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Porous glass-ceramic orbital implants from eggshell

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ABSTRACT

The Calcium silicate porous glass-ceramic material was prepared by using cheaper calcium carbonate from eggshell in this study. The key morphological characteristics of the porous glass-ceramic product were assessed and the capability of this material in body fluid was investigated. The porous glass-ceramic orbital implants derived from different eggshell contents (30 – 50 mol%) in replacement of calcium carbonate in calcium silicate glass systems were fabricated. The microstructure, phase composition, and porosity of glass-ceramic orbital implants both after fabrication at 870ºC and 1000ºC for 2 h and 5 h, and after immersion test in Simulate Body Fluid (SBF) solution for 2 weeks and 1 month were comparatively studied. The maximum contents of eggshell in making the calcium silicate glass is 40 mol%, in which a pure amorphous structure was formed for the fabrication of a glass-ceramic orbital implant. The biocompatible wollastonite phase was obtained after heat treatment at 1000ºC for 2 h. The glass-ceramic orbital implants from eggshells have a uniform distribution of an open-macropore with high porosity in the range of 35-45% for eye tissue ingrowth. Also, good chemical stability in SBF for a 2-month test was obtained in this alternative low-cost eggshell derived porous glass-ceramic for ocular prosthesis applications.

INTRODUCTION

The removal of the patient's eye has proceeded for the treatment of ocular disease and traumatic eyes. The artificial eyes or "orbital implants" are required to replace into an empty socket after surgical removal of those eye diseases (Figure 1). Orbital implants are commonly divided into two groups. A spherical-solid orbital implant is made of polymethyl methacrylate and glass, which is not costly. However, the extraocular muscles cannot directly attach to the orbital implants for the ocular prosthesis movement. Meanwhile, another spherical-porous orbital implant is made of alumina ceramic, hydroxyapatite, and polyethylene polymer [1,2]. The porous orbital implants provide an abundance of pores for ingrowth of fibrovascular tissue to fasten the implants to orbital tissues. However, the porous materials are relatively high cost and non-negligible extrusion rates increase the risk of infection [3].

Biocompatible calcium-silicate porous glass-ceramic, therefore, have been developed to overcome these problems for producing orbital implants [4]. Since, the manufacturing of calcium-silicate porous glass-ceramic uses calcium carbonate as a major raw material, the commercial calcium carbonate is replaced with the eggshell waste due to the high content of calcium oxide > 94% by weight of eggshell [5]. Previously, eggshells have been used for producing the bio-ceramic artificial bone [6] and glass foams for electronic devices [7], but it has been rarely used for making porous glass-ceramic orbital implants.

The researchers, therefore, have developed the biomedical calcium-silicate porous glass-ceramic from eggshell for producing the orbital implants. The effects of eggshell ratios and firing temperatures on their biochemical and physical properties of calcium-silicate porous glass-ceramic have been investigated. The efficiency of biocompatible phase developed in eggshell derived calcium-silicate porous glass-ceramic was discussed after *in vitro* test in simulated body fluid (SBF) for 1 month to announce the suitable material ratio and processing conditions for producing a prototype of low-cost and biocompatible calcium-silicate porous glass-ceramic orbital implants.

METHODOLOGY

The porous glass-ceramic orbital implants derived from different eggshell contents as shown in Table 1 were fabricated and tested. The glasses were prepared by melting a mixture of high purity silica oxides (SiO_2), carbonates from eggshell ($CaCO_3$), and sodium carbonate ($NaCO_3$) in an alumina crucible at 1500˚C for 1 h and then quenched in air. The rigid glass was annealed at 500˚C for 30 min and ground by planetary milling. Then, glass powder was sieved through 230 mesh stainless steel sieves. A polyurethane (PU) 45-ppi sponges as a porous template were dipped into a water-based glass slurry prepared from 40 wt% glass powder, 6 wt% PVA binder and 54 wt% water and dried for

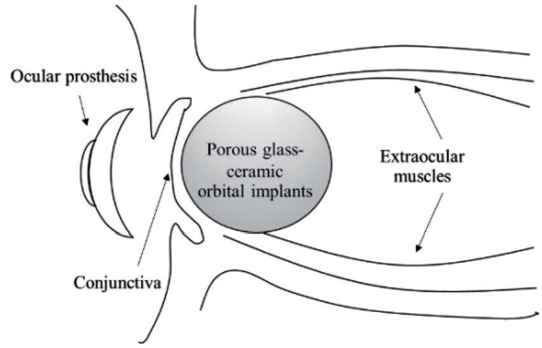


Figure 1. Schematic of a porous sphere orbital implant.

Table 1. Prepared glass compositions.

Composition (mol%)		
Eggshell ($CaCO_3$)	$NaCO_3$	SiO_2
30	10	60
35	10	55
40	10	50
45	10	45
50	10	40

24 h at room temperature, the dipped sponges were heated at 870˚C for 2 h, 870˚C for 5 h and 1000˚C for 2 h with heating rate 5˚C/min to remove the PU sponges and form the porous structures.

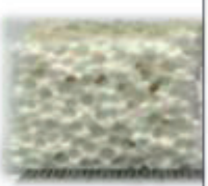
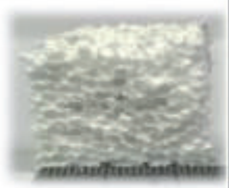
A Bruker D8 ADVANCE XRD was used to confirm crystalline phases. The porosity of glass-ceramic sample was calculated through weights determined by the Archimedes method. Microstructures of glass-ceramic samples with Au-coat were examined by SEM-EDS (JEOL JSM-6010 LV). Porous glass-ceramic samples were immersed in Kokubo's simulated body fluid (SBF, pH = 7.40) [3] at 37˚C for 1 month for *in vitro* solubility test. The weight losses (%) of samples were determined via the dry-mass change of samples after the immersion test.

RESULTS AND DISCUSSION

The maximum contents of eggshell waste in making the calcium silicate glass is 40 mol%, in which a pure amorphous structure was formed for the fabrication of a glass-ceramic orbital implant (Table 2). Meanwhile, above 40-mol% eggshell led to the recrystallization in calcium silicate glasses. The transparent glass became the opaque one suggesting the high calcium in the molten glasses is not suitable for preparing the calcium silicate glass-ceramic samples. Compared to the samples heated at 870°C, wollastonite ($CaSiO_3$) major phase accompanied and sodium-calcium silicate phase ($Na_2Ca_3Si_6O_{16}$) minor phases, which are highly biocompatible phases for implantable devices, were found in the eggshell porous glass-ceramic samples after sintering at 1000°C (Figure 2). Also, the physical appearance of samples sintered at 1000°C was very pure white compared to the yellowish samples from 870°C-sintering. The result is in good agreement with earlier studies on wollastonite phase development in calcium-silicate glasses from commercial raw materials [8-9]. Moreover, an increase in the eggshell contents affected the reduction of the peak at 2θ ~ 18º which is corresponding to the $Na_2Ca_3Si_6O_{16}$ phase (Figure 3). This was due to the $Na_2Ca_3Si_6O_{16}$ peak disappeared and wollastonite ($CaSiO_3$) became the predominant phase upon heating and CaO content [10].

Microstructures of eggshell porous glass-ceramic in Figure 4 shows a similar evolution of porous structure in glass-ceramic in the samples sintered between 870ºC and 1000ºC. The glass-ceramic orbital implants from eggshell has a uniform distribution of an open-macropore. The porosity independence of eggshell contents was in the range of 35 – 45% which is slightly less than that of bio-implants reported in the earlier study [11]. However, rough surfaces were developed in the glass-ceramic samples when the sintering temperature below 1000ºC (Figure 4(a)–(b)). This probably due to the pore residue from glass fusing with CaO to form the wollastonite phase, and the high viscosity of molten glass at high temperature prevents a smoother surface forming [12]. The presence of wollastonite crystals with a high amount of Ca/Si ratio was found on the strut surface with the normalized Ca/Si ratio ~0.8-0.9 compared to other areas (~0.12) in the glass-ceramic implants from eggshells sintered at 1000°C (Figure 4(c)–(d)). After a 1-month

Table 2. Prepared glass and porous glass-ceramic from different eggshell contents.

	Egg shell (mol%)				
	30	35	40	45	50
Melted Glass					
Porous glass-ceramic				-	-

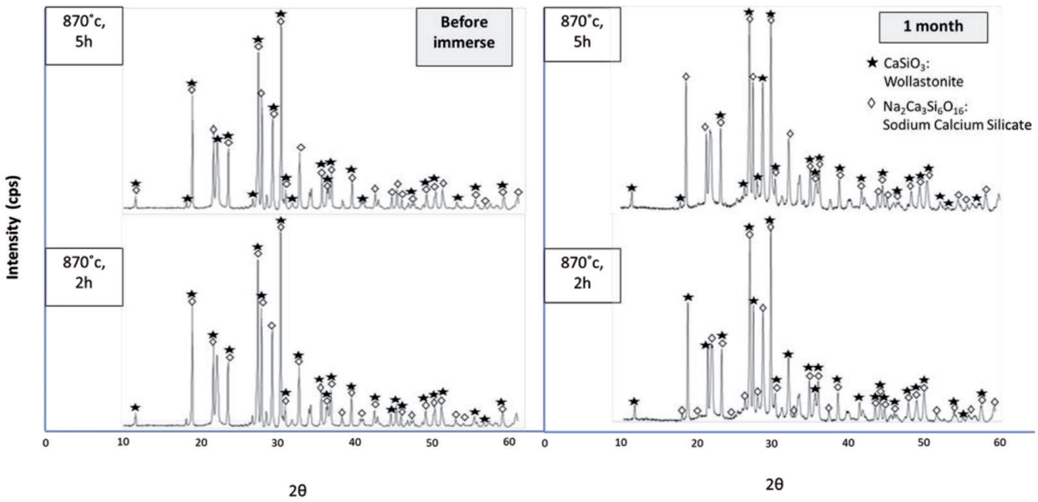


Figure 2. XRD of sintered (30 mol%) eggshell porous glass-ceramic from different eggshell contents before and after a 1-month in *vitro* test.

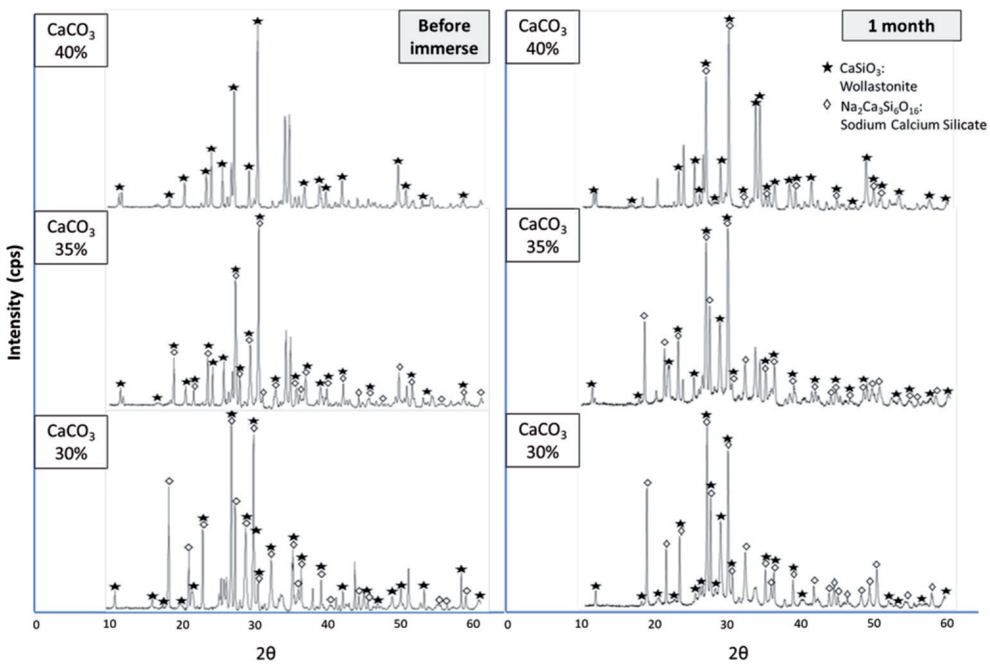


Figure 3. XRD of sintered (1000ºC for 2 h) eggshell porous glass-ceramic from different eggshell contents before and after a 1-month SBF *in vitro* test.

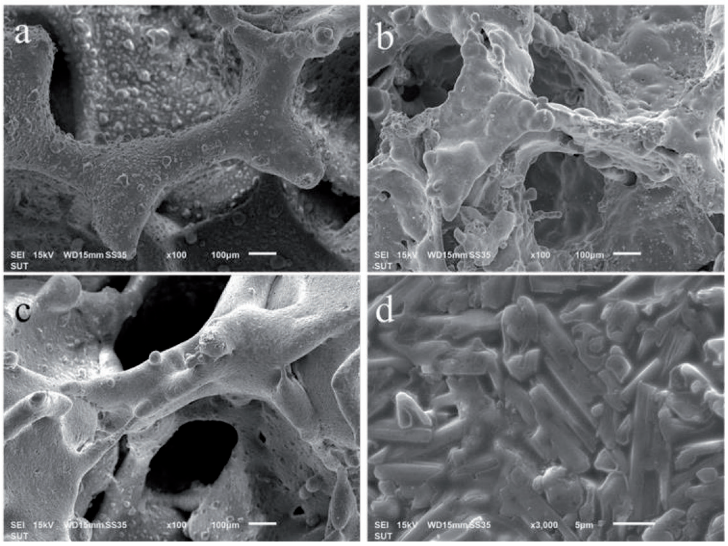


Figure 4. Microstructures of sintered eggshell porous glass-ceramic; (a) 870°C for 2 h at low magnification, (b) 870°C for 5 h at low magnification, (c) 1000°C for 2 h at low magnification, (d) 1000°C for 2 h at high magnification showing Wollastonite ($CaSiO_3$) crystals on the strut surface of porous glass-ceramic samples.

in vitro test, microstructures of porous glass-ceramic with 40 mol% eggshell was changed compared to other samples (Figure 5). This could be involved with the weight change related to the partial dissolution of the glass-ceramic sample in the SBF solution which is discussed in the next session.

After the *in vitro* test in SBF, the weight loss could take place by the direct contact between calcium-silicate based materials and SBF solution resulted in a partial dissolution and producing an ionic exchange of Ca^{2+} for $2H^+$ in materials. The reaction leads to a formation of Si–O–H groups on the surface of porous glass-ceramic samples and subsequently a partial dissolution of amorphous SiO_2 as SiO_3^{2-} [13]. Weight loss was slightly observed after a 1-months *in vitro* test in the porous glass-ceramics with 40 mol% eggshell. This probably due to the leaching out of Na ions in the $Na_2Ca_3Si_6O_{16}$ minor phase during SBF immersion that is required further investigation. However, no significant mass-losses were detected in the porous glass-ceramic implants derived from eggshells in the range of 30-35 mol% after a 1-month *in vitro* test (Figures 6 and 7). The dry weights of all eggshell porous glass-ceramic implants remained stable, which confirmed good stability in a biological environment of the glass-ceramic implants derived from eggshells in this study. Therefore, this porous glass-ceramic material is a promising alternative low-cost biomedical implant for ocular prosthesis applications.

CONCLUSIONS

In this study, biomedical calcium-silicate porous glass-ceramic from eggshell was studied for producing orbital implants. The optimum eggshell ratios and firing temperatures on their biochemical and physical properties have been investigated. The findings are as follows:

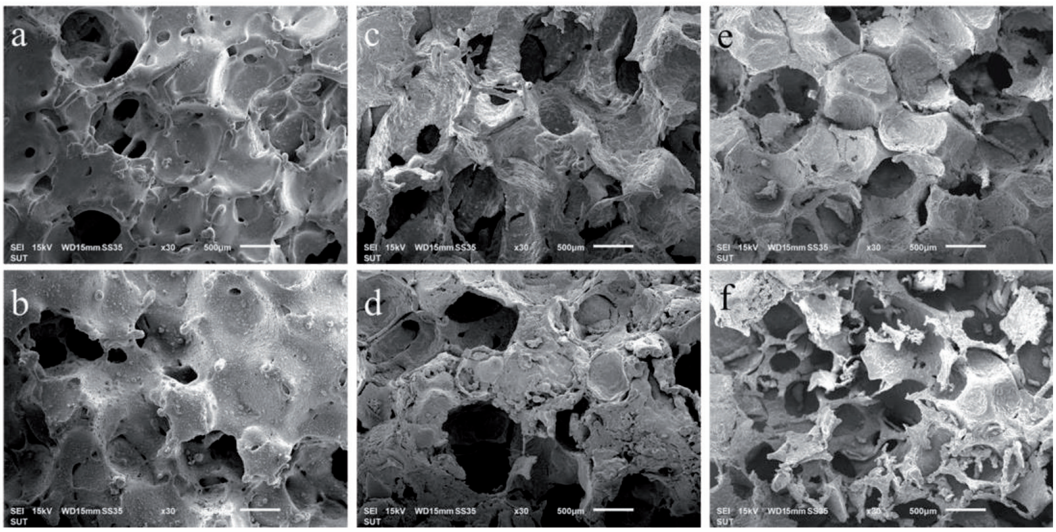


Figure 5. Microstructures of sintered eggshell porous glass-ceramic at 1000°C for 2 h; (a,b) 30 mol%, (c,d) 35 mol% and (e,f) 40 mol% eggshell: (a,c,e) before *in vitro* test and (b,d,f) after a 1-month *in vitro* test.

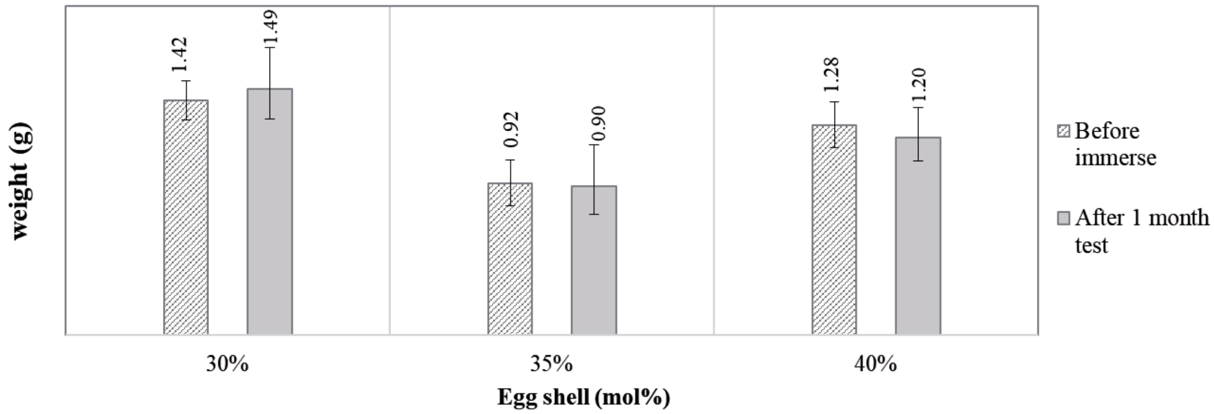


Figure 6. Weight of sintered (1000ºC for 2 h) eggshell porous glass-ceramic from different eggshell contents before and after immersion test in SBF for 1 month.

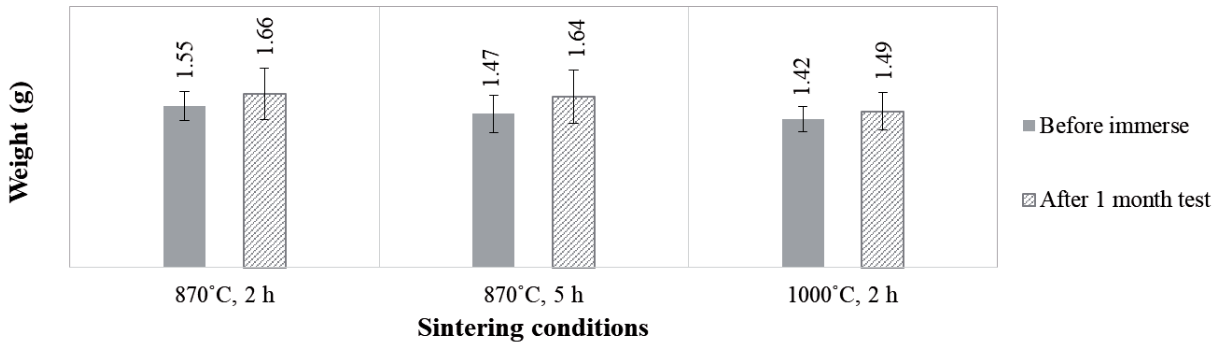


Figure 6. Weight of sintered eggshell porous glass-ceramic before and after the immersion test in SBF for 1 month.

1. The maximum contents of eggshell waste in making the calcium silicate glass is 40 mol%.

2. The biocompatible wollastonite ($CaSiO_3$) major phases were obtained after heat treatment at 1000ºC for 2 h.

3. The egg shell-derived glass-ceramic implants contained an open-macropore network with porosity over 40% allowing the fibrovascular tissue ingrowth.

4. Weight loss was found after a 1-months *in vitro* test in the porous glass-ceramics with 40 mol% eggshell indicating the eggshell glass-ceramics with good stability in the biological environment can be obtained with the eggshell at below 40 mol%.

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