

Innovation of Embedding Eggshell to Enhance Physical-Mechanical-Thermal Properties in Fired Clay Bricks via Extrusion Process

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Abstract. Eggshell functioned as a bio-filler and sintering aid added into earthenware clay compounds to make fire clay bricks via extrusion process. The main composition of eggshell is calcium carbonate (CaCO_3) while the main composition of earthenware is aluminosilicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and other oxide compounds. Calcium carbonate in eggshell can react to chemical substances in earthenware clay compound to form calcium aluminosilicate or anorthite and wollastonite or calcium silicate phase formation of the fired clay bricks. Adding 20%wt eggshell powder into clay bricks and fired at 1000°C for 5 hrs., affects to the physical-mechanical-thermal properties, i.e. high compressive strength and hardness, good thermal expansion coefficient, good true density, and low water absorption. In general, the theoretical compressive strength, hardness, and water absorption of desired refractory are more than 7.0 MPa, 6.0 HV, and less than 25%wt, respectively. Therefore, the obtained fired clay bricks added eggshell powder and fired at 1000°C for 5 hrs., are potential for use as bricks for construction and thermal insulation.

1 Introduction

Eggs have been used as foods, drugs, cosmetics, and foodstuffs. Unfortunately, eggshells are an egg product industry residue that contributes to environmental pollution as it favors microbial actions. The by-product eggshell represents approximately 11% of the total weight approximately 60 g of egg [1-2]. Eggshell is one kind of sources of calcium carbonate (CaCO_3) known as calcite which is the more stable polymorph at room temperature. An eggshell is a rich source of mineral salts, mainly calcium carbonate (94%), calcium phosphate (1%), magnesium carbonate (91%), and organic substances (4%) [2]. However, an important composition of eggshell is the calcium carbonate, which can be used in various material applications: dielectrics, dental and bone implantation, gypsum, catalysts, and also fillers used for in a variety industries such as rubber, ink, foodstuff, cosmetic, pharmaceutical, and fertilization.

Brick is a ceramic material mainly used in the building industry. There are divided into various groups on the basis of the mainly raw materials used, namely silica bricks, magnesia bricks, zirconia bricks, alumina bricks, mullite bricks, dolomite bricks, silicon carbide bricks, graphite bricks, and clay bricks [3-19]. Bricks are the major-construction and building material for a long time. The worldwide annual production of bricks is currently many thousand billion units and has trended the demand to increase every year. Conventional bricks are produced from clay and fired at high temperature. Earthenware is

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one kind of clay raw materials to produce clay brick because earthenware is the lowest price of raw material used, high percentage of iron oxide content, red or yellow color after firing, opaque, high plasticity, easily forming. Earthenware can be fired for biscuit at 1000°-1150°C. The most application of earthenware are the building bricks in block shape or rectangular building unit. There are many sources of earthenware in the provinces of Thailand such as Udon Thani (Ban Chiang), Sukhothai (Si satchanalai), Sawankhalok, Ayutthaya, Lopburi, Singburi, Kanchanburi, and Angthong which are high potential to make the good and strong traditional clay-bricks.

The annual growth rate of clay bricks using for construction, infrastructure, and industries, i.e. furnace for steel and jewelry making, materials, casting process, and others, increase continuously demand effect of the high rate of brick production for building enclosures. However, both economic and environmental problems during process need to concern on energy consuming, pollution, cost of production, and raw material sources. Therefore, one of the best ways of saving energy consumption and reducing eggshell waste is applied eggshell as a CaCO₃ filler and flux in clay bricks. In addition, recycled eggshell as a bio-filler can decrease the landfill pollution and contributes as an asset to the agriculture rather than being a waste material.

The objective of this work was to make fire clay bricks from earthenware clay mixed with eggshell (CaCO₃) powder. The obtained fired clay bricks which have good physical, mechanical, and thermal properties, lightweight, and low water absorption.

2 Experimentals

2.1 Materials and methods

Earthenware clay was obtained from Pa Mok district, Ban Norasing, Angthong province, Thailand. Hen eggshell was collected from the local cafeteria of the University. Eggshell was cleaned with tap water and let it dry in the air at room temperature for 1-2 days. The cleaned hen eggshell was ground with the rapidly porcelain ball mill to eggshell powder for 120 min.

2.2 Instruments

Extruder was used to prepare clay brick samples supplied by Petkasem Co.,Ltd., Thailand. Extruder composed of a screw to extrude the clay mixture from the hopper to the die. Barrel in the extruder can protect the mixture flow out the screw and get rid of the air containing in the mixture. Oven was used to dry the green products at 100°C for 24 hrs by using the WTB binder. Furnace was used to fire the clay bricks at 800°, 900°, 1000°, and 1100°C for 1, 3, and 5 hrs., at each firing temperature. The used furnace is Mudotemp, WW 51A model 1400°C.

2.3 Clay bricks preparation

The green products of clay brick samples were prepared according to the Table 1. The raw materials were mixed and kneaded to homogenous mixture and extrude pass through the die of extruder in a cylindrical shape having 5.00 cm diameter and 1.00 cm in thickness. The obtained clay samples or green products were dried at 100°C for 24 hrs., and then fired at 800°, 900°, 1000°, and 1100°C for 1, 3, and 5 hrs., at each firing temperature, respectively.

Table 1. Raw materials were mixed and needed to homogenous mixture and extrude pass

Samples	Earthenware clay (g)	Eggshell powder (%wt)	Water (%wt)
Formula 1	12,000	0	40
Formula 2	11,400	5	40
Formula 3	10,800	10	40
Formula 4	10,200	15	40
Formula 5	9,600	20	40

3 Results and discussion

3.1 Physical properties of clay bricks

The color of green products means the color of samples before firing as shown in Fig.1.



Fig. 1. Clay brick samples: a) the green products before drying; b) the green products after drying in an oven at 100°C for 24 hrs.; and c) the clay bricks after firing at 800°-1100°C.

Most color of clay bricks before firing or green products after kneading and extrusion are dark yellowish brown. After firing, the colors of clay bricks are reddish yellow to pale yellow.

The chemical composition of clay and chicken eggshell for clay refractory forming was measured by XRF as the data tabulated in Table2. The main composition of earthenware clay composed of 26.46%wt SiO₂, 22.32%wt Fe₂O₃, 20.66%wt Al₂O₃, and other oxide compounds. While the main composition of chicken eggshell composed of 98.101%wt CaCO₃ and the rest other oxide compounds.

Table 2. Chemical composition by XRF

Composition	Earthenware clay (%wt)	Hen eggshell (%wt)
SiO ₂	26.46	0.073
Fe ₂ O ₃	22.32	-
Al ₂ O ₃	20.66	0.035
CaO	10.55	-
MgO	8.91	0.286
Na ₂ O	4.43	0.204
K ₂ O	4.39	0.038
TiO ₂	2.28	-
CaCO ₃	-	98.101
CuO	-	0.009
P ₂ O ₅	-	0.443
SrO	-	0.013
SO ₃	-	0.798
Total	100.00	100.00

“-“ means not detected.

The physical properties (bulk density, true density, color, and water absorption) of clay brick samples added 0%, 5%, 10%, 15%, and 20% wt chicken eggshell powder fired at 800°C, 900°C, 1000°C, and 1100°C for 1, 3, and 5 hrs., are data tabulated in Table 3. Firing temperature and firing time are important factors to obtain the good clay bricks. The high firing temperature and firing time use, the better and higher strength of clay bricks obtained. The firing temperature is low less than 1000°C (800°C and 900°C), the samples are not good and low strength. However, if the firing temperature is too high more than 1000°C effect to crack on clay brick samples. Therefore, the suitable firing temperature of clay brick samples added eggshell powder is 1000°C for firing time 1, 3, and 5 hrs. Furthermore, if the percentage of chicken eggshell powder added in the clay bricks is high, the percentage value of water absorption is low and good appearance. The obtained clay brick samples added 20%wt eggshell powder are the optimum amount of hen eggshell adding. The average water absorption of adding 20%wt eggshell is equal to 14.36-14.88% consistent with the results obtained by Raut et al [9]. It means high densification effect to samples having high mechanical and good thermal properties. Furthermore, the obtained water absorption of clay brick samples has low values consistent with the theoretical values of the best refractory measured according to the Thai Industrial Standard Institute 243/2530 and the ASTM C 373-72 less than 25%wt water absorption.

Table 3. Physical properties of brick samples

Samples ^a	Bulk density ^b (g/cm ³)	True density ^c (g/cm ³)	Water absorption ^d (% wt)	Color of bricks
0-1000-1	1.80±0.04	2.05±0.01	16.69 ± 0.04	Red yellow
0-1000-3	1.83±0.01	2.07±0.02	15.79 ± 0.66	Red yellow
0-1000-5	1.83±0.03	2.12±0.07	15.37 ± 1.28	Red yellow
5-1000-1	1.71±0.03	1.97±0.05	N/A	Red yellow
5-1000-3	1.73±0.03	2.01±0.05	N/A	Red yellow
5-1000-5	1.75±0.01	2.05±0.02	N/A	Red yellow
10-1000-1	1.69±0.02	2.03±0.03	N/A	Red yellow
10-1000-3	1.67±0.01	2.02±0.03	N/A	Red yellow
10-1000-5	1.70±0.02	2.04±0.05	N/A	Red yellow
15-1000-1	1.63±0.02	1.97±0.01	N/A	Red yellow
15-1000-3	1.65±0.02	1.99±0.01	N/A	Red yellow
15-1000-5	1.64±0.03	2.00±0.02	N/A	Red yellow
20-1000-1	1.83±0.01	2.06±0.08	14.88 ± 0.89	Yellow
20-1000-3	1.70±0.02	1.98±0.02	14.69 ± 1.04	Yellow
20-1000-5	1.75±0.04	1.96±0.02	14.36 ± 0.80	Yellow

Remark: N/A means not measured.

^a means 5 pieces of clay brick samples at each condition.

^b means density including open and closed pores within the clay samples according to the ASTM B212-82.

^c means density without open and closed pores within the clay samples due to boiled in water for 5 hrs., and let them in cool water for 24 hrs., before calculation according the ASTM B212-72 and ASTM C 373-72.

^d means water absorption according to the ASTM C 373-72.

Encoded samples x-xxx-x mean amount of eggshell powder adding-firing temperature-firing time i.e. 0-1000-3 (no adding (0%wt) eggshell powder -firing at 1000°C-firing time for 3 hrs).

When the clay bricks were mixed with the eggshell powder 0%, 5%, 10%, 15%, and 20%wt effect on the color of mixture changed according to the Munsell soil color chart from dark yellowish brown to very pale yellow as reported in Table 4. The clay brick samples were prepared by extrusion in a disk-like shape, having 5.00 cm diameter and 1.00 cm thickness. All clay brick samples were fired at 800°C, 900°C, 1000°C, and 1100°C for 1, 3, and 5 hrs., at each firing temperature. The colors of clay brick samples changed to reddish yellow or yellow as reported in Table 4 due to the amount of iron oxide (Fe₂O₃) having red color consistent with the results obtained by XRF and amount of hen eggshell powder adding.

The XRD peak patterns comparison of raw materials (earthenware clay and hen eggshell powder) and clay brick samples added 0% and 20%wt hen eggshell powder fired at 1000°C for 1, 3, and 5 hrs., are shown in Fig. 2. The XRD peak patterns of earthenware clay at 2 θ (26.832°, 50.079°, and 60.026°) consistent with the JCPDS nos. 01-089-8936 (quartz), 00-003-0447 (aluminum phosphate), and 00-019-0615 (iron oxide, Fe₂O₃) are hexagonal phase formation of SiO₂-Al₂O₃-Fe₂O₃. While the XRD peak patterns of chicken eggshell powder show rhombohedral of calcium carbonate (CaCO₃) or calcite consistent with the JCPDS nos. 01-072-1937 at 2 θ (29.369°, 48.452°, 47.450°, 39.370°, and 43.118°). The XRD peak patterns of fired clay brick without adding eggshell powder and fired at 1000°C for 1, 3, and 5 hrs., are shown only hexagonal crystalline phase formation of SiO₂-Al₂O₃-Fe₂O₃ consistent with the JCPDS nos. 01-089-8936 (quartz, SiO₂), 00-049-0134 (aluminum oxide, Al₂O₃), and 00-019-0615 (iron oxide, Fe₂O₃). The XRD peak patterns of fired clay brick samples added 20%wt eggshell powder and fired at 1000°C show sharp two peaks of anorthic phase formation of JCPDS nos. 00-003-0559 calcium aluminum silicate (CaAl₂Si₂O₈ or calcium feldspar) and calcium silicate (CaSiO₃ or wollastonite) at 2 θ

(26.881°-28.776°, 23.205°, 36.650°, and 43.473°) mixed with the cubic phase formation of calcium oxide (CaO) of JCPDS no. 00-048-1467 at 2 θ (37.360°, 53.860°, and 32.200°) and consistent with the results reported by Gökhan, G. et al. [13], Cultrone, G., et al. [15], Jordan, M.M et al.[20], Xia, W., et al. [21], and Wan, X. et al. [22]. Furthermore, the XRD peak patterns of fired clay bricks added 20%wt eggshell powder and fired at 1000°C show hexagonal phase formation of SiO₂-Al₂O₃-Fe₂O₃ consistent with JCPDS nos. 01-089-8936, 00-049-0134, and 00-019-0615. The sharp XRD peak at 2 θ 28.776° belongs to calcium aluminum silicate (CaAl₂Si₂O₈ or calcium feldspar) occurring obviously when the clay bricks were fired at 1000°C for 5 hrs., consistent with the results obtained by Jordan, M.M. et al. [20]. It means completely vitreous firing effect of high mechanical and good thermal properties of products.

Table 4. Color of clay brick before and after firing

Encoded samples (% wt eggshell-firing temperature)	Color of samples after firing (Munsell soil color chart)	Color of samples after firing
0 %wt-before firing	10YR5/6	dark yellowish brown
5 %wt-before firing	10YR5/6	yellowish brown
10 %wt-before firing	10YR7/4	very pale brown
15 %wt-before firing	10YR7/4	very pale brown
20 %wt-before firing	10YR7/4	very pale brown
0 %wt-800 °C	7.5YR7/8	reddish yellow
0 %wt-900 °C	7.5YR7/8	reddish yellow
0 %wt-1000 °C	7.5YR7/8	reddish yellow
0 %wt-1100 °C	7.5YR7/8	reddish yellow
5 %wt-800 °C	7.5YR7/6	reddish yellow
5 %wt-900 °C	7.5YR7/6	reddish yellow
5 %wt-1000 °C	7.5YR7/6	reddish yellow
5 %wt-1100 °C	7.5YR7/6	reddish yellow
10 %wt-800 °C	7.5YR7/6	reddish yellow
10 %wt-900 °C	7.5YR7/6	reddish yellow
10 %wt-1000 °C	7.5YR7/6	reddish yellow
10 %wt-1100 °C	7.5YR7/6	reddish yellow
15 %wt-800 °C	7.5YR7/6	reddish yellow
15 %wt-900 °C	7.5YR7/6	reddish yellow
15 %wt-1000 °C	7.5YR7/6	reddish yellow
15 %wt-1100 °C	7.5YR7/6	reddish yellow
20 %wt-800 °C	10YR8/6	Yellow
20 %wt-900 °C	10YR8/6	Yellow
20 %wt-1000 °C	10YR8/6	Yellow
20 %wt-1100 °C	10YR8/6	Yellow

The mechanical properties (compressive strength and hardness) of clay bricks are measured according to the Thai Industrial Standard Institute 243/2520. The data comparison of clay brick samples with and without 0%, 5%, 10%, 15%, and 20% wt eggshell powder fired at 1000°C for 1, 3, and 5 hrs., at each firing temperature are shown in Table 5. The high percentage of amount eggshell powder added in clay bricks, the better and higher compressive strength and hardness values of clay bricks are. The best condition of samples firing and eggshell adding to get the highest compressive strength and hardness clay brick is 20%wt eggshell powder adding and firing at 1000°C for 5 hrs., namely sample 20-1000-5. The compressive strength and hardness values of the best condition (20-1000-5) are 8.28 MPa and 8.79 ± 0.60 HV, respectively. While the clay brick sample without adding eggshell powder fired 1000°C for 5 hrs, has the compressive strength 7.42 MPa and

hardness 7.63 ± 0.30 HV, respectively. The theoretical compressive strength and hardness values of the best fired clay brick according to the Thai Industrial Standard Institute 243/2530 and the ASTM C 373-72 should have the data more than 7.0 MPa and 6.0 HV, respectively.

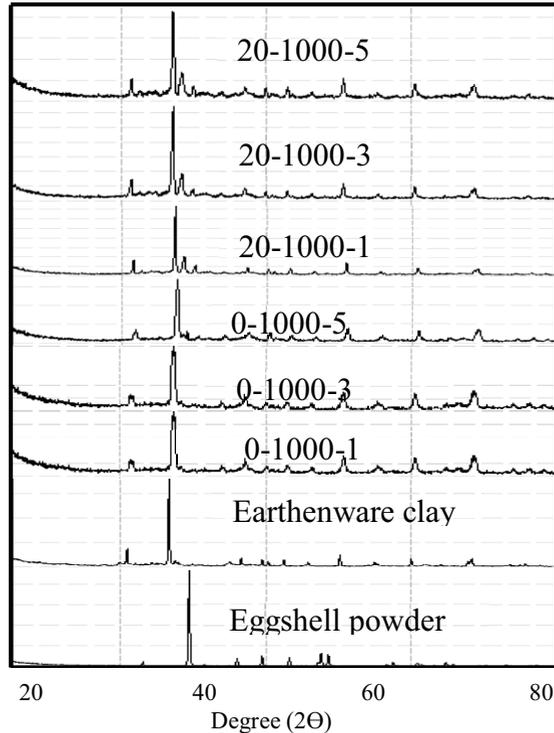


Fig. 2. The XRD peak patterns of samples: eggshell powder, earthenware clay, and fired clay bricks added 0 and 20%wt eggshell powder after firing at 1000°C for 1, 3, and 5 hrs., respectively.

The thermal expansion coefficient is one kind of the thermal properties of materials. The obtained fired clay bricks added eggshell powder and fired at 1000°C for 3 hrs., or 5 hrs., have low thermal expansion coefficient value less than those of fired clay bricks without adding eggshell powder at the same firing temperature and firing time. It means adding eggshell in fired clay bricks better than samples without eggshell adding. Thermal expansion coefficient values of clay bricks added eggshell powder and fired at 1000°C for 3 and 5 hrs., are 3.2605×10^{-6} and 2.3652×10^{-6} ($^{\circ}\text{C}$)⁻¹. While thermal expansion coefficient values of fired clay bricks without adding eggshell powder and fired at 1000°C for 3 and 5 hrs., are 4.7846×10^{-6} and 3.6566×10^{-6} ($^{\circ}\text{C}$)⁻¹. The low thermal expansion coefficient of materials has, the better thermal shock resistance is. Therefore, the fired clay brick sample added 20%wt eggshell powder and fired at 1000°C for 5 hrs., is the best condition to receive the good physical, mechanical and thermal properties.

Table 5. Mechanical properties of clay bricks

Samples*	Compressive strength (MPa)	Hardness (HV)
0-1000-1	7.05	7.27±0.20
20-1000-1	8.09	8.38±0.87
0-1000-3	7.37	7.47±0.60
20-1000-3	8.18	8.55±0.10
0-1000-5	7.42	7.63±0.30
20-1000-5	8.28	8.79±0.60

Table 6. Thermal expansion coefficient of clay bricks

Samples ^a	Thermal expansion coefficient ^b (°C) ⁻¹
0-1000-3	4.7846 x 10 ⁻⁶
0-1000-5	3.6566 x 10 ⁻⁶
20-1000-3	3.2605 x 10 ⁻⁶
20-1000-5**	2.3652 x 10 ⁻⁶

Remark:

*Encoded of samples x-xxxx-x mean amount of eggshell powder adding-firing temperature-firing time i.e. 0-1000-3 (no adding (0%wt) eggshell powder -firing at 1000°C-firing time for 3 hrs.).

** means the best condition due to the low thermal expansion coefficient effect to good thermal shock resistance.

4 Conclusions

Adding chicken eggshell powder into clay bricks can increase physical-mechanical-thermal properties of products. The higher amount of adding eggshell powder into clay bricks is, the better physical-mechanical-thermal properties of clay bricks are due to calcium oxide content caused to calcium feldspar, calcium silicate, and wollastonite phase formation. The firing temperature and soaking time is an important factors affect to densification or vitrification due to low porosity and completion of the glassy phase formation. The best condition of fired clay bio-bricks are firing at 1000°C for 5 hrs. The fired clay bio-bricks added 20%wt eggshell powder and fired at 1000°C for 5 hrs., are high compressive strength and hardness (8.28 MPa and 8.79 ± 0.60 HV), good thermal expansion coefficient 2.3652 x 10⁻⁶ (°C)⁻¹, good true density 1.96 ± 0.02 g/cm³, and low water absorption 14.36 ± 0.80%wt. The theoretical compressive strength, hardness, and water absorption values of fired refractory according to the Thai Industrial Standard Institute 243/2530 and the ASTM C 373-72 should have the values more than 7.0 MPa, 6.0 HV, and less than 25%wt, respectively. Therefore, the obtained fired clay bio-bricks added 20%wt eggshell powder and fired at 1000°C for 5 hrs., are potential to use as clay bricks for construction and thermal insulation.

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