INNOVATIVE GREEN PORCELAIN CLAY PRODUCTS EMBEDDED QUAIL EGGSHELL TO ENHANCE PHYSICAL-THERMAL-MECHANICAL PROPERTIES VIA SLIP CASTING

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ABSTRACT: *Porcelain is a ceramic material that can be applied for wares, dental and medical applications, thermal and electrical insulating materials, and ceramic molds. The main composition of porcelain clay is aluminosilicate compounds. Adding calcium carbonate into porcelain clay can be formed anorthite feldspar ($CaAl_2Si_2O_8$) to increase physical-mechanical-thermal properties and reduce firing temperature to obtain dense porcelain products. Nowadays, the biomaterials selection is concerned for green and sustainable development. In this study, the objective is focused on adding quail eggshell as a calcium carbonate source into porcelain products with 0, 5, 10, 15, and 20 %wt and fired at 600° and 700°C for 1, 3, and 5 hr at each firing temperature. The best condition is 15%wt quail eggshell adding into porcelain clay and fired at 600°C for 3 hr encoded 15-3-600. The obtained samples are low percent water absorption, high percent shrinkage, good true density value close to the theoretical density, low thermal expansion coefficient, high compressive strength, and high hardness. Furthermore, phase formation and microstructure are measured by using XRD and SEM, and reported here.*

Keywords: Phase transformation; Porcelain clay products; Slip casting; Quail eggshell; Thermal expansion coefficient

1. INTRODUCTION

At present, there are enormous community concerns, eco-friendly materials, and a growing environmental awareness throughout the world. These concerns affect to force the researchers focus to use, produce, and synthesize the new green and recycle materials i.e. biological wastes, industrial wastes, and processes that enhance the environmental quality of products, health, and nontoxic. In this perspective, biodegradability, eco-friendliness, low cost, easy formation, reuse, and nontoxic substance have become important considerations in production of new materials [1-2].

Porcelain products is an important potentially candidate materials used as dental implant, porcelain tile, castable ceramics for molten metal, advanced ceramics [3-8], ceramic membranes [9-11], and bioceramics [12-16]. Porcelain products can be used as restorative dentistry for teeth full coverage as crowns, inlays and onlay bridges, veneering agents [17-18].

Calcium carbonate is a popular filler used in many industries that is added to improve optical (brightness and opacity), thermal (thermal insulating and thermal shock resistance), mechanical (strength and young's modulus), physical (smoothness and formation), and cost reduction, including acted as a starting raw material in clay products [19-21]. There are many sources of calcium carbonate from both nature (i.e. coral, bone, minerals, pearl, shell) and synthesis.

Eggshell is also an important source of calcium carbonate. Eggs are one of the most complete foods as they contain protein, lipid, and carbohydrates which are essential for a good diet. They also contain vitamins and mineral elements which are necessary for the development of young and elderly people. Egg and its derivative are one of important raw materials to make food, drug, bakery, and cosmetic industries i.e. for manufacturing bread, cakes, crackers, ice creams, and food additive. Eggshell as by products provides approximately 11%wt of the total weight (65-70 g per egg). The main composition of eggshell composed of more than 96%wt calcium carbonate ($CaCO_3$), 1%wt magnesium carbonate ($MgCO_3$), 1%wt calcium phosphate ($CaPO_4$), and 2%wt other organic matters [22-24]. Therefore, in order to maximize the recycling opportunities for eggshells, reduce eggshell wastes, conserve the environment without pre-treatment, and increase agricultural evaluation are considered to use as an effective biomaterial. It is estimated that eggshell waste amounts are many millions tons per day from hen, duck, and bird eggs. [24]. The main composition of eggshell is calcium carbonate that can be used as a filler or additive in many products i.e. ink, pharmaceutical, animal food, cosmetic, rubber, and paint [24].

The objective of this present is to study effect of adding quail eggshell powder acted as a chemical substance or calcium carbonate source into porcelain clay products in order to increase mechanical, thermal, and physical properties of porcelain products via slip casting process. The physical properties (true density, bulk density, water absorption, and shrinkage), mechanical properties (compressive strength, compressive Young's modulus, Vickers micro-hardness), and thermal properties (thermal expansion coefficient) of porcelain products were measured and also reported here.

2. EXPERIMENTAL

Quail eggshell collected from the local cafeteria in the University, was cleaned with tap water and let it dried in the air at room temperature for 1-2 days. The cleaned quail eggshell was ground by the porcelain rapid mill to receive fine eggshell powder for 80-120 min in micron size. Porcelain clay acted as a raw material for making clay products by slip casting process. Sodium silicate acted as the deflocculant for the slip preparation was purchased from Compound Clay Co., Ltd. Thailand. The sodium silicate solution was prepared with a weight ratio between sodium silicate and water equal to 2:1. The solution of sodium silicate was added to adjust the viscosity of slip. The weight ratio of porcelain clay and sodium silicate solution was 100 Kg: 250 g.

Porcelain clay products are composed of porcelain clay added quail eggshells powder ground with a rapid mill for 80-120 min. Quail eggshell powder is varied 0, 5, 10, 15, and 20 % wt added into porcelain clay slip and casted into plaster mold as shown in Fig.1. The green porcelain samples were fired at 600° and 700°C for 1, 3, and 5 hr at each firing temperature. The fired porcelain products called finished porcelain products were characterized the physical, mechanical, and thermal properties.

a) b)

Fig (1) a) plaster mold for porcelain samples preparation and b) porcelain clay products after casting.

3. RESULTS AND DISCUSSION

Chemical compositions of quail eggshell powder were measured by XRF. The main composition of quail eggshell powder composed of 96.23%wt $CaCO_3$, 1.12 %wt MgO, 1.19 %wt P_2O_5, and 1.46%wt other oxide compounds. Quail eggshell powder has true density, average particle size, specific surface area, and average pore diameter equal to 2.30 g/cm^3, 312.86 µm, 0.68 m^2/g, and 267.90 Ã, respectively. While true density, average particle size, specific surface area, and average pore diameter values of porcelain clay are 1.70 g/cm^3, 39.98 µm, 19.92 m^2/g, and 183.30 Ã, respectively. Porcelain clay is finer than quail eggshell powder. Therefore, slip casting process for making porcelain clay products needs to add small amount of sodium silicate solution approximately 0.5-1.0 cm^3 acted as a deflocculant for colloidal dispersion or to prevent agglomeration problem of clay particles.

When porcelain slip added with/without quail eggshell powder 0, 5, 10, 15, and 20 %wt was poured in plaster molds, let it solidification for 1 day at room temperature, and then casted out of the plaster mold to obtain the porcelain green products as shown in Fig.1b. The obtained green products were fired at 600° and 700°C for 1, 3, and 5 hr at each firing temperature to measure water absorption, shrinkage, bulk density, and true density.

Water absorption and shrinkage of all samples were measured and tabulated in Table 1 and shown in Fig. 2. When amount of quail eggshell powder added in porcelain clay products increases, the percentage of water absorption values decreases whereas the percentage of shrinkage values increases. It means amount of eggshell adding effect to physical properties of porcelain products to densification. In addition, firing time and firing temperature of porcelain clay products affect to water absorption and shrinkage values as well. The longer firing time and higher firing temperature use, the lower percentage of water absorption and higher percentage of shrinkage values are.

Table 1 Water absorption and shrinkage of samples

Samples [a]	Water absorption [b] (%)	Shrinkage [c] (%)
0-1-600	0.7879±0.0469	14.0727±1.7621
0-3-600	0.7536±0.0237	14.4041±0.8705
0-5-600	0.6536±0.0099	14.4547±0.2356
0-1-700	0.7803±0.0520	14.5180±0.3914
0-3-700	0.6886±0.0496	14.6699±0.7632
0-5-700	0.6579±0.0219	14.8083±1.0296
5-1-600	0.6838±0.0133	14.5069±2.1283
5-3-600	0.6425±0.0139	14.7481±2.6139
5-5-600	0.5837±0.0252	14.8891±1.6910
5-1-700	0.6769±0.0476	15.1251±0.8851
5-3-700	0.6321±0.0798	15.3477±2.4247
5-5-700	0.5810±0.0315	15.5463±1.0807
10-1-600	0.6613±0.0536	15.1531±3.1614
10-3-600	0.5984±0.0366	15.6277±2.2823
10-5-600	0.5603±0.0370	16.2003±3.1284
10-1-700	0.6479±0.2060	15.1802±0.6206
10-3-700	0.5878±0.0232	15.4208±1.2114
10-5-700	0.5491±0.0221	15.8676±1.3396
15-1-600	0.5793±0.0146	16.0093±2.2537
15-3-600	0.5470±0.0188	16.3876±1.8437
15-5-600	0.5275±0.0145	16.5732±1.1446
15-1-700	0.5562±0.0109	16.6407±1.2502
15-3-700	0.5060±0.0343	16.7611±0.4603
15-5-700	0.4675±0.0298	16.9850±1.0647
20-1-600	0.5383±0.0356	16.0725±1.6957
20-3-600	0.4739±0.0336	16.6836±0.7721
20-5-600	0.4662±0.0317	16.6700±0.5255
20-1-700	0.5093±0.0319	16.8249±1.8758
20-3-700	0.4663±0.0131	16.5692±1.2759
20-5-700	0.4603±0.0242	15.4475±2.0989

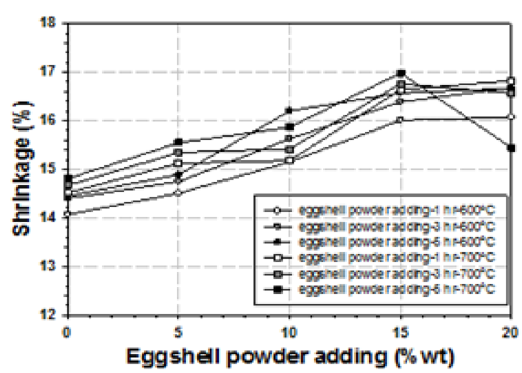
[a] samples encoded x-xx-xxx means amount of quail eggshell powder adding-firing time-firing temperature i.e. 0-1-600 (no quail eggshell powder adding-firing time 1 hr-firing temperature at 600°C).

[b] water absorption means the amount of water absorbed by a porcelain clay product under specified test condition and calculated a weight percent of the test specimen.

[c] shrinkage means the decrease in size of a porcelain clay object to drying and firing. Drying shrinkage is reversible with the return of water, but firing shrinkage is permanent due to chemical and physical changes porcelain clay undergoes when exposed to heat. In this study is firing shrinkage.

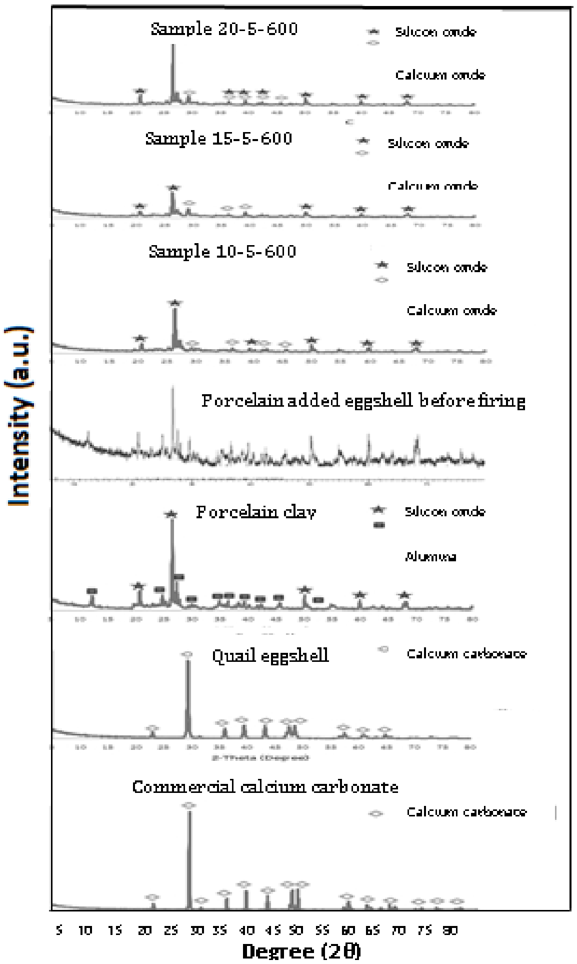
[d] bulk density of samples was measured according to the ASTM B212-82 by calculation from mass per volume. Volume is including open and closed pores within the porcelain sample.

[e] true density of samples was measured according to the ASTM B212-82 by calculation from mass per volume. Volume is not including open and closed pores within the porcelain sample.



Fig(2) The percentage of shrinkage *vs.* amount of quail eggshell powder adding.

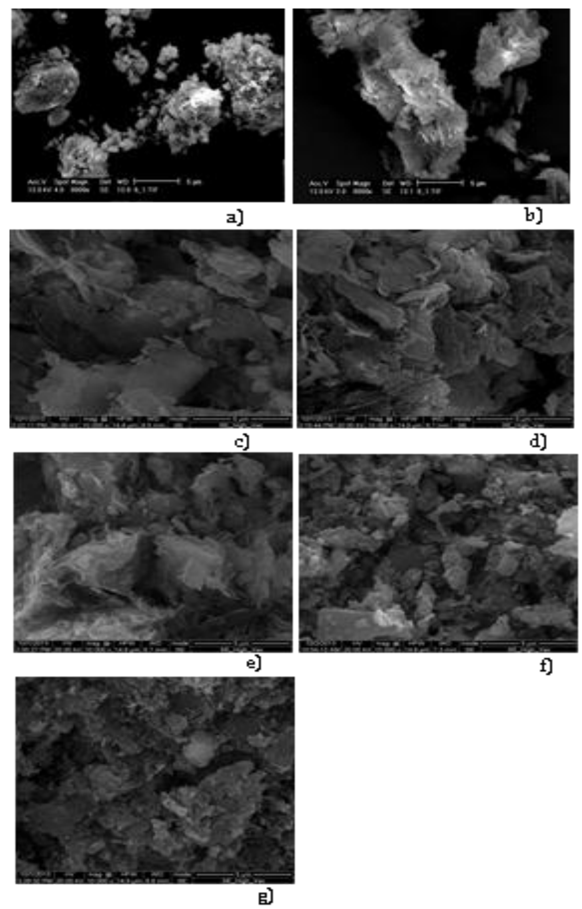
Comparison of water absorption, shrinkage, bulk and true density values of porcelain clay samples with/without quail eggshell powder adding is tabulated in Table 1 and shown in Fig.2. The best sample to obtain good water absorption, shrinkage, bulk and true density values is encoded 15-3-600 by means of adding 15%wt quail eggshell powder in porcelain clay product for firing time 3 hr, at firing temperature 600 °C.



Fig(3) The XRD peak patterns comparison of raw materials (commercial calcium carbonate, quail eggshell powder, porcelain clay) and porcelain clay samples before and after firing at 600°C.

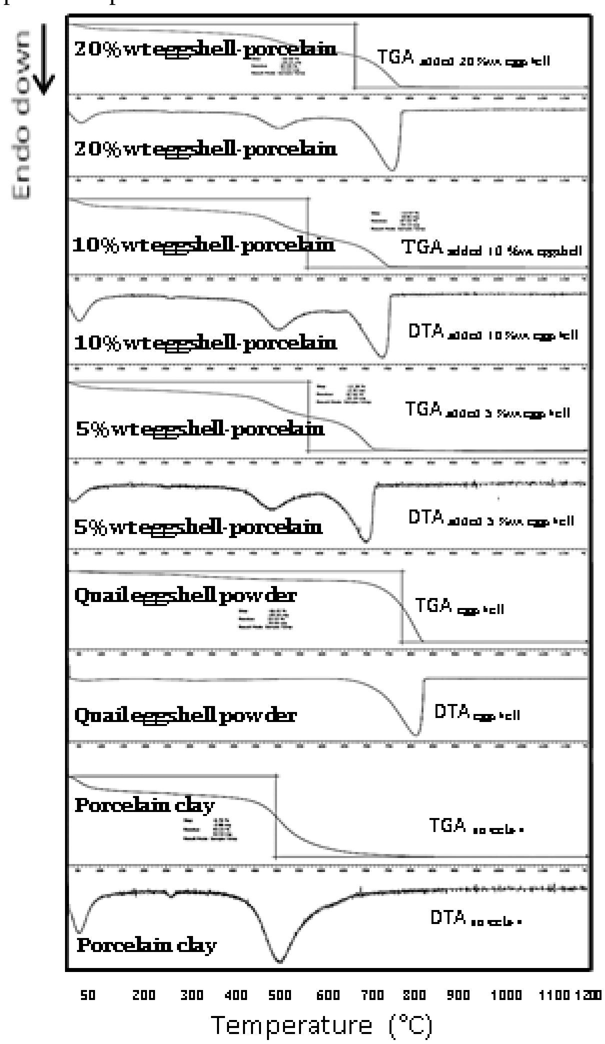
The XRD peak patterns comparison of raw materials and porcelain clay samples before and after firing at 600 °C are shown in Fig.3. The XRD peak patterns of both commercial calcium carbonate and quail eggshell show the same positions consistent with the JCPDS file no. 01-086-2341 belonging to rhombohedral structure at 2θ: 29.369°, 39.370°, and 43.118°. While the XRD peak pattern of porcelain clay is AlCaMgOSi belonging to halloysite, quartz, muscovite, and calcite structures consistent with the JCPDS file no. 00-003-0418 at 2θ: 26.566°, 20.935°, 20.790°, 10.996° and 36.422°. Furthermore, the porcelain samples added 10, 15, and 20%wt quail eggshell powder and fired 600°C are the same XRD peak positions consistent with the JCPDS no. 01-089-1459 of calcium aluminium silicate or anorthite ($CaAl_2Si_2O_8$) mixed with small amount of calcium oxide and calcite structures.

The SEM micrographs of quail eggshell powder, porcelain clay, and porcelain clay products added 0, 5, 10, 15, and 20 %wt quail eggshell powder and fired at 600°C for 3 hr are shown in Fig.4. The SEM micrographs of quail eggshell powder and porcelain clay are fine particles and particles agglomeration as shown in Figs. 4a and 4b, respectively, consistent with the results obtained by particle size analyzer measurement. Adding 0, 5, 10, 15, and 20 %wt quail eggshell powder into porcelain clay products fired at 600°C for 3 hr affects to eggshell particles filled in micro-and macro-pore of porcelain clay products. Therefore, adding quail eggshell powder in porcelain samples can increase densification and mechanical properties of porcelain products due to phase transformation from mixed phases of clay and calcite to anorthite or calcium aluminosilicate ($CaAl_2Si_2O_8$) as shown in SEM micrographs Figs. 4c-4g, respectively.



Fig(4) The SEM micrographs with magnifications of 8000 and 10000X of raw materials and porcelain clay products added 0, 5, 10, 15, and 20 %wt quail eggshell powder, respectively.

DTA-TGA curves of quail eggshell powder, porcelain clay, and 5, 10, 20 %wt quail eggshell powder added in porcelain products were measured at room temperature to 1200°C as shown in Fig. 5. DTA curves comparison of quail eggshell powder and porcelain clay suggest that quail eggshell has endothermic reaction at approximately 800°C consistent with the XRD peak due to phase transformation from calcium carbonate to calcium oxide while porcelain clay has two endothermic reactions at 50° and 500°C due to decomposition of water and organic matter contents. Porcelain samples added 5, 10, and 20%wt quail eggshell show the same three endothermic peaks of DTA curves at 50°, 500°, and in the range of 600° - 800°C, respectively. It means that adding quail eggshell powder into porcelain clay products affects to decomposition of calcium carbonate to calcium oxide and reacts to aluminosilicate composition of porcelain clay to obtain cacium aluminosilicate or anorthite phase formation ($CaAl_2Si_2O_8$). Therefore, the new phase formation of anorthite can decrease firing temperature of porcelain products.



Fig(5) DTA-TGA curves from room temperature to 1200°C of porcelain clay, quail eggshell powder, and 5, 10, and 20 %wt quail eggshell powder added in porcelain clay products.

In addition, comparison of mechanical properties of porcelain clay products with/without adding quail eggshell powder is tabulated in Table 2. The data of mechanical properties can be summarized that the quail eggshell powder adding can increase the compressive strength and hardness of samples. However, excess adding of quail eggshell powder affects to very high hardness and brittle of porcelain samples due to calcium oxide transformation to calcium hydroxide inducing moisture absorption. The best sample encoded 15-3-600 has compressive strength and hardness equal to 3444 Pa and 9.1 ± 0.20 HV, respectively. While the sample without adding quail eggshell powder encoded 0-3-600 has compressive strength and hardness equal to 2320 Pa and 7.1 ± 0.58 HV, respectively. Even though, longer firing temperature may give high compressive strength and hardness, but it is not good physical properties i.e. water absorption, true density, and shrinkage, including high energy consuming. Furthermore, the comparison of thermal expansion coefficient values with/without adding quail eggshell powder is tabulated in Table 3. The quail eggshell powder can decrease thermal expansion coefficient of fired clay samples. The samples encoded 15-3-600 has thermal expansion coefficient value equal to 6.1435×10^{-6} $(°C)^{-1}$ while the sample encoded 0-3-600 is the sample without quail eggshell adding having thermal expansion coefficient 6.3015×10^{-6} $(°C)^{-1}$ as data tabulated in Table 3. It means adding quail eggshell powder can increase thermal resistance of fired porcelain products as well.

Table 2 Mechanical properties of fired porcelain clay products

Samples	Compressive strength (N/mm^2)	Hardness (HV)
0-3-600	2320	7.1 ± 0.58
5-1-600	2063	6.8 ± 0.35
10-5-600	6255	7.6 ± 0.31
15-3-600	3444	9.1 ± 0.20
15-5-600	3844	10.2 ± 0.55
20-5-600	3750	9.6 ± 0.32

Table 3 Thermal expansion coefficient values of samples

Samples	Thermal expansion coefficient x 10^{-6} $(°C)^{-1}$
0-3-600	6.3015
15-3-600	6.1435

4. CONCLUSIONS

The optimum amount of adding quail eggshell powder in porcelain clay products is 15%wt and fired at 600°C for 3 hr. The obtained porcelain samples are good physical (low water absorption, high shrinkage, and good true density), good thermal resistance, and good mechanical (good compressive strength and high hardness) properties. The percentage of water absorption, shrinkage, true density, thermal expansion coefficient, compressive strength, and hardness of 15-3-600 are equal to 0.5470%, 16.3876%, 2.3644 g/cm^3, 6.1435×10^{-6} $(°C)^{-1}$, 3444 Pa, and 9.1±0.2 HV, respectively. While porcelain samples without adding quail eggshell powder encoded 0-3-600 having the percentage of water absorption, shrinkage, true density, thermal expansion coefficient, compressive strength, and hardness are equal to 0.7536%, 14.4041%, 2.3295 g/cm^3, 6.3015×10^{-6} $(°C)^{-1}$, 2320 Pa, and 7.1±0.58 HV, respectively. Adding quail eggshell powder as calcium carbonate source can react with aluminosilicate compound to form anorthite ($CaAl_2Si_2O_8$) phase formation within the microstructure of porcelain clay products at optimum firing temperature and firing time. Anorthite phase formation induces the porcelain products to have good physical, thermal, and mechanical properties. The obtained porcelain products added 15 %wt quail eggshell powder and fired at 600°C for 3 hr are potentially candidate materials used as dental implant, porcelain tile, castable ceramics for molten metal, advanced ceramics, ceramic membranes, bioceramics, and thermal insulation.

5. REFERANCE

[1] Thakur, V.K, Singha, A.S., and Thakur, M.K. "Graft Copolymerization of Methyl Acrylate onto Cellulosic Biofibers: Synthesis, characterization and Application" *Journal of Polymers and the Environment*, **20**: 164-174(2012).

[2] Singha A.S. and Thakur, V.K. "Synthesis and Characterization of Grewia Optiva Fiber-reinforced PF-based Composites" *Int. Journal of Polymeric Materials*, 57: 1059-1074(2008).

[3] Harabi, A. and Achour, S. "A process for sintering of MgO and CaO based ceramics" *Journal of Materials Science Letters*, 18: 955–957(1999).

[4] Boudchicha, M.R., Achour, S., and Harabi, A. "Crystallization and sintering of cordierite and anorthite based binary ceramics" *Journal of Materials Science Letters*, 20: 215–217(2001).

[5] Mecif, A., Soro, J., Bonnet, J.P., and Harabi, A. "Preparation of mullite and zircon based ceramics using kaolinite and zirconium oxide: a sintering study" *Journal of the American Ceramic Society*, 93: 1306–1312(2010).

[6] Harabi, A., Karboua, N., and Achour, S. "Effect of thickness and orientation of alumina fibrous thermal insulation on microwave heating in a modified domestic 2.45 GHz multi-mode cavity" *Int. Journal of Apply Ceramic Technology*, 9 (1): 124–132(2012).

[7] Harabi, A. and Davies, T.J. "Densification and grain growth in sintered alumina-chromia powder mixtures" *Br. Ceram. Trans., J.* 94 (2): 79–84(1995).

[8] Harabi, A., Guerfa, F., Harabi, E., Benhas sine, M. T., Foughali, L., and Zaiou, S. "Preparation and characterization of new dental porcelains, using K-feldspar and quartz raw materials. Effect of B_2O_3 additions on sintering and mechanical properties" *Materials Science and Engineering C*, 65: 33–42(2016).

[9] Bouzerara, F., Harabi, A., Achour, S., and Labrot, A. "Porous ceramic supports for membranes prepared from kaolin and doloma mixtures" *Journal of Europian Ceramic Society*. 26: 1663–1671(2006).

[10] Bouzerara, F., Harabi, A., Ghouil, B., Medjemem, N., Boudaira, B., and Condom, S. "Elaboration and properties of zirconia microfiltration membranes" *Procedia Engi neering*, 33: 78–84(2012).

[11] Harabi, E., Harabi, A., Foughali, L., Chehlatt, S., Zouai, S., and Mezahi, F.Z. "Grain growth in sintered natural hydroxyapatite "*Acta Physica Polonica A*,127:1161–1163(2015).

[12] Harabi, J.A., Belamri, D., Karboua, N., and Mezahi, F.Z. "Sintering of bioceramics using a modified domestic microwave oven: natural hydroxyapatite sintering" *Journal of Thermal Analysis and Calorimetry*, 104: 383–388(2011).

[13] Harabi, A. and Harabi, E. "A modified milling system, using a bimodal distribution of highly resistant ceramics. Part1. A natural hydroxyapatite study" *Materials Science and Engineering C*, 51: 206–215(2015).

[14] Zouai, S., Harabi, A., Karboua, N., Harabi, E., Chehlatt, S., Barama, S.E., Zaiou, S., Bouzerara, F., and Guerfa, F. "A new and economic approach to synthesize and fabricate bioactive diopside ceramics using a modified domestic microwave oven. Part 2: effect of P_2O_5 additions on diopside bioactivity and mechanical properties" *Materials Science and Engineering C*, 61: 553–563(2016).

[15] O'Brien, W.J., Boenke, K.M., and Groh, C.L. "Evaluation of some properties of an opaque porcelain fired simultaneously with the body porcelain" *Journal of Prosthetic Dental*, 72 (4): 414–419(1994).

[16] Touati, J.B., Miara, P., and Nathanson, D. "Esthetic Dentistry and Ceramic Restorations" *first ed. Taylor & Francis*, 26–30(1998).

[17] Liua, F., Suna, B., Jiang, X., Sultan Aldeyab, S., Zhang, Q., and Zhu, M. "Mechanical properties of dental resin/composite containing urchin-like hydroxyapatite" *Dental Materials*, 30: 1358–1368(2014).

[18] Chen, D. and van de Ven, T.G.M. "Flocculation kinetics of precipitated calcium carbonate induced by electrosterically stabilized nanocrystalline cellulose" *Colloidal and Surfaces A: Physicochemical Engineering Aspects*, 504: 11-17(2016).

[19] Kuusisto, J. and Maloney, T. C. "Preparation and characterization of corn starch-calcium carbonate hybrid pigments" *Industrial Crops and Products*, 83: 294-300(2016).

[20] Cao, Z., Daly, M., Clémence, L., Geever, L.M., Major, I., Higginbotham, C.L., and Devine, D.M. "Chemical surface modification of calcium carbonate particles with stearic acid using different treating methods", 378: 320-329(2016).

[21] Tullett, S.G. "Eggshell Conductance and Other Functional Qualities of Ostrich Egg" *Comparative Biochemistry and Physiology*, 78A/1: 5-13(1984).

[22] Nys, Y., Gautron, J., Garcia-Ruiz, J.M., Hincke, M.T. "Avian eggshell mineralization: biochemical and functional characterization of matrix proteins" *Comptes Rendus Palevol*, 3: 549-562(2004).

[23] Tsai, W.T., Yang, J.M., Lai, C.W., Cheng, Y.H., Lin, C. C., Yeh, C.W. "Characterization and adsorption properties of eggshells and eggshell membrane" *Bioresource Technology*, 97: 488-493(2006).

[24] Tsai, W.T., Yang, J.M., Lai, C.W., Cheng, Y.H., Lin, C.C., and Yeh, C.W. "Characterization and adsorption properties of eggshells and eggshell membrane" *Bioresource Technology*, 97: 488-493(2006).