Synthesis of eggshell based hydroxyapatite using hydrothermal method

Shahid Hussain\textsuperscript{1} and Kazi Sabiruddin\textsuperscript{1,2}

\textsuperscript{1}Discipline of Mechanical Engineering, Indian Institute of Technology Indore, Simrol, Indore 453552, India
\textsuperscript{2}Email: skazi@iiti.ac.in

\textbf{Abstract.} Eggshell are rich sources of calcium carbonate and calcium oxide, but treated as bio-waste material. The natural origin and wide availability of eggshell are suitable to synthesize hydroxyapatite having chemical composition and crystalline structure similar to human teeth and bones. In present work, eggshell powders are sintered at different temperature 200°C, 400°C, 600°C, 800°C and 900°C for 1 h time duration in muffle furnace. The sintered powders are cold compacted at a fixed load of 15 tons for 10 min duration in a hydraulic pellet press. A suitable die set having 13 mm diameter is used to prepare compacted powder samples of 6 mm height. The sintered eggshell pellets are characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Vickers hardness tester. Chemical composition of eggshell pellet changes from calcium carbonate to calcium oxide at 900°C for 1 h time duration and noticed through XRD. Increased hardness of the sintered eggshell pellet is noticed at more than 600°C temperature. The waste eggshells can be utilized to synthesize hydroxyapatite with the help of ball milling and subsequently heat treatment. A straightforward and cost effective method (i.e. hydrothermal method) is proposed for converting eggshell into hydroxyapatite. In this method, a solution of calcium oxide powder obtained from eggshell, tri calcium phosphate powder and demineralized water in stoichiometric proportions is employed as the precursor. Now, this solution is heat treated at 1050°C for 3 h time duration in muffle furnace to complete the reaction. X-ray diffraction result confirms the formation of hydroxyapatite, apart from little amount of other compounds in final product.

\textbf{Keywords:} Eggshell; Hydroxyapatite; XRD; Micro hardness; FESEM

1. \textbf{Introduction}
Hydroxyapatite (HA) is a bioactive material means ability to produce bone apatite-like material on their surfaces. The chemical composition and structure of hydroxyapatite is similar to mineral constituent of natural teeth and human bones. They can be used in dental, orthopaedic, and maxillofacial applications as its bioactivity helps in bone osseointegration and ingrowth [1]. Various techniques have been developed to synthesize hydroxyapatite powders. The synthesis techniques can be divided into two methods: wet techniques and dry techniques. In wet techniques, the reaction is carried out in solution using various solvent at different temperature. On the other hand, no solvent is used in dry methods. The wet methods can be further categorized into hydrothermal, chemical precipitation, emulsion, sol-gel, sonochemical and hydrolysis. The dry techniques include mechanochemical method and solid state method. The more convenient and effective method is hydrothermal method to produce hydroxyapatite among various synthetic routes [2]. The
hydroxyapatite can be synthesized by different biogenic materials and synthetic calcium. The hydroxyapatite obtained through biogenic materials is different in response to that of synthetic calcium based hydroxyapatite. Different biogenic materials like eggshell, seashell, coral, and cuttlefish shell have successfully been focused to obtain hydroxyapatite. In biogenic based hydroxyapatite, the properties like pore structure and chemical composition are preserved as in precursor material [3]. In this work, a solution of calcium oxide powder obtained from eggshell, tri calcium phosphate powder and demineralized water in stoichiometric proportions is employed as the precursor to carry out chemical reaction at 1050°C for 3 h time duration to synthesize hydroxyapatite [4].

2. Materials and Methods
Waste eggshells were collected from Bhopal Caterer Mess, IIT Indore, Madhya Pradesh, India. Tap water was used to clean the collected eggshell and eggshell membranes were removed manually by peeling off. Further, eggshells were rinsed with demineralized water. Then, washed eggshell were dried and crushed into very small pieces by using hammer. The powder form of eggshells particle was obtained by using planetary ball milling process (Retsch PM 100). The ratio of grinding media to eggshell was 10:1 (mass ratio). Calcium oxide was synthesized from eggshell powder by two stage heat treatment process. In the first stage, eggshell powder was placed in muffle furnace to heat at 450°C for 2 hours. Any organic residues are expected to be destroyed at this temperature. In the second stage, the obtained powder was heat treated at 900°C for another 2 hours. By releasing carbon dioxide, the eggshell transform into calcium oxide at this temperature according to the following equation (1).

\[ \text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO} \quad (1) \]

The obtained calcium oxide powder from eggshell and tri-calcium phosphate (manufacturer: Loba Make) was mixed homogeneously with demineralized water in an alumina crucible. The obtained calcium oxide powder of 0.72 g and tri-calcium phosphate of 11.62 g were mixed in 30 g demineralized water to carry out reaction according to equation (2). After mixing, this solution was heat-treated in muffle furnace (BIO-TECHNICS INDIA) and maintained at temperature 1050°C for time duration 3 h.

\[ 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \quad (2) \]

The powders is cold compacted at 15 tons and 10 min holding time in a hydraulic pellet press (25 tons, Kimaya engineering). A suitable die set having 13 mm diameter is used to prepare compacted powder samples of 6 mm height. The X-ray diffraction (XRD) analyses of the pellets were carried out using an X-ray diffractometer (Rigaku Smart Lab 3kW) with scanning speed 2°/min operating at 40 mA and 30 kV. Microstructural characterization of the pellets was conducted using a field emission scanning electron microscope (Zeiss Supra-55) under secondary electron mode. Surface hardness of the pellets were carried out using Vickers hardness tester at an indentation load of 100 g, dwell time 15 sec and indentation speed 25 micron/sec.

3. Results and discussion
The XRD patterns of the eggshell powder at room temperature, 200°C, 400°C and 600°C are shown in figure 1. It is found that in all four figures most of the characteristics diffraction peaks of eggshell powders at room temperature and different temperature are coinciding with calcite polymorphic phase of calcium carbonate. Additionally, these XRD patterns indicate that eggshell at room temperature and upto temperature 600°C are mainly composed of calcium carbonate (CaCO3) with little amount of impurities like organic matter, magnesium carbonate and calcium phosphate [5].
When eggshell powder is heated at 800°C or above, calcium carbonate is converted into calcium oxide (CaO) by releasing of carbon dioxide as depicted in Figure 2. Physical appearance of eggshell powder also changes as temperature increases from room temperature to 900°C. The color of eggshell powders at room temperature, 200°C, 400°C, 600°C and 900°C are white, light brown, brown, black and bright white respectively.

Figure 1. XRD pattern of eggshell at (a) room temperature, (b) 200°C, (c) 400°C, (d) 600°C.

Figure 2. XRD pattern of eggshell at (a) 800°C, (b) 900°C temperature.
Micro images of the eggshell powder at room temperature, 200°C, 400°C, 600°C and 900°C are shown in figure 3. Furthermore, it is noticed that remarkable difference in surface morphology of eggshell powder with an increase in heating temperature from room temperature to 900°C. Microstructure of powder at 900°C temperature is quite different than that of remaining powders.

![Figure 3. FESEM image of eggshell at (a) room temperature, (b) 200°C, (c) 400°C, (d) 600°C, (e) 900°C.](image)

The micro hardness of room temperature eggshell powder and heat treated eggshell powder at different temperature calculated by Vickers hardness tester is shown in figure 4. The hardness of eggshell powder at room temperature, 200°C, 400°C and 600°C are almost same. But hardness of eggshell powder at 900°C is almost double than that of remaining powders. This increment in hardness value may be due the transformation of calcium carbonate into calcium oxide. Figure 5 shows X-ray diffraction pattern of final product which confirms the peaks of hydroxyapatite mainly and few peaks are also belong to the other compound which is minute in amount.

![Figure 4. Hardness of eggshell at different temperature.](image)

![Figure 5. XRD pattern of eggshell based hydroxyapatite.](image)
Conclusions

a) With an increase in temperature from room temperature to 600°C, eggshell powder retaining its chemical composition i.e. calcium carbonate. But, further increase in temperature results in mainly calcium oxide.

b) The hardness value of eggshell powder is almost same, with an increase in temperature from room temperature to 600°C. With further increase in temperature leads to transformation of calcium carbonate into calcium oxide which in turn result in higher hardness value.

c) Hydroxyapatite powder has been synthesized successfully using eggshell powder.

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