

Synthesis and Characterization of Bone & Teeth Ash and Analysis of Their Influence on the Properties of Bone China

Mst. Sharmin Mostari*, Tasmia Zaman, Md. Shamimur Rahman

Department of Glass & Ceramic Engineering, Rajshahi University of Engineering and Technology (RUET), Rajshahi, Bangladesh

Email address:

sharmin015@gmail.com (Mst. S. Mostari)

*Corresponding author

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Abstract: The work was done to understand the effects of naturally occurred bone and teeth ash on the physical as well as mechanical properties of bone china products. Both bone and teeth ash was prepared following conventional thermal decomposition method. Locally found cattle bones and tooth was utilized for this purpose. Three different routes of powder or ash preparation i.e. boiling-wood firing, excavating-calcination and boiling-calcination were followed. The calcination temperature was fixed at 950°C-2 hours. After that, density and phase identification of ash was carried out. Finally, bone china product was manufactured using powder compaction and slip casting route. Firing was done at a constant temperature (1150°C-2 hours). Further characterizations (density, percent firing shrinkage, percent water absorption and modulus of rupture measurement) of the sintered samples were evaluated. Boiling-calcination route was found to be the most superlative route. However, enhanced properties of bone china were obtained by the addition of teeth ash.

Keywords: Nitrogen (N₂) Pycnometry, X-ray Diffraction (XRD), Firing Shrinkage, Water Absorption, Modulus of Rupture (MOR)

1. Introduction

Research on biomimetic and eco-friendly materials has been gaining prominence day by day in industrial and biomedical sectors. Among them calcium hydroxyapatite (HAp) is one of the potential candidates which are naturally found in teeth and bone [1].

The mineral content of bone is much greater than needed as a physiologic reservoir. Martin *et al.* reported HAp as the primary mineral content of bone and calcified cartilage. It has the desirable physiochemical attributes of stability and inertness [2, 15].

The organic (collagen) and inorganic (hydroxyapatite) constituents present in bone and teeth are found to be in the range of 70-90% and 10-30% correspondingly. The elastic modulus of HAp is found to be two orders of magnitude greater than that of collagen, which is the primary polymeric component of bone. HAp, the model mineral compound having three times greater density than most other biological

materials, provides high mechanical strength, hardness and rigidity to bone and teeth [3, 14-16].

Because of the natural abundance and excellent compatibility with anatomical environment, it has effectively drawn the attention of both entrepreneurs and researchers. This biological apatite is completely different from synthetic HAp in structure, composition and stoichiometry i.e. having Ca deficiency with the ratio of Ca/P <1.67 [2, 4]. Yet, it is extensively used in medical science as implants for the replacement of traumatized or infected and damaged body parts [4, 5]. For example- bone plates, joint replacement, ligament, vascular grafts, pyrolytic heart valves, dental implants etc. are accomplished using HAp [5].

The major concerns of cement and ceramic industries are the energy saving. While achieving this goal, the industrialists are developing persistently the idea of using alternative fuels and raw materials. Calcined bones are considered as a good source of fuel as well as raw material in these industries. Combustion of this bio-waste in cement industries diminishes the evolution or spreading of greenhouse gas and contagious

ailment [1]. Calcined bones are not only used in cement and ceramic industries but also for agricultural purposes [6].

The powder residue of burnt cattle bone, acknowledged as bone ash is being widely used as core ingredient of whitewares since the eighteen century. Until then porcelain products were used in China and Japan which were difficult to reproduce. Consequently, soft porcelain named as bone china emerged as a possible solution of hard porcelain [7].

Utilization of ~50% bone ash in bone china products has been reported previously [8]. Bone ash is supposed to provide outstanding mechanical properties i.e. greater strength, toughness to bone china. The whitish appearance of bone china is also created by bone ash which makes it an eligible alternate to porcelain [9].

Several methods like thermal decomposition, alkali hydrolysis, co-precipitation, sol-gel, hydrothermal synthesis, microwave heating etc. have been stated for the extraction of HAP from bone or teeth [10].

Hayek *et al.* successfully precipitated high quality HAP by controlling P^H and temperature through the method of alkaline hydrolysis [11]. Lehr *et al.* and Seuter *et al.* both reported the synthesis of HAP by solid state route [12]. Hydrothermal technique is also stated as an effective method of single crystal HAP synthesis. Mosebach *et al.* prepared single crystal hydroxyapatite via this route [13]. However, thermal decomposition technique is the most widely used method due to its simplicity and cost effectiveness.

In this present work, HAP was synthesized through the method of thermal decomposition and the effects of its addition on the physical and mechanical properties of bone china were observed.

2. Experimental

2.1. Methodology

Conventional calcination technique with three different preparation routes (abbreviated as R_1 , R_2 and R_3) were followed formulating $Ca_{10}(PO_4)_6(OH)_2$ (HAP). After collecting fresh bones from slaughter house, they were headed for boiling-wood firing (R_1), excavating-calcination (R_2) and boiling-calcination (R_3). On the other hand, generation of teeth ash was conducted by single R_3 route.

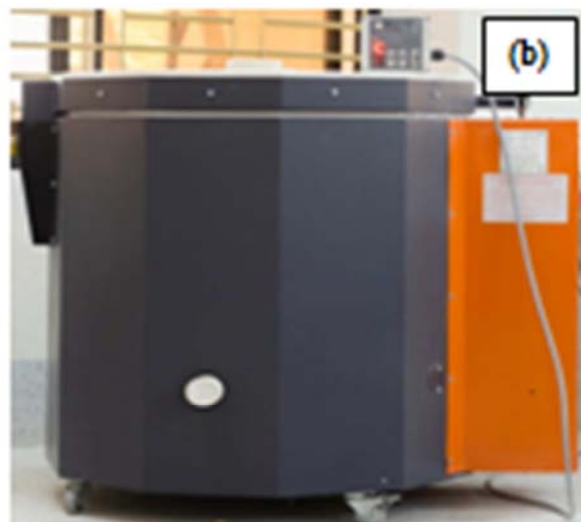


Figure 1. Different routes of bone ash preparation (a) wood fired kiln and (b) electric kiln.

In case of R_1 route, the bones were defatted and deproteinised by boiling. Then the bone sludge was burnt in a wood fired kiln (Fig. 1a), followed by rinsing with water to remove wood ash and dirt. The residues were finally kept in oven at 100°C .

While for R_2 , bone samples were decomposed under the soil for 15 days so that all flesh and organic fluid would be extinct. Finally the samples were taken out, washed thoroughly, dried at 100°C -48 hours and calcined at 950°C -1 hour in electric kiln (Fig. 1b).

Direct calcination was applied for R_3 method. Before calcination, the samples were cleaned via boiling. The calcination cycle (shown later in Fig. 4b) was identical as R_2 .

2.2. Ball Milling

Eventually whitish powder residue (Fig. 2a-c) was obtained by pulverizing all the wood fired bones and tooth in a planetary ball mill (Retsch, model no. PM 200, Germany).

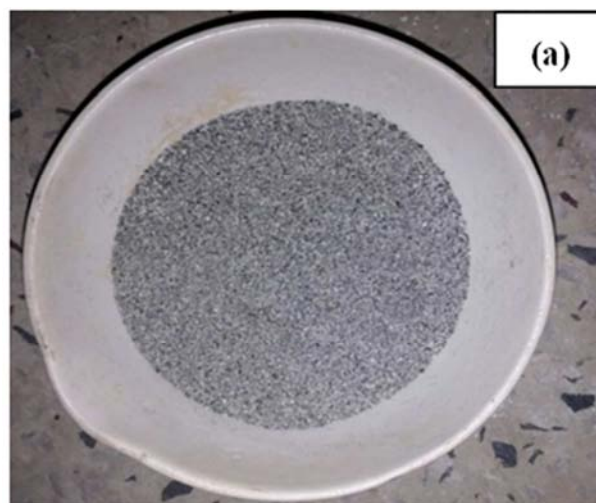




Figure 2. Powders of bone ash (a) R₁, (b) R₂ and (c) R₃.

2.3. Powder Characterization

The powder samples were taken for density measurement using Quantchrome (UP-32) N₂ Pycnometry (Fig. 3a). After that, phase analysis was performed by XRD (Fig. 3b) in between 20 to 60° with a source of Cu K_α radiation (40 kV-40 mA, step size: 0.02°) and wavelength $\lambda=1.5418 \text{ \AA}$ (Bruker D8 Advance, Germany).



Figure 3. (a) True density measuring apparatus, (b) XRD machine.

2.4. Bone China Preparation

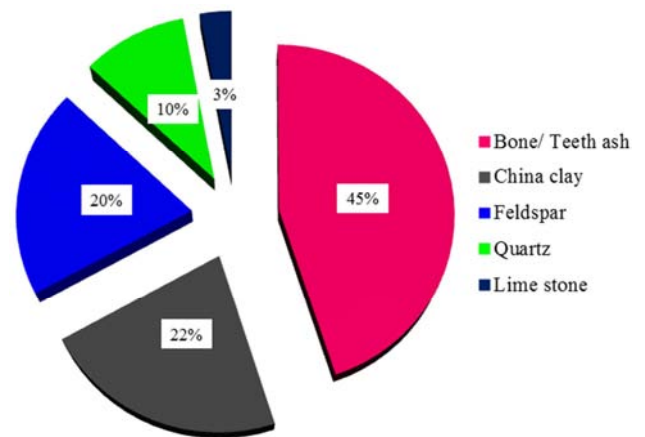


Figure 4. Pie chart for batch composition.

After the powder characterization, batch compositions were prepared for the fabrication of bone china samples, abbreviated as S₁, S₂, S₃ and S₄ for the samples originated from R₁, R₂ and R₃ respectively. Fig. 4 and Table 1. shows the weight percent of different components followed in this experiment.

Batch mixing was done by conventional ball milling. It was conducted for 6 hours using ethanol as milling media. After milling, the slurry was dried for 100°C for 12 hours.

Table 1. Batch composition of bone china.

Components	Weight percent
Bone/ Teeth ash	45
China clay	22
Feldspar	20
Quartz	10
Lime stone	03

It is to be noted that, samples were prepared by both compaction and slip casting methods. Hydraulic press was used to prepare pellet shaped (dia=32 mm) samples whereas rectangular shaped (length=100 mm, width=40 mm, thickness=10 mm) samples were made by slip casting.

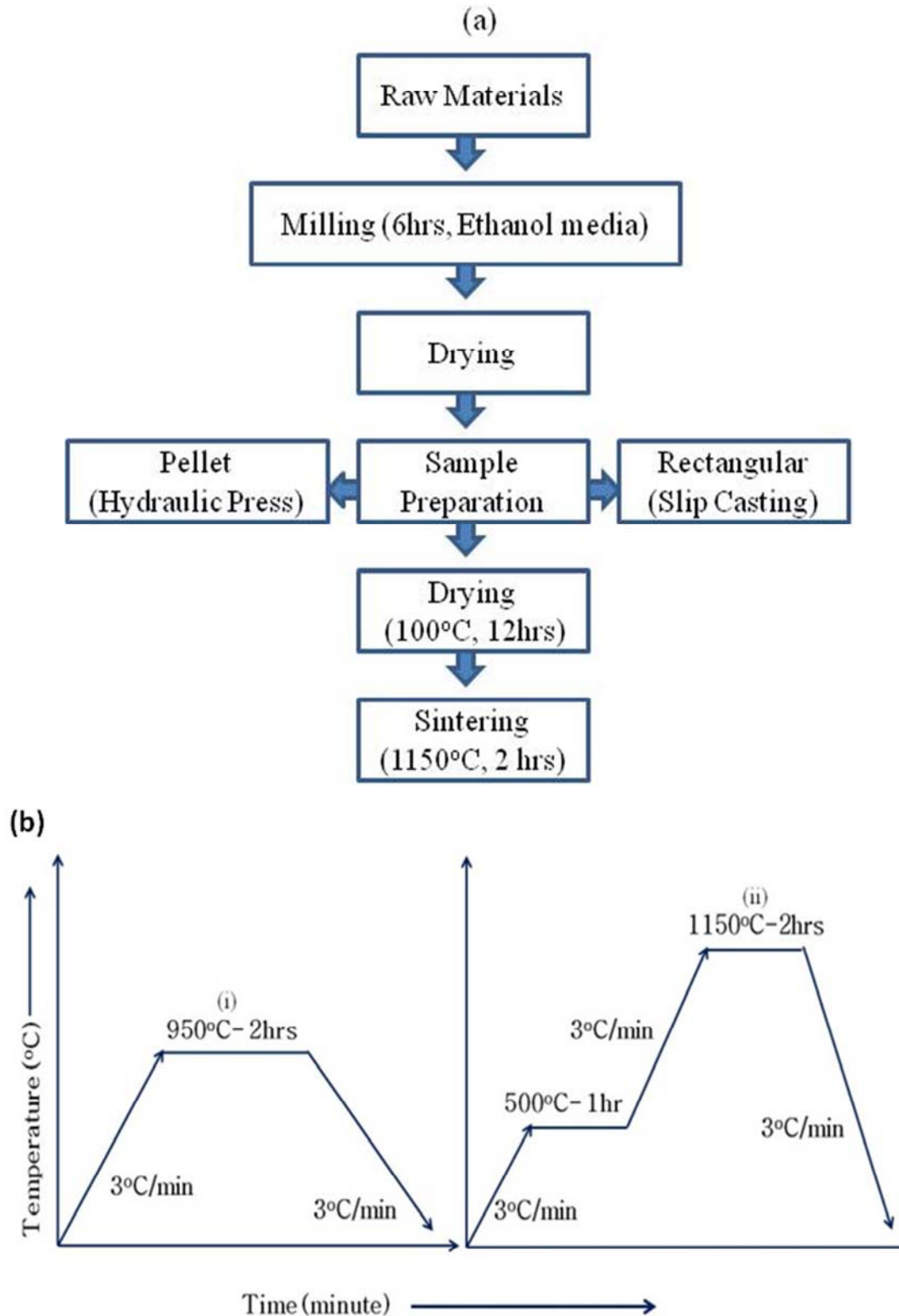


Figure 5. (a) Flow chart and (b) (i) calcination (ii) sintering cycle of bone and teeth ash.

Finally, firing was done at 1150°C for 2 hours. The experimental flow chart and calcination as well as sintering cycle are shown in Fig. 5(a-b). The density, shrinkage behavior and water absorptivity of sintered products were further evaluated. Lastly modulus of rupture (MOR) was

determined by E. J. Payne, UK three point bending tester. Calculation of flexural strength was done using (1):

$$\sigma_f = \frac{3FL}{2bd^2} \quad (1)$$

3. Result & Discussions

3.1. Powder Characterization

3.1.1. Density

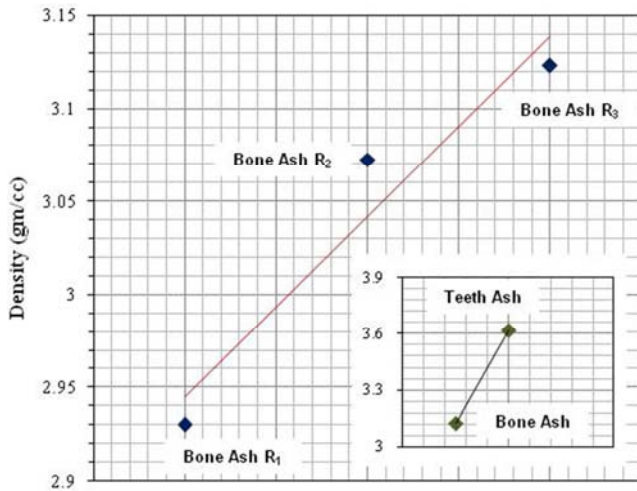


Figure 6. Variation of density of bone ash following different routes (Inset: density comparison for bone and teeth ash produced by R_3 route).

Fig. 6 shows the variation of density of the bone and teeth ash prepared in different routes. Boiling-calcination route turned out to be the best method as evidenced by highest density (3.12 gm/cc) attained for bone ash. While following the same route (R_3), teeth ash provided around 16% greater density compared to bone ash.

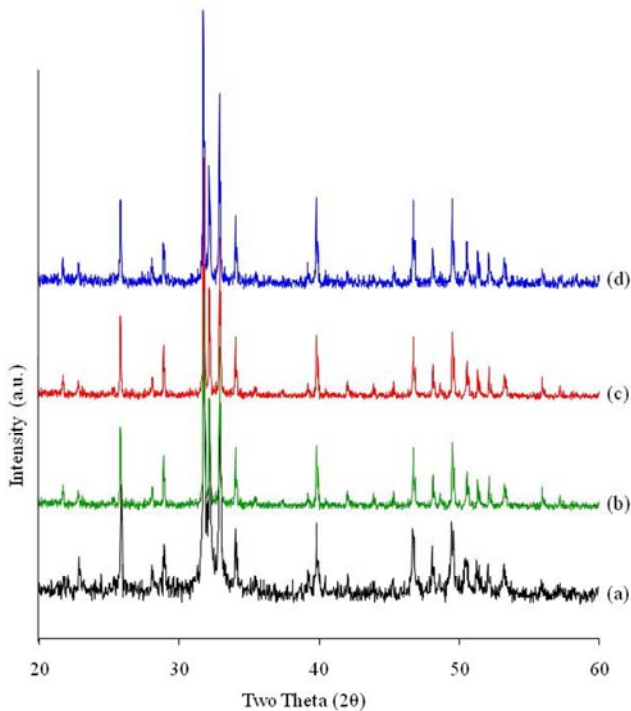


Figure 7. XRD curves for calcined powder of (a) bone ash R_1 , (b) bone ash R_2 , (c) bone ash R_3 and (d) teeth ash R_3 .

3.1.2. XRD Analysis

The XRD patterns for the calcined samples are portrayed in

Fig. 7. It reveals the presence of crystalline HAP phase having hexagonal structure along with additional second phases. Presence of impurity phase was found to be high for R_1 . Route R_3 gave highly crystalline HAP. However, the crystallinity of teeth ash was much better than that of bone ash. It indicates that, utilization of teeth ash could be more beneficial than bone ash for industrial purposes.

3.2. Bone China Preparation

3.2.1. Density Measurement

Fig. 8 depicts the density curves of the fired bone china samples. Among all the samples of bone ash, S_3 showed highest density whereas lowest density was perceived for wood fired sample S_1 . It comes with no surprise as wood firing was the most uncontrollable system generating over fired ash. The formation of grayish ash (Fig. 2a) justifies the above statement. Existence of wood ash in batch material might also have an adverse effect on overall density. The secondary peaks as evinced in XRD indicate the presence of such impurities. Conversely, S_4 sample prepared from 45% teeth ash exhibited greater density than others. Enhanced density of teeth ash might have influenced the phenomenon of better densification which was observed in the end products.

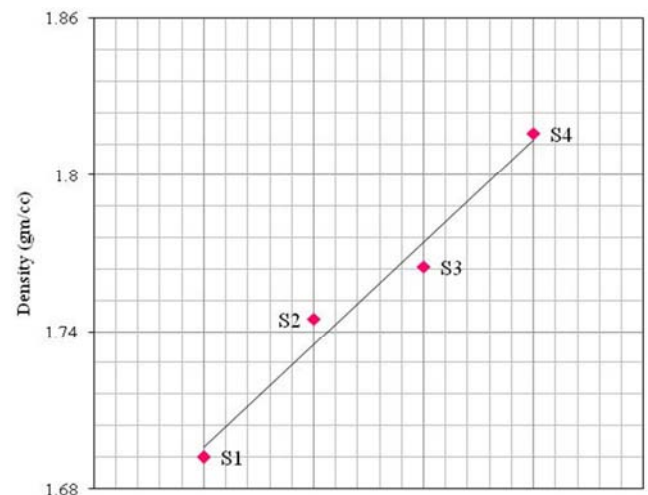


Figure 8. Density curve of bone china samples.

3.2.2. Percent Firing Shrinkage

The percent firing shrinkage vs. composition curves are shown in Fig. 9. The curve shows an increasing trend in firing shrinkage with composition. It is well-known that, higher the firing shrinkage, greater the density of a fired product. In this observation, the shrinkage behavior matched perfectly with the density curves.

Table 2. Physical and mechanical properties of bone china.

Samples	Density (gm/cc)	Firing Shrinkage (%)	Water Absorption (%)	MOR (MPa)
S_1	1.692	1.706	13.353	1.41885
S_2	1.745	1.968	11.687	2.9073
S_3	1.765	2.216	11.593	3.0359
S_4	1.816	2.659	9.271	5.115

Both particle size and presence of impurity manipulates the sintering temperature of solid body. As the S₁ samples were made of wood fired bone ash, it is obvious that it might contain excessive impurity phase. Moreover, the distribution and packing of S₁ was poor. It resulted porous structure even after firing. These factors might cause deterioration of property for S₁.

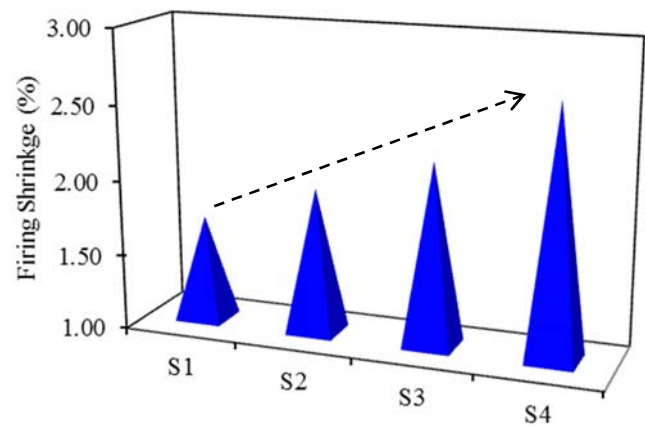


Figure 9. Chronological change in percent firing shrinkage for bone china samples.

3.2.3. Percent Water Absorption

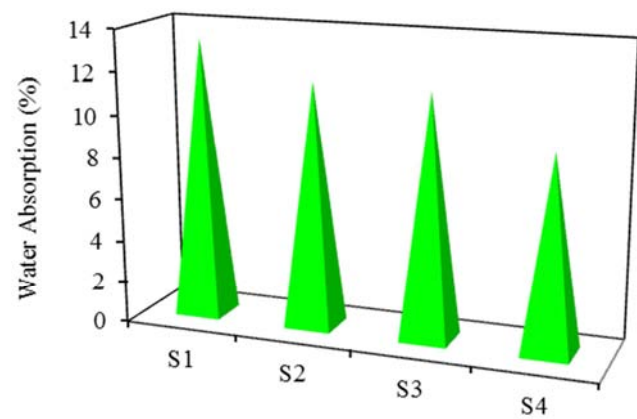


Figure 10. Variation of percent water absorption for bone china samples.

The water absorption characteristics of the densified samples were further evaluated (Fig. 10). The wood fired samples (S₁) appeared to be highly porous as evidenced by higher absorptivity. Meanwhile, similar nature of water absorption was alleged for S₂ and S₃ samples.

3.2.4. Modulus of Rupture (MOR)

Flexural strength is a property of material which quantifies the capability of resistance to deformation under bending stress. The variation of bending strength of all types of samples was examined and displayed in Fig. 11. The best modulus of rupture was provided by the sample S₄ containing teeth ash as it had better crystallinity and density with least contaminating element as shown in XRD graph.

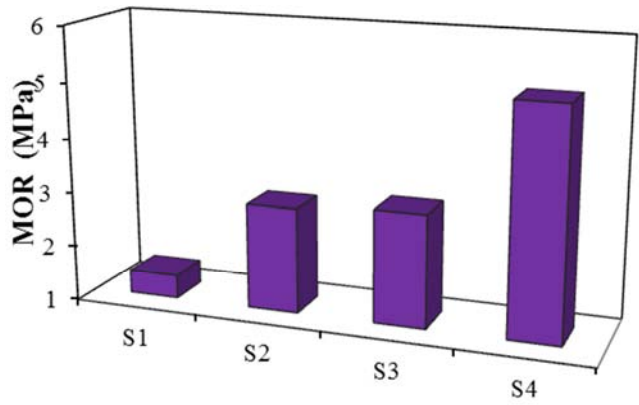


Figure 11. Flexural strength of bone china samples.

4. Conclusions

This research was conducted in searching for the optimum extraction method of HAp (bone and teeth ash) and their special applications in bone china soft porcelain. Among the three different routes, boiling-calcination (R₃) seemed to be emerged as the best route confirmed by the true density curves and X-ray diffractometry. The ash made through R₃ gave highest density of value 3.12 gm/cc. The XRD analysis revealed the existence of HAp phase for all the powdered samples whereas presence of impurity peaks was lowest for R₃.

Further, from the fabrication and characterization of bone china samples created with the aid of bone and teeth ash concludes the fact that HAp sourced from cattle sludge has greater potentiality for this application. The sample S₃ shows highest property in density (1.765 gm/cc) and also possesses better bending strength (MOR-3.0359 MPa) with minimum water absorption.

In comparison to teeth and bone ash, teeth ash was found to develop better property due to its superior crystallinity as observed in the characterization process. However, extended investigation need to be carried out to ensure the beneficial of teeth ash over bone ash.

Finally, this research suggests that, the study on cattle bone and teeth sludge is economically viable, environmentally friendly and technically sound source of raw material.

Nomenclature

Symbol	Meaning	Unit
σ_f	Flexural Strength	MPa
F	Applied Load	N
L	Length of Support Span	m
b	Width	m
d	Thickness	m

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