*Recent Research in Science and Technology 2009, 1(2): 052–057*
*ISSN: 2076-5061*
*www.recent-science.com*

PHYSICS & CHEMISTRY

# MECHANICAL PROPERTIES RELATED TO USE OF GLASS WASTE AS A RAW MATERIAL IN PORCELAIN STONEWARE TILE MIXTURES

**G. Viruthagiri, R. Gobi, B. Rajamannan**
*Department of Physics, Annamalai University, Annamalainagar- 608 002, India*

## Abstract

Porcelain represents one of the most complex ceramics, formulated from a mix of clay, feldspar and quartz are sintered to conform a glass-ceramic composite. Porcelain stoneware tile has excellent technical characteristics. Nowadays, research of new materials, for example non-hazardous wastes, that are able to replace the traditional fluxing agent 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 amount of fireclay, glass waste, feldspar and quartz. The samples were fired reaching different maximum temperatures in the range 900-1200$^0$ C, with a soaking time of 1 hour. The fired samples were characterized and the use of small amounts of glass powder in addition with feldspar and quartz showed good results of mechanical technological properties. The 10F5Q5G was the only product that can be classified as a porcelain stoneware tile due to its properties.

**Key Words**: Glass waste; Fire clay; Porcelain stoneware; Ceramics; Tiles.

## 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, and talc 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 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 [1,4-7].

Porcelain stoneware tile is a derived porcelain building material characterized by a very compact microstructure and high technical characterized [8]. The main difference between porcelain and porcelain stoneware lies on their firing schedule. The different firing process leads to big differences in the percentage of crystalline phases in the end products. Most of the reactions occurring during firing are kinetically governed processes [9] that do not reach thermodynamic equilibrium in porcelain stoneware products, since the industrial cycles are shorter than 1 hour. Thus, we can say that, because of fast firing process, porcelain stoneware is a non-equilibrium material. In some of the new engineering applications there is a clear tendency to reduce the tiles weight to lightening building and this requirement implies to increase the stoneware tile mechanical properties. 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. The effects due to the use of glass powder were investigated in laboratory experiments and discussed in terms of firing behavior and physical-mechanical properties.

## Experimental techniques

The basic raw materials used in this glass investigation were fireclay, quartz powder with 99.9% purity, powder waste (which is a material generated due to glass pieces stonecutting and washing), supplied by Govt. Ceramic Institute, Vridhachalam. The chemical analysis of the raw materials (fireclay and glass powder), determined by X-ray Fluorescence analysis (XRF) are reported in Table.1.

It was prepared by different mixture whose composition are reported in table2. The amount of glass powder waste added to mixtures was based on the amounts of CaO, $Na_2O$ and $K_2O$ of this waste.

The raw materials were mixed in an alumina ball mill using alumina milling media on water for1houre. The slurry was dried at 100º C in a rotatory drier until 8-10% of humidity.

The dried material was then crushed and sieved to pass through 500µm sieve. The resulting powders were moistered up to ~6wt / water, hand granulated and uniaxially pressed at 45Mpa in to 16 cm X 8 cm X1.5cm tiles. A total of six tiles for each composition were prepared to ensure the reproducibility of the measurements. Specimens were fired in a Laboratory electrical furnace simulating an industrial fast firing process in an air atmosphere involving basically: an average heating rate of 25ºC/min, a soaking temperature of 900º, 1000º, 1100º and 1200ºC hold 0.1 and 1hour and a furnace cooling step. The products were characterized in terms of compositional and technological properties. X-ray fluorescence attempted for chemical analysis in a PAN analytical X-ray spectrometer. Water absorption and porosity were quantified measuring the dry weight, the water- saturated weight and the weight suspended in water, according to ISO 10543-3. The modulus of rupture was measured with a three points flexural method ISO 10545-4 using a universal instron machine.

### Mechanical properties

### Role of porosity

The density or porosity affects a number of the properties of the building material but probably the most important effect is its strength [10]. Highly porous tiles are mechanically weak. Tiles with the lowest porosity have the greatest strength, thermal conductivity and heat capacity.

The sample were heated continuously in boiling water for about six hours and left to cool over night which enables the pores to get filled up with water to saturation. The saturated specimens were then weighed by immersing in water as (W1) and in air as (W2). The samples were then placed in hot air oven at 200º C and dried for about six hours to remove the water contents completely.

$$\text{Percentage of porosity} = ((W_3 - W_2)/ (W_2-W_1)) \times 100$$

$$\text{Percentage of porosity} = \frac{\text{Volume of pores}}{\text{Volume of sample}} \times 100$$

### Water absorption test

The test specimens of ceramic tile samples are in the form of bar. Weigh try ceramic tile specimens and then submerge it in water at a temperature between 55 ºC and 30 ºC. After 24 hours, take specimen from water. Each specimen shall then be removed, surface water wiped off with damp clothes and the specimen weighed again

$$\text{Percentage of water absorption} = \frac{W2-W_1}{W_1} \times 100$$

Where

$W_1$ - weight of the specimen

$W_2$ - weight of the specimen after 24 hours of immersion in water.

### Linear shrinkage

The linear shrinkage, LS(%), of fired samples has been determined by means of the following equation:

$$LS=L_p-L_f / L_p \times 100$$

Being $L_p$ and $L_f$ the length (mm) of the green and fired specimens, respectively. The liner shrinkage values obtained of six specimens were averaged for each firing temperature.

### Modulus of rupture

The modulus of rupture (MOR) was calculated for samples of rectangular cross section as

$$MOR = 3PL/2bd^2 \quad N\ cm^{-2}$$

Where P- is the force (N); L- distance between knife edges (cm); d -depth (cm); MOR, modulus of rupture (N $cm^{-2}$).

The dried material was then crushed and sieved to pass through a 500-μm screen to obtain suitable powders for pressing. The mixtures were compacted in to tiles(bar) shape 16cm×8cm × 1.5cm) by uniaxial pressing as 45Mpa. Firing was carried out in a laboratory electric furnace reaching different maximum temperatures in the range 900°-1200°C,as regular temperature intervals of 100°c, with a soaking time of 30 min and heating rate 25°C $min^{-1}$.

### Investigation techniques

A full chemical analysis using X-ray fluorescence was applied to two raw materials (glass powder and fireclay). The results of XRF are given in table.1

The extent of strength analyses were determined by measuring some physical properties such as porosity, water absorption, Linear shrinkage and modulus of rupture are tabulated in Table.3.

## Results and discussion

A homogeneous powder of porcelain stoneware composition is obtained as result of mixing ,milling and sieved steps, from table.3 the body shows a good sintering behavior. The fired samples are homogeneous and free of defects such as holes pebbles or cracks.

It is necessary to point out that the sintering process in porcelain stoneware samples does not exactly proceed by the foreseen way of a liquid phase mechanism.

For simplicity, quartz content added to the starting composition (as indicated in table.2) is used in the following discussion, instead of the actual level in the final sintered material.

Table. 1 Mechanical properties of the samples at different temperatures

| Temperature | Sample | Firing shrinkage (cm) | MOD ($N/cm^2$) | Water Absorption (%) | Porosity (%) |
|---|---|---|---|---|---|
| 900 | S1 | 4.5 | 257.69 | 16.19 | 28.94 |
| | S2 | 4.0 | 245.67 | 18.19 | 31.93 |
| | S3 | 4.0 | 264.82 | 17.76 | 31.59 |
| | S4 | 3.5 | 253.59 | 16.13 | 29.35 |
| | S5 | 3.0 | 248.27 | 15.06 | 27.71 |
| | S6 | 3.25 | 235.86 | 14.80 | 27.20 |
| 1000 | S1 | 3.0 | 257.14 | 20.65 | 34.86 |
| | S2 | 3.0 | 269.39 | 18.38 | 32.09 |
| | S3 | 3.0 | 237.19 | 17.19 | 30.46 |
| | S4 | 3.0 | 316.99 | 16.92 | 30.25 |
| | S5 | 3.0 | 316.99 | 16.38 | 29.29 |
| | S6 | 3.0 | 286.59 | 13.88 | 25.87 |
| 1100 | S1 | 8.0 | 759.92 | 9.15 | 18.21 |
| | S2 | 7.0 | 634.36 | 8.42 | 16.57 |
| | S3 | 6.5 | 409.09 | 8.22 | 16.49 |
| | S4 | 7.0 | 520.00 | 8.47 | 16.32 |
| | S5 | 8.0 | 452.00 | 8.28 | 16.61 |
| | S6 | 8.0 | 427.93 | 8.23 | 15.36 |
| 1200 | S1 | 10.0 | 519.12 | 7.07 | 14.55 |
| | S2 | 9.0 | 430.15 | 7.71 | 15.25 |
| | S3 | 7.5 | 479.28 | 6.04 | 11.90 |
| | S4 | 7.5 | 505.71 | 5.62 | 10.95 |
| | S5 | 8.5 | 465.51 | 5.98 | 11.35 |
| | S6 | 8.0 | 397.33 | 8.89 | 16.15 |

In contrast, the rate of dissolution of quartz into the glass phase was somewhat influenced by quartz particle size, despite the fact that the specimens were fired as different temperatures to reach maximum densification. This is because smaller quartz grains dissolve more rapidly than larger grains, owing to their greater surface area [11]. Densification was monitored by measuring linear shrinkage and water absorption. The $S_1$ specimens which present the highest clay content with respect to other bodies ($S_2$,$S_3$,$S_4$,$S_5$,$S_6$), showed the highest shrinkage values and the composition with quartz and feldspar added, as expected, showed small shrinkage (fig-4) The firing behavior shown by the compositions S1 toS6 present an increase of shrinkage from 1000 to 1200 ºC (fig-4), that indicate an over firing this phenomenon only occurs from 1000 to 1200ºC in $s_6$ (fig-4), it means that highest amount of feldspar extend the firing range .

Figure 1. Modulus of rupture for six different stoneware tiles samples at different temperatures

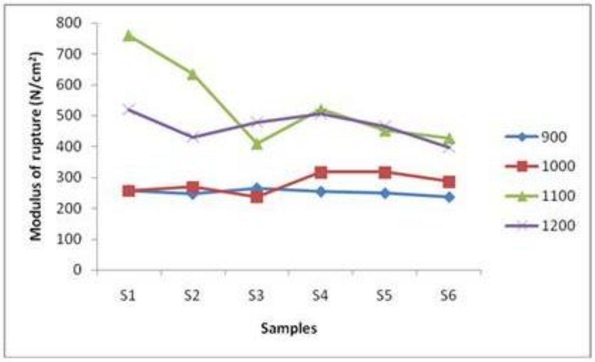



Figure 2. Water absorption for six different stoneware tiles samples at different temperatures

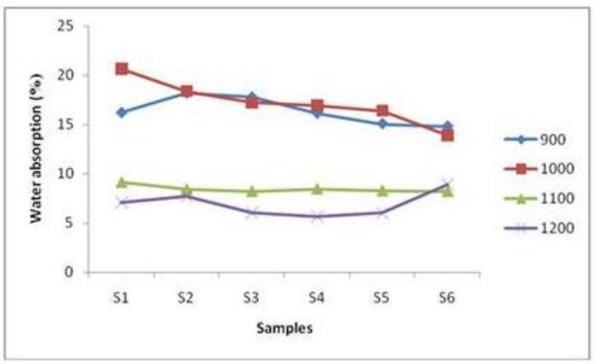
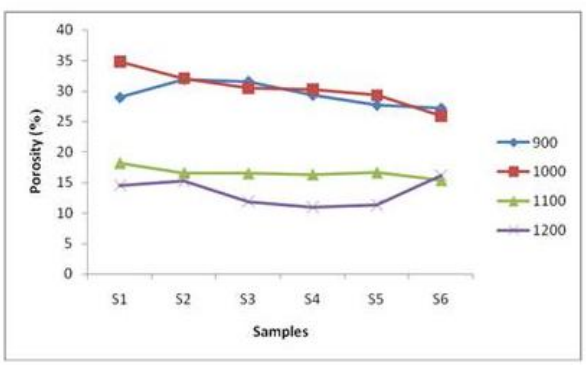
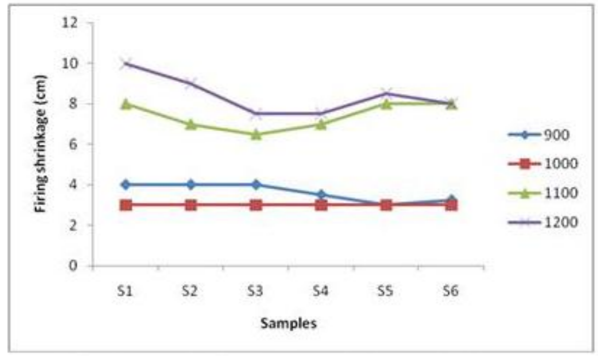



Figure 3. Porosity for six different stoneware tiles samples at different temperatures




Chemical composition of the studied materials is shown in table.1. In this table percentage of $SiO_2$,$Al_2O_3$ and $Fe_2O_3$ are comparatively reported to reference fireclay. In respect of glass waste power the percentage of $SiO_2$ and CaO are higher compare than that of other frequent components with respect to the less frequent components their variation is smaller ($TiO_2$,$Na_2O$,MgO,$P_2O_5$,$Cr_2O_3$,ZnO,BaO and PbO). The content of $Fe_2O_3$ is high (16.48%) in fire clay sample, which characterizes the studied clay materials as red clays type. Alkaline flumes contents $K_2O$+$Na_2O$) are low.

Figure 4. Firing shrinkage for six different stoneware tiles samples at different temperatures




**Tile water absorption**

Water absorption is an important parameter in ceramic tiles, that defines the class to which the product belong the standard porcelain stoneware tiles. Water absorption is used to estimate the pore ratio of tile specimens. High water absorption in tile is characterized by a high pore ratio. CNS requires the water absorption of tile be less than 16% water absorption of tiles increased by about 3-4% with the addition of quartz as can be seen in Fig-2 however, glaze formed a thin film, which helped protect the surface and reduce water absorption of porcelain stone ware tiles. It also indicates that water absorption decreased with the increase of glaze concentration application.

The materials showed low firing shrinkage at 900 and 1000$^0$C whilst at 1050 and 1200$^0$C a higher range of values is presented (Table. 3) Moreover, the ceramic bodies in this temperature tend to have a more open structure due to the transformation from kaolinite to metakaolinite. Between 950 and 1050$^0$C relevant variations occur. This behavior is related to the beginning of glassy phase formation, with likely predominance of viscous flow sintering on the material densification.

**Porosity test**

According to technical standards, tiles with water absorption values higher than 10%are classified process wall tiles [3]. The bloating phenomenon, in the form of a high concentration of coarse pores, that starts at about 1000ºC for all the tile compositions (fig-3), takes place by retention of gas within the mass when a considerable quantity of glass of adequate viscosity is present. Since the bloating is a process commonly used for the production of lightweight ceramic materials, e.g., aggregates for concrete it has been studied by several researchers [5,12,13]. The mechanism of bloating by iron(III) oxide reduction is well known; sandrolini et al [2,4] gave a detailed description of the fundamental role of iron oxide in the bloating of vitrified ceramic materials with an iron(III) oxide content between 1 and 6wt%. At elevated temperature, $Fe_2O_3$ is partially reduced with the production of oxygen as the bloating gaseous phase, generating large pores within the fired body and determining a density decrease.

Porosity was determined by the boiling method which is the standard procedure. From the Table.3 and Fig.3 the values of porosities of samples from $S_1$ to $S_6$ vary for different temperatures. Finally, since water absorption is directly related to open porosity, its value decrease in the overall temperature range.

Table – 2 : Mixtures compositions (wt%)

| Mixtures | Raw materials | | | |
|---|---|---|---|---|
| | Fire clay | Feldspar | Quartz | Glass waste |
| 10G5Q5G | 80 | 10 | 5 | 5 |
| 10F5Q10G | 75 | 10 | 5 | 10 |
| 10F5Q15G | 70 | 10 | 5 | 15 |
| 10F5Q20G | 65 | 10 | 5 | 20 |
| 10F5Q25G | 60 | 10 | 5 | 25 |
| 10F5Q30G | 55 | 10 | 5 | 30 |

Table.3 Chemical composition of the raw material (Fireclay and glass waste in wt%)

| Element composition | Fire clay mass (%) | Glass waste mass (%) |
|---|---|---|
| $Na_2O$ | 0.00 | 0.47 |
| $MgO$ | 0.00 | 0.12 |
| $Al_2O_3$ | 18.62 | 0.01 |
| $SiO_2$ | 59.60 | 73.71 |
| $P_2O_5$ | 0.00 | 0.19 |
| $K_2O$ | 0.03 | 0.07 |
| $CaO$ | 0.67 | 24.84 |
| $TiO_2$ | 2.81 | 0.00 |
| $Cr_2O_3$ | 0.00 | 0.01 |
| $Fe_2O_3$ | 16.48 | 0.56 |
| $ZnO$ | 0.00 | 0.01 |
| sro | 0.27 | 0.00 |
| Bao | 1.41 | 0.02 |
| Pbo | 0.12 | 0.00 |

**Modulus of rupture**

MOR values are shown in table.3. In all series as four different temperatures (900, 1000, 1100 and 1200ºC); an increase bend strength is observed from sample $S_1$ fired as 1100º C. 5wt%of glass while for 10wt%of glass, a small strength reduction is appreciated (fig-1). This high value may be attributed to the use of alumina in the base body composition as alumina is often used as a reinforcer. It was reported that dispersed particles increase the fracture energy by the interaction between dispersed particles and propagating crack fronts [4]. Also in the designed batch in this work, only 5%quartz is added. The α-β quartz transformation usually causes microcraks. So avoiding large amounts of quartz was advantageous.

The increased amount of liquid phase as higher temperature certainly affects negatively the mechanical strength. Generally in ceramic compositions containing clays and feldspars, thereby improving mechanical properties.

According to literature [1,2] the use of scrap-glass cause a general increase in porosity, but besides the high values of porosity (11.35-34.09%) (fig-3) the mechanical characteristics, as modulus of rupture, of the tested materials are still in accordance with the standard for porcelain stoneware.

## Conclusion

The glass powder waste shown 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 porosity, water absorption) combined with negative ones (higher values of shrinkage). The use of small amount of glass powder (5%) in association with feldspar showed good result of mechanical properties the S1 is the only product that can be classified as porcelain stoneware tile due to its properties.

## References

1. A. tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi, use of sodalime scrap-glass as a fluxing agent in a porcelain stone ware tile mix, J. Eur. Ceram. Soc. 24(1) (2004) 83-92.

2. F. Matteucci, M. Dondi, G. Guarini, Effect of soda–lime glass on sintering and technological properties of porcelain stoneware tiles, Ceram. Int. 28 (8) (2002) 873-880.

3. A.C.S. Alcantara, M.S.S. Beltrao, H.A. Olireirq, I.F. Gimienez, L.S. Barreto, characterization of ceramic tiles prepared from two clays from sergipe-Brazil. Appl. Clay Sci. 39 (2008) 160-165.

4. M.F. Abadir, E.H. Sallam, I.M. Bakr, Preparation of porcelain tiles from Egyptian raw materials, Ceram. Int. 28 (2002).303-310.

5. P. Appendino, M. Ferraris, I. Matekovits, M. Salvo, production of glass- Ceramic bodies from the bottom ashes of municipal solid waste incinerators, J. Eur. Cream. Soc., 24 (2004) 803 810.

6. R. Gennaro, P. Cappelletti, G. Ceeri, M. Gennaro, M. Dondi, G. Guarini, A. Langella, D. Naimo, Influence of zeolites on sintering and technological properties of porcelain stone ware tiles, J. Eur. Ceram. Soc. 23 (13) (2003) 2237-2245.

7. M. Compos, F. Velasco, M.A. Martinez, J.M. Torralba, Recovered slate waste as raw material for manufacturing sintered strutural tiles, J. Eur. Ceram. Soc. 24 (2004) 811-819.

8. L. Barbieri, L. Bonfatti, A.M. Ferrari, C. Leonelli, T. Mantredini, D. Seltembre Blundo, Relation between microstructure and mechanical properties in fully vitrified stone ware, in: P.Vicenzini (Ed), Ceramics: Charting the Future,Vol.34, Techna Srl, Modena, 1995, PP.99-105.

9. W.M. Carty, U. Senapati, Porcelain-raw materials, processing, phase evolution,and mechanical behaviour, J. Am. Ceram. Soc. 81(1) (1998) 3-20.

10. Davies and Walther, Direct bonding of Basic brick, J. Am. Ceram. Soc., vol 47, No.3, Mar (1964).

11. E. Sanchez, M.H. Ibanez, J. Gareia-Ten, M.F. Quereda, I.M. Hutuchings, Y.M. Xu, porcelain tile microstructure: Implications for polished tile properties, J. Eur. Ceram. Soc., 26 (2006), 2533-2504.

12. Sandrolini, F. and Palmonari, P., Role of iron oxide in the bloating of vitrified ceramic materials. Trans. J. British Cer. Soc. 1976, 75(2). 25-32.

13. Maniatis, Y. and Tite, M.S., A scanning electron microscope Examination of the bloating of fired clays. Trans. Br. Ceram. Soc., 1975, 74, 19 22.

14. A.P. luz, S. Ribeiro, use of glasswaste as a raw materialin porcelain stoneware tile mixture, Ceram. Int. 38 (2007) 761-765.

15. D.P.H. Hassselman, R.M. Fulrath, Proposed fracture theroy of a dispersion-strengthened glass matrix. J. Am. Ceram. Soc. 49 (1966): 68-72.