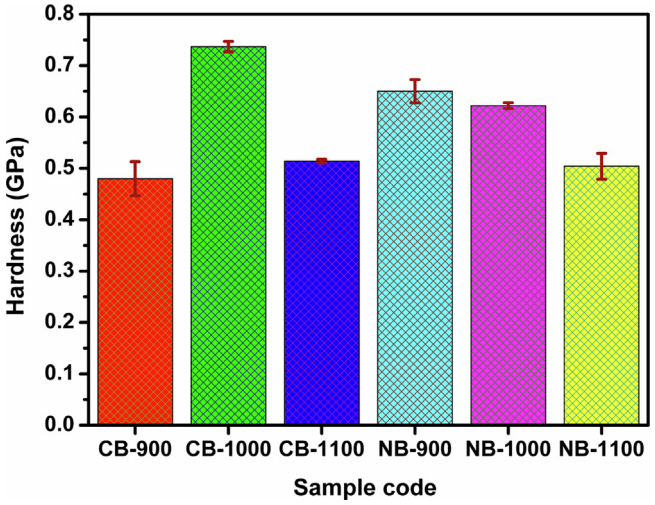

Fig. 3. Variation in hardness values of the synthesized HAp.

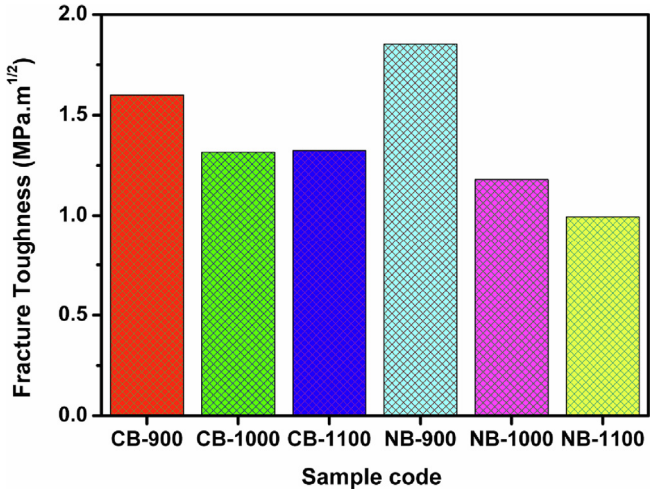

Fig. 4. Variation in fracture toughness values of the synthesized HAp.

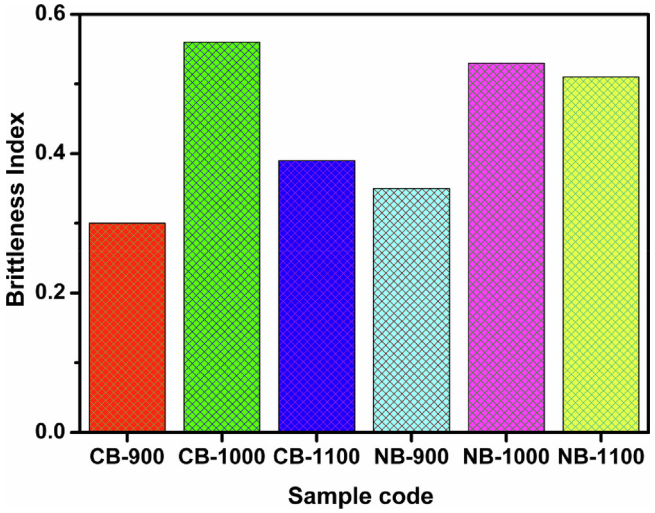

Fig. 5. Variation in brittleness index values of the synthesized HAp.

an increase in hardness until 1000 °C after which a decrease was observed. As for NB-derived hydroxyapatite, there was a steady decrease in hardness with increasing sintering temperature. The very rapid increase in hardness (0.737 GPa) for CB-1000 can be ascribed to increase in relative density [21], nonetheless, in the present work, this reason is not completely noticed. The hardness for CB-1100 and NB-derived samples decreased in spite of a consistent increase in density. This trend of a decrease in Vickers hardness can be as a result of an increased temperature-induced decomposition with the amounts of tetra-calcium phosphate (TTCP) phase included in the bulk of HAp [22]. This trend is also reflected in Fig. 4 as the fracture toughness also decreased with increasing sintering temperature from 900 to 1100 °C. However, the mechanical measurement data for CB and NB-derived HAp as obtained in this study compare well with data reported by [23,24].

The brittleness index as shown in Fig. 5 consequently showed gradients. Scaffolds with the highest microhardness values are most prone to fracture. In comparison, CB-1000 and NB-1000 have higher potential to crack when they are subjected to stress regimes.

4. Conclusion

In this study, HAp was extracted from two biogenic sources and the following conclusions were drawn:

1. The phases present in the produced hydroxyapatite bulk revealed the inclusion of TCP phases.
2. The hardness properties for NB-derived HAp were found to decrease with increasing temperature.
3. For CB-derived HAp, there was an increase in hardness until 1000 °C after which a decrease was observed.
4. The fracture toughness for all samples decreased with increasing sintering temperature from 900 to 1100 °C.
5. Comparatively, CB-1000 and NB-1000 have higher potential to crack when they are subjected to stress regimes.

CRediT authorship contribution statement

E.S. Akpan: Conceptualization, Data curation, Writing - original draft, Writing - review & editing. **M. Dauda:** Conceptualization, Supervision. **L.S. Kuburi:** Conceptualization, Supervision. **D.O. Obada:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **N.D. Bansod:** Writing - review & editing. **D. Dodoo-Arhin:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] K. Fatehi, F. Moztarzadeh, M. Solati-Hashjin, M. Tahriri, M. Rezvannia, R. Ravarian, Bull. Mater. Sci. 31 (2) (2008) 101.
[2] M. Ashuri, F. Moztarzadeh, N. Nezafati, A. Hamedani, M. Tahriri, Mater. Sci. Eng., C 32 (2012) 2330–2339.
[3] I. Manjubala, M. Sivakumar, T.S. Sampathkumar, K. Panduranga Rao, J. Mater. Sci.: Mater. Med., 11 (2000) 705–709.
[4] E.M. Rivera, M. Araiza, W. Brostow, V.M. Castano, J.R. Dıaz-Estrada, R. Hernández, J.R. Rodrıguez, Mater. Lett. 41 (1999) 128–134.
[5] D.S.R. Krishna, A. Siddharthan, S.K. Seshadri, T.S. Kumar, J. Mater. Sci. - Mater. Med. 18 (2007) 1735–1743.
[6] L. Dupoirieux, M. Neves, D. Pourquier, J. Oral Maxillofac. Surg. 58 (1) (2000) 40e46.
[7] I. Gutowska, Z. Machoy, B. Machalinski, J. Biomed. Mater. Res. Part A 75 (4) (2005) 788e793.

[8] S. Sakka, F.B. Ayed, J. Bouaziz, INTECH Open Access Publisher, 2013.
[9] Y.G. Kim, D.S. Seo, J.K. Lee, Appl. Surf. Sci. 255 (2) (2008) 589e592.
[10] S. Ramesh, A. Natasha, C. Tan, L. Bang, C. Ching, H. Chandran, Ceram. Int. 42 (6) (2016) 7824e7829.
[11] L. Ge, J. Li, Z. Zhou, B. Liu, T. Xie, J. Liu, J. Guo, Opt. Mater. 50 (2015) 25–31.
[12] K. Liu, H. Sun, Y. Shi, J. Liu, S. Zhang, S. Huang, W. Wang, Ceram. Int. 42 (2016) 10711–10718.
[13] D.O. Obada, E.T. Dauda, J.K. Abifarin, D. Dodoo-Arhin, N.D. Bansod, Mater. Chem. Phys. (2020) 122099.
[14] E.S. Akpan, M. Dauda, L.S. Kuburi, D.O. Obada, D. Dodoo-Arhin, Results Phys. (2020).
[15] E.S. Akpan, M. Dauda, L.S. Kuburi, D.O. Obada, MRS Adv. (2020) 1–10.
[16] F. Heidari, M.E. Bahrololoom, D. Vashaee, L. Tayebi, Ceram. Int. 41 (2015) 3094–3100.
[17] F. Heidari, M. Razavi, M.E. Bahrololoom, R. Bazargan-Lari, D. Vashaee, H. Kotturi, L. Tayebi, Mater. Sci. Eng. C, 65 (2016) 338–344.
[18] A. Cuccu, S. Montinaro, R. Orru, G. Cao, D. Bellucci, A. Sola, V. Cannillo, 41 (2015) 725–736.
[19] A. Farzin, M. Ahmadian, M.H. Fathi, Comparative evaluation of biocompatibility of dense nanostructured and microstructured Hydroxyapatite/Titania composites, Mater. Sci. Eng., C 33 (2013) 2251–2257.
[20] M.E. Bahrololoom, M. Javidi, S. Javadpour, J. Ma, J. Ceram. Process. Res, 10 (2009) 129–138.
[21] J. Wang, L.L. Shaw, Nanocrystalline hydroxyapatite with simultaneous enhancements in hardness and toughness, Biomaterials 30 (34) (2009) 6565–6572.
[22] S. Koutsopoulos, Synthesis and characterization of hydroxyapatite crystals: a review study on the analytical methods, J. Biomedical Mater. Res.: Official J. Soc. Biomater. Japanese Soc. Biomater. Australian Soc. Biomater. Korean Soc. Biomater. 62 (4) (2002) 600–612.
[23] S. Ramesh, C.Y. Tan, S.B. Bhaduri, W.D. Teng, Rapid densification of nanocrystalline hydroxyapatite for biomedical applications, Ceram. Int. 33 (7) (2007) 1363–1367.
[24] G. Goller, F.N. Oktar, S. Agathopoulos, D.U. Tulyaganov, J.M.F. Ferreira, E.S. Kayali, I. Peker, Effect of sintering temperature on mechanical and microstructural properties of bovine hydroxyapatite (BHA), J. Sol-Gel Sci. Technol. 37 (2) (2006) 111–115.
[25] J.K. Abifarin, D.O. Obada, E.T. Dauda, D. Dodoo-Arhin, Data Brief (2019) 104485.
[26] B.R. Lawn, D.B. Marshall, J. Am. Ceram. Soc. 62 7-8 (1979) 347–350.