New texture with black grey color of fired clay wall tiles produced from rice husk ash, brown glass cullet, and local plastic clay

W Ubolrat¹ * and P Duangkamol ²

¹,² Faculty of Engineering, Production Engineering Department, 1518 Pracharat 1 Rd., Bangsue, Bangkok, Thailand

Email: ubolrat.w@eng.kmutnb.ac.th; bmind2316@gmail.com

Abstract. Developing fired clay wall tiles by valorising waste materials and local plastic clay was objective of this study. Rice husk and glass cullet are waste materials which had been selected. They were mixed with local plastic clay of Anothong province in Thailand. All materials used were characterized their composition by X-ray Fluorescence technique. Specimens had been prepared by dry pressing and then fired at 950°C and 1050°C. Physical properties, bending strength and water absorption, were tested and compared with Thai Industrial Standard (TIS 2508-2555). In addition, X-ray Diffraction technique and Scanning Electron Microscope were used to analyse microstructure of selected specimens. The results of this experiment shows that utilizing of 60-70% brown glass cullet, 10-30% rice husk ash fired at 950°C is feasible to produce wall tiles for commercial. It provides high bending strength and low water absorption and can pass the TIS 2508-2555. Furthermore, it provides new texture with black grey colour of wall tiles.

1. Introduction

Currently, there are many community industries in Thailand. Thai government institution dedicated for SMEs. It had allocated THB 1.2 billion ($USD 37 million) to support the growth of SMEs and estimated that the fund will help SMEs to create innovation up to 100,000 products. This can increase value to the economy [1]. To comply with this policy, this paper aimed to improve competency of community industries in Anothong province of Thailand by developing new texture ceramic products. Waste materials i.e. rice husk ash from biomass power plant and brown glass cullet were selected. They were mixed with local plastic clay of Anothong province.

For saving environment, rice husk ash; waste material from the biomass power plant has been selected. Due to consuming rice husk as the fuel of boiler, the power plant generates abundant of rice husk ash. In addition to having negative effects on the environment, it leads a high cost burden to the manufacturers to dispose it. Many researches about rice husk ash (RHA) have been carried out. Effect of rice husk and rice husk ash to properties of bricks was determined by Sutas et al [2]. They summarized that bricks adding rice husk ash (RHA) have high compressive strength and density than that of adding rice husk (RH). Haslinawati et al [3] studied the effect of temperature on ceramic from rice husk ash. They founded that RHA had sintered at 1000°C contained high percentage of cristobalite. In addition, rice husk ash and fly ash were utilized to manufacture red bricks [4]. This research proposed that 15% RHA, and 15% fly ash mixed with plastic clay were appropriated to
produce bricks which fired at 1050°C. Eliche-Quesada et al [5] also studied utilization of rice husk ash and wood ash for developing clay matrix brick. The proportion of 10 wt. % rice husk ash and 30 wt. % wood ash can fulfil the standard of clay masonry units.

Moreover, glass cullet also one of waste materials have been generated from production of glass industries and discarded glass products i.e. glass bottles. From the yearly report by the pollution control department in 2016 [6], 42% of waste glass in Thailand is not utilized, amounting to 1,014,653 tons. Owing to containing fluxing agent, glass cullet can be employed as a material for reducing the firing temperature [7]. Many researchers proposed that waste glass has the potential for enhancing mechanical properties of ceramic products i.e. wall and floor tiles [8], fired clay bricks [9, 10, and 11].

In this study, combination between rice husk ash, brown glass cullet, and plastic local clay (Angthong clay) were conducted. The expected outcome was to manufacture new texture with black grey colour of fired clay wall tiles.

2. Materials and Method

2.1 Materials

Waste materials used in this research were Rice Husk Ash (RHA) and Brown Glass Cullet (BGC) which mixed with Angthong clay (Ang Clay). All of them were characterized the chemical composition by X-ray Fluorescence (XRF) which are shown in table 1.

|          | SiO₂ | K₂O | CaO | MgO | Fe₂O₃ | Al₂O₃ | SO₃ | Na₂O | TiO₂ |
|----------|------|-----|-----|-----|-------|-------|-----|------|------|
| RHA      | 92.67| 1.96| 1.18| 0.78| 0.54  | 0.56  | 0.34| 0.07 | 0.03 |
| BGC      | 72.1 | 0.2 | 10.6| 2.4 | 0.1   | 1.6   | 0.15| 12.9 | 0.05 |
| Ang Clay | 64.95| 2.46| 0.59| 1.43| 6.45  | 21.95 | 0.23| 0.41 | 0.99 |

Fluxing materials i.e. K₂O, Na₂O, and CaO (See table 1) are most contained in BGC. This indicated that fluxing materials can promote the low sintering temperature of ceramic bodies. However, SiO2 is the majority oxide containing in all materials. Mixtures of materials used are conducted by exploiting the tri axial diagram. It can formulate 36 formulas and classified into 8 groups: A, B, C, D, E, F, G, and H (See table 2).

|          | A | B | C | D | E | F | G | H |
|----------|---|---|---|---|---|---|---|---|
| RHA      | 10| 20| 30| 40| 50| 60| 70| 80|
| BGC      | 80| 70| 60| 50| 40| 30| 20| 10|
| Ang Clay | 10| 10| 10| 10| 10| 10| 10| 10|

Note that, formulas in highlight color could not be molded, due to containing RHA higher than 30 wt. %. This made the mixtures difficult to be formed. Therefore, there were 25 formulas remained to be investigated.

2.2 Method

2.2.1 Preparation the specimens. When drying until having constant weight and milling by a laboratory ball mill, all materials were sized by 297 micrometer sieve. And then, they had mixed together by dry mixing process for 30 minutes. Mixtures of formulations were sprayed with 10 wt. % of water and molded by uniaxial pressing technique in a 50x100 mm rectangular die at 100 bars and dried again at 150°C.

In order to form the hard body, all specimens were fired by 100°C C/h at maximum temperature 950°C and soaked for 1 h.
2.2.2 Testing properties of specimens. All specimens were heated up by the electric laboratory kiln, then they were suitable to be tested properties. The properties of fired specimens to be investigated are expressed as follow.

- Three points bending was exploited to determine bending strength of specimens. Water absorption test was conducted by placing specimens in water until heated up and boiled for 2 h, and soaking them under water for 24 h. Specimen’s water absorption was determining by calculating difference of dry and wet weight of them. Linear firing shrinkage of specimens was carried out by measuring specimens’ width with Vernier caliper. Difference of their before and after firing width were calculated for determining firing shrinkage. Weight loss of fired specimens was determined by weighting specimens before and after firing, then calculating their different weight. Specimens’ bulk density was investigated by Archimedes’ technique.

- Characterization microstructure of specimens Scanning Electron Microscopy (SEM) series Hitachi SU3500 and X-ray Diffractometer (XRD) series D8 ADVANCE. (BRUKER) were employed to analyse microstructure of fired specimens. However, formulas obtaining the highest and lowest bending strength were selected to investigate their microstructure.

3. Results and discussion

3.1 Fluxing materials, bending strength, and linear firing shrinkage of tested samples

$\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, and $\text{CaO}$ are fluxing contained in each mixture formulas have been calculated. They are compared with bending strength and linear shrinkage of tested specimens. It is shown in table 3. Formulas No. A4-A8, and B12-B15 are unable to be tested. Due to having high content of RHA and low content of Ang clay, they cannot be molded. All 8 formula groups show the trend of increasing bending strength and linear shrinkage, when increasing content of fluxing materials (see table 3).

### Table 3. Comparison of % fluxing material, bending strength, and % shrinkage of 36 formulas

| Group | No. | % Fluxing | Bending St. (MPa) | % Shrinkage |
|-------|-----|-----------|-------------------|-------------|
| A     | A1  | 19.63     | 8.91              | 0.06        |
|       | A2  | 17.58     | 18.18             | 3.82        |
|       | A3  | 15.53     | 14.52             | 3.67        |
|       | A4  | 13.48     | 0.00              | 0.00        |
|       | A5  | 11.43     | 0.00              | 0.00        |
|       | A6  | 9.38      | 0.00              | 0.00        |
|       | A7  | 7.33      | 0.00              | 0.00        |
|       | A8  | 5.28      | 0.00              | 0.00        |
| B     | B9  | 7.46      | 0.00              | 0.00        |
|       | B10 | 13.53     | 14.52             | 2.87        |
|       | B11 | 9.41      | 0.00              | 0.00        |
|       | B12 | 7.36      | 0.00              | 0.00        |
|       | B13 | 5.31      | 0.00              | 0.00        |
| C     | C16 | 13.53     | 21.99             | 2.33        |
|       | C17 | 13.53     | 15.08             | 2.36        |
|       | C18 | 11.48     | 5.11              | 2.09        |
|       | C19 | 9.43      | 2.36              | 1.67        |
|       | C20 | 7.38      | 0.00              | 1.65        |
|       | C21 | 5.33      | 0.00              | 1.21        |
| D     | D22 | 13.56     | 15.18             | 2.16        |
|       | D23 | 11.51     | 7.36              | 2.09        |
|       | D24 | 9.46      | 2.42              | 1.53        |
|       | D25 | 7.41      | 1.69              | 1.45        |
|       | D26 | 5.36      | 0.00              | 1.08        |
| E     | E22 | 13.53     | 11.92             | 2.03        |
|       | E23 | 9.48      | 5.10              | 1.92        |
|       | E24 | 7.43      | 2.82              | 1.72        |
|       | E25 | 5.38      | 1.38              | 0.98        |
| F     | F31 | 9.51      | 10.79             | 1.96        |
|       | F32 | 7.46      | 4.55              | 1.90        |
|       | F33 | 5.41      | 2.49              | 1.42        |
| G     | G34 | 7.48      | 11.79             | 1.88        |
|       | G35 | 5.43      | 5.12              | 1.43        |
| H     | H36 | 5.46      | 10.44             | 1.19        |

### Table 4. Comparison of % water absorption, % wt. loss, and density of 36 formulas

| Group | No. | % Water Ab | % Wt. loss | Density (g/cm³) |
|-------|-----|------------|------------|-----------------|
| A     | A1  | 9.76       | 2.05       | 1.19            |
|       | A2  | 17.74      | 4.34       | 1.61            |
|       | A3  | 19.85      | 4.08       | 1.64            |
|       | A4  | 0.00       | 0.00       | 0.00            |
|       | A5  | 0.00       | 0.00       | 0.00            |
|       | A6  | 0.00       | 0.00       | 0.00            |
|       | A7  | 0.00       | 0.00       | 0.00            |
| B     | B9  | 8.92       | 2.58       | 1.64            |
|       | B10 | 17.30      | 4.55       | 1.82            |
|       | B11 | 25.84      | 6.16       | 1.91            |
|       | B12 | 0.00       | 0.00       | 0.00            |
|       | B13 | 0.00       | 0.00       | 0.00            |
|       | B14 | 0.00       | 0.00       | 0.00            |
|       | B15 | 0.00       | 0.00       | 0.00            |
| C     | C16 | 13.44      | 2.91       | 2.17            |
|       | C17 | 23.20      | 5.09       | 2.15            |
|       | C18 | 32.05      | 6.81       | 2.14            |
|       | C19 | 36.26      | 7.41       | 2.12            |
|       | C20 | 40.72      | 9.48       | 2.06            |
|       | C21 | 47.38      | 10.75      | 2.00            |
| D     | D22 | 16.17      | 3.78       | 2.24            |
|       | D23 | 24.43      | 7.82       | 2.23            |
|       | D24 | 31.05      | 7.57       | 2.15            |
|       | D25 | 34.04      | 8.09       | 2.13            |
|       | D26 | 41.11      | 9.63       | 2.07            |
| E     | E22 | 15.53      | 3.57       | 2.31            |
|       | E23 | 22.85      | 6.48       | 2.27            |
|       | E24 | 28.25      | 8.22       | 2.21            |
|       | E25 | 35.17      | 9.79       | 2.14            |
| F     | F31 | 15.51      | 3.18       | 2.15            |
|       | F32 | 21.85      | 6.99       | 2.30            |
|       | F33 | 27.70      | 7.92       | 2.22            |
|       | F34 | 15.13      | 5.73       | 2.37            |
|       | F35 | 21.52      | 7.06       | 2.31            |
| G     | G34 | 15.13      | 5.73       | 2.37            |
|       | G35 | 21.52      | 7.06       | 2.31            |
| H     | H36 | 16.52      | 6.22       | 2.42            |
This can summarize that effect of fluxing materials promote the low sintering temperature of ceramic bodies [7-11]. They further make ceramic tiles obtain higher bending strength. Porosity of tiles are decreased and lead to increase shrinkage of specimens. Note that, although formula No. A1 and B9 have the highest fluxing material, but they have lower bending strength and % shrinkage than the other formulas of their group. This phenomenon can analyse that these two formulas have the sintering temperature less than 950\(^\circ\) C. Therefore, instead of higher banding strength and shrinkage, it makes them tend to expand their body and having more porosity.

3.2 Water absorption, % weight loss, and bulk density of tested samples

As shown in table 4, % water absorption, % wt. loss, and density have a similar trend. Water absorption is increased when bending strength is low. However, there is exception in formula No. A1 and B9. Although, they obtain the lower bending strength but they still have low water absorption. This phenomenon is the effect of close pore in their bodies which make them having lower absorption. When analysing % wt. loss of formulas in each group, it shows that higher RHA content in the formula makes the samples have high weight loss. Considering bulk density, the formulas having high content of Ang. Clay provide the higher density. As such, formulas in group A, B have lower density than the other group that having higher Ang. Clay content.

3.3 Scanning Electron Microscopy (SEM) analyzing

In order to analyze microstructure of fired samples, the formulas having highest and lowest bending strength within a group had been selected to be characterized. Formula No. A1, A2, C16, C21 were selected to be investigated. Microstructure of No. A1 has various pores (see figure1). Comparing between A1 and A2 (see figure 2), it found that A2 has the sinter body of glassy phase and has less pores than that of A1. This phenomenon has consistent with the value of bending strength which A1 has lower strength than that of A2.

![Figure 1. Scanning Electron Microscope at x3000 of No. A1](image1)

![Figure 2. Scanning Electron Microscope at x3000 of No. A2](image2)
Crystal structure of fired samples were investigated by XRD. Likewise, SEM analysis, some formulas had been selected to be analysed. XRD analysis of formula No. A1, A2, C16, and C21 are expressed in table 5.

### Table 5. Crystalline phase of selected formulas comparing with bending strength

| Formula No. | Quartz | Cristobalite low | Nepheline | Wollastonite 2M | Bending St. (MPa) |
|-------------|--------|------------------|-----------|----------------|------------------|
| A1          | 5.93   | 42.53            | 6.71      | 44.83          | 8.91             |
| A2          | 3.68   | 64.11            | 4.74      | 27.46          | 18.18            |
| C16         | 25.16  | 23.08            | 27.78     | 23.99          | 21.99            |
| C21         | 43.3   | 42.1             | 6.17      | 8.42           | 0                |

Bending strength of these 4 formulas are also indicated in table 5. It can be notice that higher content of nepheline and wollastonite phase can promote higher bending strength i.e. formula No. A2 and C16. Exception for formula No. A1, although having high content of nepheline and wollastonite phase, it obtains low bending strength. This can be summarized that formula No. A1 has sintering point less than 950o C. To be fired at this temperature, this make it expand the shape and lead to have high porosity.

### 3.5 Comparison physical properties of optimal formulas with Thai Industrial Standard (TIS 2508-2555)

#### Table 6. Comparison of bending strength, water absorption with TIS 2508-2555, and composition of optimal formulas

| Formula No. | Bending St (MPa) | % Water absorption >10% | % Wt Composition |
|-------------|------------------|-------------------------|------------------|
| TIS 2508-2555 (BIII) | 15 | Each sample must not exceed 20% | RHA | BGC | Ang Clay |
| A2          | 18.18            | 17.74                   | 20               | 70  | 10    |
| A3          | 16.32            | 19.85                   | 30               | 60  | 10    |
| B9          | 17.81            | 8.82                    | 10               | 70  | 20    |
| B10         | 18.07            | 17.3                    | 20               | 60  | 20    |
| C16         | 21.09            | 13.14                   | 10               | 60  | 30    |
| D22         | 15.18            | 16.17                   | 10               | 50  | 40    |

\[ \text{Figure 3. Scanning Electron Microscope at x3000 of No.C16} \]

\[ \text{Figure 4. Scanning Electron Microscope at x3000 of No.C21} \]
The optimal formulas i.e. No. A2, A3, B9, B10, and C16 were selected because they have high bending strength. They are compared with standard of TIS as shown in table 6. They all can achieve the bending strength and water absorption comparing with TIS 2508-2555. In addition, the composition of these formulas are expressed again in table 6.

4. Conclusion
The objective of this study was to valorise waste materials which were RHA and BGC. They all the wastes from industrial process. In addition, local clay in Anthong province was selected to be mixed with these waste materials for manufacture fired clay wall tiles. The results as described in the previous section can be concluded as follow.

- Effect of BGC can reduce sintering temperature and provide the high bending strength of ceramic bodies. Moreover, water absorption of samples were also decreased. It illustrated in SEM analysis which make samples contain high glassy phase (see figure 3).
- Utilizing of RHA provides black grey colour for wall tile ceramics. However, composition of RHA in samples should not higher than 30% (see table 6). If utilizing higher than 30%, it will lead the lower bending strength and higher water absorption (see table 3, 4). Figure 5 shows the fired ceramic specimens of formulas that achieve TIS 2508-2555. Obviously, formulas No. A2, A3, B9, and B10 express the black grey effect which attract the community company for commercial production.

![Figure 5 Samples of fired specimens at 950°C](image)

- Combination of Ang Clay in formulation, it plays a role to facilitate the plasticity of samples that make them easily moulded. In this study, it can be utilized by composition up to 40%.
- Benefits of this study are enhancing the value of waste materials for developing ceramic tiles fired at low temperature. This action is one of efforts that can save social environment.
- The further study should to investigate the lower sintering temperature of formula No. A1. Because it showed the phenomenon of expanding shape that can be modified by reducing firing temperature.

Acknowledgements
This research was funded by the King Mongkut’s University of Technology North Bangkok. Contract no. KMUTNB-61-DRIVE-027.

References
[1] Asia: Thailand to increase SMEs by over 3 million in 2018. Retrieved from https://www.rfigroup.com/rfi-group/news/asia-thailand-increase-smes-over-3-million-2018
[2] Sutas J, Mana A and Pitak L 2012 Procedia. Eng. 32 1061-1067
[3] Haslinawati M M, Matori K A, Wahab Z A, Sidek H A A and Zainal A T 2009 Int J Basic Appl Sci. 9 111–117
[4] Sultana M S, Hossain M I, Rahman M A and Khan M 2014 J. Sci. Res. 6(3)
[5] Eliche-Quesada D, Felipe-Sesé M, López-Pérez J and Infantes-Molina A 2017 Ceram. Int. 4
[6] Pollution Control Department, Ministry of Natural Resources and Environment, Thailand State of Pollution Report 2016. http://www.pcd.go.th. (accessed 3 November 2017).
[7] Braganca S R and Bergmann C P 2005 Mat Res, 8
[8] Youssef N F, Abadir M F and Shater M A O 1998 J Eur Ceram Soc, 18(12)
[9] Chidiac S E and Federico L M 2007 CAN J CIVIL ENG, 34(11)
[10] Loryuenyong V, Panyachai T, Kaewsimork K and Siritai C 2009 Waste Manage, 29
[11] Kazmi S M, Abbas S, Nehdi M L, Saleem M A, Munir M J and Mater J 2017 Civ. Eng, 29(8)