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Exploring the Effect of Sintering Temperature on Hydroxyapatite Derived from Egg Shells

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Abstract. The term hydroxyapatite $Ca_5(PO_4)_3(OH)$ is naturally occurring mineral and chemically identical to the mineral constituent of bones and solid tissues of mankind and mammals used for bone grafting, augmentation in maxillofacial surgery and in orthopedics as space filling material. However, the brittleness of pure HA materials narrows its application only to low-load bearing applications. Generally, for the improvement of the mechanical properties and the structural one, hydroxy apatite is subjected to the sintering process. Thus, an optimization of the mechanical properties and micro structure of hydroxy apatite through a suitable choice of sintering parameters is under investigation. This paper presents the effect of sintering temperature on mechanical properties of hydroxy apatite compacts. A chemical precipitation method was successfully employed to prepare hydroxy apatite powder from waste egg shells. The eggshell derived HA is a cost effective bio-ceramic for biomedical applications and an effective material recycling technology. HA derived from egg shells and 5% organic additive was cold uniaxially pressed at 2500 psi for 3 min isothermal hold. The resulting compacts were sintered at different temperatures from 900-1100 °C for dwell time of 2 h. The samples were characterized by analyzing micro structural analysis, compressive strength, porosity and radial shrinkage. Compressive strength and porosity was increased with increase in sintering temperature, while radial shrinkage was decreased with increasing sintering temperature. Structural analysis showed that inter connected pores were developed and a material with inter connected pores is thought to be a good candidate as scaffold material.

Keywords: hydroxyapatite, sintering temperature, SEM analysis, porosity

Introduction

Over the past few decades interest in bio-ceramics has increased to such a point that today they are used not only in making eye glasses tissue culture flasks and thermometers but ceramics materials are increasingly being used for the repair and reconstruction of skeletal diseases and disorders (Privadarsini *et al*., 2018; Hench, 1998; Ravaglioli and Krajewski, 1992). These materials present a capable future as the raw materials used are wastes, while employing a biological substituted apatite having some trace elements as bone substitutes, instead of synthetic apatite without them, would be more useful for bone healing (Boutinguiza *et al*., 2012). It has been reported by several researchers that HA obtained from animal bones is biologically more active as compare to the synthetic material. It appears that this benefit is connected to properties in bred from the raw material used, such as low crystallinity, non-stoichiometry and chemical composition including the presence of substituent elements such as Mg, K, Na and Sr (Ferraz *et al*., 2004; Linhart *et al.*, 2001). HA is one of the widely explored bio-ceramics for its medical applications, being a stable calcium phosphate (Sinha *et al.*, 2009) under physiological conditions. Current applications of bio-ceramics include bone grafts, spinal fusion, bone repairs, bone fillers, maxillofacial re-construction etc. (Parakasam *et al*., 2015).

On one side to reduce the cost of HA synthesis, its mechanical strength as compare to natural bones is the main demand in research. Recently, most of the research and developments are proposed to develop HA form natural resources like minerals, marine and animal bones *etc*. (Brzeziñska-Miecznik *et al*., 2016; Lowe *et al*., 2016; Mondal *et al*., 2016; Heidari *et al*., 2015; Chakraborty and Chowdhury, 2013). HA is of particular interest for bone grafting, augmentation in maxillofacial surgery and in orthopedics as space filling material. However, the brittleness of pure HA materials narrows their application only to low load bearing applications, such as tooth root substitutes, filling of periodontal pockets, cystic cavities, regions adjacent to implants, spinal fusions, contour and

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malformation defects and nonunion of long bones (Oktar and Goller, 2002). In general, HA needs to be formed into a compact or porous scaffold depending on the conditions of bone substitution before implanting in human body. Amorphous HA is no longer stable and could dissolve reliant on usage environment, while the sintered body could not dissolve so much owing to its high crystallinity. Therefore, it is possible to rectify this non-load bearing drawback by means of improving the mechanical properties substantially by sintering. Sintering of CaP is carried out by various processes. Sintering is intended to cause densification and to increase the mechanical strength of the bio-ceramics (Parakasam *et al*., 2015). In general, sintering is the term used to describe the consolidation of the product during firing. Consolidation implies that in the product, particles have joined together into strong aggregate.

A number of different studies were carried out with the aim of improving the mechanical properties. It is now well recognized that the micro-structure and properties of ceramics critically depend on processing routes and densification parameters. It has been found that, at the optimum sintering temperature of 1250 °C where the material is composed of pure hydroxyapatite phase, the samples exhibited densities >99% of theoretical value and possessed a hardness value of 6.08 GPa. Decomposition of HA starts to occur at ∼1400 °C with the formation of TCP phase. Porosity and grain size were found to play an important role in determining the properties of sintered hydroxy apatite compacts. (Muralithran and Ramesh, 2000). A researcher also studied the influence of powder processing and sintering temperature on densification, micro-structure and mechanical properties of hydroxy apatite (HA) ceramics (Nithyanantham *et al*., 2002). The processing of HA has improved its densification, micro-structure homogeneity and mechanical properties. (Habib *et al*., 2012) also studied the effect of sintering time on mechanical properties of HA compacts and found that to get improved mechanical properties like compressive strength and hardness, sintering time should be increased.

This research reflects the effect of one sintering variable *i.e*., sintering temperature on the mechanical properties including compressive strength, porosity, radial shrinkage and micro-structure of HA compacts prepared from egg shell powder. The aim of our investigation was to assess the influence of sintering time on bone substitutes derived from natural resources, such as animals' bones and teeth or hydrothermal transformation of egg shells for economic and time saving reasons. In this study, pelleted samples produced using HA powder with the addition of 5% methyl cellulose as binder. Obtained samples were sintered at 900, 1000 and 1100 °C for 2 h. Structural analysis and mechanical properties of the samples were investigated in order to determine the effects of sintering temperature on HA compacts.

Materials and Methods

Hydroxyapatite was prepared using egg shells as calcium precursor and phosphoric acid by precipitation method (Habib *et al*., 2012). The prepared HA powder along with 5% methyl cellulose as a binder was uniaxially pressed in a 17 mm steel diameter die using a load of 2500 psi for a period of 3 min. HA compacts then were sintered at 900, 1000 and 1100 °C for 2 h with ramp rate of 5 °C per min. Compressive strength of the HA compacts was measured using Shimadzu Universal Testing Machine using a load of 5KN and a ramp/strain rate of 5 mm/min. Porosity of HA compacts were measured according to ASTM C373-88 for porosity measurement. The porosity threshold was calculated by using Image J Software. Radial shrinkage was also measured by using geometric analysis. Microscopic analysis was carried out by using Scanning Electron Microscope Hitachi SU 8230.

Results and Discussion

The molecular bond structure of the synthesized material was confirmed by FTIR. As shown in Fig. 1 the band at 3433/cm displays the presence of OH group. The peak at 3804/cm is due to structural hydroxyl group. A well resolved band at 1055/cm was identical to phosphate band. Appearance of strong bands at 576 indicates the presence of phosphate ions in hydroxyapatite phase.

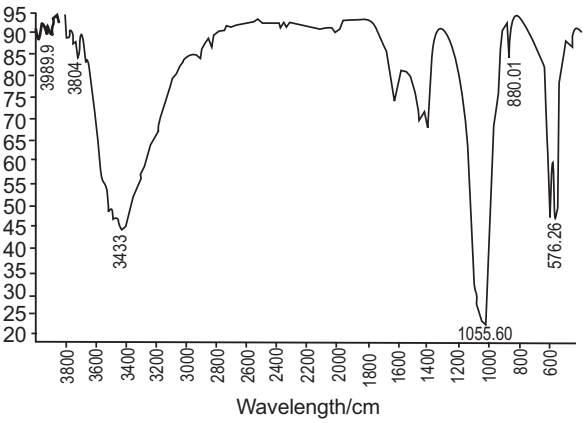


Fig. 1. FTIR of synthesized hydroxyapatite powder.

Micro structural analysis using SEM reveals a porous structure of hydroxyapatite compacts. The black portion shows the inter-connected pores, while the other portion is granular hydroxy apatite phase. From the micro-structural analysis, it is shown that with increase in sintering time the pore size and inter connectivity of pores is increased as can be seen in SEM micrographs Fig. 2. Pore inter-connection provides the way for migration, as well as for *in vivo* blood vessel formation for bone tissue remodeling (Jones *et al*., 2007; Charriere *et al*., 2003). The pores developed are inter-connected and porous hydroxy apatite with inter-connected pores is thought to be a good candidate as scaffold material for bone regeneration and as a synthetic bone substitute material. It was found that the increase in the sintering temperature induced the growth of the particle size from tens of nanometers to some micrometers for all pH values. This may be due to the diffusion of the particles at higher temperatures and formation of flake-like structures with inter-connections (Rodrý´guez-Lugo *et al*., 2018).

Porosity of compacts increased as sintering temperature increased. This may be due to the evaporation of binder from pellets leaving behind pores. Inter-connecting micropores are usually formed due to the gaseous porogen in bio-ceramics (Yan *et al*., 2004). It was observed that the density of HA sintering part increases as the sintering temperature increases from 1100 to 1300 °C. The percentage porosity of the sintered body also increases with decreasing sintering temperature (Jamadona *et al*., 2020). It was shown that pure HA starts to densify at around 800 °C and continue to densify upto 1200 °C. At this temperature, the densification is complete. Further, heating up to 1400 °C does not lead to any noticeable shrinkage (Nath *et al*., 2010). In our experiment the optimum sintering condition was obtained at 1100 °C for 2 h. The results of porosity are in accordance with the SEM images shown in Fig. 2, the porosity is increased with increasing sintering temperature (as shown in Table 1 and Fig. 3).

From Table 2 it is clear that compressive strength of the compacts increases with increase in sintering temperature. Maximum compressive strength was obtained at 1100 °C after 2 h sintering time Fig. 4. The studies also explained that the compression tests conducted on the pelleted samples sintered at 1100 °C and 1200 °C. It was revealed that the compressive strength of the samples increased with increasing sintering temperature

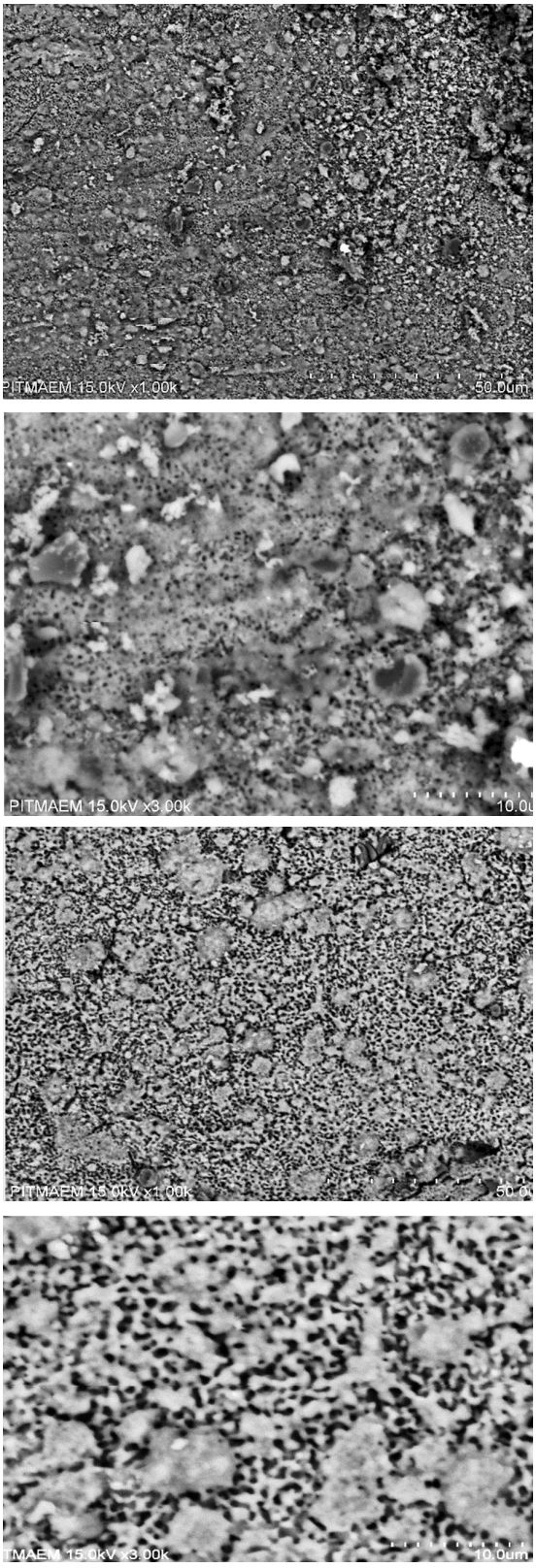


Fig. 2(a). SEM images of HA compacts sintered at 900 °C.

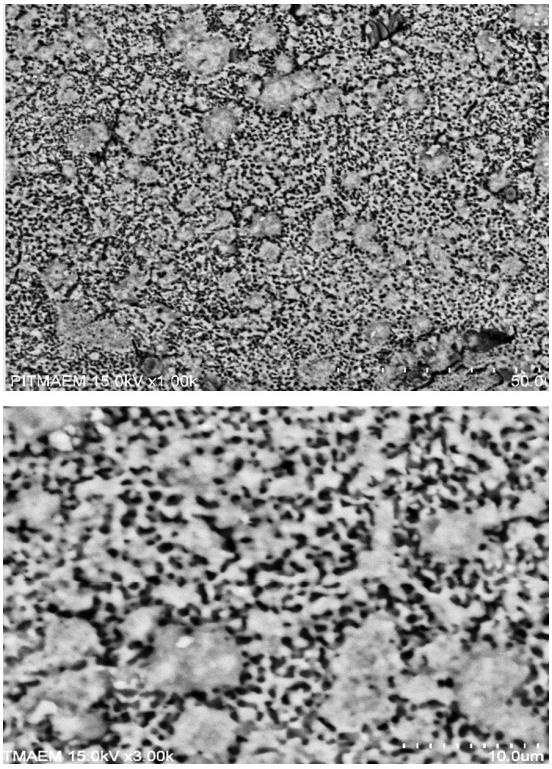


Fig. 2(b). SEM images of HA compacts sintered at 1000 °C.

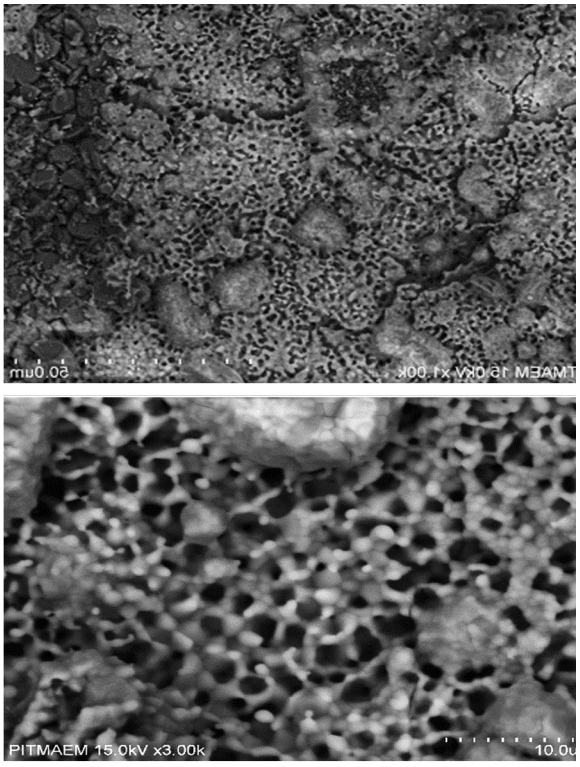
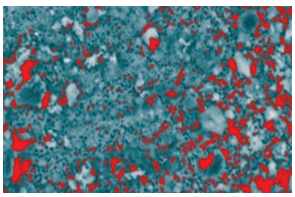
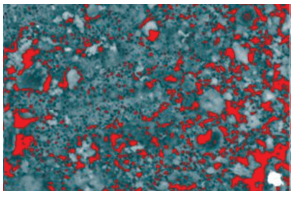
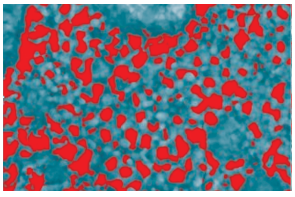


Fig. 2(c). SEM images of HA compacts sintered at 1100 °C.

Table 1. Relation between porosity and sintering temperature

Sintering temperature (°C)	Porosity (%)	Porosity threshold
900	9.54	
1000	12.68	
1100	27.17	

regardless of the calcination state of the HA powders and the urea content (Albayrak *et al*., 2016). Our results showed the same trend. As temperature of sintering increases the compressive strength increases because of the process of densification.

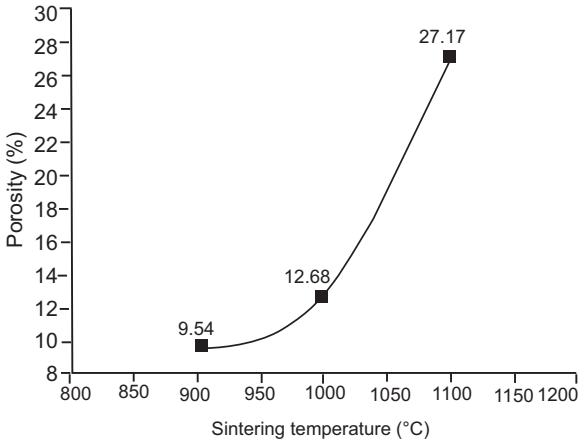


Fig. 3. Relation between porosity and sintering temperature.

Table 2. Relation between compressive strength and sintering temperature

Sintering temperature (°C)	Compressive strength (psi)
900	2920.90
1000	4627.03
1100	4968.92

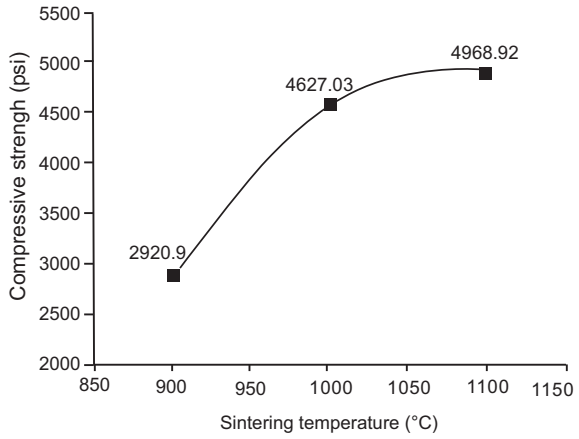


Fig. 4. Relation between porosity and sintering temperature.

Radial shrinkage. Linear shrinkage percentage was measured depending on diameteral change by using micrometer, before and after sintering:

$$\text{Linear shrinkage \%} = \frac{D_0 - D}{D} 100$$

where:

L.sh = linear shrinkage; D_o = sample diameter after pressing (mm); D = sample diameter after sintering (mm).

Table 3 and Fig. 5. shows the relation between sintering temperature and radial shrinkage. As the sintering temperature increases radial shrinkage reduces. This shrinkage also affects the mechanical properties like compressive strength. As radial shrinkage decreased the compressive strength increases due to densification process. These results are not in accordance with literature (Khalaf Al-Khazraji *et al*., 2010) results which showed that as temperature of sintering increases the linear shrinkage increases because of the evaporation of binder, moisture and the densification. This may be due to the less amount of binder in prepared pellets.

Table 3. Relation between radial shrinkage and sintering temperature

Initial radius (mm)	Sintering temperature (°C)	Final radius (mm)	Radial shrinkage (%)
18.87	900	18.56	1.64
18.70	1000	18.54	0.85
18.57	1100	18.40	0.71

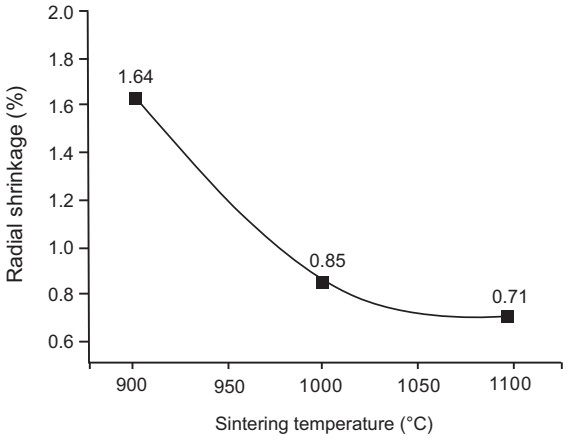


Fig. 5. Relation between porosity and sintering temperature.

Conclusion

In general, HA needs to be formed into a compact or porous scaffold depending on the conditions of bone substitution before implanting in human body. HA was successfully synthesized using waste material (egg shells) as a precursor and it was used to fabricate HA compact. The effects of sintering profiles on the synthesized hydroxy apatite (HA) pellets were investigated in terms of mechanical properties and microscopic examinations. According to the results, with increasing the sintering temperature compressive strength and porosity was increased. Compressive strength was increased due to the process of densification and porosity was increased due to the evaporation of binder. Images of SEM also showed the same trend.

Conflict of Interest. The authors declare that they have no conflict of interest.

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