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Research Article

THERMO-MECHANICAL PROPERTIES OF BIO-INSULATION FROM EMBEDDING BIRD EGGSHELL INTO CERAMICS FOR BIOENGINEERING APPLICATIONS

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ABSTRACT

Incorporating bird eggshell in porcelain can improve its physical, thermal, and mechanical properties, resulting in dense porcelain products. Calcium carbonate ($CaCO_3$) from eggshells can react with silica (SiO_2) and alumina (Al_2O_3) in porcelain clay to form calcium feldspar or anorthite ($CaAl_2Si_2O_8$), which lowers the sintering temperature to <1000 °C. In this study, 0, 5, 10, 15, and 20 vol.% bird eggshell powder was added to porcelain slips and fired at 600, 700, 800, and 900 °C for 1, 3, and 5 h. The best formula of porcelain product having good mechanical and thermal properties was obtained at 10 vol.% quail eggshell-added porcelain fired for 5 h at 900 °C. The obtained sample demonstrated a relatively low thermal expansion coefficient (1.0515×10^{-6} °C^{-1}), high compressive strength (6200 N mm^{-2}), and high hardness (12.2 ± 0.30 HV).

Keywords: Bird eggshell; Soft and hard porcelain; Hardness; Bioengineering, and Thermal Property.

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INTRODUCTION

Porcelain clay is an important type of clay that can be used to produce various products, such as clayware, fillers (in ink, paper, paint, animal feedstock, and petroleum and petrochemical products), bricks, tiles, electrical and thermal insulation, and cement for construction [1, 2]. Porcelain is produced by heating ceramic materials at a high temperature (1200–1400 °C). The toughness, translucence, and strength of porcelain relative to other types of pottery originate from vitrification and mullite formation at high temperatures. Porcelains can be divided into three types (hard, soft, and bone china), depending on the composition and source of clay used and the firing conditions [3–5].

Calcium carbonate ($CaCO_3$) is one kind of the most popular mineral fillers and diluent used in many industries i.e. polymer, ceramic, ink, paint, cosmetics, drug, animal food, paper, fertilizer, and calcium supplement [6–8]. $CaCO_3$ is an inorganic, abundant, biofriendly, renewable, and low-cost material [9–10]. Eggshell obtained from hen, duck, or bird has a rich source of mineral salts, comprising mainly $CaCO_3$ or ~96 wt.% calcite. It is a good candidate for use as a bio-ceramic filler for preparing various ceramic products [9–10]. In addition, it is a major product of the food industry and is produced in large quantities daily. Furthermore, $CaCO_3$ can increase thermal resistance, act as a processing aid, improve productivity, increase mechanical property, low specific heat, and low thermal expansion coefficient [11]. Ground eggshell is an effective liming source, as shown in Eqs. (1) and (2), and functions as a clay stabilizer [12]:

$$CaCO_3 \text{ --------> } CaO + CO_2 \tag{1}$$

$$CaO + H_2O \text{ ---------> } Ca(OH)_2 \tag{2}$$

$CaCO_3$ can react with silica (SiO_2) and alumina (Al_2O_3) in porcelain clay to form anorthite ($CaAl_2Si_2O_8$), calcium silicate ($CaO.SiO_2$), mullite ($Al_2O_3.SiO_2$), and wollastonite ($CaSiO_3$) at high temperatures, as shown in Eq. 3 [13] and Scheme 1.

$$CaO + Al_2O_3.2SiO_2 \text{ ------> } CaO.Al_2O_3.2SiO_2 \tag{3}$$

The objective of this work was to fabricate soft and hard porcelain products by adding 0, 5, 10, 15, and 20 vol.% bird eggshell powder and firing at relatively low temperatures (600, 700, 800, and 900 °C) for 1, 3, and 5 h. We added bird eggshell powder in porcelain products to reduce the firing temperature and increase the mechanical and thermal properties of porcelain products. The microstructures, phase formation, thermal expansion coefficient, specific surface area, and mechanical properties of the obtained porcelain samples were characterized using Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), dilatometer, Brunauer–Emmett–Teller (BET), and extensometer, respectively.

1. EXPERIMENTAL PROCEDURE

2.1 Materials and Methods

Bird eggshells were cleaned with tap water and left to dry in the air at room temperature for 1–2 days. The cleaned quail eggshells were grounded with the rapid ball mill for 120 min to fine micron-sized eggshell powder, as shown in Scheme 2.

Porcelain clay purchased from Compound Clay Co., Ltd., Thailand, was used as a raw material for making clay products by the slip casting process.

Sodium silicate was used as a dispersing agent or the deflocculant of porcelain clay particles for the slip preparation purchased from Compound Clay Co., Ltd., Thailand. The sodium silicate solution was prepared at a sodium silicate-to-water ratio of 20:1. The solution of sodium silicate was added to adjust the viscosity of the slip, and the ratio between the porcelain clay and sodium silicate solution was 100:0.250 kg.

2.2 Preparation of Porcelain Clay Products

The weight ratio of porcelain clay: water: sodium silicate was 10:5:0.001 kg. All raw materials were stirred for 1 h to obtain the slip or slurry. Then, 0, 5, 10, 15, and 20 vol.% bird eggshell powder was added to the slips and stirred for 45 min. After that, the porcelain slips were poured into a dried plaster mold and left to solidify in a plaster mold and cast to dry at room temperature, as shown in Scheme 3a. The dried porcelain samples were fired at 600, 700, 800, and 900 ^{o}C for 1, 3, and 5 h at each firing temperature, respectively, as shown in Scheme 3b. The physical (appearance, bulk and true density, water absorption, shrinkage, microstructure, and phase formation), thermal (thermal expansion coefficient), and mechanical properties (compressive strength, hardness, crack formation) of porcelain clay products were characterized. In addition, porcelain can be applied for bioengineering, biomedical and dental application as shown in Scheme 3c.

2.3 Instruments

2.3.1 X-ray diffraction (XRD) measurements were performed and analyzed using an analyzer (Bruker, D8 Discover) with a VANTEC-1 detector and a double-crystal wide-angle goniometer. Scans were obtained from 10° to 80° 2θ at a scan speed of 2° 2θ/min in 0.02° 2θ increments using Cu Kα radiation ($\lambda = 0.154$ nm). Peak positions were compared with standard JCPDS files to identify crystalline phases.

2.3.2 Cumulative mass and fractional distribution were measured using a particle size analyzer (Mastersizer S long bed, model Polydisperse 2.19). The samples were dispersed in a water medium and vibrated in an ultrasonic cleaner for 20 min.

2.3.3 True density of samples was measured according to ASTM B212-72 by a gas pycnometer (Quantachrome, Ultra pycnometer 1000) for raw materials (quail eggshell and porcelain clay) and soft and hard porcelain products. The true density values of raw materials and porcelain products were calculated according to ASTM C 373-72 using Eq. 4:

$$\rho = \frac{Weight\ (D)}{True\ volume} \tag{4}$$

where ρ is the true density, D is the weight of the dry sample (g), and true volume is the volume of only the solid component. It can be determined by crushing the piece into a fine powder so that all pores are destroyed and then using the gas pycnometer method for the powder.

2.3.4 The bulk densities of samples were measured according to ASTM B212-72 by a gas pycnometer (Quantachrome, Ultra pycnometer 1000) before and after the firing of porcelain products. Bulk density values of soft and hard porcelain samples were calculated according to ASTM C 373-72 using Eq. 5:

$$\rho = \frac{Weight\ (D)}{Apparent\ volume} \tag{5}$$

where ρ is the bulk density, D is the weight of the dry sample (kg), and apparent volume is the volume of sample including open pores and closed pored within the sample.

2.3.5 SEM micrographs were obtained using a scanning electron microscope (SEM, JEOL-5200). The samples were mounted on a stub using carbon paste and sputter-coated with ~0.1 µm gold to improve conductivity. An acceleration voltage of 20 kV was used with 5,000–10,000X magnification.

2.3.6 The specific surface area, pore size, and surface distributions were measured using AUTOSORB-1 (QUANTACHROME) by determining the quantity of gas adsorbed onto or desorbed from the solid surface at some equilibrium vapor pressure by the static volumetric method. The specific surface area, S, of the solid can be calculated from the total surface area and sample weight according to Eqs. 6 and 7 as follows:

$$S = S_t/W \tag{6}$$

$$S = \frac{W_m N A_{cs}}{M} \tag{7}$$

where S is the specific surface area of the solid, S_t is the total surface area, W is the sample weight, N is Avogadro's number (6.023×10^{23} molecules.mol^{-1}), M is the molecular weight of the adsorbate, and A_{cs} is the area occupied by one adsorbate molecule (16.2×10^{-20} m^2 for N_2).

2.3.7 A rapid porcelain pot mill model (RM 1105) with a speed of 500 rpm was supplied from Compound Clay Co., Ltd., Thailand. The rapid mill was composed of a porcelain pot and balls functioned by an electric motor for grinding eggshells to prepare porcelain products.

2.3.8 The hardnesses of the fired porcelain samples were measured by a hardness testing machine (Mitutoyo, MVK-H1).

2.3.9 The compressive strengths of the fired samples were measured by a universal testing machine (UTM, Hounsfield, H50KS).

2.3.10 A dilatometer (Netzsch, DIL402PC) was used to measure the thermal expansion coefficient of the fired porcelain clay products with dimensions 5 mm x 5 mm x 25 mm, as shown in Scheme 4.

2. RESULTS AND DISCUSSION

3.1 Physical Properties of Porcelain Clay Products

The physical properties of porcelain clay products such as the true density, bulk density, specific surface area, and pore diameter are tabulated in Table 1. The particle size of quail eggshell powder is bigger and rougher than that of the porcelain clay. The true density, average particle size, specific surface area, and pore diameter of quail eggshell powder were 2.30 g.cm^{-3}, 312.86 μm, 0.68 m^2.g^{-1}, and 26.79 nm, respectively, whereas those of the porcelain clay were 1.70 g.cm^{-3}, 39.98 μm, 19.92 m^2.g^{-1}, and 18.33 nm, respectively. In general, there are three types of pores formed by gas adsorption: (i) pores with openings exceeding 500 Å in diameter are macropores, (ii) pores with diameters below 20 Å are micropores, and (iii) pores with sizes between those of macropores and micropores are mesopores. Therefore, the quail eggshell powder and porcelain had mesopores.

The comparison between the particle size distributions of bird eggshell powder and porcelain clay is shown in Figures 1a and 1b. The d_{10}, d_{50}, d_{90}, and d_{avg} of bird eggshell powder grounded for 120 min were 68.21, 286.03, 596.99, and 312.86 µm, respectively, whereas the d_{10}, d_{50}, d_{90}, and d_{avg} of the porcelain clay were 0.94, 16.92, 109.07, and 39.98 µm, respectively. The particle size of the porcelain clay was smaller than that of the bird eggshell powder. Therefore, we added a small amount of sodium silicate as a deflocculant to prevent agglomeration and disperse the porcelain and quail eggshell particles within the medium.

The chemical compositions of the bird eggshell powder and porcelain clay measured by X-ray Fluorescence (XRF) are shown in Table 2. The main composition of the bird eggshell powder was $CaCO_3$ (96.23 wt.%), while other oxide compounds constituted only 3.77 wt.% of the eggshell powder. Moreover, the porcelain clay comprised SiO_2 (71.09 wt.%), Al_2O_3 (21.20 wt.%), K_2O (1.75 wt.%), and other oxide compounds (0.97 wt.%).

Table 3 shows the true and bulk density values of the porcelain clay samples with and without the addition of 0, 5, 10, and 15 vol.% eggshell powder by the slip casting process before firing. The porcelain clay samples with 20 vol.% eggshell powder demonstrated brittleness because of the excess amount of bird eggshell powder.

The water absorption, bulk and true densities of fired porcelain samples with and without 0, 5, 10, 15, and 20 vol.% bird eggshell fired at 600, 700, 800, and 900 °C for 1, 3, and 5 h are tabulated in Table 4 and shown in Figure 2. When the firing temperature increased, the water absorption and true density values of the samples also increased. At the same firing temperature, a higher percentage of bird eggshell decreased the percentage of water absorption but increased the percentage of shrinkage and true density values. The excess amount of quail eggshell above 20 vol.% caused brittleness and crack formation. The optimal condition in terms of the fired porcelain sample characteristics was the sample encoded 10-5-900. The sample 10-5-900 means 10 vol% bird eggshell powder adding-firing time 5 h-firing temperature at 900°C. The percentage of water absorption, shrinkage, average bulk density, and true density of this sample were 5.54 ± 0.62%, 16.47 ± 0.23%, 1.87 ± 0.08 $g.cm^{-3}$, and 2.42 ± 0.11 $g.cm^{-3}$, respectively. Meanwhile, the porcelain sample without bird eggshell powder (0-5-900) had a percentage of water absorption, shrinkage, average bulk density, and true density of 6.95 ± 0.18%, 14.54 ± 0.07%, 1.79 ± 0.05 $g.cm^{-3}$, and 2.29 ± 0.07 $g.cm^{-3}$, respectively.

3.2 Phase Transformation of Porcelain Clay Products

The XRD patterns of raw materials (commercial $CaCO_3$, quail eggshell, and porcelain clay) and porcelain products with 5, 10, and 15 vol.% bird eggshell powder fired at 800 and 900 °C are shown in Figure 3. The XRD pattern of bird eggshell is similar to that of commercial $CaCO_3$, consistent with the JCPDS file nos. 01-072-1937 and 01-085-1108 in terms of rhombohedral phase formation at 2θ 29.34°(104), 35.94°(110), and 39.37°(113), whereas the XRD pattern of the porcelain clay was consistent with the JCPDS file no. 01-089-

8936 that belongs to silicon dioxide or quartz (SiO_2, hexagonal phase formation) at 2θ 20.79° (100) and 26.57° (011) and JCPDS file no. 00-031-0026 of aluminum oxide (Al_2O_3) at 2θ 10.99°, 12.27°, and 20.94°, respectively. The XRD pattern of the porcelain sample with 20 vol.% bird eggshell powder before firing corresponded to $CaCO_3$, SiO_2, and Al_2O_3 of JCPDS file no. 00-003-0418 in terms of calcium magnesium aluminum silicate (CaMgAlSiO). While the XRD peak patterns of porcelain products with quail eggshell powder fired at 800 and 900 °C (5-3-800, 10-5-900, and 15-1-800) demonstrated the same peak position based on JCPDS file no. 01-089-1459 corresponding to calcium feldspar ($Al_2CaO_8Si_2$).

The SEM micrographs of samples (raw materials and bird eggshell powder-added porcelain products after firing) are shown in Figure 4. The microstructures of bird eggshell powder and porcelain clay are shown in Figures 4a and 4b. Both bird eggshell and porcelain particles were easily agglomerated. Therefore, the porcelain samples required sodium silicate as a deflocculant to disperse particles in the water medium by the slip casting process. The microstructures of porcelain samples without bird eggshell powder (0-3-900) are shown in Figures 4c and 4c-1. When the percentage of bird eggshell powder in porcelain products increased effect to good firing completion, and increased the physical-mechanical-thermal properties, as shown in Figures 4e and 4e-1 (10-5-900). However, the percentage of bird eggshell in porcelain products increased porosity (as for 15-1-800) within the microstructure, as shown in Figures 4f and 4f-1 due to CO_2 release. Furthermore, up to 20 vol.% bird eggshell powder in porcelain affects brittleness and crack development due to the release of excess CO_2.

3.3 Thermal and Mechanical Properties of Porcelain Clay Products

Raw materials (bird eggshell powder and porcelain clay) and porcelain products with 5, 10, and 20 vol.% bird eggshell powder before firing were characterized by the percentage of residue mass using TGA and thermal reaction by DTA from room temperature (27 °C) to 1200 °C, as shown in Figure 5. Bird eggshell powder had a percentage of residue mass equal to 53.55 wt.% at 820 °C. There is a low percentage of residue mass due to CO_2 decomposition during heating. While the porcelain clay had a percentage of residue mass of 93.23 wt.%, and two peak positions were observed at 50 and 510 °C due to the moisture and organic matter contents. When 5, 15, and 20 vol.% bird eggshell powder was added to the porcelain samples, they demonstrated a few degrees of peak shift in percentages of residue mass. The percentage of residue mass and three endothermic peaks of the porcelain sample with 5 vol.% bird eggshell powder was 87.60 and at 47, 480, and 700 °C, respectively, due to the moisture, organic matter, and CO_2 release from the decomposition of $CaCO_3$ to CaO, respectively. The porcelain sample with 15 wt.% bird eggshell powder had 87.03 wt.% residue mass and three types of the same endothermic peak reactions at 50, 500, and 740 °C, respectively, whereas the porcelain sample with 20 wt.% bird eggshell powder had 83.99 wt.% residue mass and the same endothermic peak reactions at 50, 500, and 760 °C, respectively. The percentage of bird eggshell powder added to porcelain clay directly affects the phase transformation to obtain $Al_2CaO_8Si_2$, consistent with the obtained XRD results. An increased percentage of bird eggshell powder lowered the percentage of residue mass but led to a higher degree of the third endothermic peak.

The data of the thermal expansion coefficient are tabulated in Table 5. The thermal expansion coefficient of the porcelain sample without bird eggshell powder (0-3-900) was equal to 6.64×10^{-6} $(°C)^{-1}$. Meanwhile, the porcelain samples 10-5-900 and 15-1-800 had low thermal expansion coefficient values equal to 1.05×10^{-6} and 1.12×10^{-6} $(°C)^{-1}$, respectively. This indicates a high melting temperature and good thermal stress resistance. Furthermore, the factors that affect the thermal properties are the amount of bird eggshell powder in porcelain products, firing temperature, and firing time. The porcelain samples with the excess amount of bird eggshell powder fired at a relatively high firing temperature and long firing time showed brittleness, i.e., sample encoded 15-3-900, 20-y-800 (y = 1, 3, and 5 h), and 20-y-900 (y = 1, 3, and 5 h), consistent with the physical property results in Table 4.

The mechanical properties (compressive strength and hardness) are tabulated in Table 6. When the amount of bird eggshell powder added in porcelain samples increased, the compressive strength and hardness of the samples increased. However, the excess of bird eggshell powder decreased both the compressive strength and hardness values due to the decomposition of CO_2 from $CaCO_3$, consistent with the obtained SEM results shown in Figures 4g and 4g-1.

3. CONCLUSIONS

Bird eggshell offers an excellent $CaCO_3$ source that can be used as a bio-ceramic filler due to low cost, abundance, and aid in increasing the mechanical and thermal properties of porcelain products. When the percentage of bird eggshell powder was added to porcelain products, it increased the true density, percentage of shrinkage, thermal resistance, and compressive strength but reduced the water absorption of the porcelains. On the other hand, adding excessive amounts of quail eggshell powder caused fracture and brittleness because

CO_2 was released from the chemical reaction of $CaCO_3$ during the firing process. In addition, firing temperature and firing time can help to control the physical, thermal, mechanical properties of porcelain products. The best conditions that achieved porcelain products with optimal characteristics included 10 vol.% eggshell powder fired at 900 °C for 5 h. Moreover, $CaCO_3$ from bird eggshell powder can react to SiO_2 and Al_2O_3 particles within the porcelain clay structure to form $Al_2CaO_8Si_2$, depending on the percentage of bird eggshell powder, firing temperature, and firing time. The porcelain samples without bird eggshell powder (i.e., 0-3-900 and 0-5-900) had a high percentage of water absorption (6.95 ± 0.18%) and thermal expansion coefficient (6.64×10^{-6} $(°C)^{-1}$) but a low percentage of shrinkage (14.54 ± 0.07%), true density (2.29 ± 0.07 $g.cm^{-3}$), and mechanical properties (2768 $N.mm^{-2}$ and 10.4 ± 0.4 HV) that resulted in incomplete densification. In this study, we obtained both hard and soft porcelain products (15-1-800 and 10-5-900), which are useful for various applications, such as dental and medical applications (tooth and artificial bone), household wares, adsorbents, catalysts, electrical insulations, spark plugs, and thermal insulators.

Declarations

The authors have no conflict of interests to state.

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Author contributions

The authors provide the experimental design, carrying out the result measurements according to the ASTM, and manuscript composition by ourselves.

Conflict of interests

The authors have no conflict of interests to state.

Data code and availability

ASTM means American Society for Testing and Materials. JCPDS means Joint Committee Powder Diffraction Standards.

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Table Captions

Table 1	Physical properties of bird eggshell and porcelain clay
Table 2	X-ray Fluorescence (XRF) of raw materials (bird eggshell and porcelain clay)
Table 3	Bulk and true density values of samples before firing
Table 4	Water absorption, bulk density, and true density of fired samples
Table 5	Thermal expansion coefficient values of fired samples
Table 6	Mechanical properties of fired porcelain clay products

Figure Captions

Fig. 1	Particle size distribution of a) bird eggshell powder after grinding for 120 min and b) porcelain clay
Fig. 2	a) The percentage of water absorption and shrinkage *vs.* the volume percentage of eggshell powder added to porcelain and b) true and bulk density values *vs.* the volume percentage of eggshell powder added to porcelain
Fig. 3	X-Ray Diffraction (XRD) patterns of raw materials and porcelain products before and after firing
Fig. 4	SEM micrographs with magnifications of 5,000X and 10,000X of a) bird eggshell powder, b) porcelain clay, c) and c-1) porcelain product without bird eggshell (0-3-900), d) and d-1) porcelain product with 5 vol.% bird eggshell (5-3-800), e) and e-1) porcelain product with 10 vol.% bird eggshell (10-5-900), f) and f-1) porcelain product with 15 vol.% bird eggshell (15-1-800), and g) and g-1) porcelain product with 20 vol.% bird eggshell (20-1-700)
Fig. 5	DTA and TGA comparisons between raw materials and porcelain products with and without bird eggshell powder

Scheme 1	Ternary phase diagram of $CaO–Al_2O_3–SiO_2$
Scheme 2	a) raw bird eggshell, b) ground rough bird eggshell, and c) ground fine bird eggshell powder
Scheme 3	Porcelain samples a) before firing, b) after firing, and c) porcelain applications
Scheme 4	Size and shape of the porcelain sample for thermal expansion coefficient measurement

Table 1. Physical properties of bird eggshell and porcelain clay

Sample	True density (g/cm^3)	Avg. particle size (Å)	Specific surface area (m^2/g)	Avg. pore diameter (Å)
Bird eggshell	2.30	312.86	0.68	267.90
Porcelain clay	1.70	39.98	19.92	183.30

Table 2. X-ray Fluorescence (XRF) of raw materials (bird eggshell and porcelain clay)

Chemical composition	**Bird eggshell (% wt)**	**Porcelain (% wt)**
Al_2O_3	-	26.20
SiO_2	0.04	71.09
K_2O	0.11	1.75
CaO	-	0.82
$CaCO_3$	96.23	-
Fe_2O_3	-	0.14
Na_2O	0.23	-
MgO	1.12	-
P_2O_5	1.19	-
SO_3	0.98	-
Cl	0.06	-
SrO	0.02	-
CuO	-	-

Table 3. Bulk and true density values of samples before firing

Samples	Bulk density [a] (g/cm$^{3)}$	True density [b] (g/cm^3)
0%vol bird eggshell adding	1.80	2.29
5%vol bird eggshell adding	1.93	2.44
10%vol bird eggshell adding	1.81	2.35
15%vol bird eggshell adding	1.98	2.52

[a] Bulk density is calculated by d = m/V, which gives the density with all pores as the following:

$$\rho = \frac{\mathit{Weight\ (D)}}{\mathit{Apparent\ volume}}$$

where ρ is the bulk density, D is the weight of the dry sample (kg), and apparent volume is the sample volume, including open pores and closed pored within the sample.

[b] The true density of bird eggshell was measured according to the ASTM B212-72 by Gas Pycnometer (Quantachrome, Ultra pycnometer 1000). The true density of eggshell powder was calculated according to ASTM C 373-72 as the following:

as following: $\rho = \frac{Weight\ (D)}{True\ volume}$

where ρ is the true density, D is the weight of the dry sample (g), and *true volume* is the volume of only the solid component. It may be determined by crushing the piece into powder form so that all pores are destroyed and then using a gas pycnometer method for powder.

Table 4. Water absorption, bulk density, and true density of fired samples (mean ± SD, n = 5)

Samples[a]	Water absorption[b] (%)	Avg. bulk density[c] (%)	True density[d] (g/cm^3)	Samples[a]	Water absorption[b] (%)	Avg. bulk density [c] (%)	True density[d] (g/cm^3)
0-1-600	7.88 ± 0.05	1.47 ± 0.37	2.28 ± 0.51	15-1-600	5.79 ± 0.01	1.55 ± 0.08	2.31 ± 0.10
0-3-600	7.54 ± 0.02	1.50 ± 0.18	2.33 ± 0.25	15-3-600	5.47 ± 0.02	1.58 ± 0.07	2.36 ± 0.09
0-5-600	6.54 ± 0.01	1.51 ± 0.05	2.34 ± 0.07	15-5-600	5.28 ± 0.01	1.60 ± 0.04	2.39 ± 0.05
0-1-700	7.80 ± 0.05	1.52 ± 0.08	2.35 ± 0.11	15-1-700	5.56 ± 0.01	1.64 ± 0.04	2.44 ± 0.06
0-3-700	6.89 ± 0.05	1.53 ± 0.16	2.37 ± 0.22	15-3-700	5.06 ± 0.03	1.65 ± 0.02	2.46 ± 0.02
0-5-700	6.58 ± 0.02	1.55 ± 0.02	2.39 ± 0.03	15-5-700	4.68 ± 0.03	1.67 ± 0.04	2.49 ± 0.05
0-1-800	6.71 ± 0.23	1.77 ± 0.07	2.25 ± 0.10	**15-1-800**	**4.29 ± 0.21**	**2.05 ± 0.09**	**2.63 ± 0.10**
0-3-800	6.77 ± 0.13	1.81 ± 0.17	2.31 ± 0.21	15-3-800	4.55 ± 0.05	1.94 ± 0.07	2.48 ± 0.10
0-5-800	6.84 ± 0.18	1.81 ± 0.10	2.32 ± 0.10	15-5-800	4.60 ± 0.23	1.99 ± 0.06	2.51 ± 0.10
0-1-900	6.71 ± 0.16	1.82 ± 0.17	2.31 ± 0.21	15-1-900	4.58 ± 0.66	1.95 ± 0.08	2.50 ± 0.09
0-3-900	6.77 ± 0.06	1.78 ± 0.13	2.27 ± 0.16	15-3-900	4.64 ± 0.40	1.99 ± 0.03	2.53 ± 0.03
0-5-900	6.95 ± 0.18	1.79 ± 0.05	2.29 ± 0.07	15-5-900	4.54 ± 0.16	1.95 ± 0.10	2.48 ± 0.11
5-1-600	6.84 ± 0.01	1.55 ± 0.05	2.30 ± 0.06	20-1-600	5.38 ± 0.04	1.43 ± 0.01	2.27 ± 0.07
5-3-600	6.43 ± 0.01	1.58 ± 0.06	2.33 ± 0.08	20-3-600	4.74 ± 0.03	1.49 ± 0.03	2.35 ± 0.30
5-5-600	5.84 ± 0.03	1.59 ± 0.04	2.36 ± 0.05	20-5-600	4.66 ± 0.03	1.51 ± 0.02	2.33 ± 0.20
5-1-700	6.77 ± 0.05	1.62 ± 0.02	2.39 ± 0.03	20-1-700	5.09 ± 0.03	1.52 ± 0.01	2.36 ± 0.07
5-3-700	6.32 ± 0.08	1.64 ± 0.05	2.43 ± 0.07	20-3-700	4.66 ± 0.01	1.49 ± 0.01	2.32 ± 0.05
5-5-700	5.81 ± 0.03	1.66 ± 0.02	2.46 ± 0.03	20-5-700	4.60 ± 0.02	1.39 ± 0.01	2.16 ± 0.08
5-1-800	6.50 ± 0.09	1.93 ± 0.09	2.44 ± 0.12	20-1-800	Not measured/ Brittle	Not measured/ Brittle	Not measured/ Brittle
5-3-800	**7.02 ± 0.09**	**2.07 ± 0.19**	**2.64 ± 0.24**	20-3-800	Not measured/ Brittle	Not measured/ Brittle	Not measured/ Brittle
5-5-800	6.72 ± 0.18	2.00 ± 0.15	2.53 ± 0.18	20-5-800	Not measured/ Brittle	Not measured/ Brittle	Not measured/ Brittle
5-1-900	6.28 ± 0.05	1.86 ± 0.09	2.36 ± 0.11	20-1-900	Not measured/	Not measured/	Not measured/

					Brittle	Brittle	Brittle
5-3-900	6.21 ± 0.07	1.85 ± 0.07	2.33 ± 0.09	20-3-900	Not measured/ Brittle	Not measured/ Brittle	Not measured/ Brittle
5-5-900	6.26 ± 0.10	1.86 ± 0.06	2.35 ± 0.07	20-5-900	Not measured/ Brittle	Not measured/ Brittle	Not measured/ Brittle
10-1-600	6.61 ± 0.05	1.53 ± 0.02	2.28 ± 0.02				
10-3-600	5.98 ± 0.04	1.58 ± 0.12	2.35 ± 0.15				
10-5-600	5.60 ±0.04	1.64 ± 0.17	2.44 ± 0.21				
10-1-700	6.48 ± 0.21	1.53 ± 0.03	2.29 ± 0.05				
10-3-700	5.88 ± 0.02	1.56 ± 0.07	2.32 ± 0.08				
10-5-700	5.49 ± 0.02	1.60 ± 0.07	2.39 ± 0.09				
10-1-800	5.55 ± 0.25	1.82 ± 0.07	2.38 ± 0.09				
10-3-800	5.56 ± 0.16	1.84 ± 0.08	2.38 ± 0.10				
10-5-800	5.31 ± 0.24	1.76 ± 0.07	2.28 ± 0.08				
10-1-900	5.43 ± 0.28	1.78 ± 0.05	2.33 ± 0.07				
10-3-900	5.37 ± 4.11	1.78 ± 0.12	2.30 ± 0.15				
10-5-900	**5.54 ± 0.62**	**1.87 ± 0.08**	**2.42 ± 0.10**				

[a] Encoded sample x-y-xxx indicates the amount of bird eggshell powder added (%vol)-firing time (h)-firing temperature (°C).
[b] Water absorption is the amount of water absorbed by a sample under specified test conditions, which is commonly expressed as the weight percent of the test specimen.
[c] Bulk density is calculated by d = m/V, which gives the density with all pores.
[d] True density is calculated by d = m/V, which gives the density without any pores within the samples.

Table 5. Thermal expansion coefficient values of fired samples

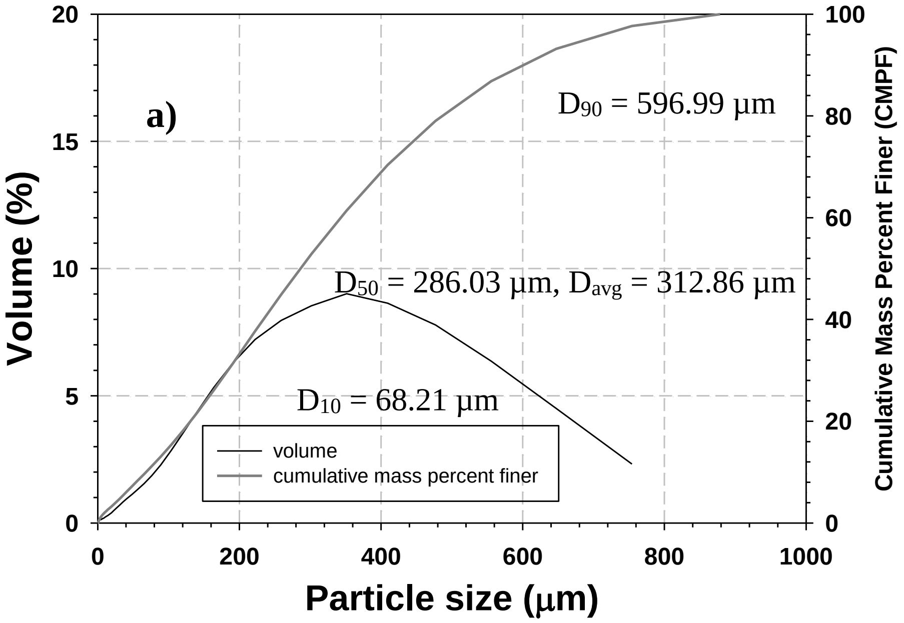
Sample [a]	Thermal expansion coefficient x 10^{-6} $(^{o}C)^{-1}$
0-3-900	6.64
10-5-900	**1.05**
15-1-800	**1.12**
15-3-900	High shrinkage, crack

[a] Encoded sample x-y-xxx indicates the amount of bird eggshell powder added (%vol)-firing time (h)-firing temperature (°C).

Table 6. Mechanical properties of fired porcelain clay products (± SD, n = 5)

Sample [a]	Compressive strength ($N.mm^{-2}$)	Hardness (HV)
0-3-900	2768	10.40 ± 0.40
5-3-800	3160	11.80 ± 0.50
10-5-900	**6200**	**12.20 ± 0.30**
15-1-800	**2012**	**16.60 ± 0.30**
20-1-700	839	9.70 ± 0.06

[a] Encoded sample x-y-xxx indicates the amount of bird eggshell powder added (%vol)-firing time (h)-firing temperature (°C).



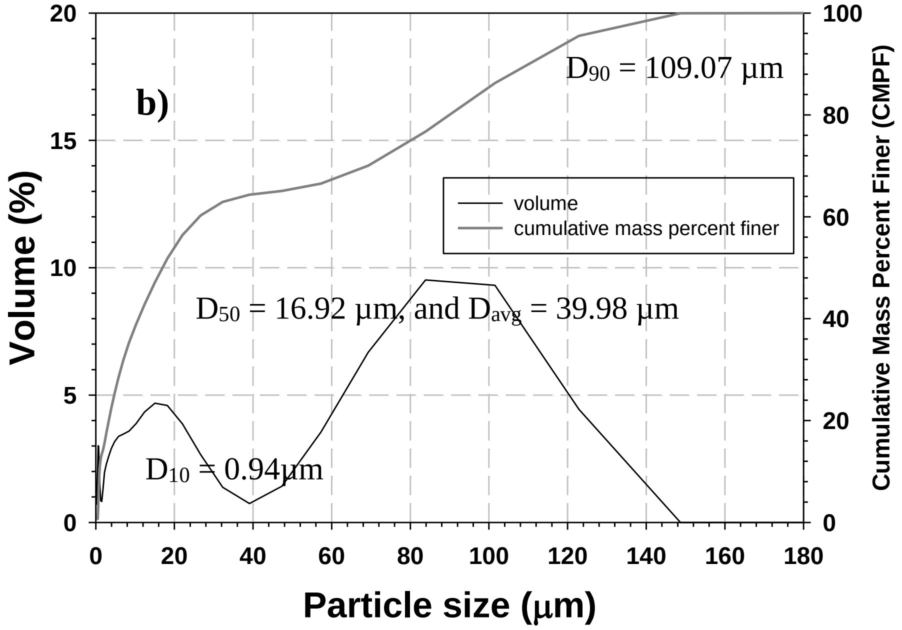


Fig.1. Particle size distribution of: a) bird eggshell powder after grinding for 120 min and b) porcelain clay

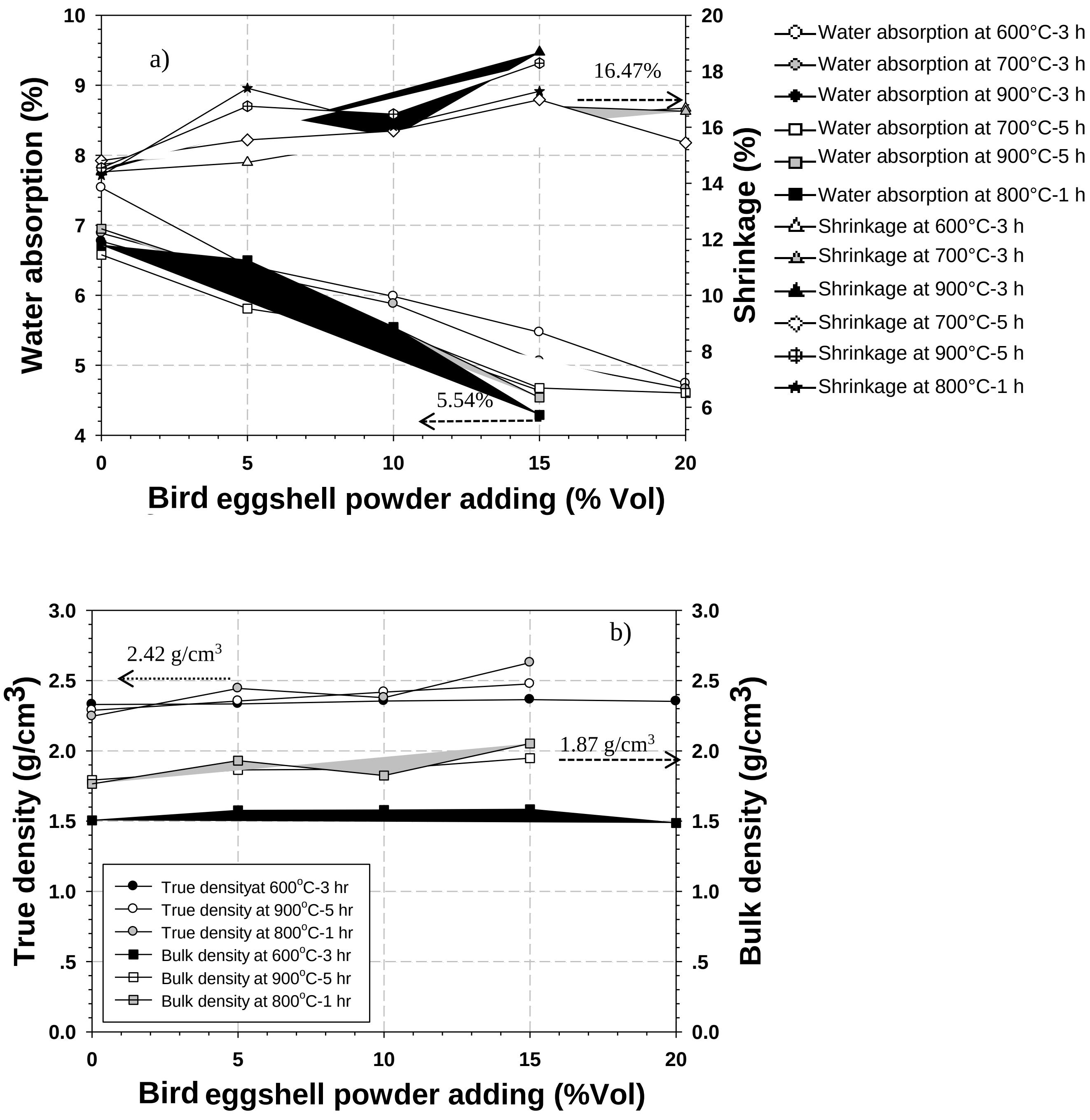


Fig.2. a) a) The percentage of water absorption and shrinkage *vs.* the volume percentage of eggshell powder added to aluminosilicate porcelain and b) true and bulk density values *vs.* the volume percentage of eggshell powder added to bioinert porcelain products.

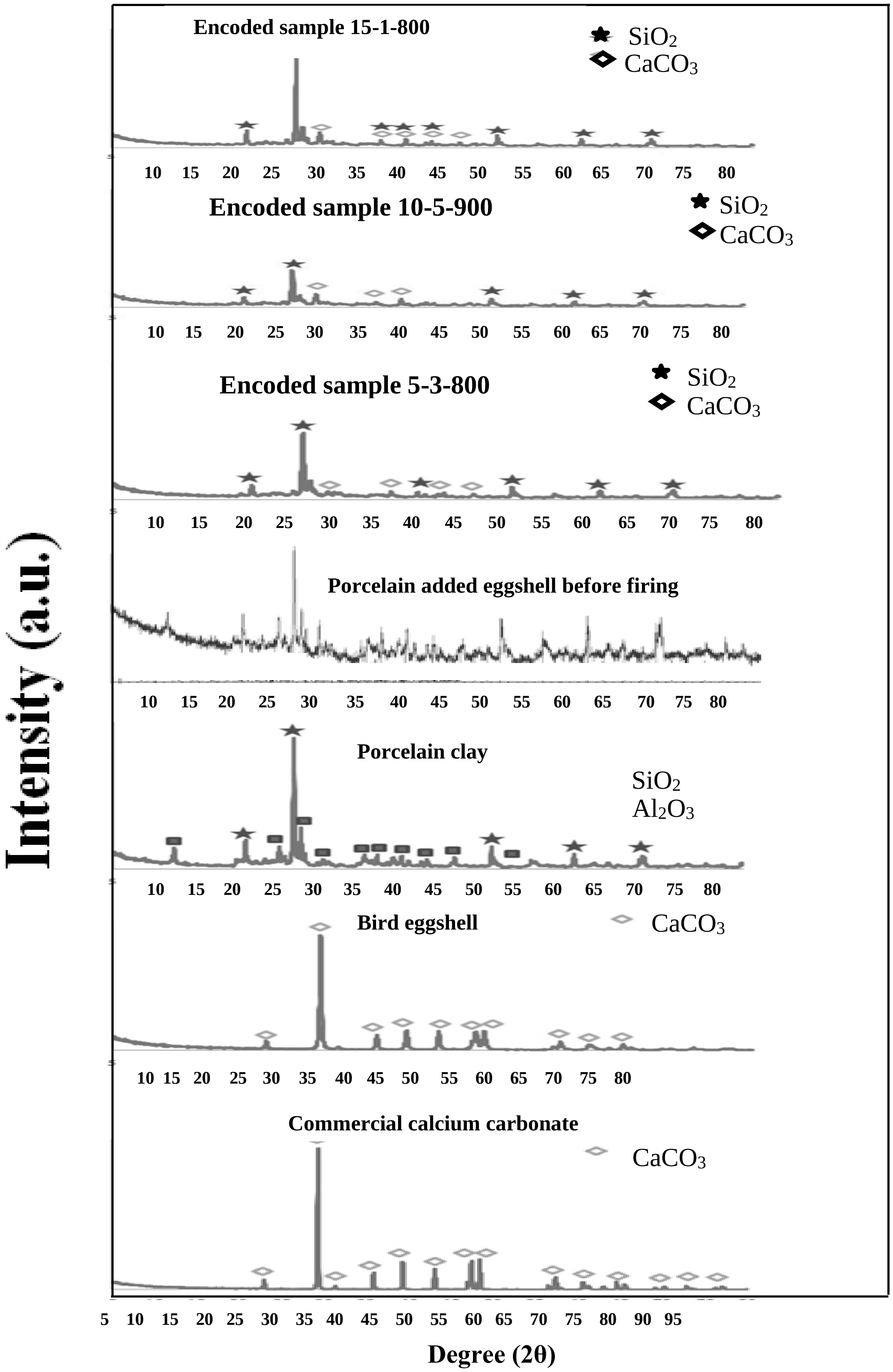
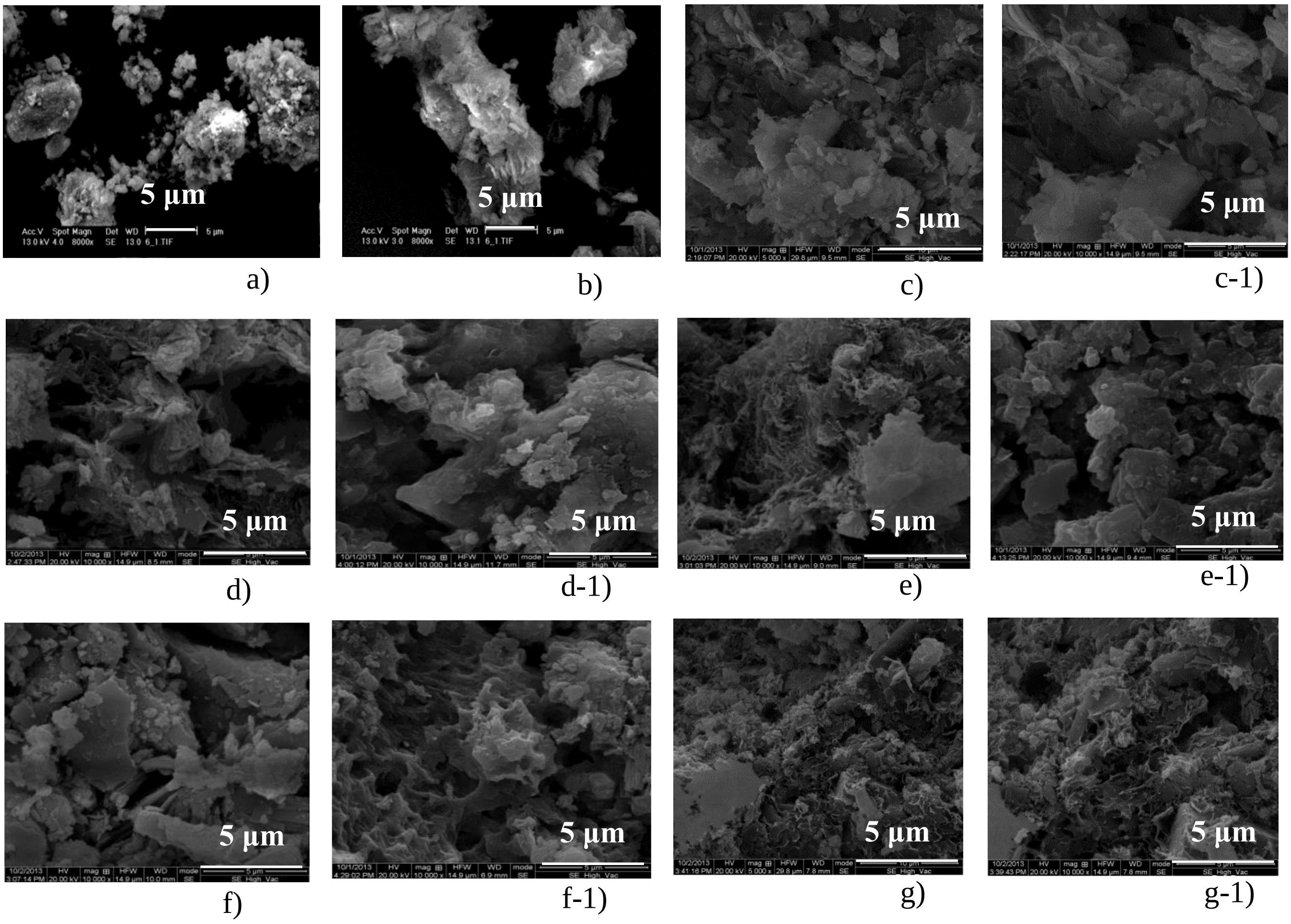

Encoded sample 15-1-800
SiO$_2$
CaCO$_3$
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Encoded sample 10-5-900
SiO$_2$
CaCO$_3$
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Encoded sample 5-3-800
SiO$_2$
CaCO$_3$
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Porcelain added eggshell before firing
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Porcelain clay
SiO$_2$
Al$_2$O$_3$
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Bird eggshell
CaCO$_3$
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Commercial calcium carbonate
CaCO$_3$
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 90 95
Intensity (a.u.)
Degree (2θ)

Fig.3. XRD peak patterns of raw materials and porcelain products before and after firing



a) b) c) c-1)

d) d-1) e) e-1)

f) f-1) g) g-1)

Fig.4. SEM micrographs with the magnifications of 5,000X and 10,000X of a) bird eggshell powder; b) porcelain clay; c) and c-1) porcelain product without adding bird eggshell (0-3-900); d) and d-1) porcelain product added 5%vol bird eggshell (5-3-800); e) and e-1) porcelain product added 10%vol bird eggshell (10-5-900); f) and f-1) porcelain product added 15%vol bird eggshell (15-1-800); and g) and g-1) porcelain product added 20%vol bird eggshell (20-1-700)

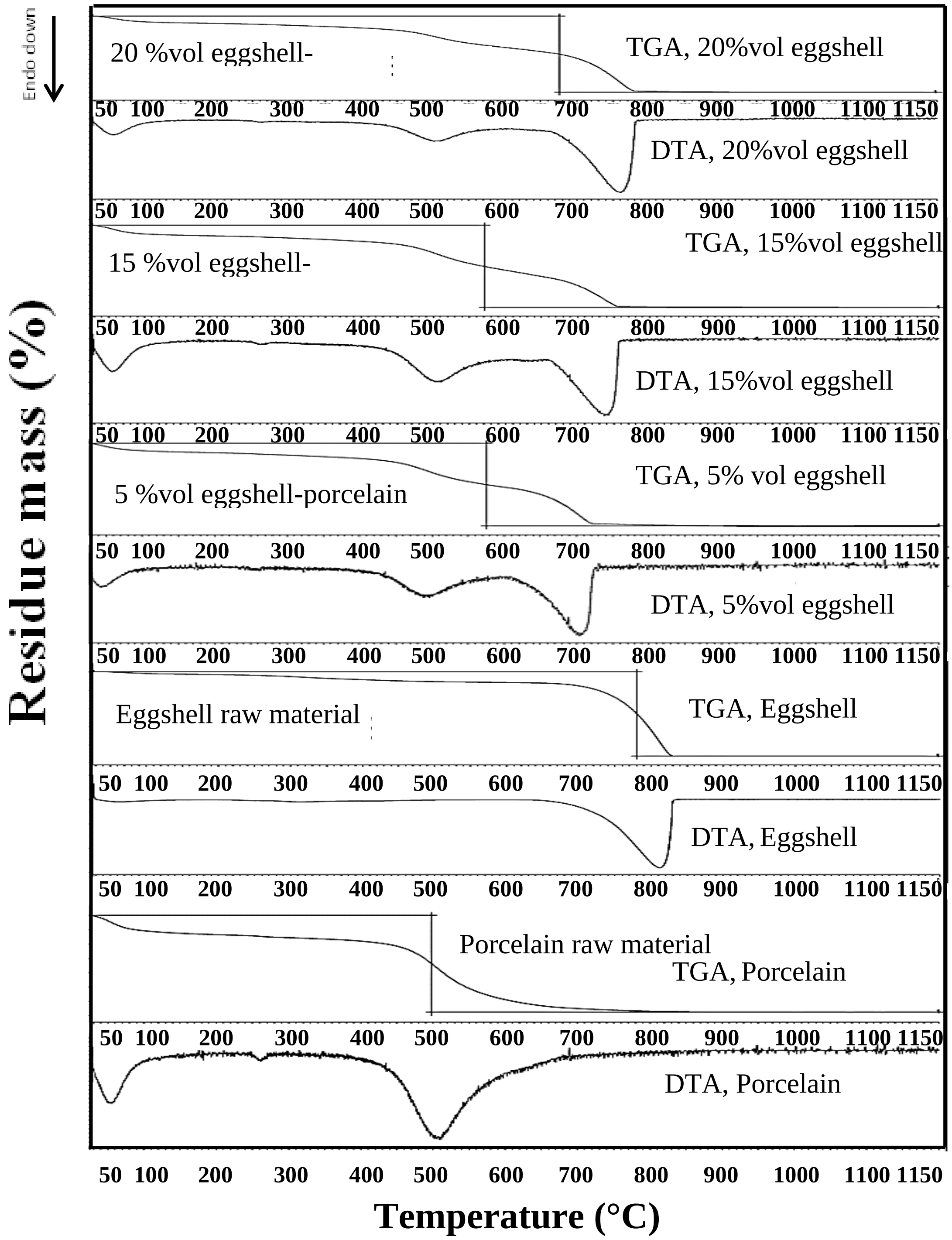
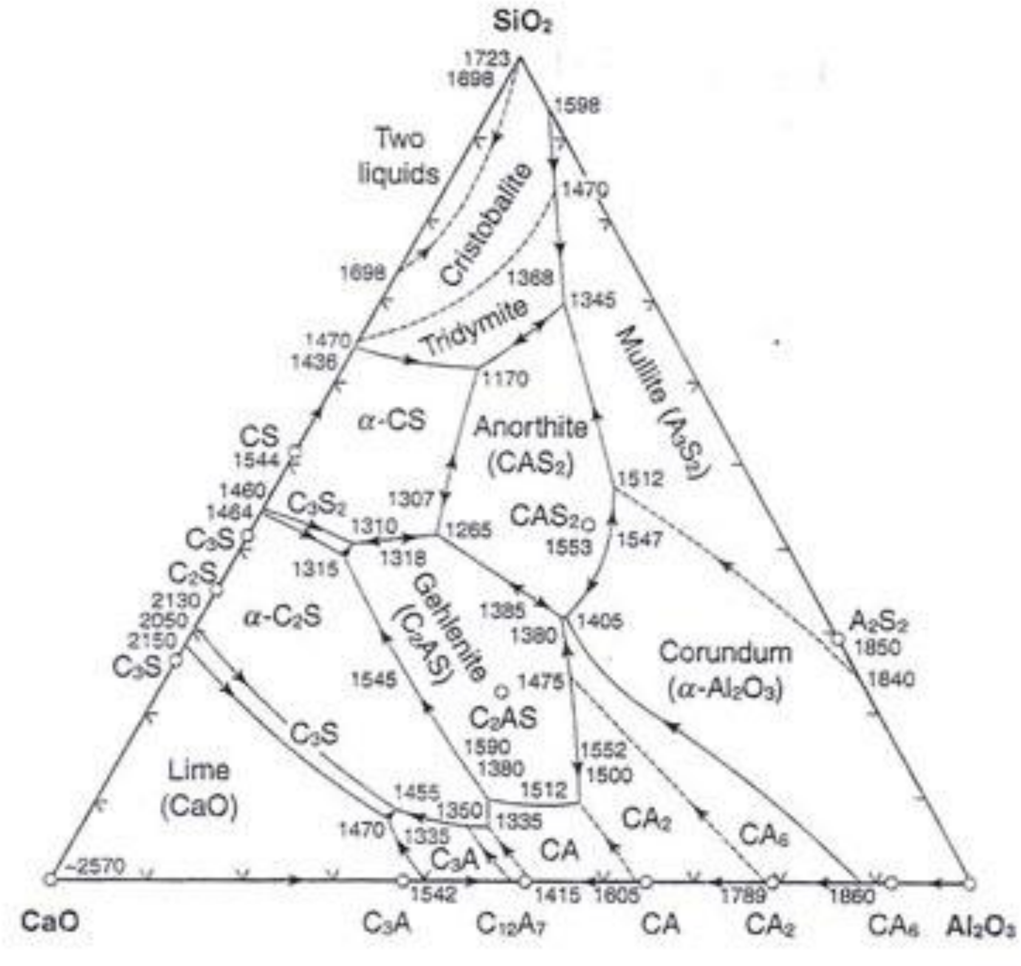


Fig.5. DTA and TGA comparison of samples between raw materials and porcelain products with/without bird eggshell powder adding



Scheme 1. Ternary phase diagram of $CaO–Al_2O_3–SiO_2$

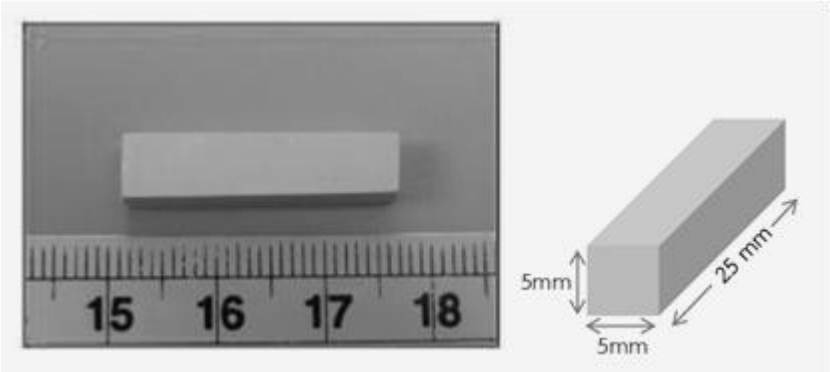
a) b) c)

Scheme 2. a) raw bird eggshell, b) ground rough bird eggshell, and c) ground fine bird eggshell powder

a) b)

c)

Scheme 3. Porcelain samples a) before firing, b) after firing, and c) porcelain applications



Scheme 4. Size and shape of the porcelain sample for thermal expansion coefficient measurement

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