

RESEARCH ARTICLE

Physical and Mechanical Properties of Porcelain Tiles Manufactured Using Nrobo- Uzo Uwani Nigerian Clay and local Raw Materials

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Abstract

Nigeria is endowed with vast natural resources for porcelain tiles manufacturing, yet it imports about 80% of this product from other countries. The physical and mechanical properties of porcelain tiles manufactured from Nrobo- Uzo Uwani clay, silica sand and feldspar sourced from Abakaliki and Ajaokuta respectively have been studied. Four different porcelain compositions were moulded into test samples by varying the compositions of clay, feldspar and silica sand and densified by firing them at temperatures of 900, 1000, 1100, 1200 °C. Common technological properties such as apparent porosity, water absorption, shrinkage, bulk density, flexural strength and compression strength were obtained from the fired samples. The results indicate that apparent porosity and water absorption decrease with temperature while bulk density, flexural and compressive strengths increase with firing temperature and silica content in the range of temperature and silica composition limits utilized in the investigation.

Keywords: Porcelain; Feldspar; Silica Sand; Flexural Strength; Compression Strength; Bulk Density

Introduction

Nigeria is ranked as the thirteenth importer of ceramic tiles in the world with its expenditure in the importation of tiles valued at over 10 billion dollars [1]. The emergence of modern ceramic tiles production in Nigeria is nascent compared to their counterparts overseas. Majority of the ceramic tiles used in Nigeria till date are still being imported mainly, nowadays from China, Spain and Brazil in spite of substantial reservoir of clay mines that can make her one of the first ten ceramic tiles manufacturing and exporting nations of the globe [2]. The compositions of the body of the tile material is based fundamentally on three raw materials: plastic clay (ball clay), which contributes the necessary plasticity for forming in the green state. It assures the mechanical strength of the tile body in drying; sodium- potassium feldspar that provides the first liquid phase during sintering, and which initiates the densification process and contributes mostly to reducing tile porosity; and finally quartz which serves as filler material and provides resistance to pyro- plastic deformation of the ceramic body during firing [3].

Clays are the major constituents of a tile body and are anhydrous complexes of alumina and silica, which are generally represented by the molecular formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [3]. There is abundant clay deposits spread across the six geo-political zones of Nigeria, each differing in chemical and mineralogical compositions depending on their geological formation. Many of these clays have been characterized and found useful for pottery and refractory bricks manufacturing [4]. Clay especially kaolin was imported as previous report claimed that Nigerian clays lacked the desired mechanical properties and mineralogical constituents for quality ceramic product manufacturing [5]. Worrisome is the fact that many important ceramics are made with colouring agents, glazes and additives considered toxic to humans and the environment [5]. There is, therefore, an absolute need for our local clay resources to be explored. The demand for tiles in Nigeria has necessitated the need to research and report potential clay resources for ceramic tiles manufacturing.

Abeid and Park [6] reported that a typical porcelain tile consists of 50% clay, 25% feldspar and 25% silica. Andreola, *et al.* [7], however, reported that a typical porcelain tile composition consists of 40- 50% illicit- kaolinitic clay, 10- 15% quartz and 35- 45% feldspar. By varying the proportion of these main constituents, it is possible to increase strength and reduce manufacturing cost. Strengthening of porcelain bodies occurs during a sintering process due to formation of favourable microstructures such as high

interlocking of fine needle- like secondary mullite, which occurs at a temperature of about 1075 °C and finely disperse quartz particles in glassy matrix, which limit the size of Griffith flaws resulting in increases in strength [8]. In another related mechanism, the heterogeneity of the porcelain structure leads to the development of compressive stresses in the vitreous phase as a result of differential thermal coefficients of the dispersed particles and the surrounding vitreous phase. The larger the compressive stress, the higher is the strength of the porcelain body [8].

Njoku, *et al.* [9] characterized the Nrobo- Uzo-uwani, Enugu state, Nigerian clay for possible use in ceramic tiles manufacturing and reported that the Nrobo clay has a similar composition with typical clays all over the world with Fe_2O_3 content of 1.09% as against less than 1.0% Fe_2O_3 content required for quality ceramic product manufacturing. They noted, however, that many clay deposits (foreign and local) have iron III oxide content in the range of 2.0 to 16.22%. They also reported that the flexural strength of the Nrobo clay attained the upper intermediate and high threshold standards for manufacturing high-quality ceramic products if processed at temperature above 900 °C. There are abundant natural resources for ceramic tiles manufacturing in Nigeria [10]. Nevertheless, about 80% of tiles used in Nigeria are imported since the few tiles producing companies are unable to meet the nation's demand for ceramic tile products [11]. The present Nigeria's economic state makes it imperative for the harnessing of our local clay minerals for the manufacturing of porcelain tiles. The objective of this study is the development of porcelain tiles using the Nrobo clay and other locally sourced raw materials.

Materials and Methods

The raw materials used for the study include clay from Nrobo in Uzo-Uwani Local Government Area of Enugu State; silica sand from Abakaliki- Ebonyi state and feldspar from Ajaokuta- Kogi state, Nigeria. The raw materials were sun-dried, crushed, ground and sieved to <160 μm prior to further use.

Chemical Analysis

The major compounds (oxides) in the Nrobo clay, Abakaliki silica and Ajaokuta feldspar were determined using an ARL Preform'X Sequential x-ray fluorescent (XRF) spectrometer equipped with Uniquant software for analyses at the Department of Geology, University of Pretoria, South Africa. The samples were mixed with boric acid for chemical analysis. The XRF result is shown in Table 2.

Sample Preparation

Four groups of porcelain samples were prepared according to Table 1. Separate specimens of each group were made and fired at 900, 1000, 1100 and 1200 °C. Each experiment was repeated three times and the average result and standard deviation were determined. The preparation of a sample consists of thoroughly mixing 1Kg of ground (<160 μm) porcelain body with 650 ml of distilled water in a beaker and manually stirring for 30 minutes for a homogenous paste to be formed. The solid constituents of the porcelain body were varied in accordance with Table 1. The resulting porcelain paste was moulded into different sizes and shapes for determining the physical and mechanical properties of the porcelain blends and stored in a desiccator.

Sample	Composition
A	50% Clay/50% Feldspar/0% Silica
B	50% Clay/10% Silica/40% Feldspar
C	50% Clay/20% Silica/30% Feldspar
D	50% Clay/25% Silica/25% Feldspar

Table 1: Composition of porcelain samples

Linear Shrinkage

Porcelain ceramic bar samples measuring 8 x 4.1 x 2.1 cm were selected from each group and line of 20 mm length was marked on them in their green state. The samples were dried in an oven at 110 °C for 5 hours and then fired to the temperatures of 900, 1000, 1100, and 1200 °C in an electric furnace for 1 hour and allowed to cool to ambient condition in the furnace. The samples were stored in a desiccator. The lengths of the marks were then re-measured. Total linear percentage shrinkage was determined using equation 1 as follows [12]:

$$\% \text{ linear dry shrinkage} = \frac{\text{Initial length} - \text{Final length}}{\text{Initial length}} \times 100 \quad (1)$$

Water Absorption

Flat porcelain bars were dried and fired to the temperatures of 900, 1000, 1100 and 1200 °C in an electric furnace, soaked for 1 hour, cooled to ambient condition, stored in a desiccator and weighed as dry weight. Thereafter, the samples were soaked in boiling water in a beaker for 1 hour and then, left in water for 24 hours. Excess water was removed from the sample surface with a moistened cloth prior to weighing with an electronic balance and recorded as soaked weight. The difference in weight was then used in calculating percentage water absorption as follows:

$$\% \text{ Water Absorption} = \frac{\text{SoakedWeight} - \text{DryWeight}}{\text{DryWeight}} \times 100 \quad (2)$$

Bulk Density/ Apparent Porosity

The bulk density and apparent porosity tests were performed using the liquid displacement method based on the Archimedes' principle [13]. Flat porcelain samples were dried at 110 °C, fired to the temperatures of 900, 1000, 1100 and 1200 °C, cooled to the ambient temperature and the weights were measured and recorded as MDRY. The samples were immersed in a beaker of distilled water and soaked for 24 hours. Excess water was removed from the samples using a moistened cloth prior to weighing and recorded as MSAT. They were then suspended in a beaker of distilled water using a string and their suspended weights were measured as MSUSP by measuring the weight of the beaker- filled with water with and without suspended porcelain sample and computing the differential weight. The bulk density and apparent porosity were calculated using the following formulae [13]

$$\rho_{\text{BUK}} = \frac{M_{\text{DRY}} \times \rho_{\text{LIQ}}}{M_{\text{SAT}} - M_{\text{SUSP}}} \quad (3)$$

$$\% \text{ Porosity} = \frac{M_{\text{SAT}} - M_{\text{DRY}}}{M_{\text{SAT}} - M_{\text{SUSP}}} \times 100 \quad (4)$$

Bending Strength

Bending strengths of fired porcelain flat samples were determined using the three-point loading scheme, which consisted of applying a gradually increasing load on the mid-point of the samples until failure occurred. The breaking load was recorded and bending strength computed using the formula stated as follows [12]

$$\text{Flexural Strength} = \frac{3PL}{2BH^2} \quad (5)$$

where P is the yield or breaking load, L is the distance between supports, B is the breath of sample, H is the height or thickness of the sample.

Compression Strength

Compression strengths of fired porcelain samples measuring 40 x 40 x 40 mm were determined using an M500- 25 CT model of computer-controlled Testometric universal materials testing machine which features winTest™ analysis software running under the Windows operating system. The samples were mounted and subjected to compressive loading at a speed of 1 mm/min and were loaded until fracture occurred.

Results and Discussion

Composition of Raw Materials

The results of x-ray fluorescence (XRF) analysis of clay, silica and feldspar used in the formulation of porcelain bodies for tile manufacturing are shown in Table 2.

Raw material	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	SO ₃	TiO ₂	P ₂ O ₅	ZrO ₂	PbO	ZnO	MnO
Clay	59.12	4.12	0.73	2.43	30.01	0.57	1.09	0.02	0.14	0.05	0.03	0.02	0.01	0.02
Silica	95.28	-	1.27	1.04	-	-	0.84	-	-	-	-	-	-	-
Feldspar	60.94	-	1.74	1.79	18.13	16.47	0.93	-	-	-	-	-	-	-

Table 2: Chemical composition of raw materials [wt%]

As seen in Table 2, SiO₂ and Al₂O₃ are the major constituents of the raw materials. Other compounds that are of minor proportions include K₂O, Na₂O, MgO, CaO and Fe₂O₃. The other oxides such as SO₃, TiO₂, P₂O₅, ZrO₂, PbO, ZnO and MnO are in trace amounts. By using a simple proportion method, it can be estimated that a ceramic blend consisting for instance of 50% clay, 25% silica and 25% feldspar would roughly be composed of 68.62% SiO₂, 19.54% Al₂O₃, 2.06% Na₂O, 4.41% K₂O, 1.92% MgO, 1.56% CaO and 0.99% Fe₂O₃. The feldspar contains 16.47% K₂O which in combination with other oxides: Na₂O, MgO, CaO and Fe₂O₃ forms a liquid phase that contributes in the densification of the ceramic body [14]. These oxides have been reported to play significant roles in vitrification, phase transformation and mullite grain growth in the ceramic bodies [14]. Table 2 also shows that both the silica and feldspar have low Fe₂O₃ content and which is capable of reducing its overall amount in the ceramic body. The composition of a ceramic body determines the microstructure of the processed body, which in turn is responsible for the properties of the ceramic material.

Physical Properties

As stated earlier, each experiment was repeated three times and the average and standard deviation of each experimental result were calculated. Average was calculated as sum of data divided by the number of experiments while standard deviation (SD) was determined using equation 6. in equation 6 is statistical data, X is average and N is number of experiments.

$$SD = \sqrt{\frac{1}{N-1} \sum (x - X)^2} \quad (6)$$

Consistency of the results is indicated by the standard deviation of results from mean value and is shown in the figures by the error bars. Figures 1-4 show the variation of apparent porosity, water absorption, linear shrinkage and bulk density of porcelain samples (consisting of different proportion of clay, silica and feldspar) with firing temperature. The results indicate that whereas the apparent porosity and water absorption of the porcelain bodies decrease with temperature, the linear shrinkage and bulk density increase with temperature in the range of temperatures that the experiment was performed. As reported by Romero and Perez [15], the microstructure of a standard ceramic or porcelain tile manufactured from a clay- silica- feldspar blend consists of quartz grains, primary mullite crystals, secondary mullite crystals, a silica-rich amorphous phase and porosity. Porosity can be open and interconnected or closed- porosity depending on the manufacturing temperature. Open porosity is formed as a result of a loss of volume associated with clay dehydroxylation (loss of hydroxyl group in clayey material) during firing at 500 °C [16]. Closed porosity develops during sintering as a result of the development of liquid phase, which progressively closes the capillaries that constitute the open porosities- leading to the reduction of open pores and formation of isolated pores with smooth and spherical cross-sections.

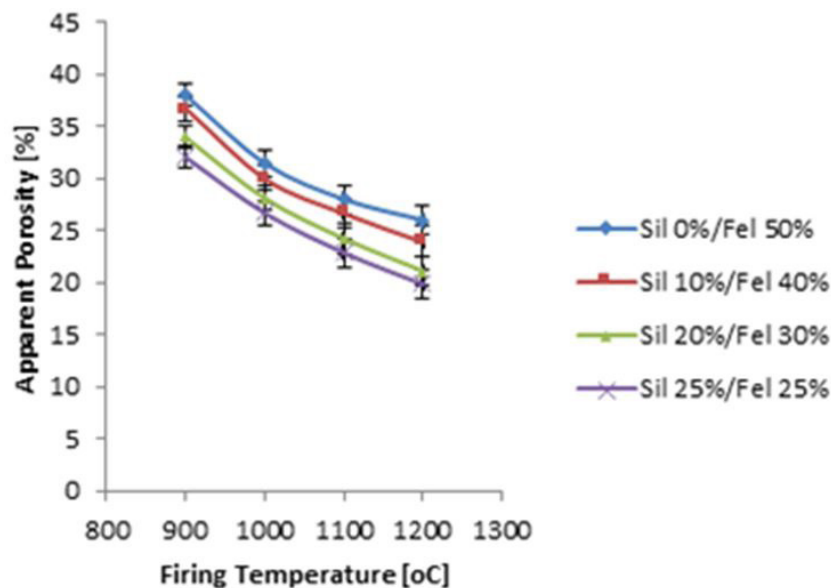


Figure 1: Variation of apparent porosity of porcelain samples with firing temperature

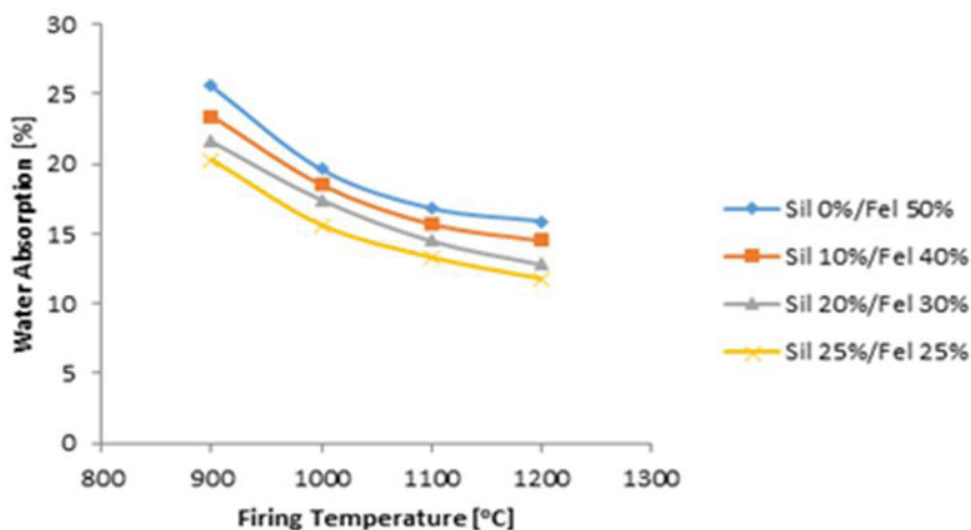


Figure 2: Variation of water absorption of porcelain samples with firing temperature

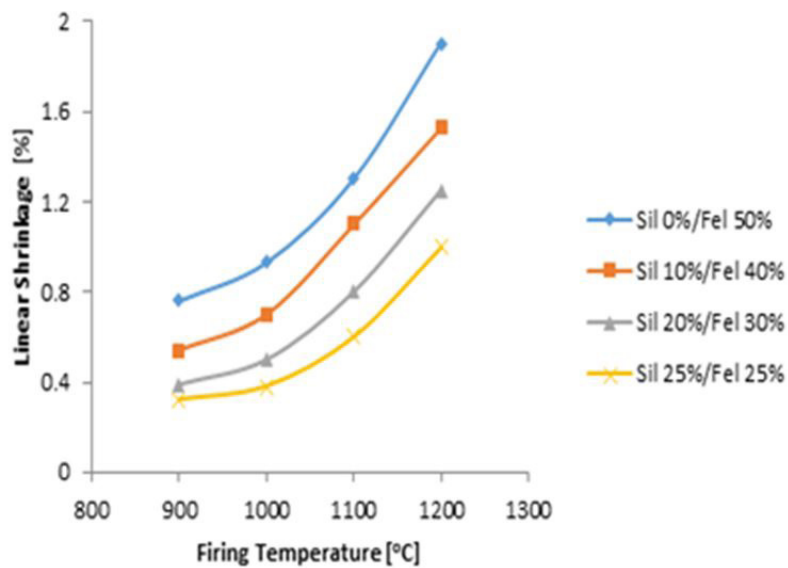


Figure 3: Variation of linear shrinkage of porcelain samples as a function of firing temperature

As shown in Figures 1 & 2, apparent porosity and water absorption decreases with firing temperature. This is attributable to a liquid phase developed from the relatively low melting point constituents of feldspar which progressively increases in volume and reduces in viscosity as the firing temperature is increased above 1100 °C and is able to fill more capillaries of pores and cracks within the ceramic body [17]. Consequently, the ceramic body's capacity to absorb water is diminished. Figures 1 & 2 also show that the specimen with 50% clay, 25% silica and 25% feldspar exhibited the least porosity and water absorption capacity while the test piece with 50% clay and 50% feldspar showed the highest of these properties. This is probably because, the viscous liquid phase dissolves silica at higher temperatures to form a glassy phase and this increases the volume of the liquid phase and its capacity to fill pores, reduces porosity and water absorption capacity of the ceramic body. Hence, large amount of silica is likely to have been dissolved in the sample with 25% silica.

Figure 4 shows the variation of bulk density of the porcelain blends with firing temperature. As can be seen, this parameter increases as the firing temperature of the porcelain wares is increased. It can also be observed from Figures 4 that the bulk density of the porcelain samples increases as the silica sand content of the triaxial ceramic body is increased. For instance, the bulk density (Figure 4) of the porcelain body (consisting of 50% clay, 25% feldspar and 25% silica) increased from 1.65 g/cm³ at 900 °C to 1.77 g/cm³ at 1200 °C resulting in 7.27% increase in bulk density of the porcelain blend. Also for the same ceramic body fired at 1200 °C, the bulk density of the specimen increased from 1.74 to 1.77 g/cm³, resulting in an increased densification of 1.72%. This suggests that increasing processing temperature rather than silica content is a more potent means of achieving densification in porcelain materials.

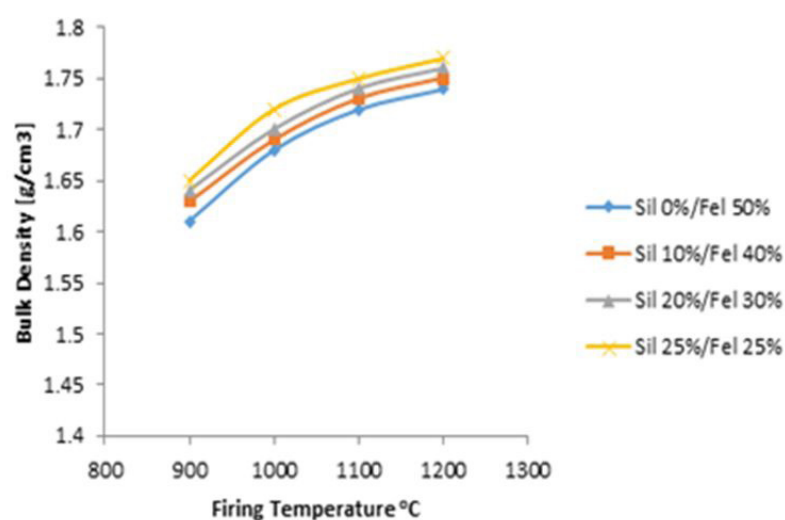


Figure 4: Variation of bulk density of porcelain samples with firing temperature

As reported in [15], densification of porcelain ware occurs during a viscous phase sintering process, with the development of a liquid phase that flows by capillary pressure in the interconnected holes between the particles, and leads to the development of ceramic bonding constituted by a glassy matrix, embedding new- crystalline phases (mullites) and part of residual crystals.

Densification appears to be rate- controlled by the solubility of solids (mainly silica) in the liquid phase and; the strong dependence of viscosity on temperature [17]. As stated in equation 7 [18], the densification rate $\left(\frac{d\rho}{dt}\right)$ of a porcelain, material can be related to the reduction in viscosity of the glassy liquid phase developed during a sintering process as follows:

$$\frac{d\rho}{dt} = \frac{Kn^{1/3}\gamma^{1/3}}{\eta} \quad (7)$$

where K and n are constants, γ and η are the surface energy and viscosity of the glassy phase. Surface energy does not change significantly with compositional changes; consequently, viscosity remains a key parameter to affect densification. Equation 7 clearly suggests that the densification of a porcelain ware increases with a reduction in viscosity of a glassy phase developed during the firing of the ceramic material. Viscosity, in turn, depends on temperature as described in equation 8, which shows that viscosity of liquids decreases exponentially with increases in temperature as follows [18]:

$$\eta = \eta_o \exp\left[\frac{\Delta F_n(T)}{RT}\right] \quad (8)$$

where $\Delta F_n(T)$ is the free activation energy of viscous flow, R is gas constant, $\eta_o = h/V_\eta$, h is Plank's constant and V_η is the volume of the kinetic unit which is responsible for fluidity. Equations 7 and 8, therefore, show that a ceramic body, undergoing a liquid phase sintering process will increase in density if its sintering temperature is increased.

Mechanical Properties

Figures 5 & 6 show the variation of compressive strength and bending strength with temperature respectively for porcelain samples fired at different temperatures. As seen in these figures, both compressive strength (Figure 5) and bending strength, (Figure 6) increase with firing temperature and with silica content up to the maximum temperature and silica content utilized in the experiment. It can be deduced from Figure 5 that compressive strength increased from 8.5 MPa to 14.62 MPa for a triaxial porcelain specimen consisting of 50% clay, 25% feldspar and 25% silica fired at 900 °C and 1200 °C, resulting in 72% increase in compressive strength. Similarly, for the same sample and the same temperatures, the bending strength (Figure 6) increased from 16.5 MPa to 35.65 MPa resulting in about twice its bending strength. Bending strength of 35.65 MPa is in the order of bending strength limit reported in international standards (EN14411 (ANNEX G) for porcelain tiles [19]. No standard requirement has been defined for compression strength by this standard.

The EN 14411 standard, however, prescribes a water absorption percentage of 0.5% for a tile to qualify to be classified as highly vitrified porcelain tiles. Porcelain sample D which was fired at 1200 °C (Table 1) and which has the optimum physical property has percentage water absorption of 11.77% and can rather be classified as a semi-porous porcelain tile [19,20]. The non- attainment of low water absorption capacity of 0.5% by the samples is attributable to the inability of the porcelain samples to achieve full vitrification at the firing temperatures since the attainment of vitrification depends on the formation of certain minimum percentage of the liquid phase to provide a bond. The minimum percentage may vary depending on the viscosity of the liquid phase, sintering temperature and holding time [21]. The Increase in strength (compression and bending) with temperature is very likely due to a more effective sintering process, which resulted in lesser porosity (Figure 1) as the firing temperature was increased.

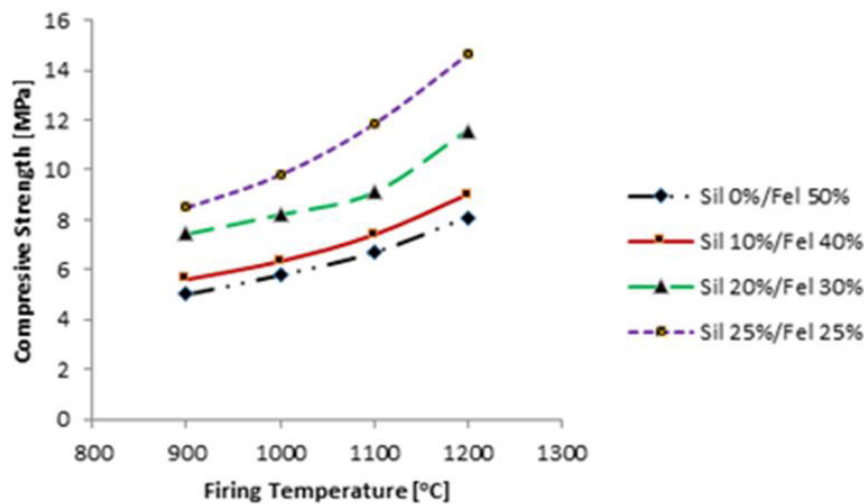


Figure 5: Variation of compressive strength of porcelain samples with temperature

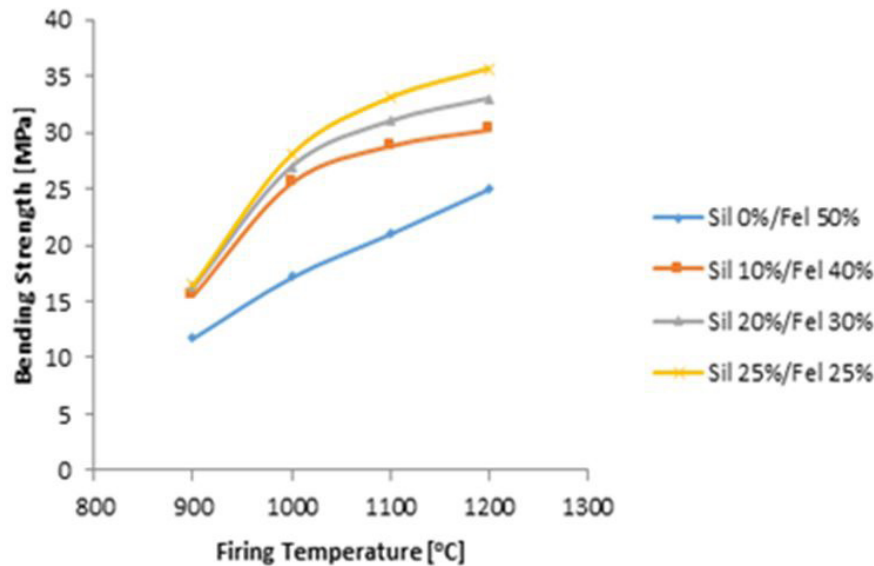


Figure 6: Variation of bending strength of porcelain samples with firing temperature

Also, silica dissolves in molten feldspar (with solubility increasing with temperature) and this increases the strength of the glassy phase formed in the porcelain material during liquid phase sintering [17]. Another mechanism that might have affected the strength of the porcelain material is the large pre-stressing effect due to residual stress at the glassy phase around the silica grains which resulted from the large discrepancy in coefficient of thermal expansion between silica grains and glassy phase and which increases with temperature [22]. Thus, the glassy matrix surrounding the quartz grains experiences a compressive stress, which acts as a pre-stress, improving mechanical strengthening.

Conclusion

Tri-axial mixtures of Nrobo clay, feldspar and silica sand from Ajaokuta (Kogi state) and Abakaliki (Ebonyi state) respectively were formulated as representative compositions of ceramic blends for tile manufacturing and were fired at temperatures ranging from 900 °C to 1200 °C. Both physical and mechanical properties of these porcelain materials were determined and the following conclusions can be made:

1. The apparent porosity and water absorption of the ceramic bodies decrease with increase in temperature and silica content while the linear shrinkage and bulk density of the porcelain samples increase with temperature and silica content in the range of the temperature and silica content used in the study;
2. The bending strength and compressive strength of the porcelain wares increase with temperature and silica content;
3. The ceramic body consisting of 50% clay, 25% feldspar and 25% silica sand showed the least water absorption and highest bending and compressive strengths;
4. The percentage water absorption of the ceramic bodies ranged between 11.77% to 25.6% which is higher than the 3% and 0.5% water absorption that is recommended for vitrified and highly vitrified porcelain tiles respectively;
5. The bending strength of the tri-axial ceramic bodies ranged between 15.47 and 35.65 MPa with the blend consisting of 50% clay, 25% feldspar and 25% silica- having a bending strength of 35.65 MPa which is in the order of the >35 MPa prescribed in the standard EN14411 (ANNEX G) for ceramic tiles.

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