Ceramics International 33 (2007) 761–765

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Use of glass waste as a raw material in porcelain stoneware tile mixtures

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Received 1 July 2005; received in revised form 12 December 2005; accepted 30 January 2006
Available online 18 April 2006

Abstract

Porcelain stoneware tile has excellent technical characteristics such as flexural strength, chemical resistance, surface hardness, etc. Nowadays, research of new materials, for example non-hazardous wastes, that are able to replace the traditional fluxing agents without changing the process or quality of the final products has been realized. The aim of this work is to study the possibility of the use of glass powder waste, in ceramic mixtures, for manufacturing of porcelain stoneware tiles. It was prepared by mixtures containing different amounts of clay, glass waste, feldspar and quartz. The samples were fired reaching different maximum temperatures in the range 1000–1250 °C, with a soaking time of 30 min. The fired samples were characterized and the use of small amounts of glass powder in addition with feldspar showed good results of mechanical–technological properties. The 25F5G was the only product that can be classified as a porcelain stoneware tile due to its properties.

Keywords: Porcelain stoneware; Glass powder; Liquid phase sintering; Environment

1. Introduction

Porcelain stoneware tiles have excellent technical characteristics that make possible their use in many different places, since high traffic, where it is necessary high mechanical resistance and surface hardness, until walls where impermeability is essential [1,2]. These products are manufactured using high amounts of fluxing agents like sodium and potassium feldspars, nefeline, talc and recently even so ceramics frits [3].

This product is a ceramic material with a very compact structure, impermeable, glazed or not, made up of crystalline phases surrounded in a glassy matrix. It is composed of low amounts of clays and kaolin, high percentage of feldspars as fluxes and some quartz sands [1,4].

The scantiness of the ceramic ores reserves, in addition to the distance of their use place has made a strong influence on the final products costs. Besides that, high efforts in research have been made for studying new materials that are able to replace the traditional fluxing agents without changing the process or quality of the final products [1,2]. For this reason, several countries have interest to reformulate the body mix composition, by partial or total replacement of one of the natural raw materials with a very cheap and readily available waste material. The use of waste material is considered viable only if the industrial process essentially remains unchanged and the quality and properties of the product do not decrease [1,3–6].

The aim of this work is to study the possibility of the use of glass powder waste, in ceramic mixtures, for manufacturing of porcelain stoneware tiles.

Glass powder waste when incorporated into a mixture, has a good potential as a new fluxing agent in replacement of traditional feldspar and makes possible to obtain a vitreous microstructure during sintering of porcelain stoneware. Considering the analogies between glass powder and sodium feldspar, the composition of the two body mix was reformulated, replacing total and part of the sodium feldspar with glass powder. The effects due to the use of glass powder were investigated in laboratory experiments and discussed in terms of firing behaviour and physical–mechanical properties.

2. Experimental

The basic raw materials used in this investigation were a kaolinitic clay from Paraíba Valley (São Paulo, Brazil),

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0272-8842/$32.00
doi:10.1016/j.ceramint.2006.01.001

supplied by Nova Canas Sociedade Agro-Industrial Ltda; sodium feldspar, supplied by Prominex Mineração Ltda, which presents melting point of 1120 °C; glass powder waste, which is a waste material generated due to glass pieces stonecutting and washing, supplied by Pilkington Brazil Ltda; and quartz powder with 99.9% purity. The grain size distribution of the raw materials presents cumulative curves that indicate 50% of the particles are below 10 μm and that all the particles have diameters below 40 μm. The chemical analysis of the raw materials, determined by inductively coupled plasma optical emission spectroscopy is reported in Table 1.

It was prepared by different mixtures whose compositions are reported in Table 2. The amount of glass powder waste added to mixtures was based on the amounts of Na_2O and K_2O of this waste and correlated with was used in works presents in literature [1,2].

The raw materials were mixed in an alumina ball mill using alumina milling media and water for 1 h. The slurry was dried at 100 °C in a rotating drier until 8–10% of humidity.

The dried material was then crushed and sieved to pass through a 425-μm screen to obtain suitable powders for pressing. The mixtures were compacted into bar shape (114 mm × 25 mm × 7 mm) by uniaxial pressing at 50 MPa. Firing was carried out in a laboratory electric furnace reaching different maximum temperatures in the range 1000–1250 °C, at regular temperature intervals of 50 °C, with a soaking time of 30 min and heating rate of 10 °C min^{-1}. After preliminary studies, the 20G specimens were fired from 1150 to 1200 °C and the others from 1200 to 1250 °C, at temperature intervals of 10 °C.

The firing behaviour was described in terms of linear shrinkage (ASTM C 326), water absorption (ASTM C 373) and the total porosity (ASTM C329-88).

The crystalline phases of the fired samples, which present the best results of linear shrinkage and water absorption, were identified by X-ray diffraction analysis (XRD, Rich Seiferst & Co. Isso-Debeyeflex 1001) with Cu kα radiation.

The flexural strength was determined using a universal testing machine (MTS 810.23M), in three-point bending fixture, 70 mm support span and with a crosshead speed of 0.5 mm min^{-1}. Abrasion resistance was performed as described in the standard ISO 10545-6. Weibull's statistical analysis was carried out on each set of data with 30 specimens.

Table 1
Chemical composition of the raw materials (wt.%)

Composition	Clay	Feldspar	Glass waste
SiO_2	50.94	69.00–72.00	72.40
Al_2O_3	28.20	16.50–19.50	0.70
Fe_2O_3	3.41	0.05–0.25	0.11
CaO	0.17	<0.42	8.60
MgO	0.84	<0.01	4.00
Na_2O	0.19	7.60–8.50	13.60
K_2O	2.02	1.00–2.00	0.30
TiO_2	0.93	–	0.02
L.O.I.	12.80	0.40–0.55	–
SO_2	–	–	0.20

Table 2
Mixtures compositions (wt.%)

Mixtures	Raw materials			
	Clay	Quartz	Feldspar	Glass waste
20G	80.0	–	–	20.0
15G	73.0	12.0	–	15.0
20F10G	60.0	10.0	20.0	10.0
25F5G	60.0	10.0	25.0	5.0

Weibull's modulus, m, was determined by squares method, adopting as probability estimator of failure $P_n = (I - 0.5)/N$, where N is the number of strength measurements and I the ranking number, with $I = 1$ for the weakest specimen and $I = N$ for the strongest [7,8].

3. Results and discussion

Densification was monitored by measuring linear shrinkage and water absorption. The 20G specimens which present the highest clay content with respect to other bodies, showed the highest shrinkage values. And the compositions, with quartz added, as expected, showed small shrinkage (Fig. 1a and b). The firing behaviour shown by the compositions 20G, 15G and 20F10G present an increase of shrinkage from 1200 to 1250 °C (Fig. 1a), that indicate an overfiring; this phenomenon only occurs from 1240 to 1250 °C in 25F5G (Fig. 1b), it means that highest amount of feldspar extend the firing range.

Water absorption is an important parameter in ceramic tiles, that defines the class to which the product belong and according to ISO 13006 standard porcelain stoneware presents values below 0.5%. Fig. 2a and b show that all the specimens present values below 0.5% and the replacement of sodium feldspar with glass powder resulted in a lower firing temperature only for the composition 20G that reach values of approximately 0.0% at 1150 °C. So all the composition can be classified in the range used for porcelain stoneware as far as water absorption is concerned.

Replacing different amounts of feldspar with glass in a porcelain stoneware mix changes the amounts of the different alkalis in the mixture [1,2]. Increasing the amount of glass powder in the mixture, the amount of calcium and magnesium increases, but the amount of alumina decreases. The firing behaviours shown by the mixtures can be attributed to the changes in composition resulting from the replacement total and partial of the feldspar with the glass, which led to differences in the viscosity of the liquid formed at the firing temperatures used to produce the porcelain stoneware tile [2,7–9]. The fired specimens of 20G mixture present insignificant variation of linear shrinkage and water absorption values in the interval of 1150–1200 °C, so it was chosen 1150 (20G), 1200 (15G and 20F10G) and 1220 °C (25F5G) as the temperatures which was reached the better values of linear shrinkage and water absorption for the mixtures.

Flexural strength depends on the material composition and dimension and morphology of the flaws. The mechanical behaviour of the specimens can be explained taking into

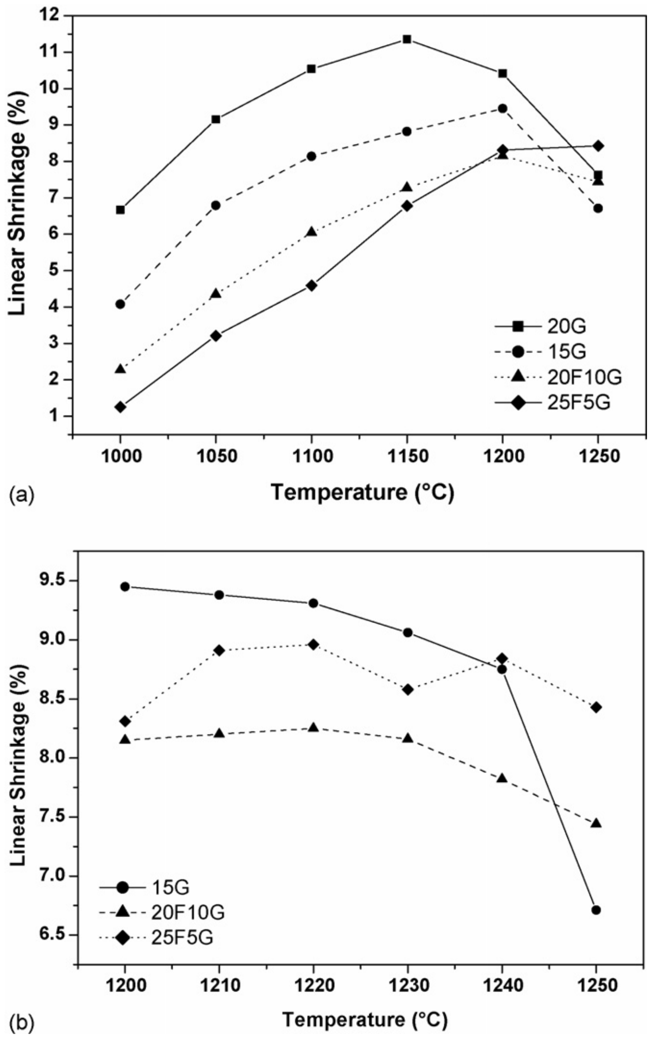

Fig. 1. Linear shrinkage of the fired samples from 1200 to 1250 °C with intervals of (a) 50 °C and (b) 10 °C.

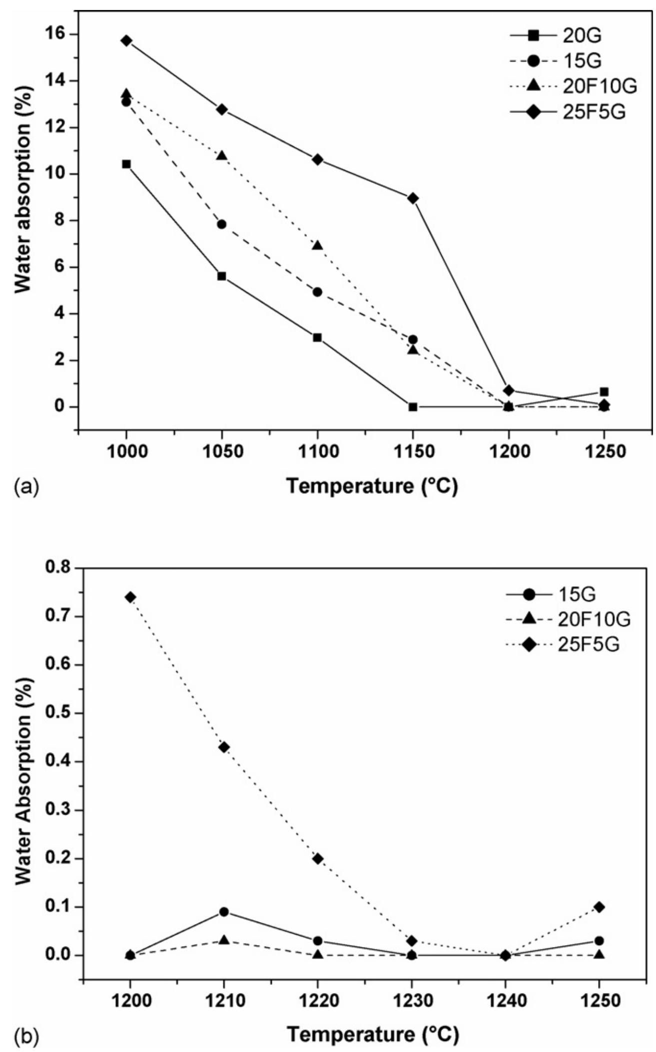

Fig. 2. Water absorption of the fired samples from 1200 to 1250 °C with intervals of (a) 50 °C and (b) 10 °C.

account the different microstructures developed during firing [10–12]. At the maximum firing temperature the average modulus of rupture values are between 39 and 46 MPa (Table 3), these values are in accordance with standard ISO 10545-4 that requires values higher than 27 MPa. The presence of feldspar and glass, favouring the developing of a more compact microstructure, with lower porosity than 20G and 15G, causes the observed increase of modulus of rupture, for 20F10G and 25F5G. The flexural strength reaches the maximum value for 20F10G, characterized by the presence of pores with narrowed sizes (Fig. 3c). The increase in Weibull's modulus is further evidence of improved microstructural homogeneity and high performance is required of porcelain stoneware tiles, so the reliability of the product represents a very important parameter.

The use of glass causes a formation of a lower viscosity of the liquid phase, that decreases with the increase of glass powder, favors the shrinkage, but also the growing of rather large closed pores (Fig. 3), that trapped in the glassy matrix during cooling [1,2,10], cause the observed expansion of 20G

Table 3
Physical mechanical properties of the fired samples

Sample	Total porosity (%)	Modulus of rupture (MPa)	Weibull's modulus (m)	Abrasion resistance (volume removed, mm^3)
20G (1150 °C)	14.0	39.0	3.4	195.3
15G (1200 °C)	13.1	40.0	7.6	191.5
20F10G (1200 °C)	12.0	46.0	10.6	188.8
25F5G (1220 °C)	12.7	44.1	7.8	164.2

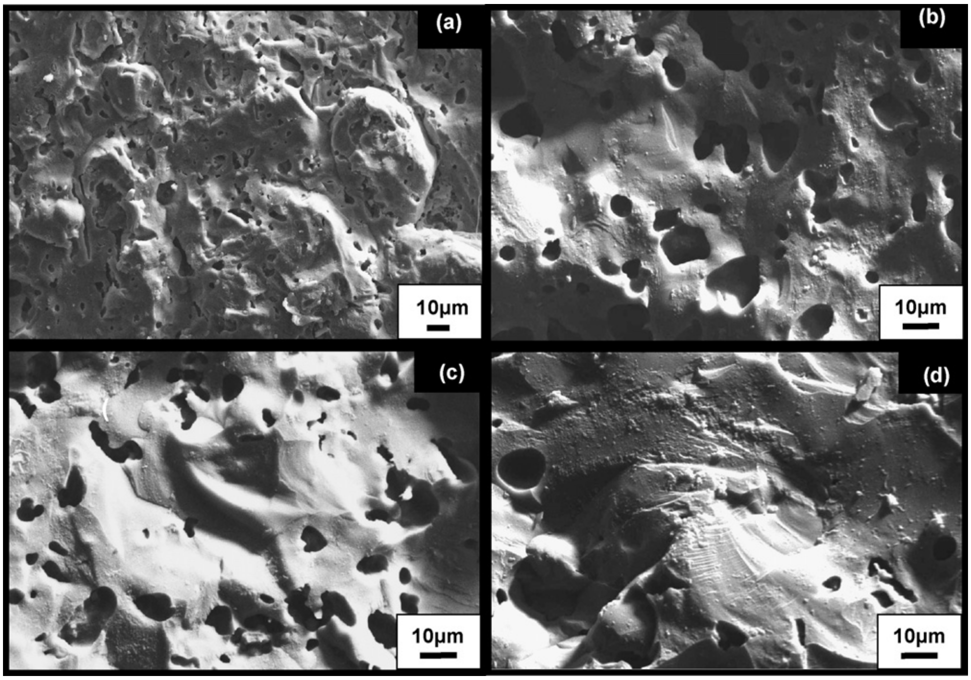

Fig. 3. Fracture surface micrographs: (a) 20G, 1150 °C 1000×; (b) 15G, 1200 °C 2000×; (c) 20F10G, 1200 °C 2000×; and (d) 25F5G, 1220 °C 2000×.

specimens at 1200–1250 °C. This is in agreement with the results of porosity. According to literature [1,2], the use of scrap-glass cause a general increase in porosity, but besides the high values of porosity (12.0–14.0%) the mechanical characteristics, as modulus of rupture, of the tested materials are still in accordance with the standard for porcelain stoneware.

The crystalline phases identified in all the samples fired are quartz and mullite (Fig. 4). Quartz is a residual mineral from the original raw materials, and mullite, formed during firing. Porcelain stoneware bodies generally contain a single mullite phase, $3Al_2O_3{\cdot}2SiO_2$, evolution pathway: the dehydroxylated kaolin, metakaolin, transforms into a nonequilibrium unstable spinel type structure, which converts to mullite above 1075 °C [10,13]. For the compositions containing glass powder some modifications in intensity and position of the peaks in the X-ray diffraction patterns indicate the presence of anorthite, and the amount of which increases with increasing percentage of glass.

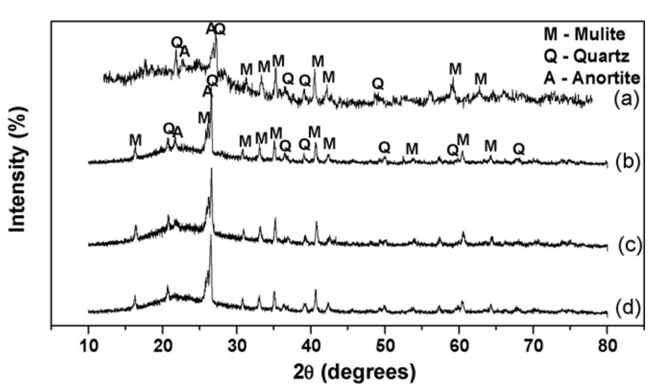

Fig. 4. X-ray diffraction patterns: (a) 20G, 1150 °C; (b) 15G, 1200 °C; (c) 20F10G, 1200 °C; and (d) 25F5G, 1220 °C.

The abrasion resistance of the fired specimens was checked according to ISO 10545-6 and measured in terms of removed sample volume (Table 3). The values are all located in the range 164.2–195.3 mm^3 for the specimens fired at high temperature, according to the maximum densification reached. According to literature [10,13], porcelain stoneware must present abraded volume values lower than 175 mm^3. 20G, 15G and 20F10G present high values of abraded volume due to the high amount of total porosity in the samples, so they cannot be classified as porcelain stoneware. In spite of the high values of porosity found in all specimens tested, the 25F5G samples present modulus of rupture, water absorption and abrasion resistance values in accordance with the standards for porcelain stoneware. So, 25F5G is the only product that can be classified as a porcelain stoneware and the others ones did not achieve all the requirements necessary, but they can be classified in other category of ceramic tile.

4. Conclusions

The glass powder waste shows to be an efficient fluxing agent when it is used as an additive in ceramic mixture. During firing glass powder waste accelerates the densification process, with some positive effects (lower open porosity, water absorption) combined with negative ones (higher values of shrinkage and high closed porosity). The use of small amounts of glass powder in addition with feldspar showed good results of mechanical and technological properties and Weibull's modulus, which is an important parameter that represents the reliability of the product. The 25F5G is the only product that can be classified as a porcelain stoneware tile due to its properties.

Acknowledgements

The authors would like to acknowledge the financial support of the Brazilian research funding institution FAPESP (Process no. 02/13491-8) and Pilkington Brazil Ltda, which support the development of this work.

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