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Microstructure evolution and physico-mechanical properties of bone china porcelain compositions using two selected kaolinite clays from Nigeria

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ABSTRACT

The microstructure evolution and physico-mechanical properties of bone china porcelain developed using two selected kaolinite clays from Nigeria were investigated. The prepared bodies were uniaxially pressed, oven dried at 105 °C and sintered at temperatures of 1000 °C and 1200 °C. Scanning electron microscopy was used to evaluate the microstructure while physical and mechanical properties were examined following standard procedures. The results showed that higher densification was observed at 1200 °C while water absorption were detected at <1% and porosity at <4% for both samples containing Ikere and Okpella kaolinite clays respectively. Improvements in terms of wear loss and strength properties were also observed to be better for samples containing Okpella kaolin compared with those containing Ikere Kaolin also at 1200 °C. This superior behavior observed at temperature of 1200 °C can be attributed to maturation phases of Anorthite, Quartz and β-TCP (Tri-calcium phosphate) at the same temperature.

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Introduction

Bone china porcelain is a type of ceramic ware that is generally known to have a translucent body with minimum content of 30% phosphate [1]. In comparison with other types of porcelain bodies, bone china porcelains possess superior aesthetic qualities and better technological properties [2,3]. Its mechanical properties almost double that of the hard porcelain, for a sintering temperature of about 100 °C lesser [4,5].

Due to the recent trends in environmental management through utilization of recycled waste materials, bone china has become one of the most attractive materials to be produced as it contains about 50% bone ash in its body composition [6]. However, the main problem observed in utilizing bone ash in porcelain compositions is the narrow sintering range it offers, making the firing of bone china porcelain require a detailed process parameter control. Bone china porcelain (BCP) standard recipe comprises of bone ash (50%), kaolin (25%) and flux (25%) [4]. In bone china porcelain, crystalline phases are formed

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Table 1
Percent composition of the bone china blends containing Ikere and Okpella kaolin.

Samples	Ikere Kaolin (%)	Okpella Kaolin (%)	Ball Clay (%)	Flint (%)	Feldspar (%)	Bone Ash (%)
BCP_1	25	–	–	–	25	50
BCP_2	15	–	10	–	25	50
BCP_3	20	–	10	5	15	50
BCP_4	–	25	–	–	25	50
BCP_5	–	15	10	–	25	50
BCP_6	–	20	10	5	15	50

by the bone ash which is mainly hydroxyapatite that disintegrate on sintering to CaO (lime), β-tricalcium phosphate (β-TCP) and H_2O. As a result of this, bone china is known to have about 70% crystalline phases and 30% liquid phase [4,7].

The growing demands for ceramic wares have made researchers to develop different ceramic products with better technical properties for decorative and household applications. Extensive studies conducted in recent times on bone china porcelain have shown its complex nature, with difficulties in understanding bone china porcelain in connection to its raw materials, processing technique, phase and microstructure evolution [5–10].

Different researches have actually been conducted on bone china porcelain which is primarily a combination of bone ash, kaolinite clay and flux, but not much have been done on considering the effect of different china clay deposits which can naturally influence the properties of the porcelain composition. The advent addition of plastic ball clay to the porcelain composition was created for this research in order to improve the physical properties of the body, while 5% silica (SiO_2) in form of flint was also added to improve the mechanical properties of the resultant bone china porcelain. The required firing strength and physico-mechanical properties of bone china is always drawn from the strength and properties of the type of kaolinite clay used in the porcelain composition.

This research is aimed at studying and characterizing the comparative effects of some selected kaolinite clay deposits on bone china porcelain composition and also to improve certain properties of bone china porcelain using the same kaolinite clay deposit. Parameters such as water absorption, porosity, shrinkage, flexural strength, wear resistance, bulk density and microstructure evaluation were conducted, so as to determine the finest kaolinite clay for bone china porcelain compositions. The outcome of this research is expected to provide some cogent thoughts on the behavior of the selected kaolinite clays in making bone china porcelain and other types of porcelain within the same firing temperature, so as to help Ceramist in Nigeria have a good knowledge of the selected kaolinite clay. The research will also tackle some problems of a number of dwindling ceramics industries in Nigeria. The idea of importation of all ceramic tableware porcelain products may be addressed if some successful outputs of this research are taken in to consideration.

Materials and method

Raw materials

The raw materials used in this research for the formulation of bone china composition are china clays from two selected deposits, ball clay, feldspar, cow bone ash and flint. China clays were obtained from two major selected deposits: Ikere and Okpella in Ekiti and Edo States of Nigeria. The cow bones were at first boiled in distilled water in order to remove flesh adherence and cartilage bits and dried in an oven at 110 °C for several hours. The dried bones were then calcined inside an electric muffle furnace at 1000 °C. The calcinated bones were ground, milled and then sieved through 150 µm sieve to produce bone ash. The remaining materials such as clays, feldspar and flint were also taken through beneficiation process. The processed raw materials were then dried in open air, milled and sieved through 150 µm sieve for further use. The mineralogical composition of the clays were investigated by using advanced diffractometer Cu-Kα radiation in the range of 2theta 10 to 90 while literature standard compositions were considered for the remaining raw materials including bone ash.

Body formulations

Six batches typical of bone china porcelain bodies were formulated using the processed materials. Three bone china bodies contained Ikere kaolin (BCP_1–BCP_3) while the other three compositions were for bone china porcelain containing Okpella kaolin (BCP_4–BCP_6). Table 1 gives the percentage blends and their corresponding sample designations.

Samples preparation

Different batches of each composed body were dry mixed and later moistened with small amount of water at 5% of the total weight mix to ensure bindability during pressing. Hydraulic press of 40KN with a 50 × 50 × 10 mm rectangular die was used to produce the tile samples. The pressed samples were first dried for 24 h in open air and later set inside electric oven at 105 °C for about 12 h. The dried samples were then sintered at 1000 °C and 1200 °C respectively in an electric muffle furnace at heating rate of 10 °C/min, then left to soak at the same temperature for about 1 h before cooling.

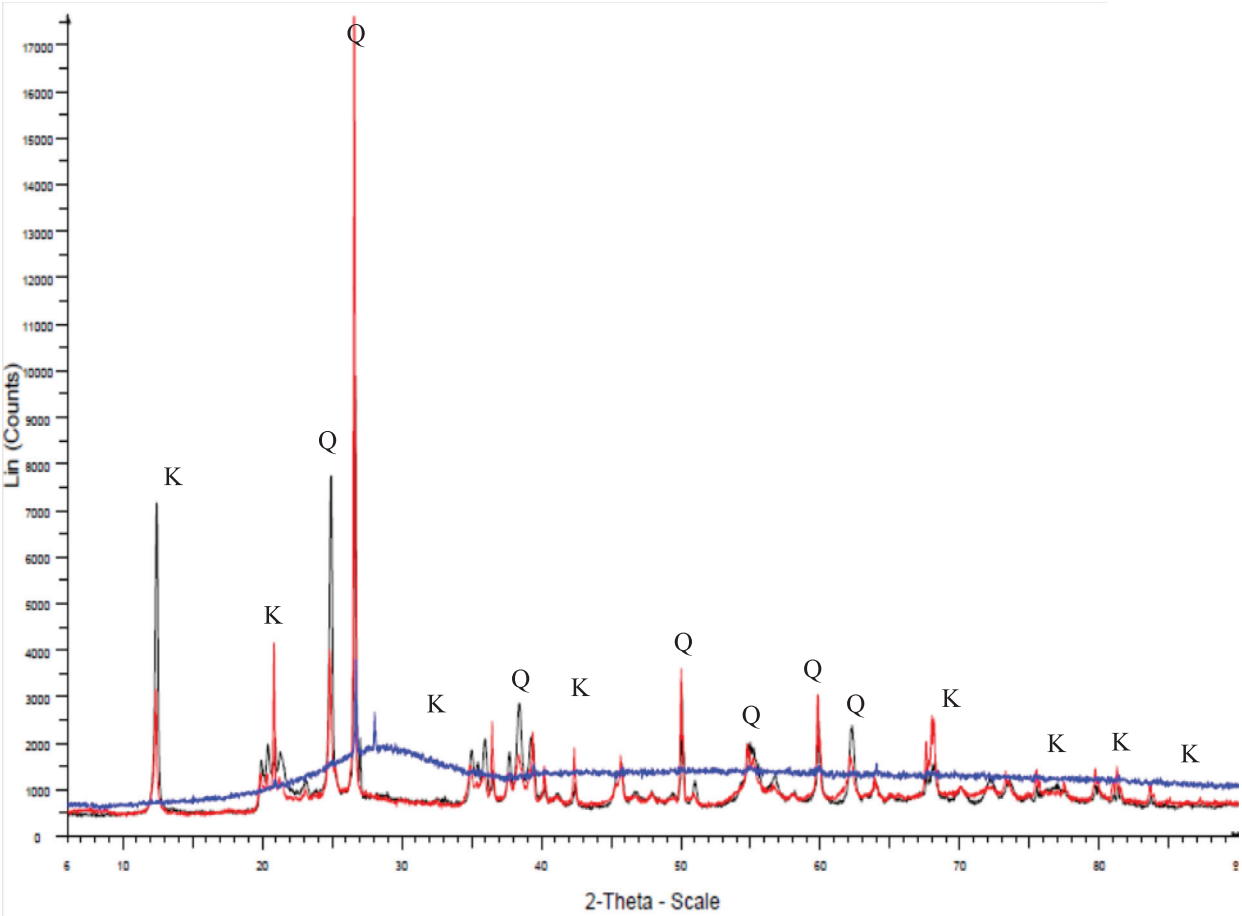


Fig. 1. XRD pattern of the superimposed mineralogical phases of all the clay samples.

Tests

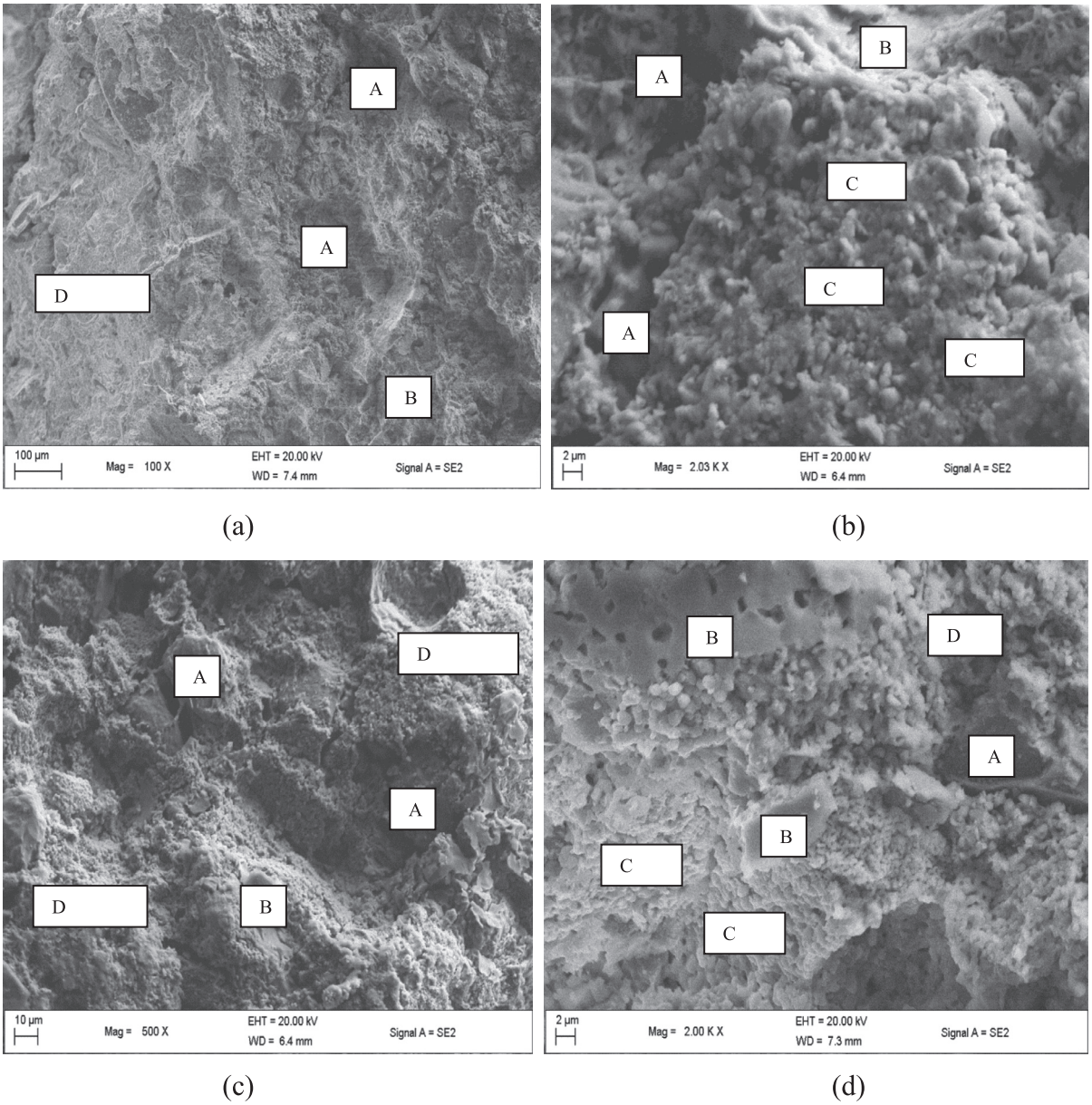
In order to study the sintered bone china porcelain bodies, different tests were conducted using standard procedures. The morphology was examined using Scanning Electron Microscopy. The physical properties were measured using standard procedures in accordance with [11–12].

A three point bending strength using Instron universal testing machine in accordance with ASTM D790 standard at 25 °C was used to examine the flexural strength of the bone china porcelain bodies. The machine was operated at a strain/load rate of 5 mm/min, and a support radius of 2 mm. Load was applied on the sample at an increase stress of 0.2 Nmm^{-1} sec^{-1} until fracture and the exact force at the point of fracture was noted. The wear rate was evaluated in accordance with ASTM G-65 guideline in a ball mill using grinding balls as grinding media at a speed of 60 revolutions for 3 min. Wear occurred due to the effects of collision forces with the introduced weight.

Results and discussion

Materials characterization

Fig. 1 illustrates the superimposed results of the mineralogical compositions of all the clay samples: Ikere kaolin, Okpella kaolin and Ball clay were used respectively (as obtained from previous work by the authors). The black peaks showed the XRD spectrum of Ikere kaolin, red peaks showed Ball clay while blue peaks showed Okpella kaolin respectively. It can be observed that all the clay samples comprise similar mineralogical phases of Quartz (SiO_2) and Kaolinite – Al_2 $(Si_2O_5)(OH)_4$. The chemical compositions of materials such as bone ash, quartz and feldspar were based on their literature standard compositions.

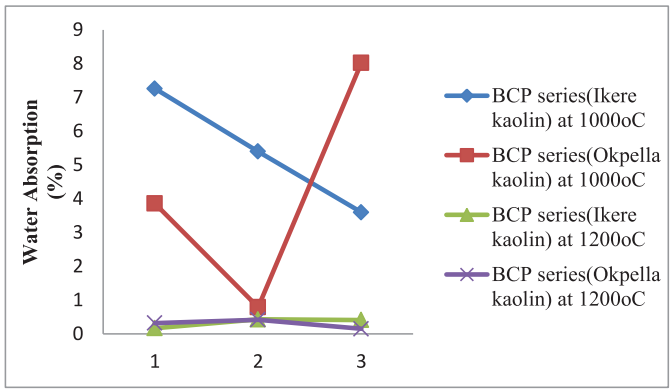


Letters	Elements	Main Phase
A	Si, Al, O, Ca	Anorthite
B	Si, O,	Quartz
C	Ca, P, O	β-Tricalcium phosphate
D	Si, Al, O, Ca, P	Mixture of β-TCP and A

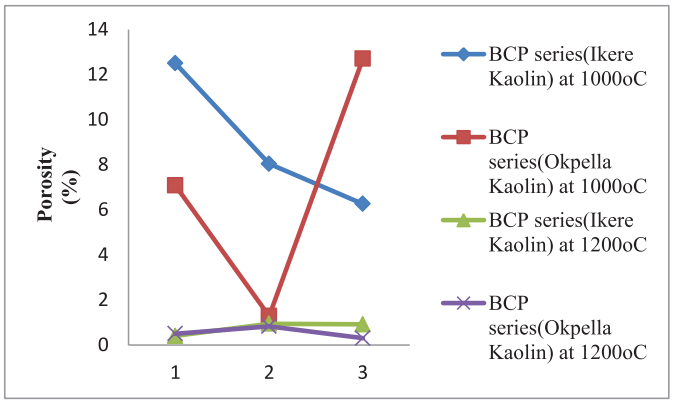
Fig. 2. The representative morphology of (a) BCP series containing Ikere Kaolin at 1000 °C, (b) BCP series containing Okpella Kaolin at 1000 °C, (c) BCP series containing Ikere Kaolin at 1200 °C and (d) BCP series containing Okpella Kaolin at 1200 °C.

Microstructure evolution

Representative microstructure of the developed bone china porcelain containing Ikere and Okpella china clays sintered at 1000 °C and 1200 °C respectively are shown in Fig. 2 (a–d). Fig. 2(a) and (b) showed morphology of the bone china porcelain compositions containing Ikere Kaolin and Okpella Kaolin both sintered at 1000 °C while Fig. 2(c) and (d) indicate representative morphology of the bone china porcelain sintered at 1200 °C. At 1000 °C: it is observed that the bone china porcelain



(a)



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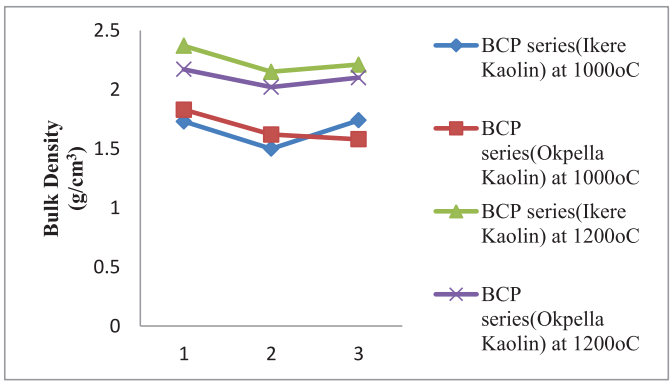
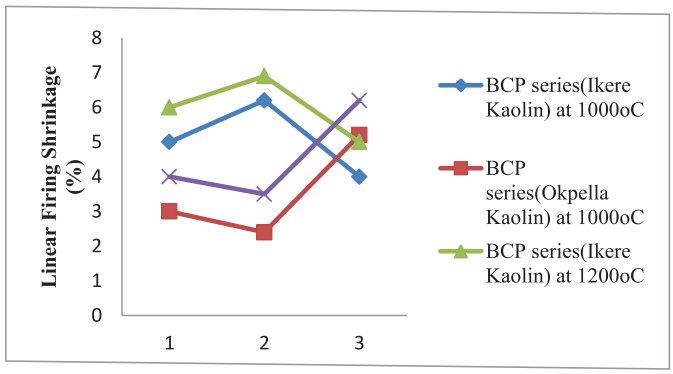


(c)

Fig. 3. (a)% water absorption (b) estimated% porosity (c) bulk density (d)% firing shrinkage.

(BCP) containing Ikere Kaolin (Fig. 2a) and Okpella Kaolin (Fig. 2b) consists of Anorthite (matrix), Quartz, hydroxyapatite and β-TCP respectively. However, the presence of albite in the Okpella kaolin aided glassy formation in BCP containing Okpella kaolin and thus contributed to better behavior in BCP_4–BCP_6 series while liquid phase was not observed in BCP_1–BCP_3 series containing Ikere Kaolin. At 1200 °C: both BCP series containing Ikere kaolin and Okpella kaolin shown in Fig. 2(c) and (d) respectively comprise of mature phases of Anorthite, Quartz, and β-TCP, which confirmed that maturation of bone china increases at elevated temperature [7]. However, liquid phase formed in BCP series containing Okpella kaolin aided close packing of the structure as shown in Fig. 2(d), which eventually aided the better properties observed in them when com-



(d)

Fig. 3. Continued

pared with BCP series containing Ikere kaolin. Also the β-TCP phase co-exists with Anorthite in the BCP containing Ikere kaolin (Fig. 2c) with similar pattern observed in BCP series containing Ikere kaolin sintered at 1000 °C (Fig. 2a). Phosphorus was detected by EDS analysis in the vitreous phase of BCP series containing Okpella kaolin, which is seen to have improved its vitrification level [13]. The stability of the Phosphate glass in the BCP series containing Okpella kaolin might be due to the presence of Na^+ from albite inherent in the Okpella kaolin deposit (Fig. 1b) which conforms to the literature [14].

Physical properties

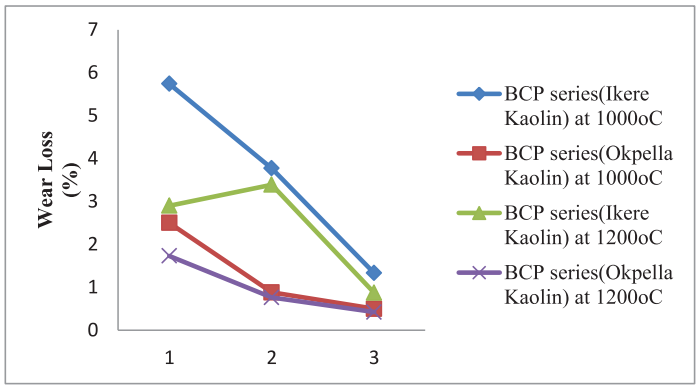
Properties such as water absorption, apparent porosity, bulk density and linear firing shrinkage were used to evaluate the physical properties of the BCP series containing Ikere kaolin and Okpella kaolin respectively and the results are shown in Fig. 3(a–d). In Fig. 3a, at 1000 °C, BCP series containing Ikere kaolin (BCP_1–BCP_3) was detected to have high water absorption at >5%, which decreases along the series to <4% for BCP_3. For BCP series containing Okpella kaolin (BCP_4–BCP_6), it was observed that the series showed lower water absorption rate at <4%, which later dropped down to 1% for BCP_5 and increased to 8% for BCP_6. However, the BCP series containing Okpella kaolin displayed improved water absorption rate when compared with that of Ikere kaolin. This better behavior might be as a result of vitreous phase obtained from the presence of albite inherent in the Okpella kaolin, overlaying the samples surface and thereby lowering water absorption rate. At 1200 °C, a significant drop in water absorption below 1% was observed for both BCP series containing Ikere kaolin and Okpella kaolin respectively, this drop can be linked to increase in vitreous phase formed at the said temperature [6]. However, BCP series containing Okpella kaolin had the least percentage water absorption rate at 0.3, which is due to the presence of albite mineral causing a formation of more vitreous phase at elevated temperature of 1200 °C.

Fig. 3b shows the percent porosity of all the samples, it is observed that a similar trend is obtained as shown in Fig. 3(a) indicating the relationship between water absorption and porosity. However, the low porosity values observed at 1200 °C in all the samples can be attributed to sealing of the open pores at high temperature.

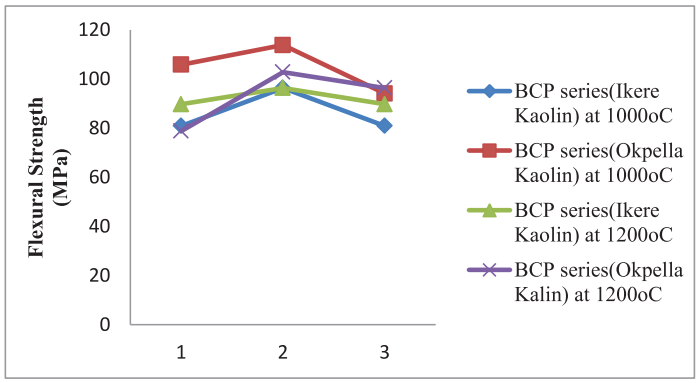
Fig. 3(c) illustrates the bulk densities of all the BCP series, it is observed that BCP series containing Okpella kaolin showed higher densification of 1.83 g/cm^3 while BCP series containing Ikere kaolin showed maximum densification of 1.73 g/cm^3 at 1000 °C. At 1200 °C, both BCP series containing Ikere and Okpella kaolin showed higher densification above 2.0 g/cm^3 and have their bulk densities within the range of 2.0–2.5 g/cm^3 due to more vitreous phase formed at the elevated temperature. Bulk density is mostly influence by porosity and amount of vitreous phases in the microstructure [15]. Fig. 3(d) showed the results of percent firing shrinkage, for 1000 °C, the BCP series containing Okpella kaolin showed lower shrinkage behavior which decreases across the series and then increased to 5% at BCP_6 while BCP series containing Ikere kaolin also showed a higher shrinkage property, which was seen to increase across the series until a drop was observed below 5% for BCP_3. At 1200 °C, the BCP series containing Okpella kaolin showed similar trends as observed at 1000 °C but with a difference of higher firing shrinkage rate while BCP series containing Ikere kaolin also behaved in similar manner. Increase in shrinkage is actually normal in ceramics as temperature increases but should not exceed 5% [16]. However, BCP series containing Okpella kaolin displayed least shrinkage rate which satisfied the expected requirement.

Mechanical properties

Fig. 4(a) represents the wear loss of all the BCP series containing Ikere and Okpella kaolin respectively. At 1000 °C, the BCP series containing Okpella kaolin displayed a reduced wear loss rate as the percent wear loss decreased across the series from 2.9% to <1%, while BCP series containing Ikere kaolin displayed initial high wear loss rate at 5.74%, then it eventually dropped across the series to <2%. However, at 1200 °C; the BCP series containing Okpella kaolin further showed a low wear



(a)



(b)

Fig. 4. (a)% wear loss (b) flexural strength.

loss rate at 0.5%, while the BCP series containing Ikere kaolin had <0.6% as the wear loss rate. The superior wear loss rate seen in BCP series containing Okpella kaolin can be attributed to the more vitreous phase formation (resulting from the albite presence in the Kaolin) on the surface of the samples reducing material loss [17]. The BCP series containing Ikere kaolin displayed better wear loss only at 1200 °C as some vitreous phase were formed at that temperature.

Fig. 4(b) showed the results of the flexural strength of all the BCP series containing Ikere and Okpella kaolin sintered at 1000 °C and 1200 °C respectively. It was observed that a superior flexural strength of 113.8 MPa and 102.8 MPa was obtained for BCP series containing Okpella kaolin at 1000 °C and 1200 °C respectively. However, for the BCP series containing Ikere Kaolin, a maximum flexural strength of 96.3 MPa was obtained at both 1000 °C and 1200 °C respectively. Ceramic properties such as densification, porosity and vitrification has been known to influence strength which was obviously seen in BCP series containing Okpella kaolin while that of Ikere Kaolin was spotted to have limited level of the same properties.

Conclusions

Microstructure evolution and physico-mechanical properties of bone china porcelain compositions using two selected kaolinite clays from Nigeria have been studied. The results obtained revealed that:

- Kaolin deposits can influence the microstructural evolution and physico-mechanical behavior of bone china porcelain.
- In terms of mineralogical constituents, Ikere china clay contains Kaolinite and Quartz while Okpella china clay had Quartz and ordered Albite ($NaAlSi_3O_8$).
- Scanning Electron Microscopy revealed that the samples containing both Ikere and Okpella kaolin sintered at 1000 °C and 1200 °C respectively had microstructural phases of Anorthite (matrix), Quartz, β-TCP and mixture of β-TCP + A. However, samples containing Okpella Kaolin possess a better vitreous phase which has a positive influence on its properties due to the presence of Albite mineral.
- In terms of physical properties such as water absorption, porosity, bulk density and linear firing shrinkage: both BCP series containing Ikere and Okpella kaolin sintered at 1000 °C and 1200 °C respectively displayed a very good result.

However, samples containing Okpella displayed a superior result which can be attributed to a vitreous phase present to seal pores and increase densification.

- In terms of mechanical behavior: BCP series containing Okpella kaolin displayed maximum strength of 113.8 MPa/102.8 MPa both at 1000 °C and 1200 °C respectively while a reduced wear loss rate was also observed in the same samples, which makes them better than that of Ikere Kaolin.
- The sintering temperature at which a better behavior of all the bone china porcelain compositions can be obtained is 1200 °C.
- Bone china porcelain containing Okpella kaolin deposit showed overall better promising results, which can be attributed to the presence of Albite in the kaolin deposit.
- Addition of 5% flint which is in conformity with literature body composition of bone china porcelain in the BCP_3 and BCP_6 is also seen to have contributed positively in reducing the shrinkage and distortion level at high temperature.

Conflict of interest

The Authors declare no conflict of interest and that this work has not been previously published anywhere.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.sciaf.2019.e00066.

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