

Effect of microstructure on mechanical properties of porcelain stoneware

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Abstract

This work examines the effect of microstructure (aspect ratio of mullite crystals and proportion of crystalline and amorphous phases) as well as different physical features (bulk density, closed and open porosity and absolute density) on the mechanical properties of a standard porcelain stoneware composition (50% kaolinitic clay, 40% feldspar and 10% quartz) fired in the 1200–1300 °C temperature interval using a fast firing schedule. The mechanical behaviour was evaluated in terms of bending strength, Vickers microhardness, fracture toughness and Young's modulus. After viewing the results, it can be concluded that increased σ_f , H_v and E values were mainly due to open porosity, percentage of mullite phase and morphology of secondary mullite needles, whereas closed porosity and quartz particles have no influence on these properties.

Keywords

Mullite; Porcelain stoneware; Mechanical properties; Traditional ceramics; Microstructure-final

1. Introduction

Porcelain stoneware tile is a ceramic building material with high bending strength and abrasion resistance. It is generally used in pavements, as wall covering and as ventilated facades. In recent years, it has experienced the greatest increase in production and sales of all ceramic building materials.

Porcelains typically have a triaxial composition comprised of about 50% clay, 25% flux and 25% filler. Fired bodies containing these three components result in a grain and bond microstructure, which has large grains or filler (usually quartz) held together by a finer bond or matrix comprised of mullite crystals and a glassy phase. In relation to its raw material composition (clay, quartz and feldspar), porcelain stoneware is considered to be a triaxial porcelain material. However, porcelain stoneware tile is produced using a fast firing schedule (temperature rates up to 60 °C/min), in which the tiles are inside the furnace no longer than 60–90 min. This is in contrast to the lengthy (several hours) process employed in porcelain

manufacture. Consequently, the microstructure of porcelain and porcelain stoneware is different because the firing process affects the ratio of crystalline to amorphous phases in the end products. Mullite and glass are the major phases in porcelain. In porcelain stoneware tile, quartz is more abundant than mullite.

Concerning mechanical properties of porcelain bodies, several theories have evolved, which assume that strength can be attributed to factors such as mullite content and morphology, as well as quartz particles and porosity.

Various studies have shown that the strength of a porcelain body is related to felt-like interlocking of fine mullite needles. Consequently, the strength increases with increasing mullite content. This assumption was first proposed by Zoellner.¹ However, at times, the beneficial effect of mullite content is not evident. Several researchers have not found a clear relationship between mullite content and bending strength^{2, 3 and 4} and a recent study on the influence of composition on mechanical behaviour of porcelain tile⁵ has shown that mullite significantly worsen the fracture energy, which invalidates the mullite hypothesis as a mechanism to strengthen the porcelain tile.

The function of quartz in the strength of a porcelain body has also been taken into consideration. Some authors suggest that the mismatch in the thermal expansion coefficient, α , between quartz particles ($\alpha \approx 15\text{--}26 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and the silicate glass matrix ($\alpha \approx 5\text{--}8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) generate a compressive stress on the matrix, which leads to strength reinforcement in the porcelain bodies. According to this theory, a higher residual quartz content results in higher strength. Nevertheless, other researchers have reported that such a relationship is not very clear and the dependence even seems to be the opposite.^{4 and 6} Mattyasovszky-Zsolnay⁷ reported that the bending strength of porcelain bodies is strongly dependent on quartz particle size and that to assure a suitable compressive prestress to the vitreous phase, the added quartz particles must be within the 10–30 μm range. If the quartz grains are very fine, they are highly dissolved in the glass matrix, whereas if grains are too coarse, they induce crack generation. More recently, other authors have supported this idea and reported similar results in silica and sanitary porcelains.^{2, 8 and 9}

In addition, other studies have also found evidence of the influence of the microstructure of porcelain bodies on the bending strength. Thus, several authors have suggested a close relationship between the amount of glassy phase present in the fired body and bending strength^{2 and 4} or fracture toughness.¹⁰ In contrast, other studies have claimed that an increase in the vitreous phase decreases the mechanical resistance of porcelain bodies.⁶

Porosity has also been shown to affect mechanical properties. It was reported that the Young's modulus decreases with increasing porosity^{10 and 11} and at equivalent porosities, specimens with small pores were found to have a higher Young's modulus than specimens with large pores.¹²

As mentioned above, because of the fast firing process, the microstructure shown by porcelain and porcelain stoneware is rather different. The effect of microstructure on the technological properties of porcelain stoneware products has been studied over the past few years and, similar to porcelain, the effect of microstructure on mechanical properties is not well established. Thus, several studies suggest that internal porosity is the main factor affecting Young's modulus and the flexural strength of stoneware.^{13, 14 and 15} Some authors claim that mechanical improvement is mainly influenced by the stresses set up in the glassy matrix, which are induced by the quartz grains rather than the amount or size of mullite.^{16 and 17} Other researchers maintain that mullite content plays a major role in resistance to deep abrasion, owing to both its hardness and a toughening mechanism originating from differences in thermal expansion and elastic modulus between the glassy and mullite phases, which induce compression at grain boundaries^{18 and 19} and toughness of porcelain stoneware increases as the quantity of crystallising mullite increases.²⁰ Finally, it has been also suggested that the mechanical characteristics of stoneware increase with decreasing percentage of the glassy phase.²¹ However, although much effort has been made to enhance the mechanical properties of porcelain stoneware tiles, the effect of mullite crystal morphology has not received significant consideration.

The aim of this work is to study the evolution of mechanical properties on firing in porcelain stoneware and to establish the influence of microstructure, taking into consideration percentage, shape and size of mullite crystals. For this purpose, a standard porcelain stoneware body was fired between 1200 and 1300 °C using a fast firing process. The mechanical properties of the end products have been correlated with their physical and microstructural features, which have been determined in previous work.^{22, 23 and 24}

2. Materials and methods

Raw materials used in the present investigation were kaolinitic clay and feldspar (provided by Compañía Europea de Arcillas, S.A. and designed as AR-2097-G and FC-100 respectively), and quartz sand (facilitated by IETcc, CSIC). Chemical composition, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), and mineralogical

composition determined by X-ray diffraction (XRD) are shown in Table 1. All the above materials were crushed, ground and finally powdered to <160 μm prior to further use.

Table 1. Chemical and mineralogical analyses of raw materials used in this work.

	Content (wt%)		
	Kaolinitic clay	Feldspar	Quartz sand
SiO₂	58.10	69.86	98.88
Al₂O₃	27.60	16.45	1.08
Fe₂O₃	1.58	0.06	0.31
CaO	0.26	0.54	0.08
MgO	0.40	0.06	< 0.10
Na₂O	-----	2.28	< 0.07
K₂O	1.62	10.20	< 0.10
TiO₂	0.65	0.05	0.57
MnO	0.01	-----	0.01
P₂O₅	0.16	-----	< 0.10
LOI	9.40	0.50	0.28
Mineralogical composition	70.6% kaolinite 12.7% illite 10.6% quartz 6.1% others	65% microcline 20% albite 13% quartz 2% others	Mainly quartz microcline as minor phase

A standard porcelain stoneware composition was prepared by mixing 50% kaolinitic clay, 40% feldspar and 10% quartz. Batches (300 g each) were prepared by milling the constituents with distilled water (1:1) for 30 min in a planetary ball mill (TURBULA) using alumina balls as the grinding media. The resultant slurry was oven-dried overnight at 110 °C, powdered in a porcelain mortar and pestle, and sieved to pass –100 mesh (150 μm). The resulting powder was moistened by spraying it with distilled water (6 wt%) and was uniaxially pressed at 40 MPa in a steel die. Discs of 20 mm diameter and 5 mm height were shaped from 3 g of powder. Square tiles (30 g each) of 50 mm \times 50 mm \times 8 mm dimensions were prepared for bending strength measurements. After drying in an oven at 110 °C, the compacts were placed on alumina rollers in an electric furnace and fired between 1200 and 1300 °C, following a typical fast firing process used by the ceramic tile industry. The samples were heated for ~30 min to the required

temperature, soaked for 15 min and then cooled in the furnace at 50 °C/min to room temperature. Because of the high fluxing agent content, stoneware bodies exhibited pyroplasticity when fired at temperatures higher than 1300 °C, and thus it has not been feasible to correlate the microstructure of those specimens with their mechanical properties.

The bulk density, B (g/cm³), and open porosity, ε_o (%), were measured according to ASTM C373-88. The total porosity of the sample, ε_T (%) is determined as $\varepsilon_T = (1 - B/AD)$, where AD (g/cm³) is the absolute density of the sample, which was previously measured according to ASTM C329-88. The close porosity, ε_c (%), is then calculated as the difference between ε_T and ε_o .

The microstructure of fired specimens was examined by scanning electron microscopy (SEM, Philips XPERT microscope) using an accelerate voltage of 20 kV. For SEM observation, the specimens were Au–Pd coated (Balzers SCD 050 sputter). The analysis of porosity evolution during firing was accomplished on samples polished to 1 μ m finish with diamond pastes after initial grinding with SiC powder. For analysis of phase assemblages and morphology, the fresh fracture surfaces were etched for 4 min in 15% HF solution, washed ultrasonically with distilled water and ethylic alcohol, dried and subsequently Au–Pd coated.

Quantification of phases was carried out by Rietveld analysis. Finely powdered porcelain stoneware samples were mixed with ~30% high purity calcined α -Al₂O₃ as internal standard. The mixture was homogenized by hand milling for 5 min in an agate mortar with acetone. Powder diffraction patterns were collected at room temperature (Siemens D5000 (CuK α radiation) diffractometer) working at 40 kV and 30 mA. Intensities were collected by step-scanning in the 10–70° (2θ) range, with steps of 0.03° and a counting time of 8 s for each step.

Bending strength, σ_f , was measured according to UNE-EN 843-1 in an electronic universal tester (Servosis) on 10 test pieces of 50 mm \times 10 mm \times 8 mm by a three-point loading test with a span of 36 mm and a crosshead speed of 3 mm/min. Vickers microhardness, H_v , and fracture toughness, K_{IC} , measurements were performed using the indentation technique with a load of 1000 g for a dwell time of 15 s (Matsuzawa Hardness tester). Samples were ground with silicon carbide paper and then polished using 6, 3 and 1 μ m diamond pastes prior to measurement. For each case, an average of 10 measurements was taken. The cracks were measured immediately after indentation, thereby minimising any subcritical crack growth caused by residual stresses. Crack measurements were only made on indents that were well defined without chipping and

for cracks that did not terminate at pores. Young's modulus, E , was measured by the resonance frequency method (Grindosonic analyser).

3. Results and discussion

Fig. 1 shows the variation of bending strength in porcelain stoneware as function of firing temperature in the 1200–1300 °C range. The value of σ_f increases with firing temperature, reaching a maximum value at 1280 °C. Above that temperature, firing leads to reduced strength. To better depict this behaviour, Fig. 2 shows the variation of bending strength as a function of different physical features of the fired bodies. It is noted that bending strength is not dependent on the closed porosity of the piece because porcelain stoneware samples fired at 1270 and 1300 °C show similar σ_f values even though their closed porosity is very different. What does seem to have a positive effect on bending strength is the open porosity of the sample. Fig. 2 clearly shows that σ_f increases at the 1200–1250 °C interval when a reduction in open porosity close to 40% occurs. However, the bending strength continues to increase in samples fired in the 1250–1270 °C range when the open porosity is almost constant, with an average value of 3.53%. This result indicates that although bending strength is influenced by open porosity, it is not the only factor having an effect. Regarding the relationship between bending strength and density, there is a wide scattering of data in the representation of absolute density, whereas bulk density shows similar behaviour to open porosity, as these properties are directly related.

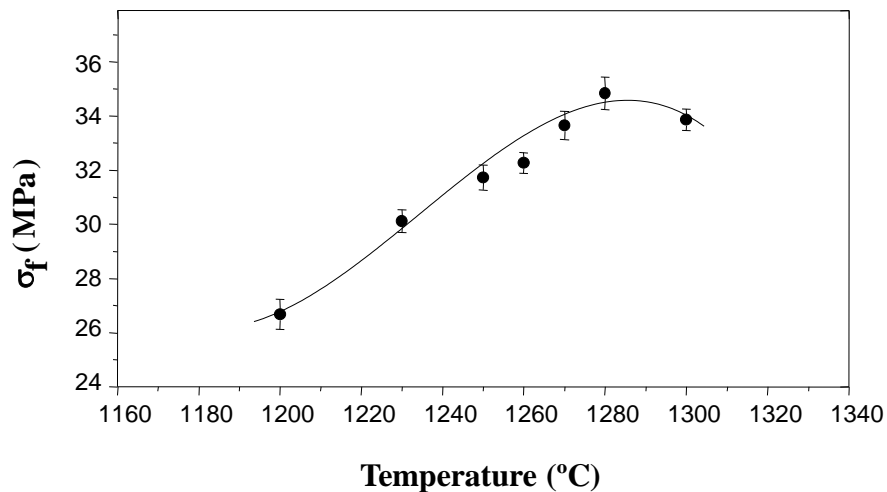


Fig. 1. Variation of bending strength in porcelain stoneware as a function of firing temperature in the 1200–1300 °C range.

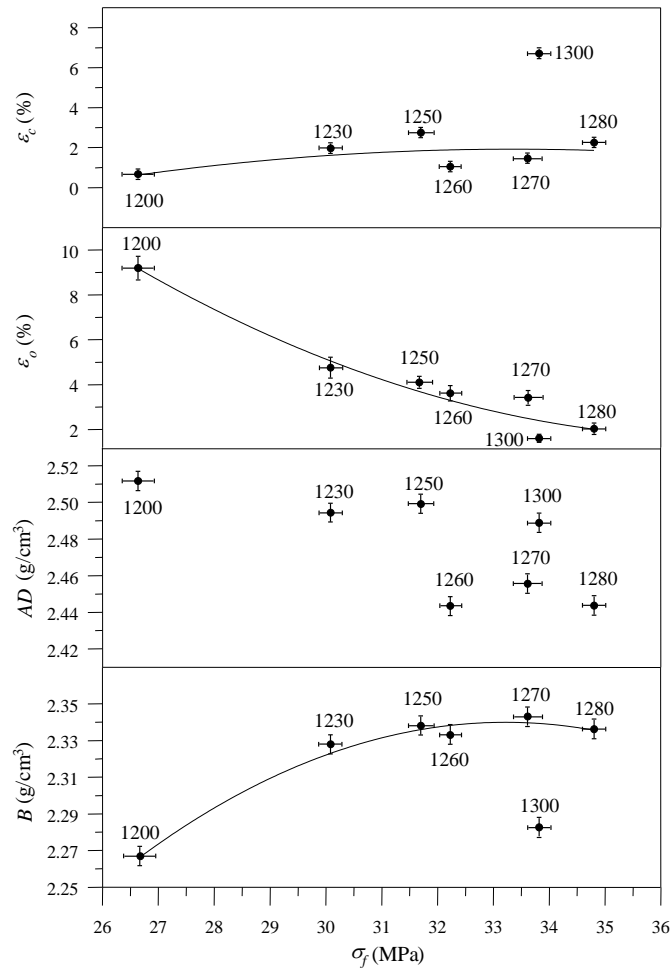


Fig. 2. Variation of bending strength as a function of different physical features of the fired porcelain stoneware (close porosity (ϵ_c), open porosity (ϵ_o), absolute density (AD) and bulk density (B)).

Fig. 3 shows the variation of bending strength as a function of the contents of quartz, mullite and the glassy phase obtained by the Rietveld method. σ_f increases in the 1200–1230 °C interval, in which the percentage of mullite increases nearly 20% and continues to increase in the 1230–1300 °C interval, when the mullite content is almost constant with an average value of 14.3%. Although this result is consistent with the hypothesis of mullite, which suggests that higher mullite content results in greater bending strength, 1⁸ 19^{and} 20 it also suggests the existence of another factor having influence on the flexural strength of porcelain stoneware specimens. A similar trend is depicted by the glassy phase curve, which shows an enhancement of σ_f in the 1200–1230 °C interval, in which the percentage of the glassy phase increases about 7% and continues to increase in the 1230–1300 °C interval, where the glassy phase is roughly constant with an average value of 60%. Concerning quartz particles, Fig. 3 shows how the

percentage of this phase seems to have no influence on σ_f . This is because bending strength increases in the 1230–1300 °C interval when quartz content is constant and even increases in the 1200–1230 °C interval when the percentage of quartz decreases. This result contradicts the prestressed theory, which proposes that quartz particles produce strong compressive stresses on the glassy phase with consequent mechanical property enhancement. In a recent study, De Noni et al.⁵ have found that quartz particles have a decisive contribution on increasing the fracture energy in porcelain tile, either by increasing the state of compressive residual stress in the glass matrix, or by promoting a combination of the mechanism of crack deflection and microcracking. However, the results are in good agreement with the results given by Maity and Sarkar²⁵, which show that quartz particles have an adverse effect on the flexural strength of porcelain compositions.

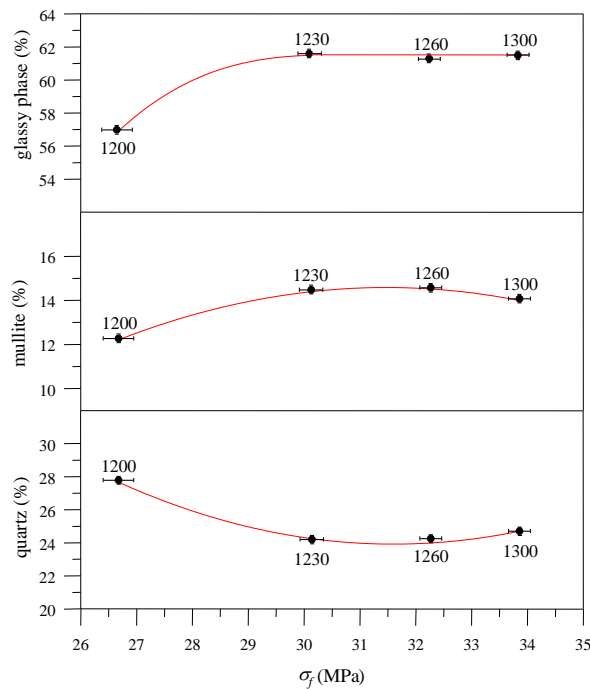


Fig. 3. Variation of bending strength in porcelain stoneware as a function of the contents of crystalline and glassy phases.

Fig. 4 depicts the variation of bending strength as a function of the aspect ratio showed by secondary mullite needles developed at the different firing temperatures. It can be seen that both factors are directly associated. σ_f improves throughout the whole temperature interval when the aspect ratio increases from 7:1 at 1200 °C to 50:1 at 1300 °C. Fig. 5 shows micrographs of porcelain stoneware specimens fired at different temperatures in the 1200–1300 °C interval. The increase in bending strength in Fig. 3 takes place at the 1230–1260 °C interval and concurs with

the arrangement of Type III secondary mullite crystals to form clusters or packs of needles, as has been observed by the authors in previous work focused on the study of microstructural evolution during the firing of porcelain stoneware.²⁴ Thus, at 1250 °C, bigger mullite needles begin to appear that show a considerable growth in both longitudinal and axial axes. A detailed observation of this growth suggests that mullite fibres, with an aspect ratio >30:1, join together and give rise to clusters or packs of needles.

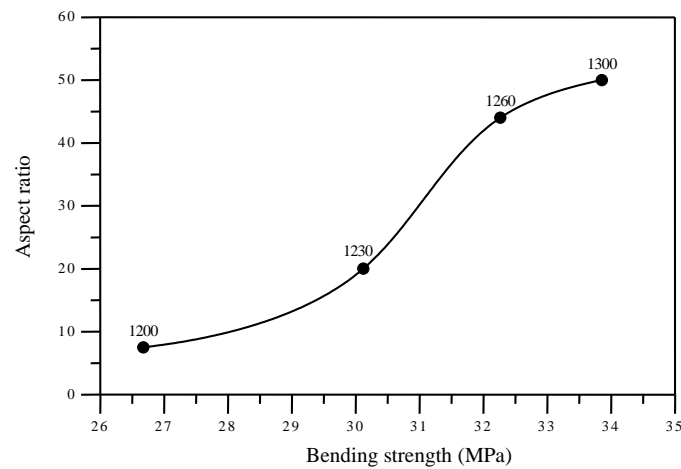


Fig. 4. Variation of bending strength in porcelain stoneware as a function of the aspect ratio shown by secondary mullite needles developed at different firing temperatures

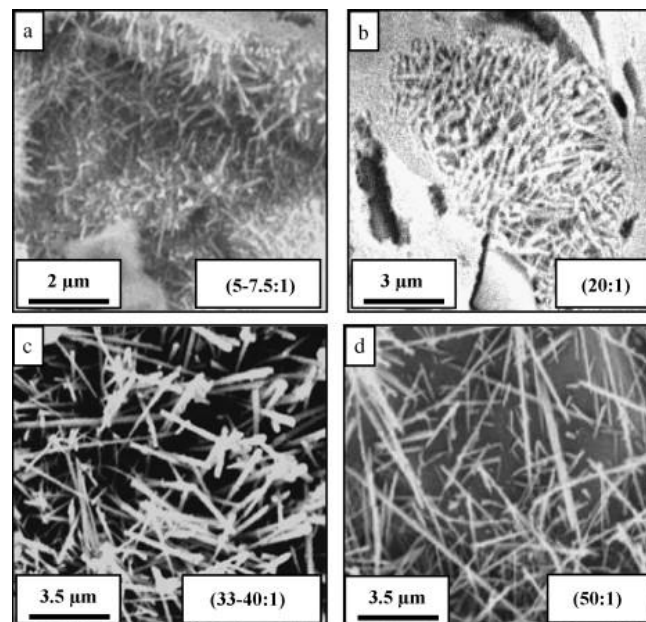


Fig. 5. SEM images of freshly fractured etched porcelain stoneware pellets fast fired at different temperatures. (a) 1200 °C, (b) 1250 °C, (c) 1260 °C and (d) 1300 °C.

After viewing the results showed in Fig. 1, Fig. 2, Fig. 3 and Fig. 4, it can be concluded that increased strength in the present porcelain stoneware composition was mainly due to open porosity, percentage of the mullite phase and morphology of secondary mullite needles. It is noteworthy that, although the influence of the first two factors has been referenced in earlier investigations of triaxial porcelain, there is no previous evidence of the importance of aspect ratio of mullite crystals on the mechanical properties of such materials.

Table 2 displays the values of the Vickers microhardness (H_v), Young's modulus (E) and fracture toughness (K_{IC}) of porcelain stoneware samples after fast firing in the 1200–1300 °C interval. Fig. 6 and Fig. 7 depict the variation of Vickers microhardness and Young's modulus as function of different physical features and phase compositions of the fired bodies. It is noted that all curves show similar behaviour to bending strength curves, which indicates that these properties are related and that the factors responsible for σ_f increasing also govern Vickers microhardness and Young's modulus. It is remarkable that the body fast fired at 1300 °C shows the highest values of E and also the maximum values of close and total porosity, which is in disagreement with the presumption that the Young's modulus decreases with increasing porosity. The Young's modulus–porosity correlation has been the subject of several investigations and numerous equations can be found in the literature. For example, the following dependence of E on porosity (P) has been proposed by Boccaccini and Boccaccini²⁶: $E(P) = E_0(1 - P^{2/3})^s$, where $E(P)$ and E_0 are the Young's modulus of the porous body and of the pore-free material respectively and s is a factor depending on pore shape and orientation. Nevertheless, in complex multi-phase systems such as porcelain stoneware, the correlation with the proposed theoretical models is difficult to find out.¹⁴

Table 2. Mechanical properties of porcelain stoneware samples after fast firing in the 1200–1300 °C interval.

	H_v (GPa)	E (GPa)	K_{IC} (MPa·m ^{1/2})
1200°C	4.6	48	1.3
1230°C	4.9	49	1.2
1250°C	5.3	61	1.3
1260°C	5.2	61	1.2
1270°C	5.3	61	1.4
1280°C	5.7	57	1.3
1300°C	5.5	65	1.4

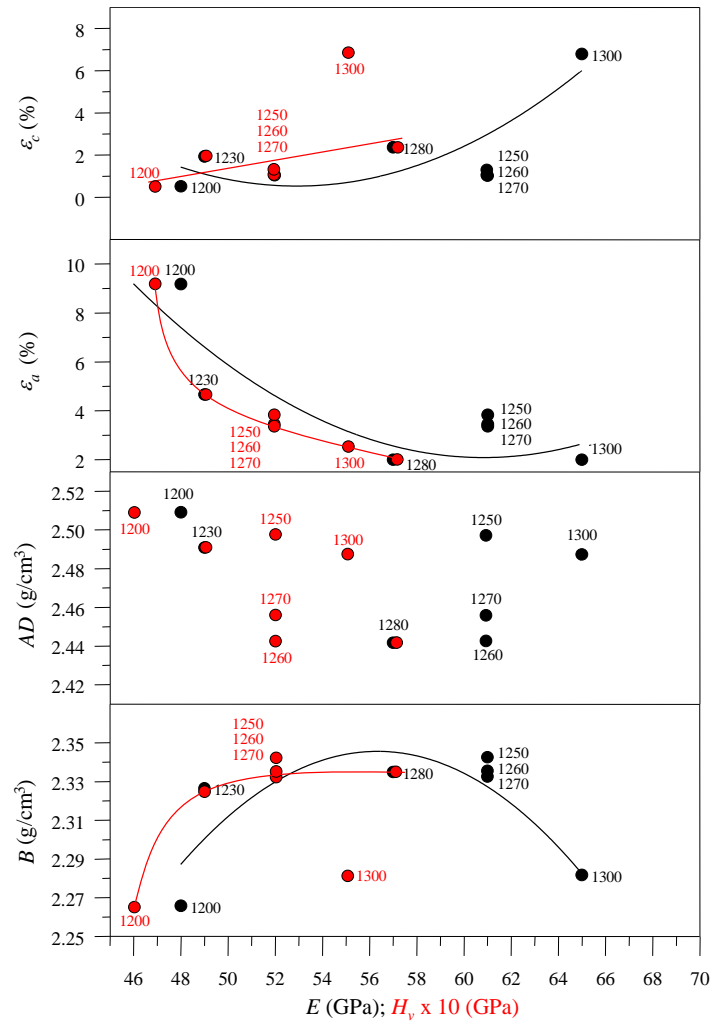


Fig. 6. Variation of Vickers microhardness and Young's modulus as a function of different physical features of the fired porcelain stoneware.

The increase found in E with porosity can be explained by taking into account the aspect ratio of mullite needles, which at 1300 °C have reached their maximum length (50:1) and have growth inside the pores, leading to a strengthening of the porcelain stoneware body. Finally, in Table 2, it is noted that the fracture toughness remains constant in the 1200–1300 °C interval, with an average value of 1.3 MPa m^{1/2}. This is independent of the firing temperature and, therefore, of the physical properties and microstructural features of the fired body.

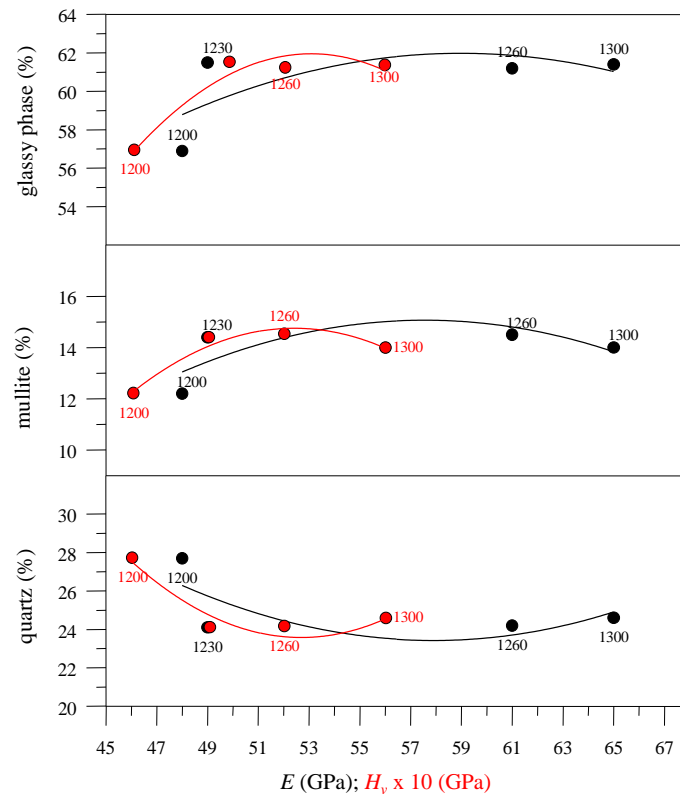


Fig. 7. Variation of Vickers microhardness and Young's modulus as a function of the contents of crystalline and glassy phases.

4. Conclusions

A mixture of 50% kaolinitic clay, 40% feldspar and 10% quartz was selected as a representative composition of commercial porcelain stoneware tiles produced via a fast firing process. After correlating different mechanical properties with several physical features and phase compositions, the following conclusions can be made:

1. Bending strength is not dependent on closed porosity, but is reliant on open porosity of the sample.
2. The results are consistent with the hypothesis of mullite, because higher mullite content results in greater bending strength and contradicts the prestressed theory because quartz particles have no influence on σ_f .
3. Bending strength is directly associated to the aspect ratio shown by secondary mullite needles. An increase in the aspect ratio of crystals was observed to increase the bending strength, which reaches maximum values when mullite needles join together and give rise to clusters.

4. Vickers microhardness and Young's modulus show behaviour similar to bending strength curves, which indicates that these properties are governed by the same factors.
5. Fracture toughness is independent of the firing temperature and, therefore, of the physical properties and microstructural features of the fired body.

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References

1. A. Zoellner, Some chemical and physical properties of porcelain, *Sprechsal*, 41 (1908), pp. 471–473
2. O.I. Ece, Z. Nakagawa, Bending strength in porcelains, *Ceram Int*, 28 (2002), pp. 131–140
3. G. Stathis, Effect of firing conditions, filler grain size and quartz content on bending strength and physical properties of sanitaryware porcelain, *J Eur Ceram Soc*, 24 (2004), pp. 2357–2366
4. S.L. Correia, A.P.N. Oliveira, D. Hotza, A.M. Segadães, Properties of triaxial porcelain bodies: interpretation of statistical modeling, *J Am Ceram Soc*, 89 (2006), pp. 3356–3365
5. A. De Noni Jr., D. Hotza, V. Cantavellas Soler, E. Sánchez Vilches, Influence of composition on mechanical behaviour of porcelain tile. Part II. Mechanical properties and microscopic residual stress, *Mater Sci Eng A*, 527 (2010), pp. 1736–1743
6. J.M. Amigó, J.V. Clausell, V. Esteve, J.M. Delgado, M.M. Reventós, L.E. Ochando, *et al.*, X-ray powder diffraction phase analysis and thermomechanical properties of silica and alumina porcelains, *J Eur Ceram Soc*, 24 (2004), pp. 75–81
7. L. Mattyasovszky-Zsolnay, Mechanical strength of porcelain, *J Am Ceram Soc*, 40 (1957), pp. 299–306
8. K. Hamano, Y.H. Wu, Z. Nakawaga, M. Hasegawa, Effect of grain size of quartz on mechanical strength of porcelain bodies, *J Ceram Soc Jpn*, 99 (1991), pp. 149–153
9. G. Stathis, A. Ekonomakou, C.J. Stournaras, C. Ftikos, Effect of firing conditions, filler grain size and quartz content on bending strength and physical properties of sanitaryware porcelain, *J Eur Ceram Soc*, 24 (2004), pp. 2357–2366
10. S.A.F. Batista, P.F. Messer, R.J. Hand, Fracture toughness of bone china and hard porcelain, *Br Ceram Trans*, 100 (2001), pp. 256–259
11. B.O. Aduda, F.W. Nyongesa, Role of aspect ratio in elastic modulus–porosity relationship of triaxial porcelain, *Br Ceram Trans*, 99 (2000), pp. 206–211
12. R. Pickup, Effect of porosity on Young's modulus of a porcelain, *Br Ceram Trans*, 96 (1997), pp. 96–98
13. C. Zanelli, M. Dondi, C. Guarini, M. Raimondo, I. Roncarati, Influence of strengthening components on industrial mixture of porcelain stoneware tiles, *Key Eng Mater*, 264–268 (2004), pp. 1491–1494
14. P.M.T. Cavalcante, M. Dondi, G. Ercolani, G. Guarini, C. Melandri, M. Raimondo, *et al.*, The influence of microstructure on the performance of white porcelain stoneware, *Ceram Int*, 30 (2004), pp. 953–963

15. M. Dondi, G. Ercolani, C. Melandri, C. Mingazzini, M. Marsigli, The chemical composition of porcelain stoneware tiles and its influence on microstructural and mechanical properties, *Interceram*, 48 (1999), pp. 75–83
16. L. Carbajal, F. Rubio-Marcos, M.A. Bengochea, J.F. Fernández, Properties related phase evolution in porcelain ceramics, *J Eur Ceram Soc*, 27 (2007), pp. 4065–4069
17. A.De Noni Jr., D. Hotza, V.E. Cantavella Soler, E. Sánchez Vilches, Effect of quartz particle size on the mechanical behaviour of porcelain tile subjected to different cooling rates, *J Eur Ceram Soc*, 29 (2009), pp. 1039–1046
18. M. Dondi, G. Guarini, C. Melandri, M. Raimondo, P.M.T. Cavalante, C. Zanelli, Resistance to deep abrasion of porcelain stoneware tiles: key factors, *Ind Ceram*, 25 (2005), pp. 71–78
19. C. Leonelli, F. Bondioli, P. Veronesi, M. Romagnoli, T. Manfredini, G.C. Pellacani, *et al.*, Enhancing the mechanical properties of porcelain stoneware tiles: a microstructural approach, *J Eur Ceram Soc*, 21 (2001), pp. 785–793
20. E. Sánchez, M.J. Orts, J. García-Tena, V. Cantavella, Porcelain tile composition effect on phase formation and end products, *Am Ceram Soc Bull*, 80 (2001), pp. 43–49
21. L. Esposito, A. Salem, A. Tucci, A. Gualtieri, S.H. Jazayeri, The use of nepheline–syenite in a body mix for porcelain stoneware tiles, *Ceram Int*, 31 (2005), pp. 233–240
22. J. Martín-Márquez, J.Ma. Rincón, M. Romero, Effect of firing temperature on sintering of porcelain stoneware tiles, *Ceram Int*, 34 (2008), pp. 1867–1873
23. J. Martín-Márquez, A.G. De la Torre, M.A.G. Aranda, J.Ma. Rincón, M. Romero, Evolution with temperature of crystalline and amorphous phases in porcelain stoneware, *J Am Ceram Soc*, 92 (2009), pp. 229–234
24. J. Martín-Márquez, J.Ma. Rincón, M. Romero, Mullite development on firing in porcelain stoneware bodies, *J Eur Ceram Soc*, 30 (2010), pp. 1599–1607
25. S. Maity, B.K. Sarkar, Development of high-strength whiteware bodies, *J Eur Ceram Soc*, 16 (1996), pp. 1083–1088
26. D.N. Boccaccini, A.R. Boccaccini, Dependence of ultrasonic velocity on porosity and pore shape in sintered materials, *J Nondestruct Eval*, 16 (1997), pp. 187–192