FABRICATION OF CERAMIC FLOOR TILES FROM INDUSTRIAL WASTES

Nuttawat Kummoonin[1], Manat Jaimasith[2], and Worapong Thiemsorn[1*]

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Abstract

The present study focuses on the recycling of red mud waste (RM) from zinc hydrometallurgy, furnace slag (FS), and recycled cullet (RC) for manufacturing vitrified floor tile products. Incorporation was attempted aiming at designing new formulations intended to be less costly and possessing low water absorption and high flexural strength. The floor tiles containing RM 60-70 wt%, FS 10-20 wt%, and RC 10-20 wt% were uniaxially pressed. The green tiles were vitrified at 900-1050°C in an oxidizing atmosphere in a gas furnace with a firing rate of 5°C/min for 30 min. The fabricated floor tiles were tested for linear shrinkage, water absorption, apparent density, and flexural strength. The chemical and mineralogical analyses by X-ray fluorescence and X-ray diffraction (XRF and XRD) were also investigated. Microstructural evolution was carried out by scanning electron microscopy (SEM). The floor tiles fired at 1050°C showed linear shrinkage at 11 ± 0.45% approximately, a density of 2.4 ± 0.09 g/cm^3, and low water absorption at 2.6 ± 0.36%. The flexural strength was achieved at 26.31 ± 0.46 MPa due to the formation of needle-like crystals of mullite, wollastonite, and the flake crystals of anorthite. The dominant compositions were SiO_2, Al_2O_3, CaO, Fe_2O_3, Na_2O, and ZnO. The results indicated that all the industrial wastes (RM, FS, and RC) could be used for floor tile production. The new products, composed (in wt%) of 70RM, 15FS, and 15RC and fired at 1050°C, fulfilled the requirements of the Thailand industrial standard 2398-2551.

Keywords: Industrial waste, ceramic floor tile, furnace slag, recycled glass, red clay

Introduction

Due to the growth of economic industry in Thailand, every year huge amounts of industrial wastes are produced. The levels of solid wastes (SW), which are expected to increase continuously, should urgently be controlled and managed. At the present time the disposal of SW takes place in 3 ways; dumping on land or at sea, recycling or utilization for agricultural/constructional purposes, and finally incineration (Montero

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[1] *Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: 0-5394-3405; Fax.: 0-5389-2262; E-mail: wthiemsorn@hotmail.com*

[2] *Department of Materials Science, Faculty of Science, University of Phayao, Phayao 56000, Thailand.*

* *Corresponding author*

et al., 2009). Recently, various kinds of SW have been constructively applied to resources in recycling research, and related achievements are seen in science and engineering applications. Many authors have investigated the incorporation of different types of SW in the manufacture of traditional ceramic materials (Dondi *et al.*, 1997; Dondi *et al.*, 2002; Hojamberdiev *et al.*, 2011; Junkes *et al.*, 2011).

According to their potential, SWs are theoretically useful for ceramic tile manufacture with their low cost of raw materials, savings in energy, and the high quality of the final tiles. Recycling of SW generated by industries as alternative raw materials is not a new thing and has been done successfully in a lot of countries including Thailand (Thiemsorn and Kaewthip, 2009; Thiemsorn *et al.*, 2009; Wattanasiriwech *et al.*, 2009). The constructional ceramic industry is the most obvious technological activity sector to absorb SW due to the large quantity of raw materials used by the sector and the large volume of products in construction which is important in a developing country like Thailand. The reasons for SW recycling in the construction industry i.e. bricks, tiles, and window glass generally are : the exhaustion of natural resources, the conservation of non-renewable resources, preoccupation with environmental matters, and reduction in waste disposal costs (Pisciella *et al.*, 2001; Menezes *et al.*, 2002; Menezes *et al.*, 2005; Poungkaew *et al.*, 2010).

In this context, we report the first result when 3 industrial wastes from northern and eastern areas of Thailand, i.e. red mud waste (RM), furnace slag (FS), and recycled cullet (RC) were used to produce ceramic floor tiles resulting in 3 main advantages: (i) the use of zero natural raw materials (ii) a decrease of the firing temperature, and (iii) the elimination of abundant pollutant waste. Large amounts of RM are generated from the zinc hydrometallurgy process. This waste is disposed of in landfill sites, but this is not a sustainable solution for environmental consideration because the waste contains hazardous elements (Pb and Cu) which can contaminate natural water sources. FS is formed in iron manufacture from iron ore, the combustion residue of coke, and fluxes such as limestone and other materials. When a mixture is melted at high temperature, slag would be separated from the molten iron and then rapidly cooled into an amorphous solid. RC from waste bottles or windows is a non-dangerous waste. When RC is incorporated into a ceramic mixture, it has a good potential as a new fluxing agent to replace traditional feldspar and makes it possible to obtain a vitreous microstructure during the vitrification of ceramic materials (Thiemsorn and Kaewthip, 2009). Those wastes, featuring a high content of SiO_2, Al_2O_3, Na_2O, CaO, MgO, and Fe_2O_2 (Table 2) could be used to produce ceramic floor tiles with low water absorption and high flexural strength.

The aim of this work is to design new formulations for ceramic floor tile from RM, FS, and RC fired at 900, 950, 1000, and 1050°C measuring 20 × 20 × 1.3 cm with water absorption less than 5% and a flexural strength of more than 20 MPa which would fulfill the requirements of the Thailand industrial standard 37-2529 (TIS 2398-2551; The Thai Industrial Standards Institute).

Materials and Methods

Raw Materials and Batch Preparations

In this work, 3 industrial wastes with the potential of being reclaimed through their use as alternative raw materials were selected from the northern and eastern areas of Thailand. RM (Mining Industry, Tak), FS (Smelting Process, Chiang Mai), and RC (Kaew Sing (2000) Ltd., Khon Kaen) were collected. The standard batch of conventional floor tiles used as a reference consisted of 100% red clay (Ohm Ceramic Roof Co., Ltd., Chiang Mai). The red clay has already been analyzed and is used regularly as a raw material by Ohm Ceramic Roof Co., Ltd. Table 1 shows the chemical and mineralogical compositions of red clay (Sangleng, 2010).

The compositions of the other wastes are also shown in Table 2. All these raw materials were dry-ground and then passed through a 100 µm mesh in accordance with ASTM standard ASTM E 11:95 (ASTM, 2001).

The raw materials were characterized by the determination of their apparent density according to the Archimedes method, and particle size distribution using a particle size analyzer (Mastersizermodel MSS Serial No: 33544/756, Malvern Instruments Ltd., Malvern, UK). The chemical composition was determined using an X-ray fluorescence spectrometer (XRF) (Magix Pro MUA/USEP T84005, Koninklijke Philips N.V., Amsterdam, Netherlands). X-ray diffraction (XRD) analysis

Table 1. Chemical and mineralogical compositions of the red clay

Chemical composition (wt%)								
SiO_2	Al_2O_3	K_2O	CaO	MgO	CuO	TiO_2	Fe_2O_3	LOI*
69.61	18.01	0.94	0.11	1.62	0.35	0.36	3.00	6.00
Dominant mineralogical composition**								
Quartz (SiO_2), Iron silicate ($Fe_2O_3.SiO_2$), Kaolinite ($Al_2O_3.2SiO_2.2H_2O$), Potassium feldspar ($K_2O.Al_2O_3.6SiO_2$), Mica ($K_2O.MgO.Fe_2O_3(Al_2Si_2O5.2H_2O$)								

* *Loss on ignition*

** *Reported by Sangleng, 2010*

Table 2. Chemical composition of industrial wastes

Industrial wastes	**Composition (wt%)**										
	SiO_2	**Al_2O_3**	**Na_2O+ KO**	**CaO**	**MgO**	**CuO**	**ZnO**	**PbO**	**TiO_2**	**Fe_2O_3**	**LOI***
RM	40.06	5.15	5.16	20.30	1.76	0.35	0.97	0.61	-	15.07	10.87
FS	61.01	17.58	1.17	11.37	2.02	-	-	-	0.40	5.14	-
RC	72.40	0.70	13.90	8.60	4.00	-	-	-	0.02	0.11	0.20

* *Loss on ignition*

Table 3. The proportion of the floor tiles for the formulations (wt%)

Industrial wastes	**Formulations**					
	B0	**B1**	**B2**	**B3**	**B4**	**B5**
Red clay*	100	-	-	-	-	-
RM	-	70	70	70	70	70
FS	-	-	10	15	20	30
RC	-	30	20	15	10	-

* *Red clay used as reference (Conventional floor tile)*

was done using Cu-Kα radiation in the range (2θ) 10°-70° (X'Pert Pro MPD, Koninklijke Philips N.V., Amsterdam, Netherlands). Crystalline phases were identified by comparing the intensities and positions of the Bragg peaks to those listed in the Joint Committee on Powder Diffraction Standards (JCPDS) data files : Anorthite (00-002-0523), Diopside (00-011-0654), Gypsum (00-036-0432), Hematite (01-073-0603), Kaolinite (01-075-0938), Mica (01-079-1668) and Quartz (01-083-2456) (International Centre for Diffraction Data, 2012).

A relevant ternary system was chosen to guide the formulations of the floor tiles as shown in Table 3. The dry mixtures were homogeneously mixed for 30 min using a porcelain pot mill and then passed through a 40 mesh (420 μm, ASTM). The moisture content (moisture mass/dry mass) was adjusted to 10%.

Method of Making Floor Tile

Eight hundred grams of mixture was uniaxially pressed by a hydraulic press at 5 MPa in the form of rectangles 20 × 20 × 1.3 cm. The pressed green tiles were dried in air overnight and fired at 900, 950, 1000, and 1050°C in an oxidizing atmosphere in a gas furnace with a firing rate of 5°C/min for 30 min and then were cooled normally. The forming, temperature, and firing cycle used in this work were chosen to simulate an actual forming/firing processes used at Ohm Ceramic Roof, Co., Ltd.

Characterization of Fabricated Floor Tile

Linear shrinkage values were evaluated from the variation of the length of the rectangular tiles (TIS 2398-2551). Apparent density values were determined by the Archimedes method. Water absorption values were determined from weight differences between the as-fired and water-saturated tiles after immersion in boiling water for 2 h (TIS 2398-2551). The flexural strength of the fired floor tiles was determined with the 3 point bending test at a loading rate of 0.5 mm/min (compressive strength data logger 100KN, Universal testing machine, model LRX, Lloyd Co., Ltd., Leicester, UK). Phase compositions were identified by XRD. The microstructures of the fracture surfaces of the fired floor tiles were examined using a scanning electron microscope (SEM) (JSM-5910 LV, JEOL Ltd., Tokyo, Japan). A CIELAB colorimeter (X-Rite CDM, X-Rite, Inc., Grand Rapids, MI, USA) for indicating the color of selected floor tiles was also used. The chromatic difference between the reference and the selected floor tiles was expressed as: $\Delta E^* = (\Delta L^* + \Delta a^* + \Delta b^*)$, where ΔL^*, Δa^*, and Δb^* are the differences of the CIE-Lab parameters L^*, a^*, and b^*. Chemical resistance was evaluated in accordance with ASTM C 650-97 (ASTM 1997, by hydrochloric acid solution (3% v/v)and potassium hydroxide solution (100 g/l) used as the indicators.

Results and Discussion

Characterization of Industrial Wastes

The chemical compositions of the wastes are given in Table 2. In terms of chemical composition, SiO_2 was the most abundant component, followed by Al_2O_3 and CaO compared with the red clay (Table 1). These oxides can be formed in crystalline silicate and aluminosilicate phases to increase the strength of fired tiles. The wastes also contain a reasonable amount of Na_2O, K_2O, Fe_2O_3, CaO, MgO, and ZnO. These oxides are considered fluxes. They can influence the vitrification behavior of the floor tiles during firing (Segadães, 2006).

Figure 1 presents the particle size distribution of the raw materials. It can be observed that the raw materials have about 85-90% of the particles with an equivalent diameter lower than 70 μm and from 10 to 20% of the particles with an equivalent diameter lower than 2 μm. Average particle sizes are shown in Table 4. It was found that the average particle sizes of the wastes are smaller than that of the red clay (<31.80 μm). These results point out that the wastes have a granulometry smaller than the processed conventional floor tile which is expected to have a high degree of vitrification at low temperature (Ronogajec *et al.*, 2000; Menezes *et al.*, 2005). The densities of the wastes as shown in Table 4 are higher than that of the red clay (>1.52 g/cm^3), except for the RM, which is expected to have a high density and the strength of floor tiles (Ronogajec *et al.*, 2000). The wastes have different colors that came from different Fe_2O_3 contents, which means that a floor tile appeared in either brownish or dark brownish colors depending on the batch formulation.

The XRD analysis of the raw materials

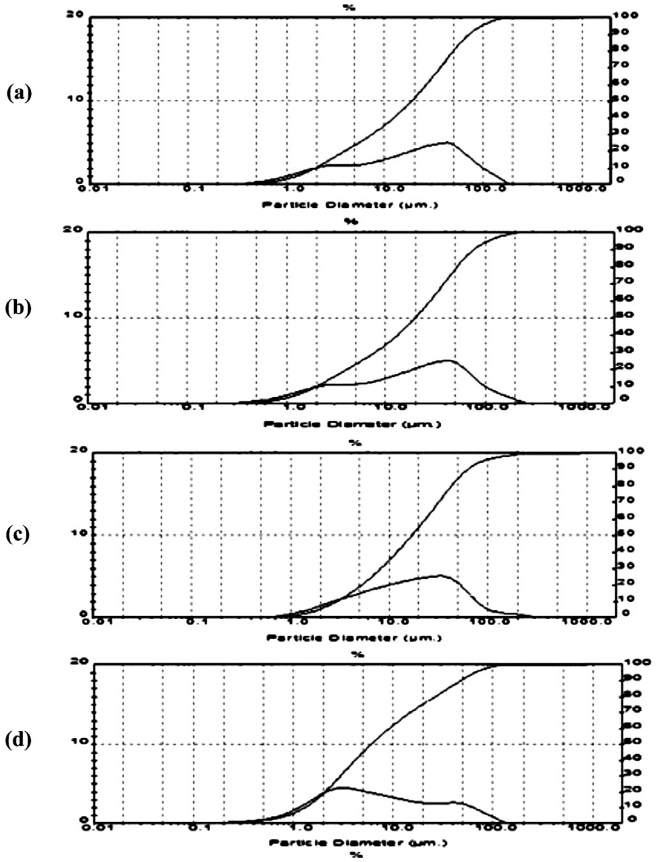

Figure 1. Particle size distributions of the industrial wastes: (a) red mud waste, (b) furnace slag, (c) recycled cullet, and (d) red clay (x-axis: Particle diameter (µm) and y-axis : Relative frequency (%))

Table 4. Physical properties of red clay and industrial waste powders

Raw material	Color	Average particle size (µm)	Apparent density (g/cm^3)
Red clay	Red	31.80 ± 0.84	1.52 ± 0.29
RM	Brown	15.85 ± 0.59	1.48 ± 0.27
FS	Black	29.20 ± 0.20	2.63 ± 0.18
RC	White	29.74 ± 0.90	2.50 ± 0.14

is shown in Figure 2. The RM exhibited crystalline peaks (Figure 2(a)) that are characteristics of quartz (SiO_2), gypsum ($CaSO_4.2H_2O$), and anorthite ($CaO.Al_2O_3.2SiO_2$). The FS exhibited both amorphous and crystalline phases that are quartz, anorthite, hematite (Fe_2O_3), and diopside ($CaO.MgO._2SiO_2$), as shown in Figure 2(b). For the RC in Figure 2(c), it is completely the amorphous phase representing only 1 broad peak. These results can be expected as the presence of the high strength of aluminosilicate and calciumsilicate crystals came from the RM and FS and the liquid phase came from the FS and RC causing the vitrification of the fired floor tiles. The red clay (Figure 2(d)) contains quartz, mica ($K_2O.MgO.Fe_2O_3(Al_2Si_2O5.2H_2O)$, kaolinite ($Al_2O_3.2SiO_2.2H_2O$), potassium feldspar ($K_2O.Al_2O_3.6SiO_2$), and iron silicate ($Fe_2O_3.SiO_2$), as shown in Table 1. It is expected that the presence of mullite, free quartz, and the liquid phases resulted after firing at the critical temperature.

Major Macro-Performance Analysis of Fabricated Floor Tile

The quality of the ceramic tiles after firing at the vitrification temperature, i.e. firing at 1050°C in this work, was determined on the basis of linear shrinkage, apparent density, water absorption, and flexural strength. In this work, the 2 parameters such as the RC/FS ratio and firing temperature were studied relating to the properties of the fabricated floor tiles.

Figure 3 shows the variation in linear shrinkage when the RC content and firing temperature were increased. Note that, at any given percentage of RC, the shrinkage of the fabricated floor tiles is higher than in the red clay floor tile (low fluxing agent) used as the reference. This is related to the RC being rich in alkaline flux (Na_2O and K_2O) which tends to accelerate the vitrification process. The series of shrinkage of the fabricated floor tiles are B3 > B4 > B5 > B2 > B1 > the reference.

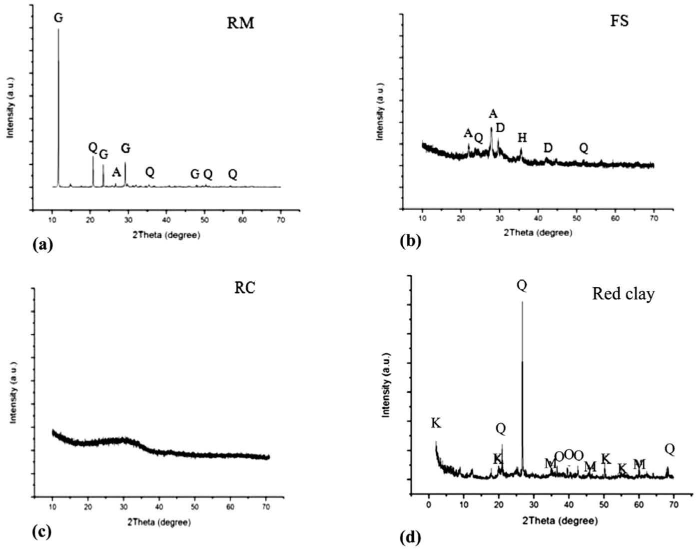

Figure 2. XRD patterns of the industrial wastes: (a) red mud waste (RM), (b) furnace slag (FS), (c) recycled cullet (RC), and (d) Red clay. Note G isgypsum ($CaSO_4.2H_2O$), Q is quartz (SiO_2), A is anorthite ($CaO.Al_2O_3.2SiO_2$), H is hematite (Fe_2O_3), D is diopside ($CaO.MgO.2SiO_2$), K is Kaolinite ($Al_2O_32SiO_2\ 2H_2O$), and M is Mica $K_2O.MgO.Fe_2O_3(Al_2Si_2O5.2H_2O)$

The highest shrinkage values appearing in the formulation B3 are because of the critical content of RC (15 wt%) caused by the liquid phase sintering. At a high RC content (formulations B1 and B2), the shrinkages shifted toward the higher RC content due to the expansion of the liquid phase at the firing temperatures (Raimondo *et al*., 2007; Thiemsorn and Kaewthip, 2009; Souza *et al*., 2010). Further, the highest shrinkage values appear at 1050°C for all formulations due to the coarsening and complete liquid phase sintering, as can be confirmed with the water absorption, apparent density, and flexural strength. In general, an increase of the firing temperature results in an increase of the shrinkage (Raimondo *et al*., 2007; Hojamberdiev *et al*., 2011) which is an important property of ceramic tiles and a small alteration that may occur. The shrinkage values for the tiles were found to be between 5.0 and 10.8%, indicative of good dimensional control. This range is within the acceptable limits for industrial production of vitrified floor tiles (Souza *et al*., 2010) included with the TIS 2398-2551.

Figure 4 depicts the water absorption values for the fabricated floor tiles. This physical property is very important, because it is related to the open porosity of the fired products. As expected, the formulation B3 shows lower water absorption values than the formulations B4, B5, and the reference, respectively. The decreases in water absorption values suggest that the high Na_2O and K_2O contents in RC improve vitrification behavior during firing. This is probably due to the reduction of the viscosity of the liquid phase, which accelerates the vitrification process (Segadães, 2006). Hence, the liquid phase formed during firing fills the pores and decreases the open porosity level which was reached to 2.64 ± 0.36% for the formulation B3.

Furthermore, the water absorption is related to the open porosity as a function of the firing temperature. The water absorption values of all formulations slightly decrease in the overall temperature range. The lowest water absorptions appeared at 1050°C due to the formations of liquid phases, especially the Na_2O-Al_2O_3-SiO_2 and K_2O-Al_2O_3-SiO_2 systems that mainly originated from the high RC content (formulation B3). Increasing temperatures cause both an increase in liquid phase amount and a decrease in the liquid phase viscosity. Under the surface energy forces created by the fine pores contained in the ceramic body, the liquid phase tends to approach the particles and, therefore, open porosity decreases (Kingery *et al*., 1976; Martín-Márques *et al*., 2008), like the results in Figure 4. The results confirmed that the

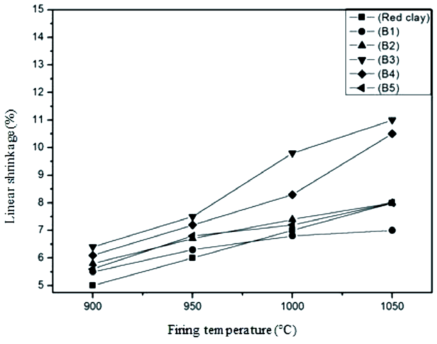

Figure 3. Linear shrinkage of the fired tile for different formulations versus firing temperatures

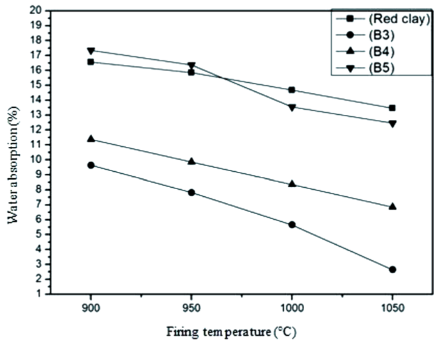

Figure 4. Water absorptions of the fired tile for different formulations versus firing temperatures

formulation B3 fired at 1050°C can be used to fabricate a floor tile that compared well with the reference.

In fact, the total porosity refers to the open and closed pore changes during firing also as a function of the firing temperature. Kingery *et al*. (1976) established 2 different steps of vitrification. The first shows a decrease in open porosity, which is coincident with an increase in the sample shrinkage. In the second step, the ceramic body could be represented as a conjunction of small and closed pores. The surface energy forces inside each pore give rise to a negative pressure, which tends to the decrease of the density. However, the densities of the fabricated floor tiles in this work depict a similar trend to that of linear shrinkage, which slightly increases with increasing the RC content and firing temperatures, as shown in Figure 5. The series of apparent densities of the fabricated floor tiles are B3 > B4 > B5 > B2 > B1 > the reference. It is expected that the tiles made from the industrial wastes and fired at lower than 1050°C, especially the formulation B3, vitrified within the first step without closed

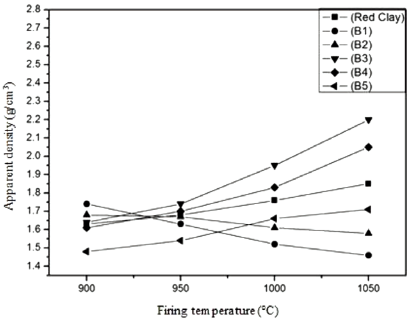

Figure 5. Apparent densities of the fired tile for different formulations versus firing temperatures

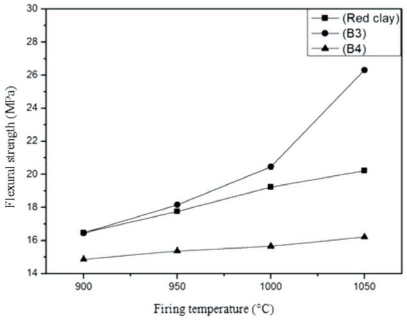

Figure 6. Flexural strength of the fired tile for different formulations versus firing temperatures

Table 5. The properties of the formulation B3 compared with conventional red clay tile used as the reference and the TIS 2398-2551

Properties	Red clay tile	Formulation B3	TIS 2398-2551(LMF*)
Water absorption (%)	13 ± 0.56	2.64 ± 0.36	< 3.0
Flexural strength (MPa)	19 ± 0.16	26.31 ± 0.46	> 25

* *LMF is a low medium ware absorption level of floor tile following the TIS 2398-2551*

Table 6. CIELAB parameters of the formulation B3 and conventional red clay tiles used as the reference fired at 1050°C

Tile formulation	CIELAB parameter			
	L^*	a^*	b^*	ΔE^*
Red clay	+ 43.18	+ 19.69	+ 19.55	ref.
B	+ 58.42	+ 6.30	+ 23.76	6.06

$+a^*$ = red, $-a^*$ = green, $+b^*$ = yellow, $-b^*$ = blue, $+L^*$ = bright, L^* = dark pores and a large bubble which is called bloating. The results confirmed that the formulation B3 fired at 1050°C shows the apparent porosity (2.64 ± 0.36%) fulfilling the TIS 2398-2551 (<3%).

Figure 6 shows the flexural strength of the fired floor tiles. The flexural strength increases with raising the RC content and the firing temperatures. Clearly, the maximum values of the flexural strength of the formulations B3 and B4 fired at 1050°C are 26.31 ± 0.36 MPa and 16.20 ± 0.46 MPa, respectively. In this work, the formulation B3 is the only component shown to completely improve the flexural strength to be higher than the reference, which is closely correlated to all the other properties investigated. Generally, the flexural strength of fired tiles is lowered by the presence of the liquid phase; however, the formulation B3 shows a value of the flexural strength higher than TIS 2398-2551 (>25 MPa).

For the performed properties, the formulation B3 was submitted to industrial-scale tests which were done at Ohm Ceramic Roof Co., Ltd., located in Chiang Mai, Thailand. The tiles for the industrial test were produced in the same way as those used by the company, although they were fired at 1050°C. The water absorption and the flexural strength are properties which, according to TIS 2398-2551, define the floor tile product class, as shown in Table 5. The formulation B3 obtained in this work shows a higher quality than the reference red clay tile and then is classified as a low medium ware absorption level (LMF).

Figure 7 demonstrated the formulation B3 and the reference floor tiles in the dimensions 20 × 20 × 1.3 cm fired at 1050°C. The tiles are a regular shape, homogeneous, and free of defects such holes, warps, or cracks. The color of the reference tile is a reddish color generated by Fe_2O_3, TiO_2, and CuO impurities (Table 1) which act as coloring agents in the ceramic body, while the formulation B3 is a bright brownish color induced by Fe_2O_3, TiO_2, MnO, and CuO

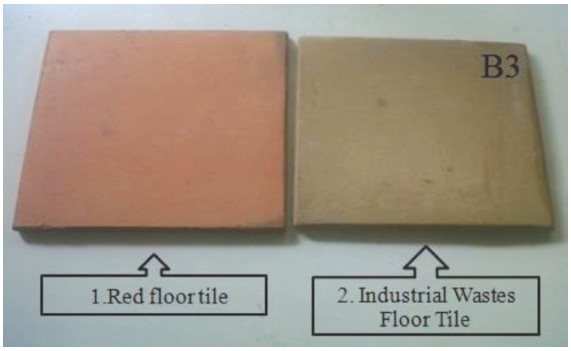

Figure 7. The comparison between the reference and the formulation B tiles in the dimensions 20 × 20 × 1.3 cm

Table 7. Chemical resistance tests of the formulation B3 and conventional red clay tiles fired at 1050°C

Solution	Formulation	
	Reference	B3
Hydrochloric ; 3%v/v	Affected	Affected
Potassium hydroxide ; 100 g/l	Not affected	Not affected

which came from the RM and FS wastes. The total chromatic difference with respect to the reference tile was expressed in Table 6. The main changes concern the a^* and b^* parameters. The a^* value of the formulation B3 is less than the reference whereas the b^* is reversed for a bright brownish appearance exhibiting the higher value of the L^*. However, the color of the formulation B3 tile could normally be improved by using either a ceramic body stain or ceramic engobe.

Microstructure Analysis of Fabricated Floor Tiles Fired at 1050°C

The values of linear shrinkage, water absorption, apparent density, and flexural strength correlate also with the crystalline phases formed during the vitrification process. The XRD pattern shown in Figure 8(a) establishes that the reference tiles fired at 1050°C contains 4 predominant crystalline phases, quartz (SiO_2), mullite ($3Al_2O_3.2SiO_2$), pseudobrookite (Fe_2TiO_3), and rutile (TiO_2). Meanwhile, the XRD pattern of the formulation B3 (Figure 8(b)) shows the wollastonite ($CaO.SiO_2$), mullite ($3Al_2O_3.2SiO_2$), anorthite ($CaO.Al_2O_3.2SiO_2$), quartz (SiO_2), calciumsulphate anhydrite ($CaSO_4$), and hematite (Fe_2O_3) as the major constituents included in the amorphous phase. The XRD of patterns of these tiles differ slightly from each other. The mullite, wollsatonite, anorthite, and quartz crystallines are the factors that contribute to the increase of the flexural strength of the fired floor tile. A mullite phase was formed in the reference tile by the transformation of kaolinite (Hojamberdiev *et al.*, 2011) following 2 steps: (1) decomposition of kaolinite to metakaolinite and (2) transformation of metakaolinite to mullite.

$$Al_2O_3.2SiO_2.2H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O\text{; at } 650^{\circ}C$$

$$Al_2O_3.2SiO_2 \rightarrow 1/3(3Al_2O_3.2SiO_2) + 4/3SiO_2\text{; at} > 960^{\circ}C$$

The formation of mullite in the reference tile was clear. Probably, a small amount of mullite was formed in the formulation B3 tile by the recrystallization of the high Al_2O_3 liquid phase, however it was difficult to detect due to the volume fraction and extremely small size (Thiemsorn and Kaewthip, 2009).

According to the chemical compositions, RM, FS, and RC, apart from the content of SiO_2 and Al_2O_3, show a relatively large amount of CaO and alkali oxides (Table 3). The formations of wollastonite and anorthite in the formulation B3 tile, which improve the flexural strength after firing at 1050°C, are the result of the interaction between the CaO and the decomposed metakaolinite and quartz, and other aluminosilicate phases in the composition (Asar *et al.*, 2010; Hojamberdiev *et al.*, 2011). The formation of wollastonite

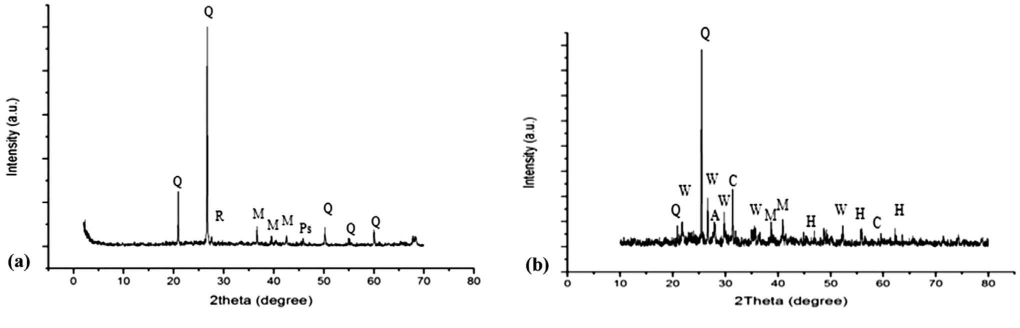

Figure 8. XRD patterns of the industrial wastes: (a) the reference tile (b) the formulation B3 tile. Note M is mullite ($3Al_2O_3.2SiO_2$), W is wollastonite ($CaO.SiO_2$), Q is quartz (SiO_2), A is anorthite ($CaO.Al_2O_3.2SiO_2$), H is hematite (Fe_2O_3), Ps is Pseudobrookite (Fe_2TiO_3), C is calciumsulphate anhydrite ($CaSO_4$), and R is rutile (TiO_2)

can be explained by the reaction of calcium oxide with decomposed quartz as follows:

$$CaO + SiO_2 \rightarrow CaO.SiO_2 \text{ ; at} > 900^oC$$

The formation of anorthite can also be explained in 2 ways: (1) the reaction of metakaolinite with calcium oxide and (2) the reaction of mullite and calcium oxide in the presence of quartz.

$$Al_2O_3.2SiO_2 + CaO \rightarrow CaO.Al_2O_3.2SiO_2\text{; at} > 1000^oC$$

$$3Al_2O_3.2SiO_2 + 3CaO + 4SiO_2 \rightarrow 3(CaO.Al_2O_3.2SiO_2)\text{; at} > 1000^oC$$

The formations of mullite, wollastonite, and anorthite in the formulation B3 confirmed the feasibility of RM, FS, and RC wastes being used as raw materials for floor tile production with an improvement in the fired properties and a reduction of the firing temperature.

Figure 9(a) and 9(b) shows SEM micrographs on the fracture of the reference and formulation B3 tiles, respectively, fired at 1050°C. There can be observed the typical grains and bond microstructure of fired tiles consisting of different grains. The results show that the reference tile contains mullite, anorthite, quartz, and large pores remained at the matrix, whereas in the formulation B3 tile a large number of wollastonite, anorthite, and residual quartz crystals are present. According to the presence of the liquid phase in the formulation B3, the microstructure shows a closely dense structure relating to the low water absorption (2.64%) and the flexural strength (26.31 MPa) compared with the reference tile.

Chemical Resistance of Fabricated Floor Tiles Fired at 1050°C

Table 7 shows the chemical resistance test of the reference and the formulation B3 tiles fired at 1050°C. Both tiles are inert to a potassium hydroxide solution but are affected by hydrochloric acid by which a small amount of Pb and Cu might be leached after a long time test. However, this problem can generally be solved by coating with either an engobe or ceramic glaze.

Conclusions

A mixture of 70 wt% RM, 15 wt% FS, and 15 wt% RC (formulation B3) was selected as a representative composition of ceramic floor tiles produced by an actual forming/firing processes used at Ohm Ceramic Roof, Co., Ltd., Chiang Mai. The formulation B3 floor tile showed a good vitrification behavior after firing at 1050°C. The fired tiles were homogeneous and free of defects. Linear shrinkage, water absorption, apparent density, and flexural strength determinations showed

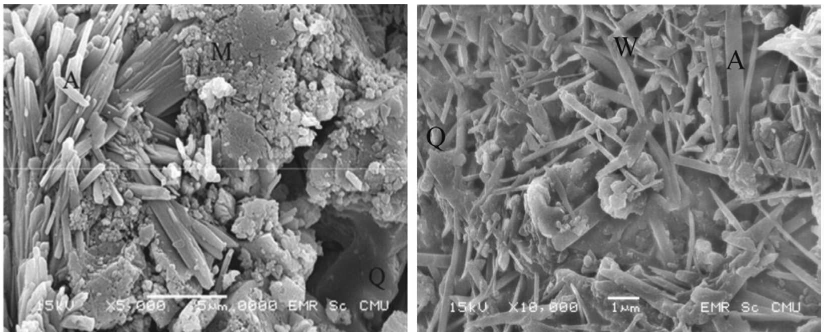

Figure 9. SEM observations on the fracture of the reference and the formulation B3 tiles fired at 1050°C: (a) the reference tile (b) the formulation B3 tile. Note M is mullite ($3Al_2O_3.2SiO_2$), W is wollastonite ($CaO.SiO_2$), Q is quartz (SiO_2), A is anorthite ($CaO.Al_2O_3.2SiO_2$)

the changes which the tile reached to vitrify by the liquid phase mechanism. This phenomenon was due to wollastonite, mullite, anorthite, and quartz formations included with the liquid forms, which originated an improvement in the fired properties. The linear shrinkage is 10.8%, water absorption is 2.64%, apparent density is 2.4 g/cm^3, flexural strength is 26.31 MPa, and basic solution resistance of the formulation B3, which fulfilled with the requirements of the Thailand industrial standard 2398-2551 (TIS 2398-2551).

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