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Mechanical measurements of pure and kaolin reinforced hydroxyapatite-derived scaffolds: A comparative study

D.O. Obada [a,*], E.T. Dauda [b], J.K. Abifarin [a], N.D. Bansod [c,*], D. Dodoo-Arhin [d]

[a] *Department of Mechanical Engineering, Ahmadu Bello University, Zaria, Nigeria*
[b] *Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria, Nigeria*
[c] *Department of Chemistry, Mahatma Gandhi Arts, Science and Late N.P. Commerce College, Armori Dist., Gadchiroli, (M.S.), India*
[d] *Department of Materials Science and Engineering, University of Ghana, Legon, Ghana*

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ABSTRACT

This study describes the mechanical properties of pure hydroxyapatite (HAp) and kaolin reinforced hydroxyapatite (K-HAp) produced from non-separated animal bones using compression pressure under different sintering regimes. The HAp microparticles were synthesized separately using a facile heat treatment method and reinforced with 15 wt% of beneficiated kaolin (HAp/15 wt% BK) using the sol–gel method. The HAp and K-HAp derived scaffolds were fabricated by cold pressing with a compaction pressure of 500 Pa. Next, the scaffolds were sintered at 900 °C, 1000 °C and 1100 °C with a 2 h dwell time in air atmosphere. Subsequently, the mechanical properties of the scaffolds were examined. The effect of sintering temperature and compaction pressure on the hardness and the compressive strength of the pure and reinforced HAp showed that at all points of measurement (with and without compaction pressure), the mechanical properties increased with an increase in sintering temperature, and the most significant mechanical properties were obtained at 1100 °C. The values of hardness at the maximum sintering temperature (1100 °C) are 0.93 and 1.09 GPa with and without the application of compaction pressure, respectively, for pure HAp-derived scaffolds and 0.74 and 0.78 GPa with and without the application of compaction pressure, respectively, for K-HAp-derived scaffolds. The compressive strength for K-HAp had the value of 7.84 MPa as compared with 0.69 MPa for the non-reinforced HAp matrix with the application of compaction pressure (500 Pa). The findings show that the mechanical properties of the synthesized kaolin reinforced HAp in relation to the scaffolds produced with the low compaction pressure of 500 Pa is suitable for human trabecular bone.

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1. Introduction

Hydroxyapatite (HAp), a popular calcium phosphate has huge chemical similarities to the inorganic component of bone matrix and has the potential to promote biological activity for inducing bone tissue growth. One critical part of tissue engineering is the use of tissue-inducing scaffolds to direct tissue development. A near perfect scaffold for tissue engineering should be biocompatible, have an acceptable pore structure with a robust mechanical strength [1,2]. The scaffold acts as a substrate that temporarily aids cell growth and tissue development. This mostly occurs in-vitro initially and eventually in-vivo. In line with these, the mechanical integrity amongst other functions cannot be overemphasized. Unfortunately, the mechanical integrity of pure HAp is poor [20]. It has been reported that the compressive strength of human trabecular bone is within the range of 2–12 MPa [3,4] which has necessitated the reinforcement of hydroxyapatite via the addition of reinforcements such as silicon carbide (SiC), aluminium oxide (Al_2O_3), zirconium dioxide (ZrO_2) and metal fibers [5]. Unfortunately, most bioinert ceramic and metal reinforcements tend to reduce the biocompatibility and bioactivity of HAp. Consequently, the investigation of siliceous materials such as kaolin and zeolites

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* Corresponding authors.
E-mail addresses: doobada@abu.edu.ng (D.O. Obada), narh.bn@gmail.com (N.D. Bansod).

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have recently received much attention [6,7]. These reinforcements are capable of enhancing the inherently low mechanical properties of synthesized HAp to reach a compressive strength which is comparable to properties of trabecular bone. Kaolin has over time been used as a reinforcing agent [7], because it shows good mechanical strength and it is nontoxic. Kaolin is known to be an abundant hydrated aluminium silicate that consists mainly of microporous particles [21–25]. Kaolin has also been applied for the replacement of human bone. To put in context, these merits of kaolin motivated the hypothesis that the inclusion of kaolin as reinforcement for HAp matrix could improve the mechanical properties of HAp based composites. Some studies have shown that the inclusion of kaolin in hydroxyapatite matrix can improve the biocompatibility and mechanical properties [16–20].

In light of these, in this contribution, we report a comparison of the mechanical characteristics of pure and reinforced hydroxyapatite scaffolds which were prepared by a simple and reproducible low pressure compaction protocol.

2. Materials and methods

The Non-separated biowastes (animal bones) which may include an approximate percentage of caprine, galline, porcine or other bones were scavenged from an abattoir dumping site in Zaria, and kaolin was collected from a deposit in Kankara, Nigeria and was beneficiated. Prior to use, the kaolin was sun-dried for 48 h and grinded using a mortar and pestle. The properties of the kaolin have been explained in our previous work [8,9]. The animal bones were properly cleaned using tap water. In order to deproteinize, the washed bone samples were boiled for 3 h and dried at 150 °C for 8 h. The dried powders were then heat treated at temperatures of 900 °C, 1000 °C and 1100 °C and labelled as HA-900, HA-1000, and HA-1100, respectively, while as-received sample was labelled as RB.

Imaging of the surface characteristics of the powders were observed using a scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX). The outcomes of the EDX were used to compute the calcium to phosphate (Ca/P) ratios, while optical micrographs were obtained using an optical microscope (Leica DM 750).

The synthesis of the kaolin reinforced hydroxyapatite (K-HAp) with 15 wt% of kaolin was conducted by the sol–gel method. In a typical reaction, the HAp powders were dissolved into 100 mL tap water under vigorous stirring for 1 h. Next, the viscous sol was mixed with 15 wt% of kaolin and left under stirring for 1 h. The resulting sol was allowed to mix under step-wise increase in temperature until dryness at 200 °C. The products were further oven-dried at 60 °C for 1 day, pelletized by uni-axial compaction at a pressure of 500 Pa into square shaped pellets of 25 × 25 × 25 mm and heat-treated at 900 °C, 1000 °C and 1100 °C for a dwell time of 2 h to obtain the K-HAp scaffolds. The sintered kaolin reinforced powdery samples were labelled as K-HAp 900, K-HAp-1000 and K-HAp-1100 in all discussions in this study. The same scaffold preparation protocol was followed for pure HAp.

Microhardness measurements of the samples were conducted on the square shaped samples 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 compressive strength of the HAp and K-HAp scaffolds was performed using a universal testing machine (UTM), equipped with a 5 kN load cell and the variations in compressive strengths of the scaffolds sintered at different temperatures with compaction and no compaction pressures were analyzed and comparisons were made.

3. Results and discussion

The representative micrographs of HAp and K-HAp samples are presented in Fig. 1. As observed, the interconnected structure of pure HAp is retained after heat treatment. Observing the microstructures of K-HAp, irregularly oriented microspheres of HAp and aluminosilicate crystals with whiskers morphology are formed on the surface at all the points of measurements (sintering temperatures). The surfaces of all the samples were covered with nano and micro sized crystals revealing the typical microstructure of HAp. It is evident that the level of formation of the apatite layer increased with the addition of kaolin with numerous spheroidal oriented particulates which are fused with the appearance of more

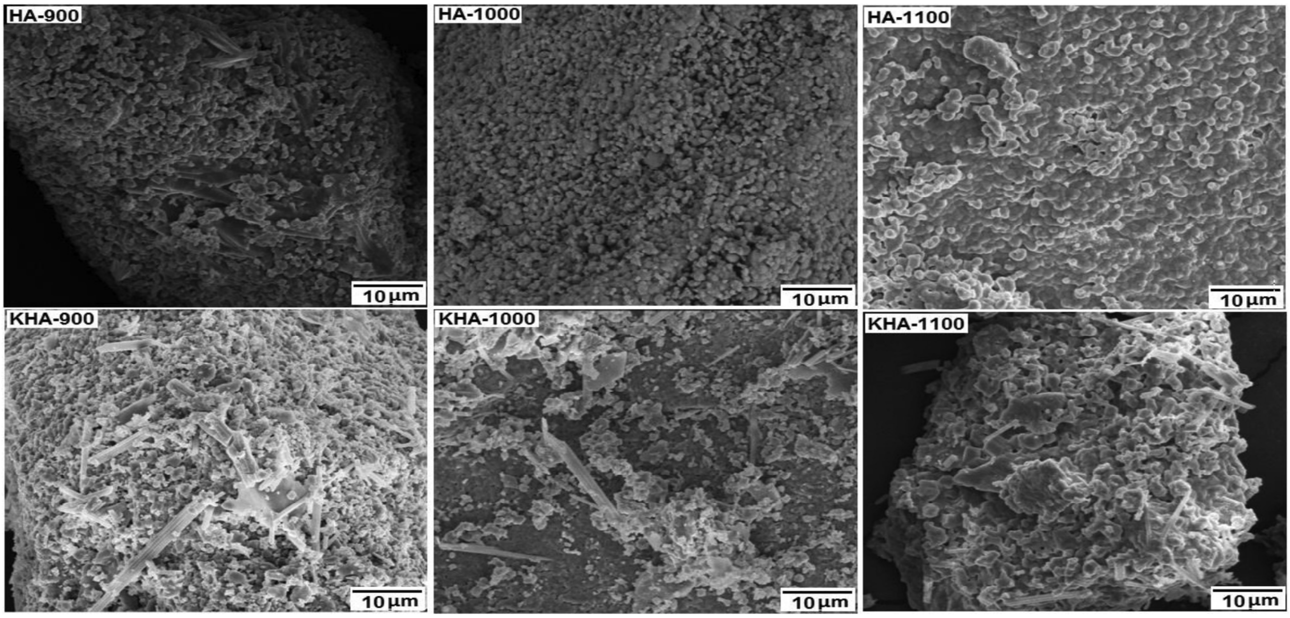
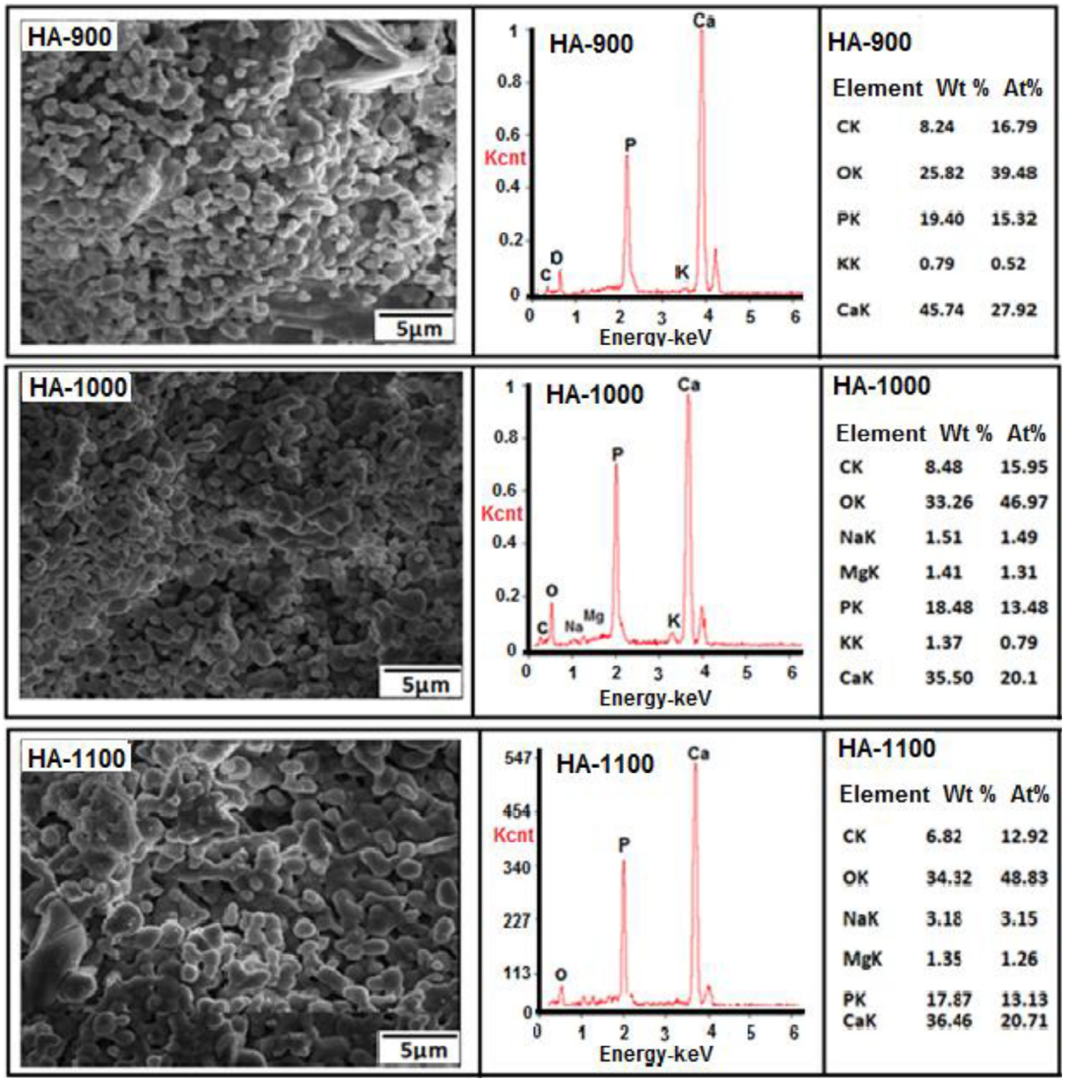


Fig. 1. SEM images of HAp and K-HAp samples.

conspicuous agglomerates. The kaolin addition in the hydroxyapatite matrix caused huge changes in the microstructure of the HAp, advancing the fact that silicate-based biomaterials have huge effects on the particle size orientations [10].

Figs. 2 and 3 reveal the corresponding EDX spectrum for HAp and K-HAp samples, respectively. It is seen that calcium (Ca), phosphorus (P), oxygen (O), carbon (C) and potassium (K) were inherent in all the samples. In addition, a large amount of oxygen is observed in all the spectra. From the EDX analysis, the Ca/P ratio was within the range of 1.47–1.98, which has similarities with the natural apatite ratio in hard tissue and similar ratios were reported in our previous study [26]. It was found that the concentration of phosphorus remained relatively constant but the calcium concentration decreased with increasing temperature up to 1000 °C and declined with a further increase in sintering temperature. The EDX analyses for K-HAp (900–1100) further revealed the presence of silicon (Si) and aluminium (Al) in the EDX-spectrum. The optical micrographs as shown in Fig. 4 revealed internal morphology of the powders as light passed through. With increasing sintering temperature, residual matter from the images of HA-900 and KHA-900 were seen to disappear, leaving a purer/clearer morphology as observed on images HA-1100 and KHA 1100. These trends have an influence on the mechanical properties as inherent residual matter may trigger the appearance of tetra-calcium phases which lowers the mechanical properties of HA-derived scaffolds.

Mechanical measurement results for hardness and compressive strength evaluations are as shown in Figs. 5 and 6. The trend reveals an increase in the mechanical properties at all points of testing. For pure HAp-derived scaffolds, the values of hardness at the maximum sintering temperature are 0.93 and 1.09 GPa with and without the application of compaction pressure, respectively. Comparatively, with and without the application of compaction pressure, the mechanical properties for the kaolin reinforced HAp scaffolds show a reduction in hardness values except for scaffolds at sintering temperature of 1100 °C. This can be ascribed to an increase in relative density and a decrease in the pore ratio (see SEM images: Fig. 1), hence, an increase in hardness values. With no compaction pressure, it was observed that hardness and compressive strength all increased with sintering temperature. At the highest sintering temperature (1100 °C) and under 0 and 500 Pa compaction pressure respectively, the values of hardness, for K-HAp scaffolds was 0.74 and 0.79 GPa, respectively. The most significant compressive strength for the prepared scaffolds was obtained



HA-900

Element	Wt %	At%
CK	8.24	16.79
OK	25.82	39.48
PK	19.40	15.32
KK	0.79	0.52
CaK	45.74	27.92

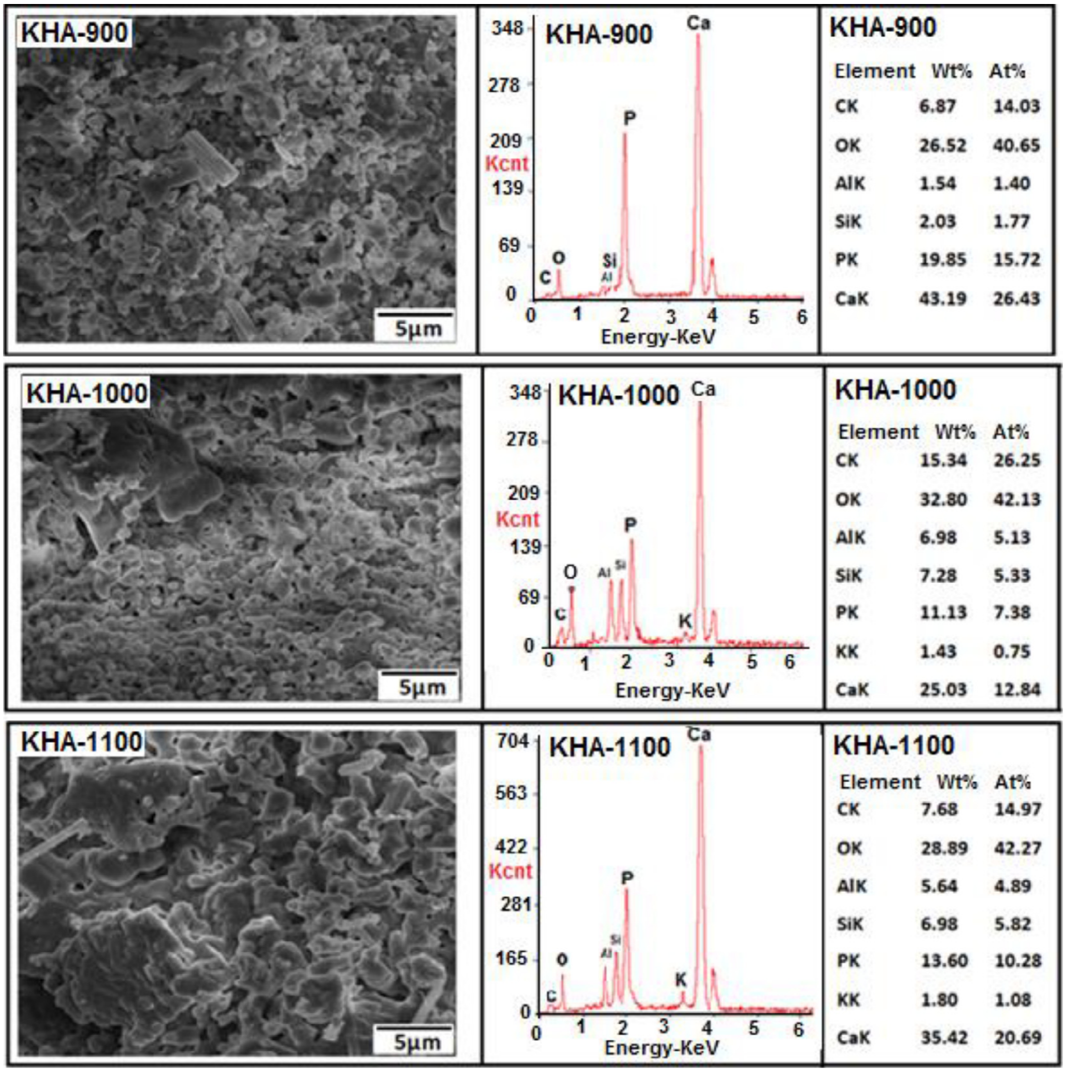
HA-1000

Element	Wt %	At%
CK	8.48	15.95
OK	33.26	46.97
NaK	1.51	1.49
MgK	1.41	1.31
PK	18.48	13.48
KK	1.37	0.79
CaK	35.50	20.1

HA-1100

Element	Wt %	At%
CK	6.82	12.92
OK	34.32	48.83
NaK	3.18	3.15
MgK	1.35	1.26
PK	17.87	13.13
CaK	36.46	20.71

Fig. 2. SEM/EDX micrographs of pure HAp samples.



KHA-900

Element	Wt%	At%
CK	6.87	14.03
OK	26.52	40.65
AlK	1.54	1.40
SiK	2.03	1.77
PK	19.85	15.72
CaK	43.19	26.43

KHA-1000

Element	Wt%	At%
CK	15.34	26.25
OK	32.80	42.13
AlK	6.98	5.13
SiK	7.28	5.33
PK	11.13	7.38
KK	1.43	0.75
CaK	25.03	12.84

KHA-1100

Element	Wt%	At%
CK	7.68	14.97
OK	28.89	42.27
AlK	5.64	4.89
SiK	6.98	5.82
PK	13.60	10.28
KK	1.80	1.08
CaK	35.42	20.69

Fig. 3. SEM/EDX micrographs of K-HAp samples.

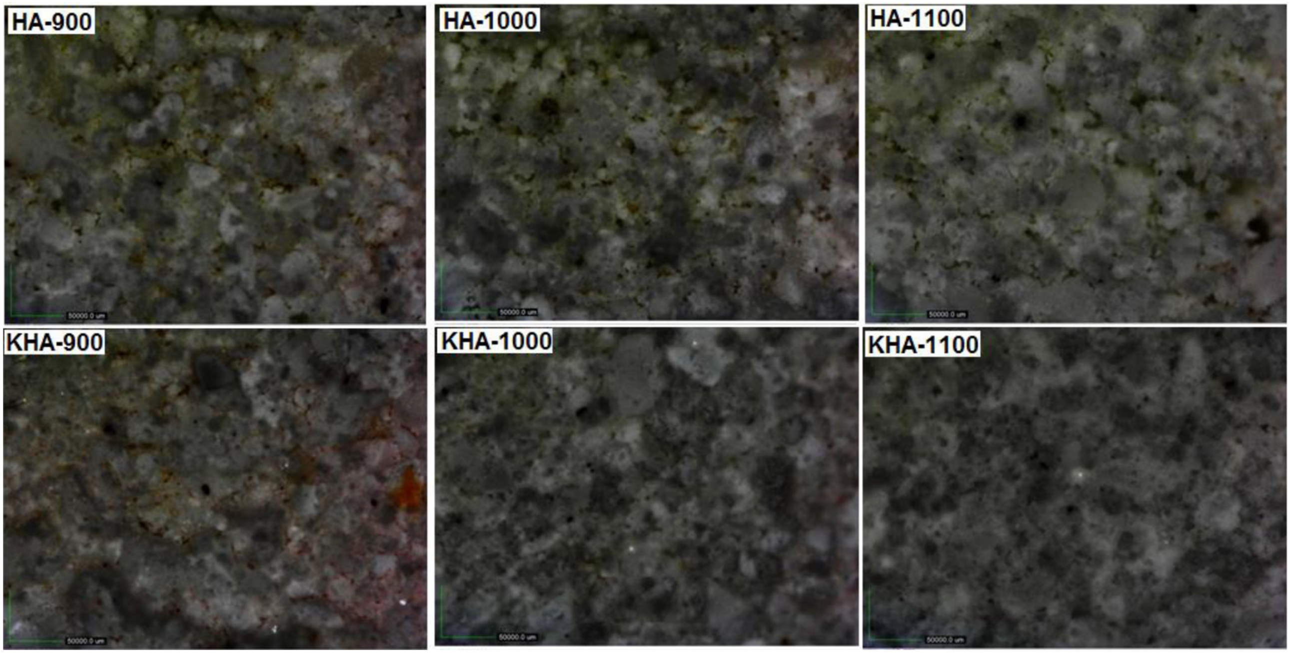


Fig. 4. Optical micrographs of HA and K-HA samples.

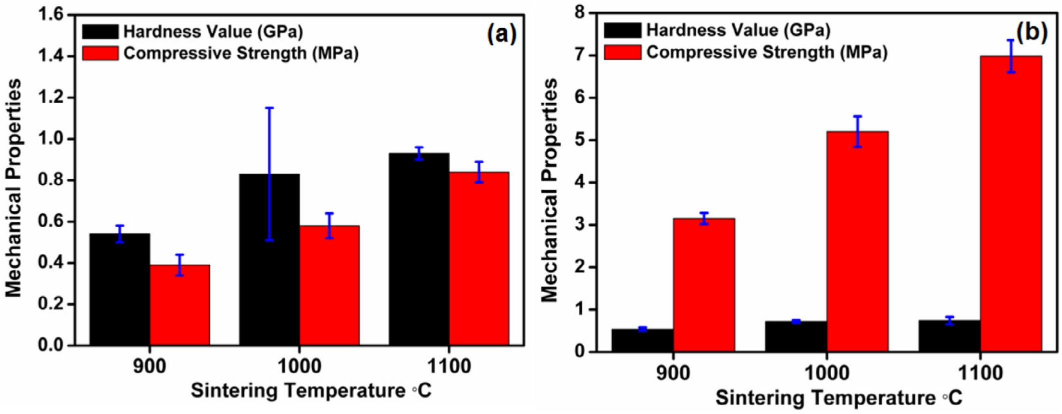


Fig. 5. Mechanical properties of (a) HAp and (b) K-HAp with no compaction pressure.

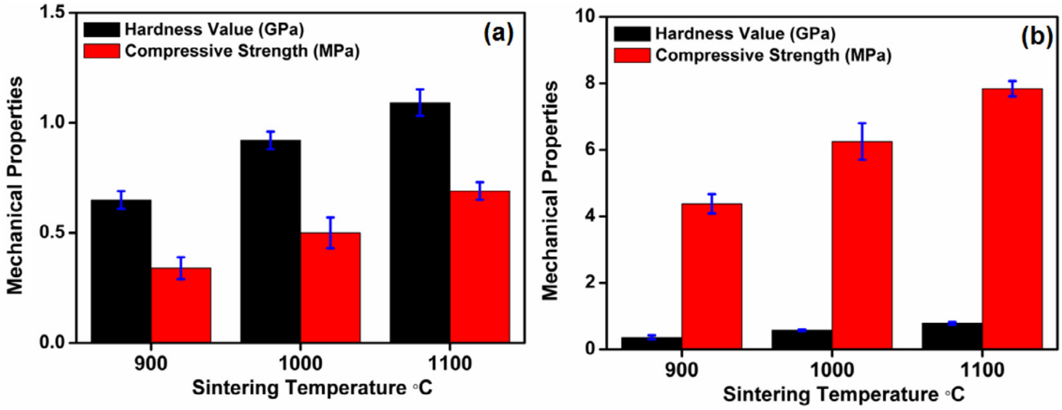


Fig. 6. Mechanical properties of (a) HAp and (b) K-HAp with compaction pressure of 500 Pa.

at 1100 °C and had the value of 7.84 MPa for K-HAp as compared with 0.69 MPa for the non-reinforced HAp matrix (Pure HAp). The mechanical measurement data obtained for the produced scaffolds as reported in this study were within the values reported in other studies [11–15].

4. Conclusions

In this study, hydroxyapatite was reinforced with kaolin and the chemical and mechanical characteristics of the pure and reinforced hydroxyapatite based materials were evaluated. The following conclusions can be drawn:

1. The Ca/P ratio of the produced pure and kaolin reinforced HAp (HA and K-HA) showed gradients at different sintering temperatures, and this can be attributed to an increase or decrease in calcium (Ca) concentration.
2. The high oxygen level in the samples as revealed by EDX means that the hydroxyapatite samples have the tendency to retain much moisture.
3. The compaction pressure (500 pa) used during the production of HAp and K-HAp scaffolds enhanced the densities during heat treatment which influenced mechanical properties.
4. The most significant compressive strength for K-HAp composite was obtained at 1100 °C and had the value of 7.84 MPa as compared with 0.69 MPa for the non-reinforced HAp matrix (Pure HAp).
5. The findings show that the mechanical properties of the synthesized biomaterial in relation to the scaffold produced with the low compaction pressure of 500 Pa is suitable for human trabecular bone

CRediT authorship contribution statement

D.O. Obada: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **E.T. Dauda:** Supervision. **J.K. Abifarin:** Data curation, 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.

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