Porous alumina via protein foaming-consolidation method

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Abstract

We have succeeded in developing a novel method for preparation of porous alumina using egg yolk both as consolidator and foaming agents. Slurries of alumina powders and yolk were prepared by stirring the mixture with various alumina-to-yolk ratios (1.00, 0.83, 0.75, and 0.65) for 3 h and the resulting slips were poured into cylindrical shaped stainless steel molds and followed by foaming and consolidation through drying at 110, 150, 160, and 180 ^{o}C. The dried green bodies of the samples were then burned to remove the pore creating agent at 600 ^{o}C for 1 h, followed by sintering at 1550 ^{o}C for 2 h. Alumina porous bodies with volume shrinkage of 29.3-39.9% were obtained. The compressive strength of the 1.00 alumina-to-yolk ratio's sample was 4.57 MPa at 50.4 % porosity and it decreased significantly to 1.07 MPa at 71.7% porosity with alumina-to-yolk ratio of 0.65. Pore size distribution measurement showed that macropores of the sintered alumina porous bodies increased with the increased alumina-to-yolk ratio and temperature of drying process and were found in the range 50 – 900 µm. These results have opened a novel preparative way for porous ceramics especially alumina-based porous materials designed for biomedical applications.

Keywords: Protein foaming-consolidation; ceramics; porous; characterization

1. Introduction

Porous ceramics have a wide range of engineering applications ranging from filtration membranes and catalyst supports to biomaterials and thermally or acoustically insulating bulk materials or coating layer. The requirements for the ceramic matrix and the pore structure may vary depending on type of application. For effective thermal insulation it is favourable to have closed porosity whereas, on the other hand, filters and membranes require open porosity. In the bioceramics field it is desirable to use porous ceramic implants with certain porosity to promote integration with biological tissues. [1]

So far, a number of routes, such as polymeric foam impregnation, gel casting, and freeze drying have been used for the consolidation of the power suspensions into porous bodies. In polymer foam impregnation process, ceramic replica of the polymer foam is prepared by soaking polyurethane foam of desired pore size in a ceramic powder suspension followed by squeezing the excess slurry out by rolling, drying the slurry impregnated polymer foam, careful burnout of organics and sintering.[2] In gel casting, a ceramic powder suspension containing organic monomer and cross linking agent is foamed by using a blowing agent followed by setting through *in situ* polymerization on the monomer. Gel casting produces porous ceramics with a combination of open and closed pore microstructure having superior mechanical properties in wide range porosities. However, the process has limitations with respect to the control of pore size.[3] In freeze drying process, controlled crystallization of ice is used for consolidation of aqueous powder suspensions into bodies and sublimation of the ice crystals under reduced pressure resulted in porous structure.[4]

Preparation of the tri-modal pores ceramic structure has been recently reported using foaming and starch consolidation method.[5] Different particles such us poppy seed[6],

polystyrene[7], PVAC[8], and wheat particles[9] were used as a pore-forming agent or template for producing porous ceramics.

Proteins such as ovalbumine and bovine serum albumin have been used for the foaming and setting of aqueous ceramic powder suspensions for preparation of porous ceramics[10-11]. Lyckfeldt and Ferreira[12] reported a starch consolidation process for preparation of porous ceramics.

Recently, porous alumina has been attracting considerable attention for scaffold applications, especially for cell loading and bone grafts. Its biomedically interesting characteristics are contributed by biocompatibility, inertness and chemical stability. Thus, various methods have been developed to produce porous alumina with a big variety in distribution, which finally determine its suitability for many applications.

In this paper, we would like to present a novel method for development of porous alumina using egg yolk as both consolidating and foaming agent. The effect of alumina-to-yolk ratio and drying temperature on physical properties like pore size, porosity and strength of sintered products will be reported as well.

2. Materials and methods

2.1 Materials

Commercial alumina powder (Sigma-Aldrich, Inc. USA), with a characteristic mean diameter of 0.25 μm (measured using a Nano S, Malvern, UK) and a surface area 0.39 m^2/g (measured by N_2 adsorption, Autosorb-1 model, Quantachrome, USA) was used in the present study. Protein used was yolk that freshly isolated from chicken egg procured from local market. Thermogravimetry analysis (Pyris Diamond model, Perkin Elmer

Instruments, USA) was carried out to understand the details of the yolk burn-out in ambient air at a heating rate of 10 °C/min.

2.2 Scaffold fabrication

Slip was prepared by dispersing the alumina powder in yolk. The slurry was stirred in beaker glass with rate of 150 rpm for 3 h. Four samples were prepared by varying alumina-to-yolk ratios: 1.00, 0.83, 0.75 and 0.65. The slurry was cast in cylindrical open stainless steel mold and heated in an air oven at 180 °C for 1 h. Castor oil was used as lubricant for easy mold removal. The drying temperature was varied as 110, 150 and 160 °C for slurry with alumina-to-yolk ratio of 1.00 also. The dried samples were then heated in a SiC furnace (Protherm, Turkey) at a 10 °C/min rate up to 600 °C for removal of the yolk and followed by 1 h holding. Then heating was continued at a rate of 2 °C/min up to 1550 °C ended by 2 h dwell time at the temperature.

2.3 Rheological analysis

The rheological property of the slurries was measured in a ThermoHaake VT 550 viscotester with a measuring system of concentric cylinders using sensor type of SV-DIN. All rheological measurements were conducted at shear rate from 10 to 1000 s^{-1} at ambient temperature. The viscosity values were derived from shear stress plots versus shear rates.

2.4 Scaffold Characterization

The porosity of the as-sintered alumina ceramics was determined by the apparent density and dimensions of the specimens. The apparent density of sintered samples obtained was measured in Electronic densimeter MD300S, Alfa Mirage). The theoretical density of fully

densified alumina (3.98 g cm^{-3}) was used as reference to calculate the total volume fraction of porosity. The pore size, interconnection among pore and also the grain structure were examined using scanning electron microscopy (JEOL 5600, Japan) and field emission scanning electron microscopy (JSM 6700 F model, JEOL, Japan).

2.5. Mechanical testing

The mechanical strength of the porous alumina scaffolds was measured using a universal testing machine (Lloyd LR10K plus) by diametrical compression at a loading rate of 0.5 mm min^{-1} with scaffolds of 3:2 height-to-width ratio, typically 10 mm diameter and 15 height. Five scaffolds were used to determine the average maximum compressive strength. Sintered samples of 10 mm diameter and 15 mm length were used for diametrical compression testing. The elastic modulus on compression was calculated from relationship between stress and strain at the initial linier portion of the curves.

3. Results and discussion

3.1 Rheological behaviour

Fig. 1 shows the influence of alumina-to-yolk ratio (w/w) on the viscosity of slurry at different shear rate. All the viscosity measurements were carried out within 3 h after stirring with rate of 150 rpm at ambient temperature. Though the slurries showed large difference in viscosity (9.32. Pa s-12.62 Pa s) at low shear rate (10 s^{-1}) the viscosity values are close at high shear rate.

As can be seen from Fig. 1, all the slurries exhibited shear thinning (pseudoplastic flow) behaviour, i.e., apparent viscosity decreases with shear rate. Pseudoplasticity in ceramics slurries usually arises because of the existence of an interparticle network, which

undergoes a gradual breakdown with increasing shear rate, causing the typically observed decrease in viscocity of slurries. The viscosity value of the slurries at high shear rate (1000 s^{-1}) is in the range 0.6-1.1 Pa s indicating that the slurries are pourable under shear[9].

3.2 Thermogravimetric analysis of the yolk

Fig. 2 shows a TGA diagram of yolk recording a total multi step weight loss of 100%. The figure revealed that the first drop in TG appeared at ~100 °C with a weight loss of 55 % from yolk which is due to water evaporation. The second drop occurs in the range of ~100 – 375 °C and experienced ca 22.5 % weight loss which contributed to the removal of lipids. In the temperature range of 375 – 525 °C, the decomposition of proteins occurred with a weight loss of 22.5%. From the graph, it is also evident that at 525 °C, the yolk was completely burned out. Thus, the heating was set up to 600 °C with a dwell time of 1 h to allow ample time for the complete burnout of the yolk for creating pores.

3.3 Characterization of alumina ceramic samples after sintering

The effect of alumina-to-yolk ratio on porosity and sintering shrinkage of the prepared samples can be seen by comparing all samples. Table 1 lists the effects of the different alumina-to-yolk ratio on physical properties (shrinkage and porosity) of the samples. All slurries were stirred for 3 hours with 150 rpm rate and then they were cast in cylindrical stainless steel mold and heated in an air oven at 180 °C for 1 h.

A volume shrinkage of 29.3–39.9 % volume shrinkage was observed over sintering. Porosity of the samples increases as the amount of pore former increases. Porosity of the samples prepared from slurry with alumina-to-yolk ratio of 0.65 to 1.00 was in the range 50.4– 71.7%. Porosity characterization is based on the presence of open pores which are

related to properties such as permeability and surface area of the porous structure. High porosity usually means a high surface area/volume ratio, and thus favors cell adhesion to the porous body and promotes bone regeneration.[13] Generally, the strength of a porous ceramic is strongly affected not only by the strength of the ceramic wall (or strut), but also by the surface flaws on the strut. In order to evaluate the mechanical properties of the samples, compressive strength tests were conducted. The stress increased linearly with the elastic response for all the fabricated samples and then dropped rapidly due to fast fracture. However, the compressive strength was remarkably increased from 1.07 to 4.57 MPa by decreasing the porosity from 71.7 to 50.4 vol.%, as shown in Fig. 3.

Studies on brittle porous materials have demonstrated a relationship between the compressive strength and relative density. The generic expression has the following form[15]:

$$\sigma_{fc} = C(R)^{3/2} \qquad (1)$$

where σ_{fc} is compressive strength, C is a geometric constant characteristic of the unit cell shape, and R is relative density as a percentage of the theoretical value for non-porous massive material. The relative density is related to porosity p by:

$$p = 1 - R \qquad (2)$$

So the relationship between compressive strength and porosity can be expressed as the following form:

$$\sigma_{fc} = C(1 - p)^{3/2} \qquad (3)$$

Based on this Eq. (3), it easy to conclude that the compressive strength of porous ceramics decrease with an increase in porosity, which were represented well by our results.

Fig. 4 shows the FESEM pictures of macro- and microstructures of porous alumina samples prepared from different slurry compositions. The macrostructure shows the pores of 50 - 600 μm diameter (Fig. 4a-b). Diametrical compressive strength of porous alumina samples prepared by the present method decreased from 4.57 to 1.07 MPa when porosity increased from 50.4 to 71.7%. As the amount of yolk increased more micropores found, thus showing poorer densification of particles (Fig. 4c-d). The mechanical properties of a porous material depend on porosity, density of the material.[14] It is worthwhile mentioning that the density of a porous body decreases with the increased level of porosity. Since a higher density usually leads to higher mechanical strength while a high porosity provides a favorable biological environment, a balance between the porosity and density for a porous body must be established for the specific application.

Fig. 5. shows the SEM cross–section of porous alumina samples prepared with varied drying temperatures at alumina-to-yolk ratio of 1.00. The macrostructures show that as the drying temperature incresed, the pore size of porous alumina bodies increased as well. Sintered porous alumina prepared in this work shown pore size increased from 130 to 900 μm as drying temperature increased from 110 to 160 °C. It can be explained that slurry drying at low temperatures resulted in low foaming capacity, hence poor pore generation (Fig. 5a). Pores are surrounded by ceramic walls and struts showing a dense and fine microstructure. Pore interconnectivity observed was not uniform; likely good pore interconnectivity can be associated with big foaming capacity of slurry. The density of

porous sintered bodies from slurry with drying temperature increased from 110 to 160 °C was 28.56% to 57.2 % of the theoretical value of alumina. Previously, we have reported that when the drying time increased, the pores size of alumina bodies increased as well in the range of 100 - 1200 μm.[16]

In protein foaming process developed by Garrn et.al[16] aqueous alumina powder suspensions containing Bovine Serum Albumin (BSA) undergo consolidation on heating at 80 °C. However, the alumina slurries containing yolks found both foaming and consolidating on drying above 110 °C in few minutes. Compared to the protein foaming process which produces porous ceramics with pore size in the range of 50-300 μm the present method is useful for the preparation of porous alumina ceramics with large pores (up to 900 μm). [17]

4. Conclusion

A simple process for preparation of porous alumina ceramics using egg yolk both as consolidating and foaming agent has been demonstrated. The physical properties (pores size, shrinkage, porosities and compressive strength) of the samples were controlled by adjusting the initial yolk contents employed in the slurry and temperature of drying process. Sintered alumina bodies with a porosity of 50.4–71.7% and diametrical compressive strength of 1.1–4.6 MPa were obtained. With macropores of 50 – 900 μm in diameter, the obtained porous alumina are suitable for scaffold application in biomedicine.

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Tables

Table 1. Measured volume shrinkage and porosity of the samples produced with various alumina-to-yolk ratios in the slurries

Alumina-to-yolk ratio (w/w)	1.00	0.83	0.75	0.65
Volume shrinkage (%)	29.3	32.5	36.4	39.9
Porosity (%)	50.4	54.7	70.3	71.7

Figure legends

Fig. 1. The influence of alumina-to-yolk ratio on the rheological properties of slurries.

Fig. 2. TGA diagram of yolk.

Fig. 3. Compressive strengths of the samples as a function of the porosity.

Fig. 4. FESEM cross–section of porous alumina prepared with suspension with varied alumina and yolk contents: (a) 0.75, (b) 0.65 and grain structure of walls: (c) 0.75, (d) 0.65.

Fig. 5. SEM cross–section of porous alumina prepared with varied drying temperatures: (a) 110, (b) 150, and (c) 160°C. Alumina-to-yolk ratio = 1.00.

Fig. 1

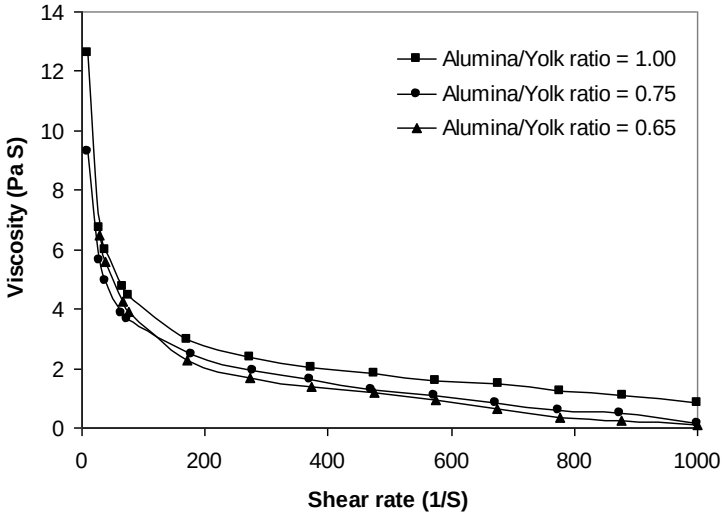


Fig. 2

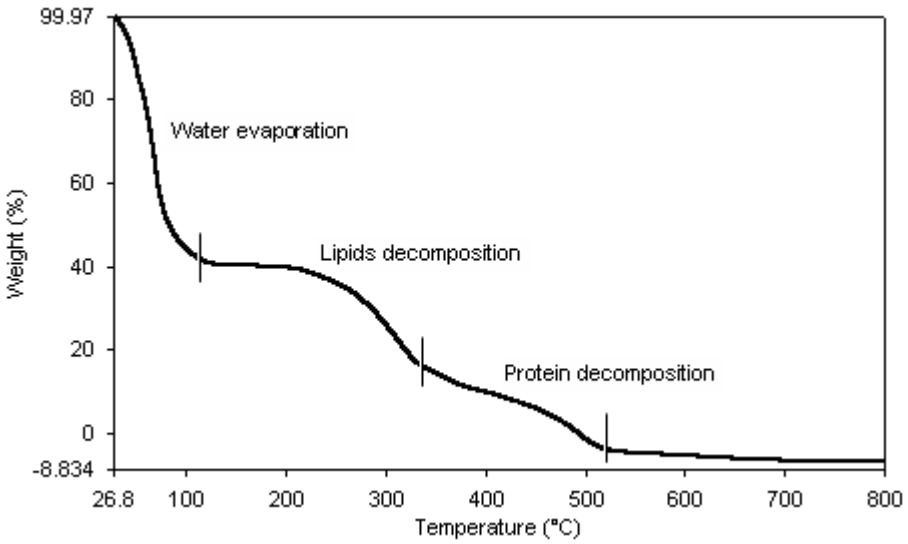


Fig. 3

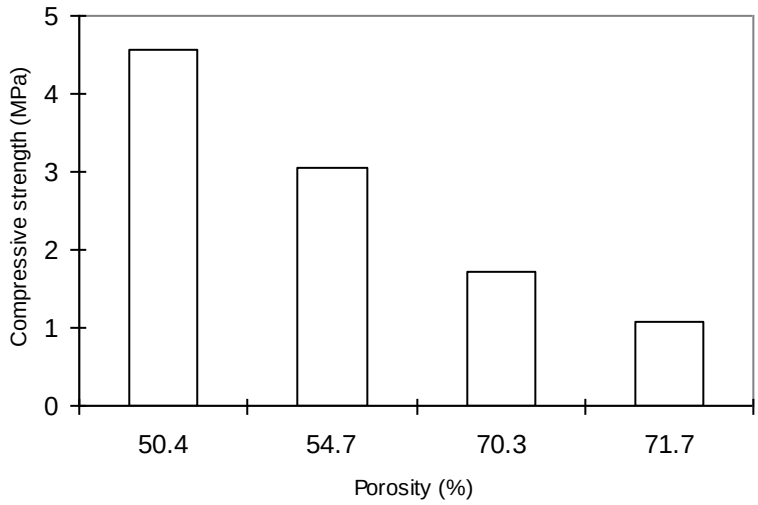
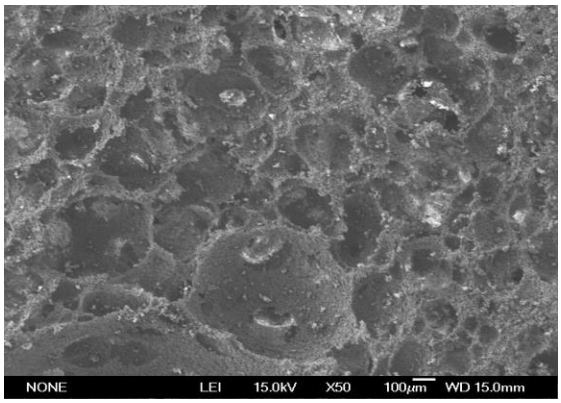


Fig. 4



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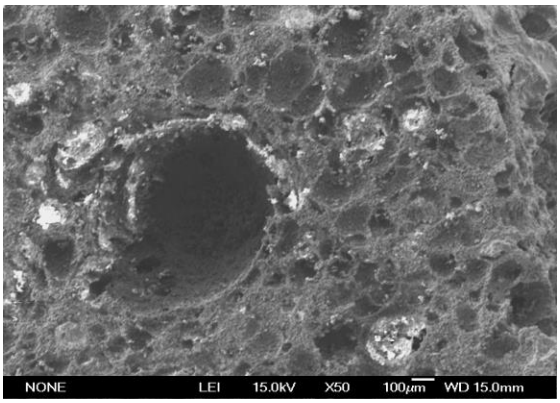

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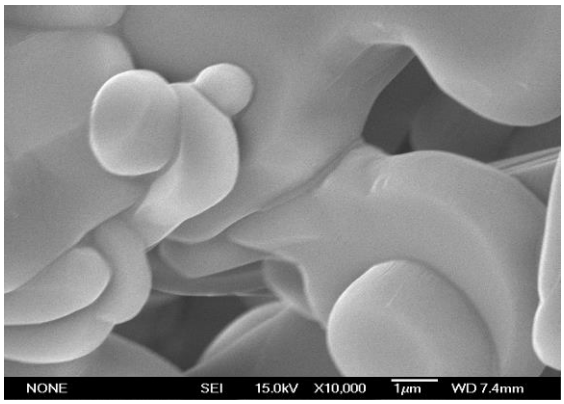

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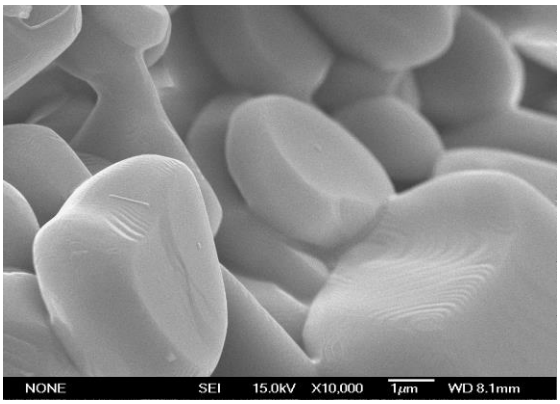

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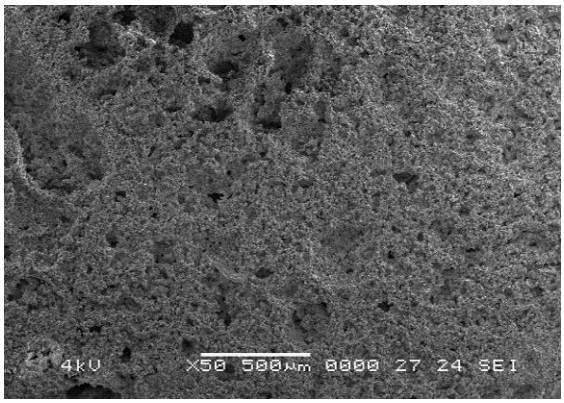
Fig. 5



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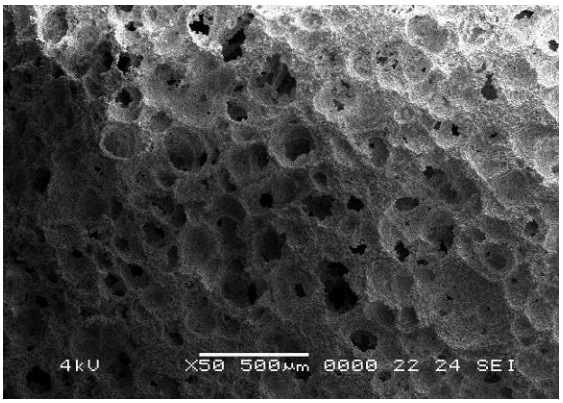

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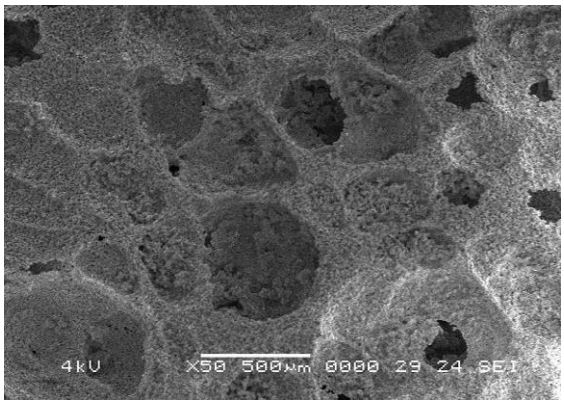

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