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Formulation of High Reflection Engobe and Their Industrial Uses for Earthenware Wall Tile

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Abstract— **The aim of this paper is to reveal the correlations between the white/high reflection engobe (WRE) composition and their properties for earthenware wall tile industry. The engobes were formulated using (wt%) porcelain clay (PC) 72-80, recycled cullet (RC) 9-10, borax 9-10 and TiO_2 0-9. The mixtures were wet ground for 30 min in a pot mill and their specific gravity was controlled at 1.6 g/cm^3. The engobe slips were spray coated on earthenware wall tiles different thicknesses at 160-250 µm. The engobed tiles were single-fired at 950-1100°C in a gas furnace for 15 min. The coefficient of thermal expansion (CTE) was determined by dilatometer. The adhesion ability was investigated by tape-peel method. The whiteness and reflection values were determined by colorimeter and spectrophotometer, respectively. The phase composition and microstructure were evaluated by x-ray diffractometer and scanning electron microscope, respectively. The results showed the WRE composing microline, anatase, albite, anorthite, quartz and corundum had the CTE values nearby the wall tile. The whiteness and reflectance reached to the highest values at 4.76 wt%TiO_2 and layer thickness at 250 µm. At high temperatures, the whiteness and reflection slightly decreased due to the formations of mullite and rutile. The optimization of WRE composed (in wt%) of PC 76.19, RC 9.52, borax 9.52 and TiO_2 4.76% representing whiteness 95.51%, reflectance up to 85% by controlling the thickness at 250 µm and temperature at 1000°C.**

***Keywords*— Whiteness, Reflection, Engobe, Wall tile, Earthenware**

I. INTRODUCTION

Engobes can be described as a coating layer on ceramic surfaces, especially on ceramic wall tile to produce the desired colours and properties. A ceramic wall tile consists of a polycrystalline aluminosilicate substrate covered by an engobe and a glaze layers. The surface property of engobed wall tile (it means surface ability against light reflection) is one of the interesting characteristics of a wall tile, which affects on the surface ability and white/high light reflection as now called WRE [1]. In the traditional engobes used in wall tile industry, white and high reflection ability usually originates through matt of glaze matrix by addition of high concentrations of whiting agents i.e. kaolin, $CaCO_3$, ZrO_2, ZnO, TiO_2, into the batch [2].

The engobe is very important section in the tile production because this thin layer between the tile body and the ceramic glaze improves the coefficient of thermal expansion (CTE) matching and prevents solutions of coloring impurities, ensure a high reflection and a high degree of whiteness. It is prepared using kaolin and white clay, which provides whiteness and plasticity, various strong fluxing agents such as frit, cullet, borax generating the glassy phase formation, feldspar and quartz, which allow control of mixture melting point and CTE. Moreover, the whiting agents can be added in order to improve the whiteness and reflection [3].

Nowadays, the WRE concept has improved the quality of engobes by development of composition with more smooth surface, whiteness and desirable optical properties at the similar firing conditions [4]-[6]. For example, the high reflection engobe deposited onto the tile, and the infrared transparent glaze placed onto the engobe. Light reflection is reflected from the engobe, crosses again the glaze and eventually leaves the tile, whereas the color is obtained by the visible spectrum of additive colorings dispersed in the glaze [7], [8].

The aim of this paper is to reveal the correlations between the WRE compositions and their properties on order to apply for earthenware wall tile industry (Northern, Thailand). With regard to the industrial process, this work is carried out with the same production and provided into two parts. At first part, the study is focused on engobe compositions in order to obtain the highest whiteness and reflection. Second part is observed on the effects of thickness and firing temperature for the best performance engobe in order to apply onto the earthenware wall tile.

II. EXPERIMENTS

2.1 Raw materials

Earthenware wall tiles were supplied by Ohm Ceramic Roof Co., Ltd. (Chiang Mai, Thailand). Commercial powders: porcelain clay (PC), recycled cullet (RC) and borax ($Na_2O.2B_2O_3.10H_2O$) cooperated with TiO_2 (Lab grade; Unilab) were used to prepare a white/high reflection engobe (WRE). All raw material powders were ground and sieved to

<35µm particle size. The mean particle sizes were determined by laser particle size analyser (Mastersizer model MSS Serial No: 33544/756, Malvern Instruments Ltd., Malvern, UK) followed by X-ray fluorescent spectrometer (XRF; Philips Magix pro, PW2540) operating with Rh X-ray tube of 4 kW for chemical composition analysis.

2.2 Engobe preparation

Two groups of engobes were formulated as shown in Table 1. The various formulas were used to investigate the effects of borax, RC and TiO_2 on whiteness, reflectance and properties. All formulas were mixed with water in order to obtain slurries (1.6 g/cm^3), which were sprayed onto 10x10 cm^2 earthen wall tiles to produce the coatings with different thicknesses of 160-250 µm. The engobed tiles were dried in air for 24 h and single-vitrified in the range of 950-1100^{o}C for 15 min with firing rate 5^{o}C/min and then were normally cooled to ambient temperature.

TABLE I
FORMULATIONS OF ENGOBES

Sample code	Composition (wt%)			
	PC	RC	Borax	TiO_2
Group I				
B1	95.24	-	-	4.76
B2	85.71	9.52	-	4.76
B3	76.19	9.52	9.52	4.76
Group II				
B3	76.19	9.52	9.52	4.76
B4	72.73	9.09	9.09	9.09
B5	80.00	10.00	10.00	-

2.3 Characterization

1) Phase and microstructure evolutions: The phase constituents of all raw materials as well as the evolution of crystalline phases on the engobe after vitrify were determined by X-ray diffractometer (XRD; Rigaku Miniflex II) with CuK_α radiation for 2θ from 10^o to 80^o with a scanning rate of 12^o/min. Data base (X′pert HihgScore Plus version 2.1, Panalytical B.V. Almelo, The Netherlands, Powder Diffraction Files) was used for the phase identification. The microstructure observations of the surface engobes were carried out by scanning electron microspectometer (SEM; SEM-JEOL JSM-5910LV, Tokyo, Japan) at an acceleration voltage of 20 kV.

2) Thermal expansion: The coefficient of thermal expansion (CTE; α) of tile and engobes were measured on a dilatometer (Linseis L75) using a silica probe and a heating rate of 5 ^{o}C/min up to 800^{o}C.

3) *Thickness*: The vitrified tiles were cut and then ground by SiC abrasive paper, followed by polishing with alumina paste (1 µm). The thickness of selected engobe was determined by optical microspectometer (OM; Optical Microscope, Olympus BX60M with Camera, Cannon EOS 1000D).

4) Adhesion abilities: The adhesion abilities of selected engobes were observed by tape-peel method [9]. The engobed tile was weighted (w_1) and re-weighted (w_2) after peel testing. The weight loss (WL) was calculated following the Eq. 1:

$$\% \text{ WL} = [(w_1\text{-}w_2)/w_1] \times 100 \qquad (1)$$

5) Whiteness and reflectance: The whiteness of engobe was measured by colorimeter (Color Difference Meter, X-Rite$^®$Inc., Grand Rapids, MI, USA) and calculated by whiteness equation following the Eq. (2). The reflectance was determined by spectrophotometer (Lambda 35 UV-Vis Spectrometer, Perkinelmer Inc.) operating in the range of 400-1000 nm in air atmosphere.

$$\text{Whiteness} = 100 - [(100\text{-}L^*)^2 + a^{*2} + b^{*2}]^{1/2} \ (2)$$

where L^* = the degree of whiteness; a^* = the variation between green and red colors; and b^* = the variation between blue and yellow colors.

III. RESULTS AND DISCUSSION

3.1 Characteristics of raw materials

Table 2 gives the chemical compositions of raw materials. The PC and RC were enriched in SiO_2, Al_2O_3 and K_2O while the Na_2O, CaO and MgO contents were greater in RC. The total amount of coloring oxides (Fe_2O_3, MnO and TiO_2) in PC was approximately at 0.62 wt% which is normally used as main component in whitewares and white engobes. The RC and borax act as fluxing agent due to high alkali and alkaline contents in both raw materials. As for borax, B_2O_3 is main component which is low melting point oxide at 450-465^{o}C leading the increase of melt ability [10]. TiO_2 is a white oxide with a high NIR solar reflectance used in ceramic glaze and engobe [8].

TABLE II
CHEMICAL COMPOSITIONS OF RAW MATERIALS

Raw materials	Composition (wt%)			
	PC	RC	Borax	TiO_2
SiO_2	62.70	70.78	-	-
Al_2O3	26.82	1.22	-	-
Fe_2O3	0.59	0.49	-	-
Na_2O	0.84	13.26	16.23	-
K_2O	3.35	0.17	-	-
CaO	0.14	6.86	-	-
MgO	0.01	5.82	-	-
MnO	0.01	0.01	-	-
P_2O_5	0.05	0.01	-	-
TiO_2	0.02	0.04	-	100.00
B_2O_3	nil.	nil.	36.65	-
LOI	5.47	1.35	47.12	-
Mean size (µm)	12.82	26.46	131.77	0.39

LOI: Loss on ignition

Concerning to smooth surface of engobe, in this work, the particle sizes of raw materials were controlled to <35 µm. As shown in Table 2, all raw materials were less than 35 µm, especially for TiO_2 showed fine powder at 0.39 µm.

3.2 Effects of engobe formulations

As the formulas, they were developed as a function of RC and borax contents in order to receive the required properties of engobe such as whiteness, reflection, adhesion ability as the formulations shown in Table 1.

1) Morphology of engobes: Fig. 1 demonstrates the XRD patterns collected on the engobed surfaces of Group I samples. The patterns show that crystal structures were formed directly from the raw materials used in the engobes after vitrify at 1000°C. Microcline ($K_2O.Al_2O_3.2SiO_2$), quartz (SiO_2) corundum (Al_2O_3), and anatase (TiO_2), phases formed as a consequence of phase transformation of PC and TiO_2 during firing. Both corundum and anatase are whiting and opaque phases in the engobes. The amorphous phase results from the melting of alkali and alkaline oxides cooperated with B_2O_3 and SiO_2 introduced in the adhesion ability of engobes onto the tile surfaces. In semi-quantitative comparison in Table 3, the microcline and corundum phases decreased slightly with decreasing PC content from 95.27 wt% in B1 to 76.19 wt% in B3. On the other hand, the anorthite ($CaO.Al_2O_3.2SiO_2$) and albite ($Na_2O.Al_2O_3.6SiO_2$) are generated from the reaction of $CaO+Na_2O+Al_2O_3+SiO_2$ and re-crystallization by RC and borax additions as found in B2 and B3 patterns. An even stronger presence of amorphous phase by the well defined peak shape occurs in B3 because of the high contents of Na_2O and B_2O_3 employed into the formulation as replacement of borax.

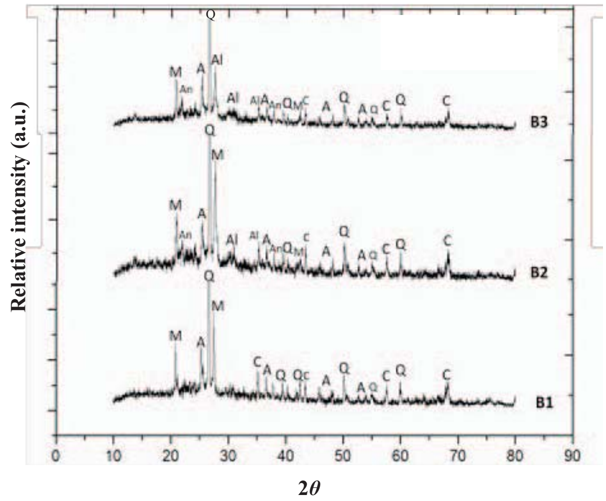


Fig. 1 XRD patterns of engobed tile as a function of RC and borax contents (Group II) vitrified at 1000°C for 250 µm of engobe layer; M: Microcline, C: Corundum, Al: Albite, An: Anorthite, Q: Quartz, and A: Anatase

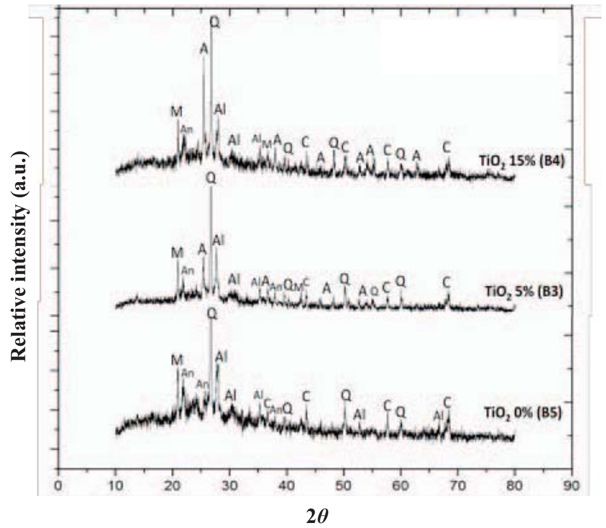
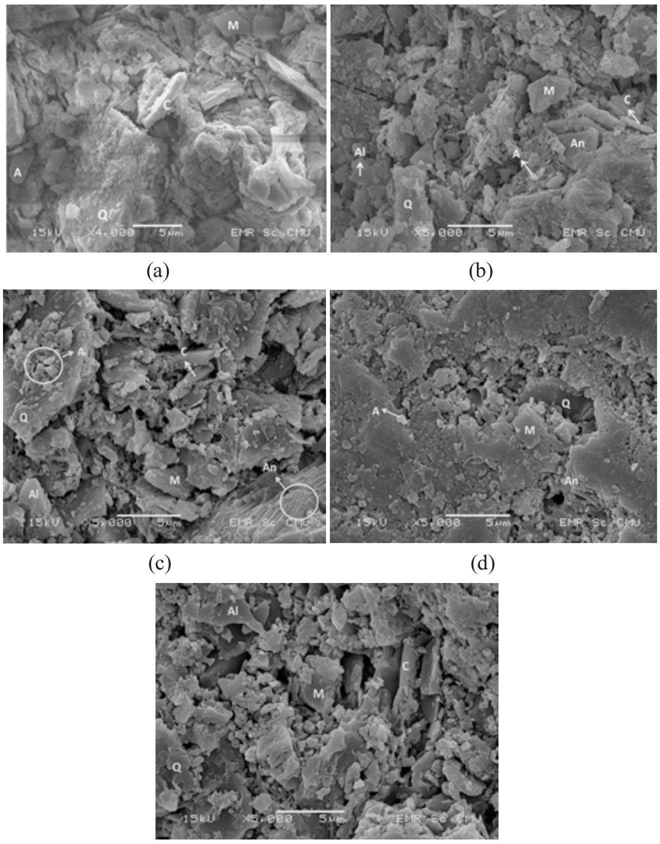


Fig. 2 XRD patterns of engobed tile as a function of TiO_2 content (Group III) vitrified at 1000°C for 250 µm of engobe layer; M: Microcline, C: Corundum, Al: Albite, An: Anorthite, Q: Quartz, and A: Anatase

The transformation of Group II samples as a function of TiO_2 content are illustrated in Fig. 2. The XRD patterns showed that the three engobes consisted of quartz, corundum, albite, anorthite, microcline and liquid phase, respectively. The B4 appeared the increase of anatase peaks due to the greater amounts of TiO_2 up to 9.09 wt% and no peaks of anatase appeared in the B5. The liquid phase increased with increasing RC and borax contents, in the other hand, the microcline and corundum phases also increased with increasing PC content as the series of B5>B3>B4.

2) Microstructure of engobes:



(a) (b)

(c) (d)

(e)

Fig. 3 SEM observations on the surface of engobes vitrified at 1000°C (a) B1 (b) B2 (c) B3 (d) B4 and (e) B5; M: Microcline, C: Corundum, Al: Albite, An: Anorthite, Q: Quartz, and A: Anatase

SEM observations were based on examination of the engobe surfaces of Group I and II vitrified at 1000°C as demonstrated in Fig. 3. The surfaces of the engobes were composed of various polycrystalline: microcline, corundum, albite, anorthite, quartz, liquid and anatase phases, except in the B5 sample where were similar in the XRD observations. As the results in Group I, the crystal sizes of the microcline, corundum and quartz decreased due to the reaction with RC and borax and transformation to albite and anorthite crystals during firing as shown in Fig. 3 (a)-(c), respectively. The polycrystalline seem almost coherent by liquid phase sintering from RC in B2 and RC cooperated with borax in B3 existing in the formulations.

In case of Group II, it was found that the increases of PC, RC and borax contents allowed the formation of crystal growth and shrinkage resulting to a more incoherent microstructures as shown in B5 (Fig. 3 (e)). Comparison between B3 and B4 samples, the microstructures of B4 looked like a greater compaction due to the increase of fine TiO_2 powder from 4.76 wt% to 90.09 wt%.

TABLE III
XRD SEMI-QUANTITATIVE ANALYSIS OF ENGOBES

Phase	Sample code				
	B1	B2	B3	B4	B5
Microcline	****	***	**	**	**
Corundum	****	*****	*****	****	***
Albite	-	*	***	***	****
Anorthite	-	**	**	**	**
Quartz	*****	*****	*****	****	****
Anatase	***	***	***	****	-
Liquid	*	**	***	**	****

3) Properties of engobes: Table 4 lists the coefficient of thermal expansions (CTE) of engobes and their surface characteristics.

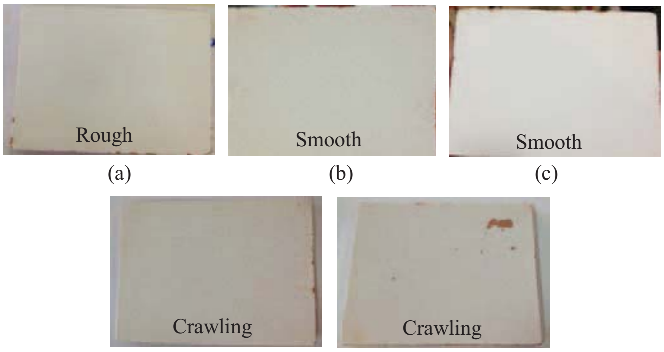
TABLE IV
PROPERTIES OF ENGOBES AND THEIR SURFACE

Sample code	Properties			
	CTE ($\times10^{-6}/^{o}C$) at 200-600 °C	WL (%)	Whiteness (%)	Smoothing
Tile	0.419	-	-	Smooth
B1	0.387	2.35	97.52	Rough
B2	0.428	2.41	95.70	Smooth
B3	0.511	0.43	95.51	Smooth
B4	0.411	0.42	92.34	Crawling
B5	0.462	0.43	89.01	Crawling

According to Table 4 the CTEs of Group I were higher than the earthenware tile due to a greater of fluxing oxides from RC and borax which is one of the most effective properties for fitting of the engobe-tile and avoiding surface curvature. The CTE increased slightly to the amount of borax as replacement of PC in the engobe. Because RC and borax encourage glass formation during firing that give a greater vitrification to the engobes as the series of B3>B2>B1. Moreover, the linear shrinkage (LS) of engobe depends directly on their CTE, that means, the LS of B3 is higher than B2 and B1, respectively. However, the CTEs of Group I is closed to the tile resulting the good fitting and smooth surface as shown in Table 4 and Fig 4.

The CTEs of Group II also closed to the tile but had high shrinkage as the series of B5>B4>B3 due to the increase of RC and borax contents and fine particle of TiO_2. These results cause to greater LS by liquid phase conducting the agglomeration of melted engobe as called crawling (Table 4 and Fig. 4).

The CTE value of B3 and the tile were 0.511 $\times10^{-6}$ $^{o}C^{-1}$ and 0.419 $\times10^{-6}$ $^{o}C^{-1}$, respectively. Both CTE values were small difference suggesting a good match between the B3 and the tile [11]-[14]. Moreover, the good fitting of B3 on the tile can be described by beside engobe and tile interface as shown in Fig. 5.



(a) (b) (c)

(d) (e)

Fig. 4 Typical images of smoothing and whiteness of engobes vitrified at 1000°C and engobe layer at 250 µm (a) B1 (b) B2 (c) B3 (d) B4 and (e) B5

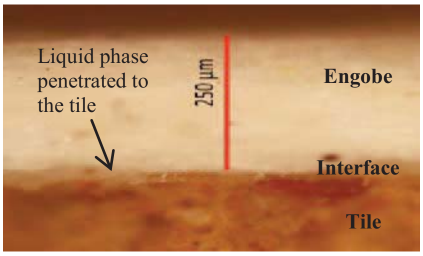
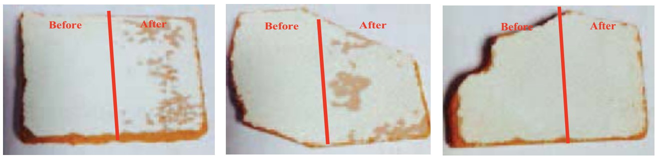


Fig. 5 The optical image of B3 sample on the tile vitrified at 1000°C

It was found that the B3 had a shiny appearance meaning further vitrification and bond well to the tile. The interface is stronger because the liquid phase of B3 increases from RC and borax which in turn produce a more fluid and more penetrating in engobe at 1000°C. These changes affect directly to the adhesion ability of engobes represented in term of WL as shown in Table 4 and Fig. 6.



(a) (b) (c)

Fig. 6 Typical images of test-peeling of engobes vitrified at 1000°C and engobe layer at 250 µm (a) B1 (b) B2 and (c) B3

The WL values decreased from 2.35% (B1) to 0.43% (B3) due to the strong bonding as found in the interface of B3 and the tile.

Again in Fig. 4, the smoothing and whiting of Group I and II engobes looked like with the three different surfaces such as rough, smooth and crawling. The smoothing depends on the vitrification existing the liquid phase and polycrystalline in engobe as described above. In the other hand, the whiting increased with increasing RC and borax totally at 19.08 wt% and 4.76 wt% TiO_2. The whiteness decreased, after that, when the RC and borax were greater than 19.08 wt% and TiO_2 was greater than 4.76 wt%. In this work, the whiteness comes from the vitrified surface cooperated with corundum (Al_2O_3) and anatase (TiO_2) presenting whiteness approximately at >99% and >97%, respectively. Fig. 4 (c) demonstrates the surface of B3, where the presence of smoothest and whiteness up to 95.51%.

A correlation between surface characteristics and reflection seems also to exist because the white vitrified and smooth engobe has higher reflectivity in comparison the white devitrified and rough engobe [3], [13], [15] as demonstrated in Fig. 6

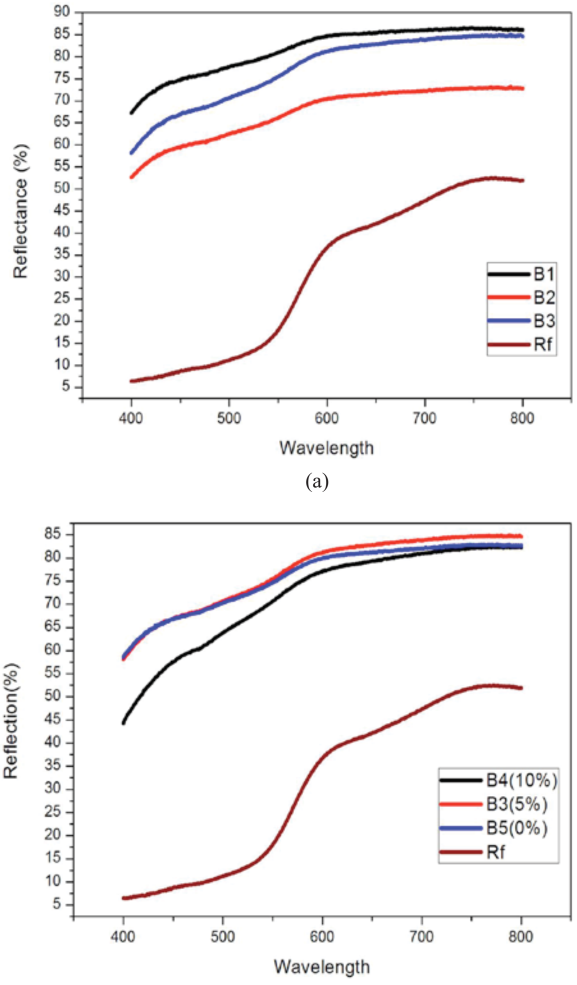


Fig. 7 Reflection of engobes vitrified at 1000°C and engobe layer at 250 µm (a) Group I samples and (b) Group II samples, Noted: Rf as the red tile

In Group I engobes in Fig. 8 (a), the B1 and B3 are the best performing ones, with reflection as high as 85% and 80%, respectively. The high reflection of B1 comes from high proportion of corundum and anatase with a high reflection of about >90% [16] and 87% [8], respectively. While the corundum decreased and the liquid phase occured due to the replacement of PC by RC and borax. According to the smooth vitrified surface of B3, the reflection of B3 was lower significantly than B1. The B4 and B5 as illustrated in Fig. 7 (b) achieve good reflection as well, but both formulations are not considered for more investigation as they are lesser whiteness and crawling performance on the surface. The lower reflection, that means, comes from the high liquid phase making the engobes more vitreous as discussed above [3].

As the results of engobe formulations, B3 engobe was achieved without any defect on the surface and very good for all criteria representing white/high reflection engobe (WRE). B3 was chosen and applied onto the earthenware tile with different thicknesses of engobe layer and vitrification temperatures.

3.3 Effect of thickness of engobe layer

In this work, the thickness of engobe layer was investigated as a function only of whiteness and smoothing. Fig. 8 demonstrates the optical images of B3 engobed onto the tile with different thicknesses in the range of 160-250 µm and vitrified at 1000°C.

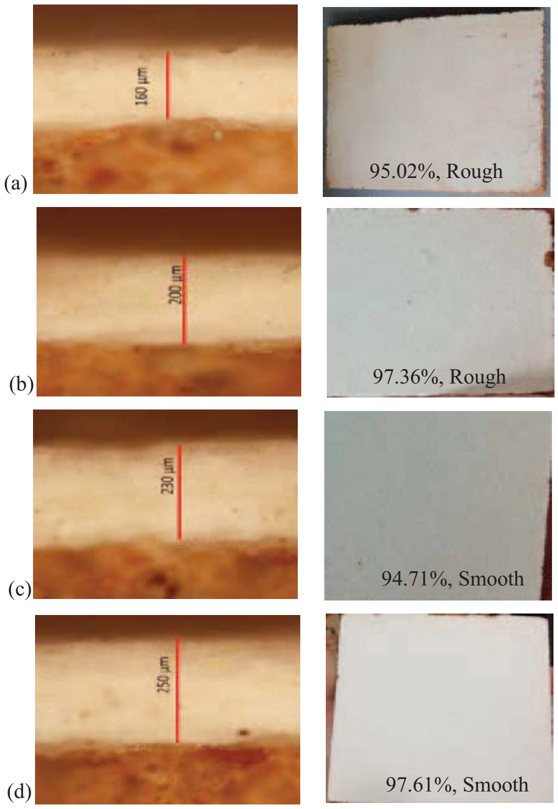


Fig. 8 The optical images of B3 as a function of thickness vitrified at 1000°C (a) 160 µm (b) 200 µm (c) 230 µm and (d) 250 µm

It was found that all samples had shiny appearance came from the vitrification and bond well to the tile. The slight increase of smoothing was obtained passing from 160 µm to 250 µm due to the increases of degree of vitrification and compaction of engobes. Moreover, the thicker layers of coverage can be reached, and are enough to mask also the tile and ensure the best performance. Whiteness values of all samples are similar, that means, it is independent on layer thickness of engobe. In this case, the engobe layer was controlled constantly at 250 µm for apply onto the tile.

3.4 Effect of vitrification temperature

1) Morphology of vitrified engobes: The results of phase transformation of B3 with increasing vitrification temperature are demonstrated in Fig. 9.

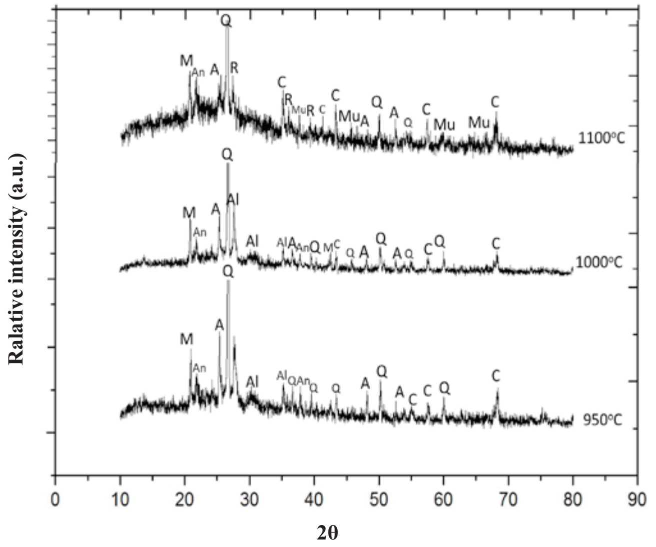


Fig. 9 XRD patterns of B3 as a function of vitrification temperature for 250 µm of thickness; M: Microcline, C: Corundum, Al: Albite, An: Anorthite, Q: Quartz, A: Anatase, R: Rutile, and Mu: Mullite

Based on the results, microcline, corundum, albite, anorthite, quartz and anatase were detected in the sample vitrified at 950 and 1000°C. It showed a significant change of B3 engobe when vitrified from 1000°C to 1100°C. The new phase of mullite ($3Al_2O_3.2SiO_2$) was developed due to the transformation of clay existing in PC and the reaction between corundum and quartz starting at 1050°C [17]. A part of the anatase phase was changed to rutile phase when temperature raised to 1100°C. The broad peak was also appeared clearly, showing a highly liquid phase.

2) *Properties of engobes:* The whiteness and smoothing of B3 engobe vitrified at 950, 1000, 1000°C are given in Table 5 and Fig. 10. It was found that the B3 sample reached to the best performance i.e. white and smooth whereas the rough surfaces were obtained when vitrified at 950 and 1100°C. At 950°C, the fluxing agents (RC, borax, alkali and alkaline oxides) cannot be transformed to liquid phase leading devitrification of polycrystalline. While the liquid phase increased abundantly leading crawling of B3 when temperature raised to 1100°C as called overfiring.

TABLE V
WHITENESS AND SMOOTHING OF B3 VITRIFIED AT 950-1100°C

Vitrification temperature ($^{\circ}$C)	Whiteness (%)	Smoothing	Homogeneous of whiteness
950	95.29	Rough	Heterogeneity
1000	95.51	Smooth	Homogeneity
1100	93.10	Rough	Heterogeneity

(a) (b) (c)

Fig. 10 Typical images of smoothing and whiteness of B3 at different vitrification temperatures and engobe layer at 250 µm (a) 950°C (b) 1000°C (c) 1100°C

The whiteness of B3 engobe decreased slightly with increasing temperature. The reason is the formations of mullite and rutile during firing at 1100°C. The whiteness of mullite phase (27%) is lesser than corundum phase (>99%), in the other hand, the whiteness rutile phase is about 94.7-95.5, which is also lesser than anatase phase (>97%).

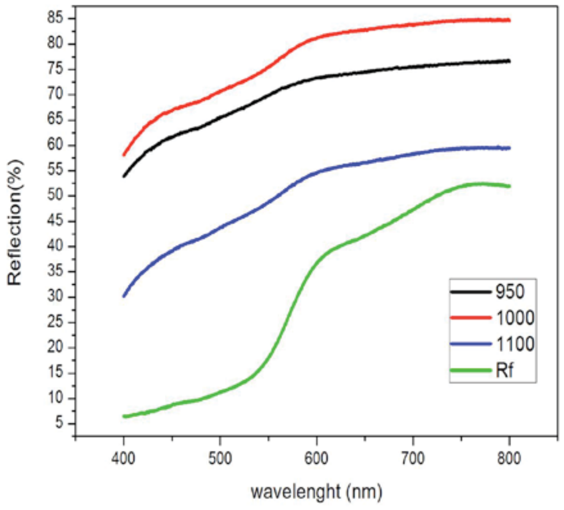


Fig. 11 Reflection of B3 at different vitrification temperatures and engobe layer at 250 µm

The reflections of B3 engobe with different temperatures are demonstrated in Fig. 11. The results showed that the highest reflection (85%) was obtained at 1000°C due to the white vitrified and smooth engobe as discussion above. Moreover, the reflectivity of rutile is approximate at 75% [18], which is lower than corundum and anatase, respectively. As the results, the white/high reflection engobe (WRE) was obtained for vitrification at 1000°C.

IV. CONCLUSIONS

This work described the procedure through which the engobe with high reflection and whiteness as called the white/high reflection engobe (WRE) was obtained by controlling in raw materials, composition, layer thickness and vitrificatrion temperature. B3 engobe composting 76.19 wt%porcelain clay (PC), 9.52 wt%recycled cullet (RC), 9.52 wt%borax and 4.76 wt%TiO_2 was chosen to apply onto the earthenware wall tile. The surface characteristics depend strongly on liquid phase formation and phase transformation during firing. B3 had a shiny appearance with the thickness layer at 250 μm meaning further vitrification and bond well to the tile which in turn produce a more fluid and more penetrating in B3 engobe at 1000^{o}C. The smoothing of engobe came from the high degree of vitrification and compaction of polycrystalline. The whiteness and reflection depend directly on the smoothing of surface cooperating with corundum and anatase contents. B3 showed the whiteness at 95.51%, reflection at about 85%, which was successfully produced the WRE for earthenware wall tile in industrial scale.

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REFERENCES

[1] L. Esposito, P. Generall, A. Tucci, and S. Nuzzielo, “Hardness of glazed ceramic tiles: comparison between mohs hardness and vicker indentation method,” *Ceram. Acta.*, vol. 5(4-5), pp. 13-21, 1993.

[2] M. Romero, J. M. Rincon, and A. Acosta, “Crystallization of zirconium-based glaze for ceramic tile coating,” *J. Eur. Ceram. Soc.*, vol. 23, pp. 1629-1635, 2003.

[3] C. Ferrari, A. Libbra, A. Muscio, and C. Siligardi, “Design of ceramic tile with high solar reflectance through the development of a functional engobe,” *Ceram. Inter.*, vol. 39, pp. 9583-9590, 2013.

[4] R. Levinson, P. Berdahl, H. Akbari, W. Miller, I. Joedicke, J. Reilly, Y. Suzuki, and M. Vondram, “Methods of creating solar-reflective nonwhite surfaces and their application to residential roofing materials,” *Solar Ener. Mater. Solar Cells*, vol. 91(4), pp. 304-314, 2007.

[5] A. Synnefa, M. Santamouris, and K. Apostolakis, “On the development, optical properties and thermal performance of cool colored coatings for the urban environment,” *Solar Ener.*, vol. 81(4), pp. 488-497, 2007.

[6] S. Kültür and N. Türkerí, “Assessment of long term solar reflectance performance of roof coverings measured in laboratory and in filed,” *Build. Environ.*, vol. 48, pp. 164-172, 2012.

[7] R. Levinson, P. Berdahl, and H. Akbari, “Solar spectral optical properties of pigments- Part II: survey of common colorants,” *Solar Ener. Mater. Solar Cells*, vol. 89(4), pp. 351-389, 2005.

[8] T. Thongkamluang, T. P. Limsuwan, and P. Rakkwamsuk, “Preparation and application of high near-infrared reflective green pigment for ceramic tile roofs,” *Inter. J. Applied Ceram. Technol.,* vol. 8(6), pp. 1451-1458, 2011.

[9] G. A. Davidson, “A modified tape-peel technique for preparing permanent qualitative microfossil slides,” *J. Paleolimnol.*, vol. 1, pp. 229-234, 1988.

[10] “Borax data sheet,” Riotinto Minerals, US.

[11] G. R. Santos, M. C. Pereira, M. O. Dionysio, S. D. Souza, and M. R. Morelli, “Whiteness process of tile ceramics: using a synthetic flow as a modifier agent of color firing,” *Hyper. Interact,* vol. 224, pp. 137-142, 2014.

[12] M. Romero, J M. Rincón, and A. Costa, “Effect of iron oxide on the crystallization of a diopside glass-ceramic glaze,” *J. Euro. Ceram. Soc.*, vol. 22, pp. 883-890, 2002.

[13] C. Li, G. W. Kaatawar, and P. Yand, “Effects of surface roughness on light scattering by small particles,” *J. Quanti. Spcetro*., vol. 89, pp. 123-131, 2004

[14] H. Bodur, “Development of engobe compositions for local roof tiles,” M. Sc. Thesis, Engineering and Sciences of Izmir Institute of Technology, Izmir, Turkey, June 2010.

[15] S. B. Felisbino, K. W. Milanez, H. G. Riella, and A. M. Bernardin, “Influence of glaze particle size distribution on surface tension and gloss,” in *Proc. Qualicer*, 2004, p. 201.

[16] R. H. French, H. Müllejans, and D. J. Jones, “Optical properties of aluminum oxide: Determined from vacuum ultraviolet and electron energy-loss spectroscopies,” J. Amer. Ceram. Soc., vol. 81(10), pp. 2549-2557, 1998.

[17] I. Johari, S. Said, B. Hisham, A. Bakar, and Z. A. Ahmad, “Effect of the change of firing temperature on microstructure and physical properties of clay bricks from Beruas (Malaysia),” *Sci. Sinter.,* vol. 42, pp. 245-254, 2010.

[18] S. Teixeira and A. M. Bernardin, “Development of TiO2 white glazes for ceramic tiles,” *Dyes and Pigments*, vol. 80, pp. 292-296, 2009.