PYROPLASTICITY IN PORCELAIN TILES

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ABSTRACT

Clay bodies exhibit pyroplasticity when they are fired. Basically they get soft again in the heat of the kiln and can deform under their own weight. This property is especially important when firing products with very low porosity like porcelain tiles, due their content in melting materials. In this way, five raw materials, kaolin, talc, an albite, a phyllite and clay were used in a study to form porcelain tile pastes resistant to pyroplasticity. After raw materials analysis (XRF and XRD), a mixture design with constraint limits was used to compose the pastes, resulting in thirteen compositions (five factors and one centroid). All compositions were mixed, wet ground (<44μm), dried and pressed (450kgf/cm²) in rectangular plates (10cm×5cm). The pyroplasticity was determined by the measure of the plate bending caused by temperature variation in an industrial roller kiln. All results were analyzed using response surfaces with data obtained by analysis of variance (ANOVA).

1. INTRODUCTION

Pyroplastic deformation is the bending of a ceramic specimen caused by gravity during heat treatment. It can be defined as the loss of shape of a product during its firing. Pyroplasticity is related to an excess of liquid phases formed during firing or to a reduced viscosity of these phases. Specifically for ceramic tiles fired in roller kilns, when the tiles are moving along the kiln carried by the rollers it is possible that a tile can bend to accomplish the roller rotation because the tile is subjected to vertical forces due its own weight. As a result the tile production is affected by curvatures arising in the final product. The pyroplastic deformation occurs more frequently in highly vitrified pastes like porcelain tiles.

The pyroplastic deformation magnitude is determined by the pyroplastic index (PI), pointing out the tendency to deformation of a specimen with fixed dimensions subjected to gravity during its firing under specific conditions. The procedure used to determine the pyroplasticity index consists in measuring the curvature of a specimen during its firing over two refractory supports:

$$IP = \frac{sb^2}{l^4} \qquad (1)$$

where s is the maximum deformation (cm), b is the bar thickness (cm) and l is the distance between supports (cm). The pyroplastic deformation develops as a function of the vitrification of the ceramic body during its firing. As the ceramic body temperature rises inside the kiln there is a gradual increase in the amount of liquid phase formed in it. The liquid phases develop due the partial fusion of the most meltable components of the paste. As the temperature rises, the most refractory components are progressively dissolved by the liquid phases, increasing considerably the volume of the latter.

The firing zone temperature, the heating rate and the time in which the specimens remain at the maximum temperature are variables that can affect the pyroplastic deformation because it depends on the thermal work to which the specimens are subjected [8,2].

Regarding the raw materials used to produce ceramic bodies highly vitrified, feldspars develop an important role in porcelain tile pastes. In fact, the great densification and high mechanical resistance showed by these ceramic materials after firing are due the action of feldspars [8,5,3].

Feldspars are largely used in ceramic materials with high densification like porcelain tiles, vitreous china, porcelains and semi-gres tiles [9,3]. During firing their fusibility and ability to form eutectics with other components are remarkable, making it possible to reach a high densification even at low temperatures. The main characteristic the originates these properties is the alkali content in the mineral. The theoretical amount of potassium and sodium oxides in potassium and sodium feldspars are 16.9% and 11.8% in a weight basis, respectively [6,7]. As the alkali amount approaches the theoretical value, the commercial value of the feldspar rises. The amount of feldspar used in ceramic materials depends on its melting characteristic, i.e., the amount of alkali present in the mineral used [10,11].

In turn, the use of talc in ceramic pastes results in an increase in their resistance to stains, if the talc amount is higher than 1.6% in weight [2]. Also, it can raise the mechanical resistance up to 30% [6]. Some studies show the use of talc in ceramic materials seems to favour the polishing process when the porosity is low. Talc also reduces the thermal expansion coefficient of the ceramic materials and increases their whiteness when in presence of zirconium dioxide [4,1].

2. MATERIALS AND METHODS

Five minerals were used in this study: a clay, a kaolin, an albite, a phyllite and a talc. The chemical analysis was determined by X-ray fluorescence (Philips PW2400, melted sample) and the phase (mineralogical) analysis by X-ray diffraction (Philips PW1830, CuKα, 0° to 75°, analysis with X'Pert HighScore software).

After raw material chemical and phase analysis a statistical design was used to study the influence of each mineral on the pyroplasticity of porcelain tile pastes. The chosen design was mixture design, suitable for the purpose of analysis. As not all raw materials can be used as the major component in a ceramic paste, restrictions were imposed in the design (constrained limits). Using five factors (raw materials) at two levels (maximum and minimum amount in the paste) and one general centroid thirteen formulations were composed. The formulations were designated as M01 to M13, the last one as the centroid, table 1.

Formulation (wt. %)	Kaolin	Phyllite	Talc	Albite	Clay
M01	50.0	20.0	10.0	10.0	10.0
M02	20.0	50.0	10.0	10.0	10.0
M03	20.0	20.0	40.0	10.0	10.0
M04	40.0	20.0	10.0	20.0	10.0
M05	20.0	40.0	10.0	20.0	10.0
M06	20.0	20.0	30.0	20.0	10.0
M07	40.0	20.0	10.0	10.0	20.0
M08	20.0	40.0	10.0	10.0	20.0
M09	20.0	20.0	30.0	10.0	20.0
M10	30.0	20.0	10.0	20.0	20.0
M11	20.0	30.0	10.0	20.0	20.0
M12	20.0	20.0	20.0	20.0	20.0
M13 (C)	26.5	26.5	17.0	15.0	15.0

Table 1. Mixture design for the analysis of pyroplasticity in porcelain tiles

The maximum and minimum limits used for kaolin were 20% and 50% (mass fraction). The limits for the other minerals were: 20% to 50% for phyllite; 10% to 40% for talc; 10% to 20% for albite; 10% to 20% for clay. The limits were established in function of the ordinary amount of each raw material in a porcelain tile paste and in function of their chemical and phase composition. In order to determine the real influence of talc on the pyroplasticity the limits used for this mineral were increased: 10% to 40% in weight. The literature reports the effect of talc in reducing the viscosity of the formed glass phase.

The raw materials were dried (110°C, 24h), fragmented (laboratory hammer mill), mixed according table 1 to form the compositions and stored. In sequence, each formulation was ground (laboratory eccentric mill, 1,60g/cm^3, 3% to 4% residue in 325 mesh Tyler (44μm)), dried again (110°C, 24h), disaggregated and mixed with 6% of water, forming a granulated paste. Each paste was compacted by uniaxial pressing (laboratory press, 450kgf/cm^2) in compacts with 47mm×100mm. The compacts were dried and disposed in a refractory tray supported by their edges at 45° with the plane of the tray (figure 1).

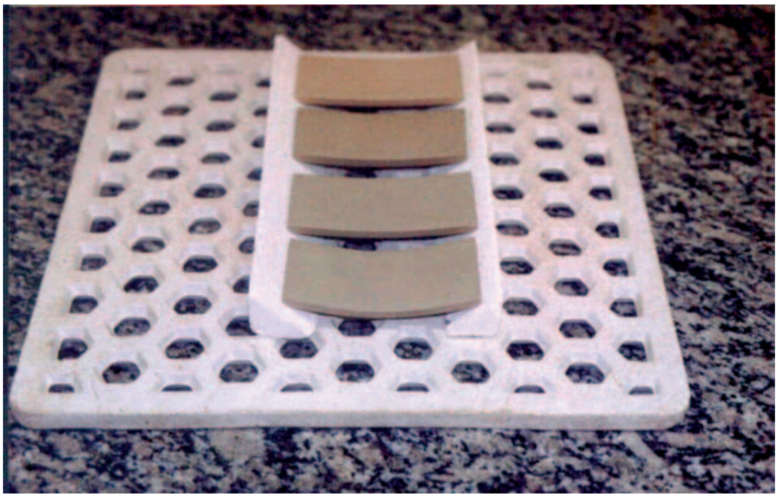

Figure 1. Samples on a refractory tray after sintering

The specimens of each formulation were fired in an industrial roller kiln at 1,195°C during 6min at maximum temperature, in a thermal cycle of 50 minutes. Four samples were chosen by chance in each running, three samples for each formulation (n=3). After sintering the maximum deflection of the samples was measured.

The technique used to analyze the results was multiple regression. The regression analysis consists to estimate the unknown parameters of the regression model or the adjustment of the data to the model and the validation of the model. The second step is used to study the adequacy of the chosen method to represent the response behaviour and the quality of the adjustment obtained.

If the validation result shows the model is not adequate the model must be modified and the parameters estimated again. Therefore the regression analysis is an iterative process, from the first adjustment to the attainment of a satisfactory model that can be used and adopted. The evaluation of the model parameters is performed by the mean squares method. The method validation is made by evaluation techniques used to test and estimate the adequacy and adjustment of the used model, mainly the hypothesis regression test (F and t) and the R^2 estimation.

3. RESULTS AND DISCUSSION

The chemical and phase analysis of all raw materials are showed in table 2. Analyzing the results apparently the most refractory minerals are the kaolin and the clay due their content in alumina; however, the clay contains iron oxide (1.6% wt.) in its composition and the kaolin contains potassium and iron oxides (1.3% and 2.0%

in weight, respectively). The kaolin is formed by kaolinite and illite as major phases and quartz and goethite as contaminations. The clay is formed by kaolinite and is contaminated with quartz and anatase.

Mineral (%)	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI	Phases
Phyllite	73.2	15.8	0.3	1.5	0.0	0.6	2.3	0.0	5.5	Q, M, K, G
Clay	62.7	22.0	2.2	1.6	0.1	0.5	0.7	0.0	9.6	Q, K, A
Kaolin	50.0	33.8	0.4	1.3	0.0	0.4	2.0	0.0	11.7	Q, K, I, G
Albite	78.0	11.6	0.1	0.2	0.7	0.4	1.1	6.3	1.0	Q, Ab, M
Talc	72.1	1.5	0.1	0.8	0.1	20.1	0.1	0.0	5.8	Q, T, C
Q is quartz, M is muscovite, K is kaolinite, G is goethite, T is talc, C is chlorite, I is illite, A is anatase and Ab is albite										

Table 2. Chemical and phase (mineralogical) analysis of the raw materials

Regarding the albite, it is contaminated with quartz and muscovite, containing a small amount of potassium oxide (1.1% wt.). Actually it is a mixed feldspar and not really an albite. The phyllite contains a small amount of potassium and iron oxides and is formed by kaolinite, quartz, goethite and muscovite and is used as a soft flux. Finally, the mineral identified as talc is contaminated with quartz and chlorite; its small amount of magnesia reveals the small amount of talc present in its composition.

The pyroplastic index was determined for all compositions by means of analysis of variance (ANOVA) and the results plotted in response surfaces. According table 3, analysis of variance for the pyroplastic index measured for all 13 formulations, the most suitable model is the quadratic model because the F test is more significant for it. The quadratic model presents 93% confidence.

ANOVA for the pyroplastic index	Main effects			Error			Confidence tests		
	SS	DF	MS	SS	DF	MS	F	p	R^2
Linear	6.92	4	1.73	2.81	8	0.35	4.92	0.03	0.71
Quadratic	2.75	6	0.46	0.06	2	0.03	14.56	0.07	0.99
Cubic	0	0	0	0	0	0			
Total Adjusted	9.67	10	0.97						
SS means sum of squares, DF degree of freedom, MS mean square									

Table 3. Variance analysis (ANOVA) for the pyroplastic index ($\times 10^{-5} cm^{-1}$)

The results from the ANOVA analysis were plotted in response surfaces, figure 2. Analyzing the response surface it is clear the effect of the albite in the pyroplastic deformation. This result occurs due the content in sodium oxide in albite, while the maximum amount of albite used was only 20% and albite is not a pure sodium feldspar. The clay also causes a strong influence in the pyroplasticity of the studied system, probably due its content in iron oxide in a non-crystalline form – no phase was identified containing iron oxide in its composition.

In turn, the talc mineral has a small influence on the pyroplasticity of the system studied, despite the large amount used (40% wt.). Apparently the presence of sodium oxide in ceramic compositions is related to the decrease in the viscosity of the formed liquid phase in the ceramic system, causing the observed pyroplasticity.

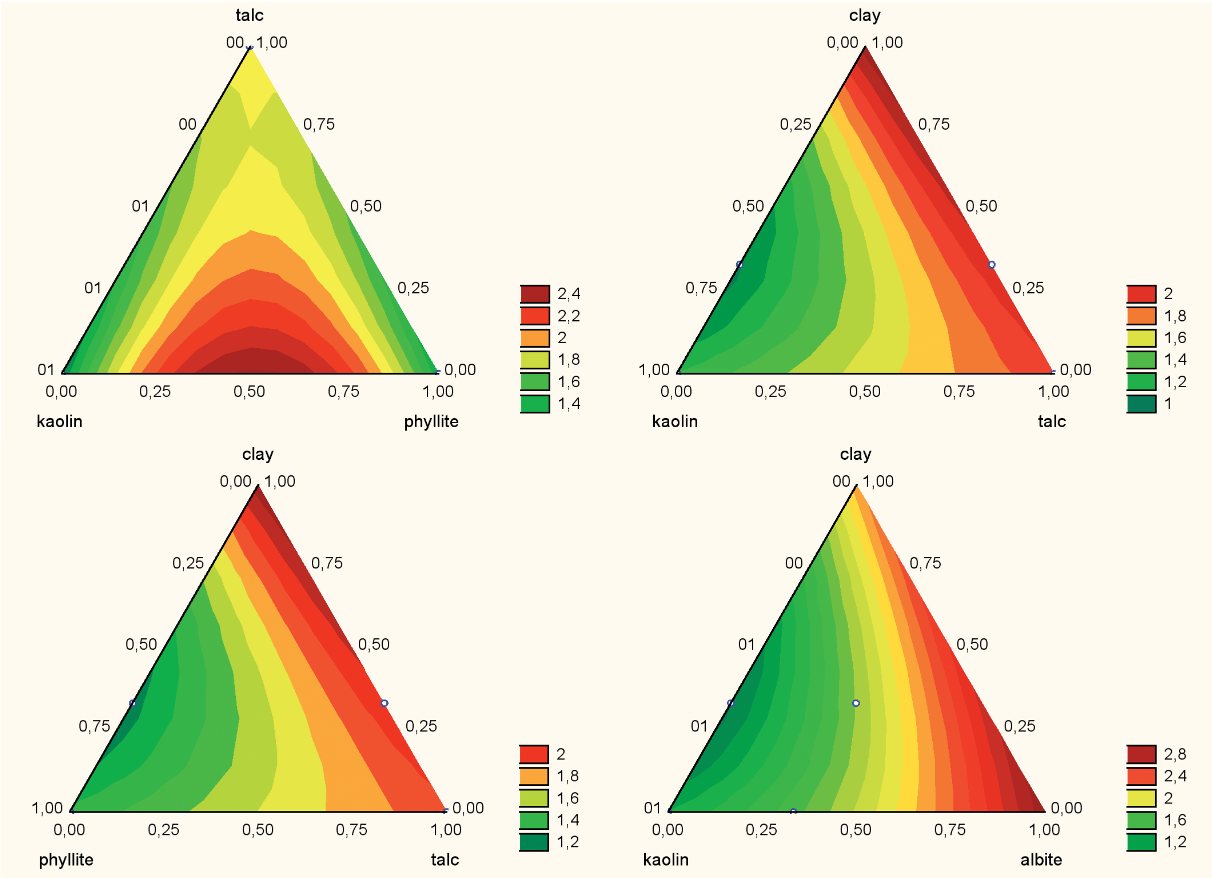

Figure 2. Response surfaces for the pyroplastic index of the studied system

4. CONCLUSION

The use of mixture design in the study of ceramic formulations and the use of multiple regression and response surfaces is a powerful procedure in the evaluation of the individual effect of raw materials in the final properties of ceramic products. The strongest influence in the pyroplastic deformation was caused by the mineral albite. The clay mineral used also caused some influence, but the isolated talc did not influence pyroplastic deformation very much, despite the large amount of this mineral that was used.

The next step in this study will be the determination of the mineral phases formed after the sintering. Probably this new study will show the real influence of the talc content in the ceramic systems. Also, it will reveal the role played by the iron oxide in phase formation.

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