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Traditional and glass powder porcelain: Technical and microstructure analysis

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Abstract

The properties of traditional porcelain (TP) were compared to a porcelain (GP) where the feldspar was replaced by recycled glass powder in the formulation. The porcelain showed characteristics and properties similar to that of TP. Therefore GP can be used in many applications except those, which demand a very high strength. The SEM investigation showed that GP contained primary mullite, quartz and glassy phase and that TP contained secondary mullite. GP can be fired at 1240 °C while TP can only be fired at 1340 °C. The reduction in firing temperature and the use of a cheaper substitute for feldspar makes GP an attractive economical alternative.

Keywords: Glass powder; Microstructure; Porcelain; Waste materials

1. Introduction

A traditional porcelain is a triaxial body that is composed mainly of quartz, feldspar and kaolin. Feldspar is the most expensive raw material and therefore its replacement would represent a significant reduction in final costs. Feldspar is a fluxing agent used to reduce the firing temperature. The glassy phase in the fired component is formed by feldspar decomposition and interaction with crystalline phases. During observation of this glassy phase it was noted that it is composed of alkaline silicates and resembles the composition of a soda–lime glass. This work is based on this fact and investigates the use of milled powder obtained from recycled soda–lime glass as a fluxing agent for porcelain.

A traditional porcelain (TP) and a porcelain containing glass powder [glass powder porcelain (GP)] were tested. TP and GP were prepared, processed and fired under the same experimental conditions so as to make the data more comparable. Technical parameters such as water absorption, bulk density and modulus of rupture were reported. The microstructure was also investigated using scanning electron microscopy.

Many researches were undertaken using alternative material replacing quartz, however few have been done replacing feldspar, mostly researchers have tried different kinds of feldspar, feldspatic rocks, nepheline syenite, etc.[1–3] The difficulty is to find a material that does not contain impurities such as oxides that can colour the material because porcelain should be as white as possible. Therefore recycled colourless glass is suitable for this work.

2. Experimental procedure

Two batch formulations were tested. One batch composed of 25% quartz, 50% kaolin and 25% feldspar (traditional porcelain—TP) and another batch composed of 50% of kaolin, 25% quartz and 25% powdered soda–lime glass (glass powder porcelain—GP). Glass powder was used in the second batch replacing feldspar, which is normally used in traditional compositions. The main observations show the role of the glass powder as a fluxing agent.

Table 1 shows the chemical analyses of the raw materials.

The crystalline phases in raw materials were determined by X-ray diffraction. The results show in the kaolin the presence of kaolinite ($Al_2\,Si_2\,O_5\,(OH)_4$) as

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the main phase and muscovite (($K\ Al_2\ (Al\ Si_3\ O_{10})\ (OH)_2$) plus illite ($K\ Al_3\ Si_3\ O_{10}\ (OH)_2$) as secondary phases. It was screened to pass 325 mesh (<45 µm). Feldspar, sieved to pass 270 mesh (<53 µm), mainly revealed microcline ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$).

The quartz passed through the 325 mesh (45 µm). This particle size is used in the majority of Brazilian industries. Because of this a particle size of 45 µm was selected instead of quartz particle sizes between 10 and 30 µm recommended by the literature for the maximum strength of porcelain.[4–6]

The glass powder was obtained from high transparency soda–lime glass pots and bottles without colouring oxides. The glass was milled and sieved to 270 mesh (<53 µm).

The raw materials selected were dry milled in a ball mill for 30 min in order to homogenize the mixture. The milling time to give the optimum samples properties was previously determined. Eight percent of forming water was then added and the mixture sieved to 20 mesh prior to pressing. The final dimensions of the samples were 8 mm×20 mm×60 mm after pressing.

Table 1
Chemical composition of the raw materials

	Kaolin	Feldspar	Glass powder	Quartz
SiO_2 (%)	46.96	67.02	70	99.81
Al_2O_3 (%)	38.05	19.22	2	0.12
Fe_2O_3 (%)	0.46	0.19	<0.1	0.08
MnO (%)	0.008	0.007	–	0.002
MgO (%)	0	0	–	0.01
CaO (%)	0.02	0.06	6	0.01
Na_2O (%)	0.03	3.75	20	0.03
K_2O (%)	1.14	9.42	–	0.06
TiO_2 (%)	0.03	0	<0.1%	0.073
P_2O_5 (%)	0.108	0.035	–	0.02
LOI (%)	13.2	0.3	–	0.1
Total (%)	99.99	100	98.0	99.9

The samples were dried for 48 h in air and then at 110 °C for 24 h in an electric furnace. No further change in weight occurred during this time once the specimens were dry. The dried pieces were then weighed and measured to obtain weight loss and dry density.

The samples were fired in an electric furnace at a heating rate of 150 °C/h until they reached a peak temperature within the 1200 °C to 1420 °C range. The samples were soaked at temperature for a period of 30 min.

To make the study comparative samples with the same dry density (1.80 g/cm^3) were used in each of the two batches. This value was easily obtained for both formulations by changing the quantity of forming water and forming pressure.

3. Results and discussions

3.1. Technical properties

The technical parameters of TP and GP are summarised in Table 2.

Table 2 shows that the firing temperature that gave the maximum strength was approximately the lowest value of water absorption. It can be remarked that the maximum strength and maximum bulk density were achieved at the same firing temperature. These factor and physical properties are illustrated in Figs. 1–3.

The use of glass powder resulted in a lower firing temperature for GP, e.g. 100 °C lower than for TP. Fig. 1 shows that 0.39% of water absorption and 8.8% of linear shrinkage occurred for the 1240 °C GP samples. Whilst the 1340 °C TP samples attained values of 0.34% water absorption and 12.2% of linear shrinkage. These temperatures were considered to be appropriate for the firing of these porcelains. The lower firing temperature is an advantage for GP and confirms that the glass powder is a strong flux. Llorens[7] reports that a low shrinkage is not usual for a strong flux. Conversely GP

Table 2
Water absorption, bulk density and modulus of rupture (MOR)[a]

Firing temperature (°C)	Traditional porcelain			Glass powder porcelain		
	Water absorption (%)	Bulk density (g/cm^3)	MOR (MPa)	Water absorption (%)	Bulk density (g/cm^3)	MOR (MPa)
1200	5.52	2.22	23.8	2.13	2.25	30.7
1220	–	–	–	1.35	2.26	33.4
1240	2.55	2.35	27.7	0.39	2.28	37.9
1260	–	–	–	0.15	2.23	33.9
1280	1.53	2.41	36.0	1.06	1.84	19.6
1320	0.46	2.47	37.7	–	–	–
1340	0.34	2.48	45.7	–	–	–
1380	0.22	2.42	40.6	–	–	–
1420	0.59	2.16	25.0	–	–	–

[a] Comparison between traditional porcelain (TP) and glass powder porcelain (GP) related to firing temperature.

shows a shorter temperature range for firing than TP. This indicates that more careful control is required during the firing process of this porcelain.

Fig. 2 shows the effect of firing temperature on MOR. At the lowest firing temperature GP showed the highest strength of 30.7 MPa at 1200 °C while TP showed strength of 23.8 MPa. The greatest MOR value for GP (38 MPa) was obtained at 1240 °C, which decreased with a further increase in temperature. TP reached a greater MOR value (46 MPa) at higher firing temperature of 1340 °C.

Bulk density is a property that has a strong influence on MOR. Generally the higher the bulk density the higher the MOR.[8,9] With reference to Figs. 2 and 3 it can be seen that MOR is a function of bulk density and is related to firing temperature. With reference to Fig. 3 it can be seen that the same behaviour of the MOR (Fig. 2), as related to firing temperature, was demonstrated by bulk density. TP showed the highest densification reaching 2.48 g/cm^3 and highest MOR value at a firing temperature of 1340 °C. GP attained a density value of 2.28 g/cm^3 at 1240 °C. As was previously shown, both formulations had a low degree of water absorption. Therefore it follows that GP must have a greater amount of closed porosity.

GP could not reach higher values of densification even if it started from the same drying density value as for TP. Therefore it is believed that the GP formulation will not be able to yield porcelain of very high strength. However a strength value of 38 MPa is sufficiently high enough for the majority of porcelain applications including porcelain stoneware.

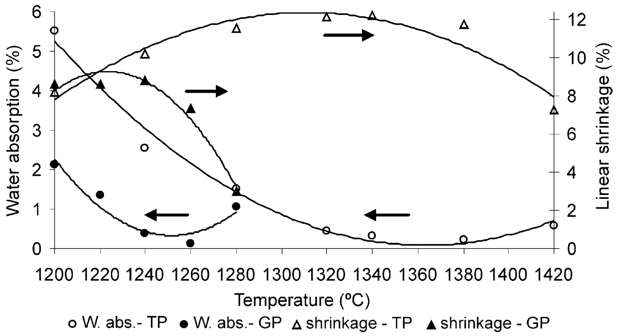

Fig 1. Effect of firing temperature on water absorption and linear shrinkage. TP: traditional porcelain. GP: glass powder porcelain.

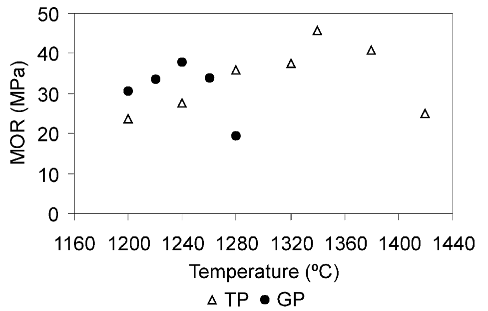

Fig. 2. Effect of firing temperature on modulus of rupture (MOR).

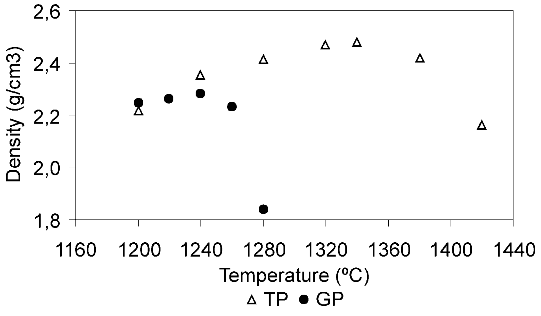

Fig. 3. Effect of firing temperature on bulk density.

3.2. Microstructure

The comparison of TP and GP microstructures is shown in Fig. 4. This study was undertaken for the appropriate firing temperature with respect to the physical properties for each batch. Therefore TP was investigated for a firing temperature of 1340 °C and GP for a temperature of 1240 °C.

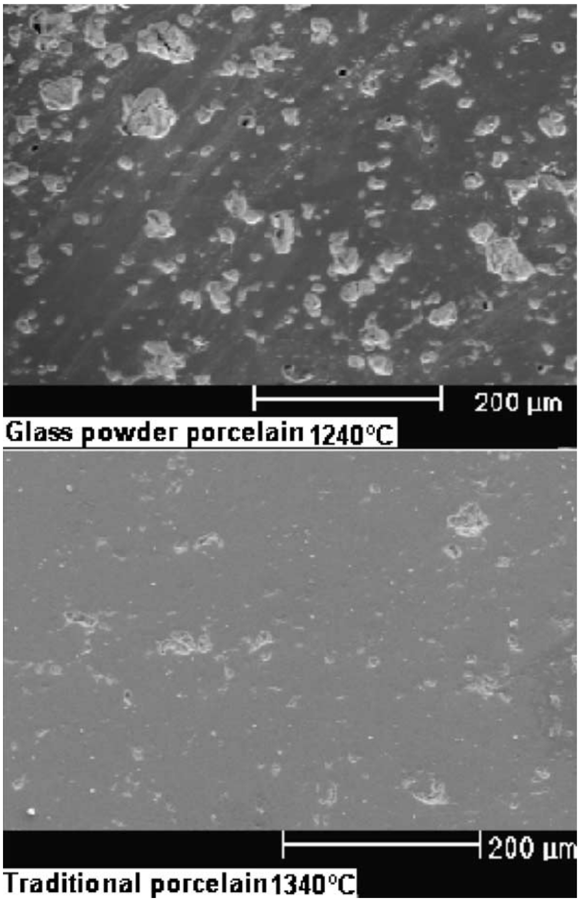

Fig. 4. SEM photomicrographs. Traditional porcelain (TP) fired at 1340 °C and glass powder porcelain (GP) fired at 1240 °C.

Fig. 4 shows that GP has a higher quantity of closed porosity and larger bubbles than TP. According to Oral,[10] these bubbles can be associated with a flaw and significantly reduce the strength of the porcelain.

Fig. 5 shows the microstructures of the etched samples. It can be noted that secondary mullite was only present in TP. This phase has morphology of prismatic needles. According to Carty,[11] the felt-like interlocking of mullite needles contributes to an increase in MOR. This is another factor besides lower porosity that explains the higher strength of TP. This hypothesis is conclusive when it is considered that the amount and particle size of the quartz was the same for both formulations as the SEM results show. Quartz is considered to be the principal phase that determines and limits porcelain strength.[12,13] The quartz particle size is represented in Fig. 5. In addition GP contains more voids, which were probably once glassy phase regions. The presence of glass powder, which does not form secondary mullite, replaced feldspar but is responsible for the smaller quantity of crystalline phase.

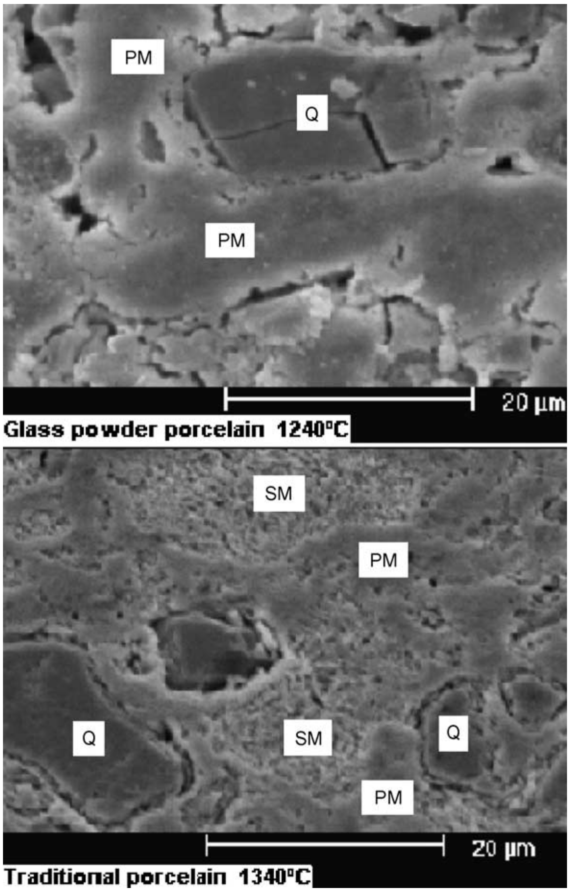

Fig. 5. SEM photomicrographs. Traditional porcelain (TP) fired at 1340 °C and glass powder porcelain (GP) fired at 1240 °C. SM: secondary mullite. PM: primary mullite. Q: quartz. Etched HF 20% for 10 s.

The study of Cordelair et al.[14] showed that the utilisation of recycled glass replacing a part of quartz was responsible for a reduction in thermal stress, and that can contribute for a higher strength. This could not be analysed here due to the low cooling rate used. An investigation of the thermal expansion behaviour will be showed in the part II of this work.

At a higher magnification (Fig. 6) the difference between the morphology of primary and secondary mullite becomes clear. According to Schüller[12] primary mullites are in the form of scaly crystals and secondary mullites are needle shaped crystals. The differences between the properties of the molten glassy phase, such as viscosity and the chemical compositions of GP and TP, would explain why secondary mullite only appears in TP. This confirms that secondary mullites are formed from the recrystallization and dissolution of alumino-silicates within the melt. Thus the chemical composition of the melt is very important. This statement is in accordance with Mörtel et al.,[15] but

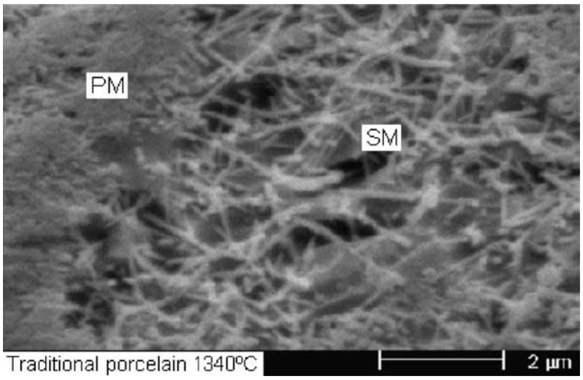

Fig. 6. SEM photomicrographs. Traditional porcelain (TP) fired at 1340 °C. SM: secondary mullite. PM: primary mullite. Etched HF 20% for 10 s.

Table 3
EDX analysis of selected regions in SEM photomicrograph[a]

Letters (Fig. 7)	Region (Fig. 7)	Elementary analysis	Main phase	Secondary phases
A	Feldspar	Si, Al, O, K, Na	Secondary mullite	Glass phase, feldspar relicts
B	Clay	Si, Al, O	Primary mullite	Clay relicts
C	Clay	Si, Al, O	Primary mullite	Clay relicts
D	Particle (light gray)	Si, Al, O	Clay relict	
E	Particle (light gray)	Si, Al, O	Clay relict	
F	Particle (dark gray)	Si, O	Quartz	

[a] Traditional porcelain (TP) fired at 1340 °C.

Table 4
EDX analysis of selected regions in SEM photomicrograph[a]

Letters (Fig. 8)	Region (Fig. 8)	Elements	Main phase	Secondary phases
A	Clay	Si, Al, O, Na	Mullite	Clay relicts and glass phase
B e C	Matrix	Si, Al, O, Na, Ca	Glass phase (corroded by HF)	Clay relicts, mullite
D	Particle (dark gray)	Si, O	quartz	

[a] Glass powder porcelain (GP) fired at 1240 °C.

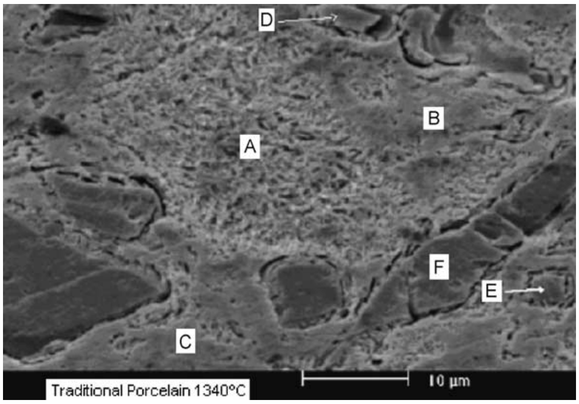

Fig. 7. Traditional porcelain (TP) fired at 1340 °C. Selected regions for EDX analysis.

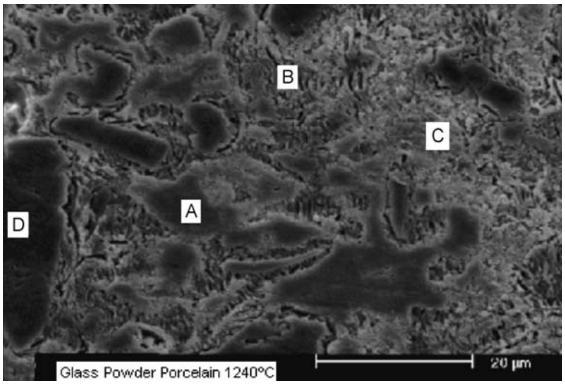

Fig. 8. Glass powder porcelain (GP) fired at 1240 °C. Selected regions for EDX analysis.

they realized experiments with feldspar of different chemical compositions. In addition, Iqbal and Lee[16] showed that primary mullite and secondary mullite have different chemical composition and they are formed in different regions because of the specific composition of those regions (clay relicts, feldspar relict, etc).

The amount of Al_2O_3 (2% as shown in Table 1) within the glass composition is less than that contained in the feldspar (20%). Therefore there was insufficient Al in GP for the formation of secondary mullite. This is a hypothesis to be considered. A second hypothesis considers the low mobility and diffusion of Al within GP porcelain with respect to the high Al content in clay relict. It can be also concluded that secondary mullite does not crystallize at the expense of primary mullite. These suppositions can be only considered within the range of firing temperature (1200–1280 °C) studied in this work.

The EDX analysis was realized simultaneously with microstructure observations, which supported the identification of the phases. The results of this analysis are shown in Fig. 7 and Table 3 for TP, and in Fig. 8 and Table 4 for GP.

4. Summary and conclusions

Porcelain with excellent technical characteristic was produced which had similar properties to a traditional porcelain. From the results obtained in this work it can be concluded that the use of recycled soda–lime glass powder as a fluxing agent to replace feldspar in porcelain is viable.

The appropriate firing temperature for GP was 1240 °C and for TP it was 1340 °C. Therefore the use of glass powder permitted a decrease of 100 °C in firing temperature to be made. This would mean a reduction in production costs which makes the utilisation of GP very attractive.

The firing curve (water absorption and linear shrinkage × firing temperature) shows that GP has a behaviour typical of a strong flux. GP has an advantageously low firing temperature, but a shorter sintering range compared to TP.

After firing at the appropriate temperature the modulus of rupture and bulk density were higher for TP. However, it is interesting to note that because of a high MOR (38 MPa) and low water absorption (0.39%) GP porcelain attained the technical specifications of a porcelain stoneware.

The microstructural analysis revealed that the ideal firing temperature occurred when the glassy phase covered the entire sample surface and had a sufficient time to react with the crystalline phases. However higher temperatures were deleterious to the properties of porcelain due to an increase in porosity. This porosity is due to the release of oxygen from the decomposition of Fe_2O_3 decomposition and gas expansion within the pores. The higher amount of closed porosity in GP porcelain explains why this porcelain did not attain a higher bulk density.

SEM investigations showed that the low MOR values in the GP samples were a consequence of closed porosity. The TP samples only contained secondary mullite and this phase may have contributed to the higher strength of TP. This observation is valid because the amount of quartz in the microstructure and the quartz particle size were similar in both formulations. Therefore quartz grains of 45 μm did not undergo significant dissolution and contributed to the strength of TP and GP.

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