COMPARATIVE STUDY OF THE DETERMINING PARAMETERS OF THE CHEMICO-PHYSICAL AND MECHANICAL BEHAVIOUR OF DIFFERENT PORCELAIN TILES

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ABSTRACT

Porcelain tile chemical and mineralogical composition together with materials processing, thermal cycle in the kiln and final operations (lapping, polishing, etc.), are the key elements determining porcelain tile end quality, not just in relation to tile mechanical properties, but also to its absorption capacity and surface reactivity.

In this work, the relationships between surface porosity, microstructure, thermal cycle and mechanical properties (Knoop hardness, fracture toughness (K_{IC}) and abrasion resistance ratio, based on Hutchings' abrasion model) have been studied. Polished porcelain tiles from two major Spanish producers have been used in the study, which has allowed drawing several conclusions regarding the foregoing relationships. Surface porosity is shown to be a useful indicator of porcelain tile quality, when the composition, materials processing, thermal cycle and final operations are well known and controlled.

1. INTRODUCTION

In the striving to develop constructive solutions for floorings or facade claddings, which display excellent mechanical properties and an attractive aesthetic appearance, porcelain tile presents itself as one of the firmest candidate materials. Since its commercial appearance in the international market at the beginning of the 1980s, porcelain tile properties have improved substantially, with particular attention also being paid to the tile's appearance, which can now be found reproducing a multitude of finishes.

The general designation 'porcelain tile' encompasses a wide field of commercial ceramic tiles included in group BIa (Dry-pressed ceramic tiles with water absorption E<0.5%), governed by the ISO 13600 and UNE 67-087 standards. A very compact product is involved, with a fully vitrified mass, comprised of feldspars, white clays, quartz and kaolin (as major components), which are dry pressed, traditionally unglazed, and subjected to a single firing. The essential characteristics of porcelain tile products used for flooring and wall cladding are: extremely low porosity, which provides it with excellent mechanical and chemical properties and prevents significant water absorption, making it frost resistant, and thus very appropriate for use as flooring or exterior wall cladding in cold zones. It is also highly resistance to chemical agents and cleaning products and, in addition, has very good resistance to abrasive wear and erosion, making it suitable for heavily trafficked areas. A high-performance product is thus involved, with high added value, appropriate for wall cladding, floorings and mosaics.

The manufacturing companies have made porcelain tile a constantly evolving material, testing the incorporation of different additives into the base body to achieve different aesthetic effects (colouring oxides, whiteners, gloss modifiers, etc.).

Porcelain tile is, today, a key product in Spanish industrial ceramic production. Even though it is the most recent type of ceramic product to appear on the market, Spanish production, which began in 1988, has a full range of porcelain tile products, which increase as demand grows. The strategic importance of the product is obvious, as one of the internationally most widely recognised ceramic products, even though the situation of the international ceramic tile market has evidenced light stagnation in the last three years.

The efforts made by the sector to keep at head of global production, in regard to both the volume of materials made and product quality, have been notable. The last 15 years have witnessed significant investments in technological modernisation, which have enabled increasing productivity and reducing manufacturing costs. In this sense it may be noted that the dissemination of spray drying, dry pressing and single firing, as well as the use of kilns fuelled by natural gas, integrated jointly with the spray dryers in cogeneration systems which, at present, supply the ceramic tile sector with over 80% of all their electric consumption.

As the official publications of all the data for the year 2004 are not yet available, the most recently published definitive reports date from 2003[1] and[2]. According to these, the ceramic tile sector is made up of 294 companies, of which 221 are concentrated in the so-called ceramic cluster of Castellón (75.17% of the total number of companies in the sector), and which account for 94.5% of Spanish production. Castellón is followed by Valencia province, with 19 factories, Barcelona with 16, and Girona with 7.

The ceramic tile sector in Spain has consolidated itself as the second world producer (after China). Note that even though in respect to the year 2002 – when the maximum figures to date were reached in value and volume – a slight reduction in both magnitudes has taken place, the data clearly highlight the strategic importance of the Spanish floor and wall tile industry on the domestic stage – importance in national wealth – and in the international scenario, by its leadership position.

The principal weak points of this product are its price – somewhat higher than that of conventional stoneware tiles – and the loss of properties it evidences (both mechanically and in regard to stain resistance) in the polished product, with the appearance of surface pores as a result of the abrading operations performed on the natural product, which debilitate the tile[3,4]. The present study addresses the relation between porosity and mechanical behaviour, linking this, in turn, with the ceramic product processing stages (milling and firing). Finally the study demonstrates the validity of using porcelain tile surface porosity as a variable for controlling porcelain tile quality, when the other processing parameters used are known (particle size distribution after milling, composition of the raw materials and characteristics of the firing cycle), because this can be related to different mechanical properties (Knoop hardness, impact hardness, fracture toughness and abrasion resistance) of the polished porcelain tile.

2. MATERIALS AND METHODS

To conduct this study, samples of two different types of commercial polished porcelain tile were used, each type being supplied by a different, major tile manufacturer. The tile types were referenced A and B. Twelve test specimens were then cut from each tile type, about 30x30x8 mm in size.

After appropriately preparing these test specimens, a mesh grid of 2x2 mm was made in ink on the surface of the specimens, to facilitate subsequent inspection and the photographic surface mapping of the areas around the tested regions.

Six test specimens of each tile type were destined for microindentation testing, four specimens were for testing impact hardness by LDL, one was for a compositional study, and one was for microstructural analysis. Each test specimen of the microindentation groups underwent a total of 35 Vickers indents at 1 kgf and 8 Knoop indents at 100 gf, 200 gf, 300 gf and 500 gf (32 indentations in all), following the recommendations regarding the optimum extension of the measurement field for characterising ceramics by microindentation tests, set out by Jianghong Gong in[5]. We also performed 25 tests per test specimen of the subgroup for LDL testing. A database was then created containing the records of the 384 Knoop indentations, 420 Vickers indentations and 200 LDL hardness measurements. After conducting the mechanical characterisation tests, we performed the photographic mapping of the surface porosity of the squares in which the different tests were located with a JEOL Mode, JSM-6400 SEM at 7 kV and magnification of 500x, obtaining a total of 13,800 images.

We used a Matsuzawa Model MXT70 microdurometer, a Proceq Equotip LDL impact hardness rebound tester, and the compositional study of the families was conducted by X-ray fluorescence (XRF) and X-ray diffraction (XRD) with a Siemens D5000 diffractometer. For the microstructure analysis, the samples selected were attacked with a 10% hydrofluoric acid solution for 20 seconds, and using the SEM at 20 kV.

The images of surface porosity were processed with an artificial vision software programme specially developed by HIDECIT S.L.

Knoop hardness was calculated from the typical expression:

$$HK = \frac{14{,}229 * L}{d^2}; \quad L[Kgf]; \quad d[mm],$$

this also yielded, from the measurement of the Knoop indents, the value of the relation $\frac{E}{H}$ for the different types of porcelain tiles studied, using the formula proposed by Marshall, Noma and Evans[6]:

$$\frac{b}{a} = \frac{1}{7{,}11} - 0{,}45 \cdot \left(\frac{H}{E} \right)$$

whose validity has been widely confirmed for use in ceramics[7].

The Vickers microindentations originated a regime of low plastic saturation under the indenter, producing Palmqvist-type crack morphologies, according to[8], because the relation 'c/a' did not exceed the value 2.25 in any measurement. Under these working conditions, the most appropriate model for calculating the fracture toughness was shown to be that proposed by Evans and Davis[9]:

$$K_{IC} = 0.4636 \cdot \left(\frac{P}{a^{3/2}} \right) \left(\frac{E}{H_V} \right)^{0.4} \cdot 10^F$$

$$F = -1.59 - 0.34B - 2.02B^2 + 11.23B^3 - 24.97B^4 + 16.32B^5$$

$$B = \log\left(c/a \right)$$

$$c/a \geq\approx 2$$

The study of abrasion resistance was performed using the model proposed by Hutchings, whose validity for use in porcelain tile has been demonstrated by T. Cavalcante and others, in[3]. According to Hutchings[10], abrasion resistance can be determined from:

$$Q = k \left(\frac{W^{1.25} d^{0.5}}{A^{0.5} K_{IC}^{0.75} H_V^{0.5}} \right)$$

As we have used the coefficient of abrasion ratio (CAR) in our study, which has been redefined from the original model, in order to make this variable depend only on factors intrinsic to the material targeted for wear:

$$CAR = \frac{Q \cdot A^{0.5}}{W^{1.25} d^{0.5} k} = \frac{1}{K_{IC}^{0.75} H_V^{0.5}}$$

where:

- "k" is a coefficient of fit independent of the material
- "W" is the applied load,
- "A" is the area of apparent contact,
- "d" is the mean characteristic length of the abrasive particle,
- "K_{IC}" is the measured local fracture toughness, and
- "H_V" is the Vickers hardness calculated on the measurements of the track in a plastic saturation regime.

3. RESULTS AND DISCUSSION

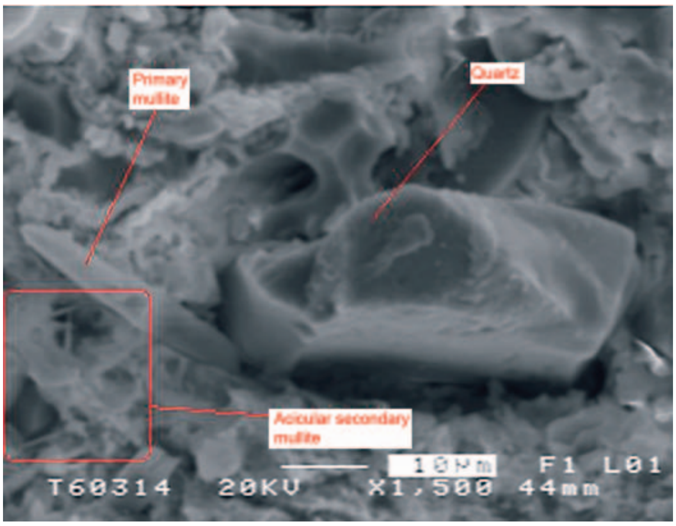
3.1. MINERALOGICAL AND MICROSTRUCTURAL ANALYSIS

The mineralogical study of the tested products (green and finished) was obtained from the fluorescence and diffraction results set out in Table 1. They show that the green formulation of the two types differed notably. Type A displayed a greater percentage of sodium feldspars (albite) than B; and B a greater amount of kaolin than A. As the firing cycles were the same, A would be expected to produce a more compact and vitrified product than B, but with a smaller amount of mullite. The mineralogical analysis of the finished product evidences that the hypothesis of equality in the firing cycles is incorrect; the porcelain tile of the B family had undergone a longer firing cycle, clearly evinced by the presence, together with primary mullite, of acicular formations of secondary mullite (Picture 1). In finished product A, the duration of the firing cycle has been insufficient for all the primitive albite to fuse and transform into glassy phase, and albite can clearly be identified in the microstructural analysis (Picture 2). The glassy phase of B, on the other hand, is more stable when exposed to acid attack than that of A; the SEM microstructural examination of the attacked test specimens shows the effects of the sintering and diffusion of quartz and mullite crystals in the glassy matrix (Picture 3).

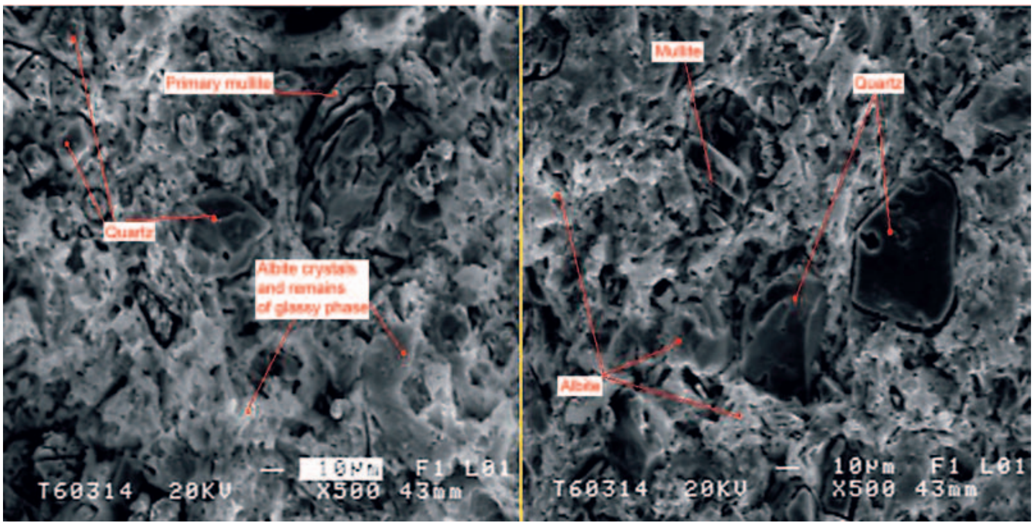
The microstructural analysis enabled drawing further interesting conclusions relating to the raw materials particle size. In this sense, the A family is characterised by displaying highly heterogeneous crystal sizes and shapes and large elements of quartz and primary mullite can frequently be identified (Picture 2). On the other hand, the B family exhibits a greater homogeneity in its microstructure; the identified crystals are smaller and more uniform (Picture 3). This analysis allows concluding that the raw materials milling process occurred more intensely in B than in A. This finding will subsequently allow us to understand better the results of the surface porosity analysis.

MINERALOGICAL COMPOSITION		
	A	B
RAW MATERIALS:		
Feldspars [%]	47.3	39.0
Clays [%]	30.5	37.2
Quartz [%]	18.2	20.5
Zircon [%]	4.0	3.3
FELDSPARS		
Albite [%]	43.8	30.7
Orthoclase [%]	3.5	8.4
Clays		
Kaolinite [%]	26.7	33.9
Illite [%]	3.8	3.3
CRYSTALLINE SPECIES IN THE FINISHED PRODUCT:		
Quartz [%]	64.0	78.5
Zircon [%]	18.0	12.0
Mullite [%]	7.0	9.5
Albite [%]	11.0	0
GLASSY PHASE	77.5	72.5

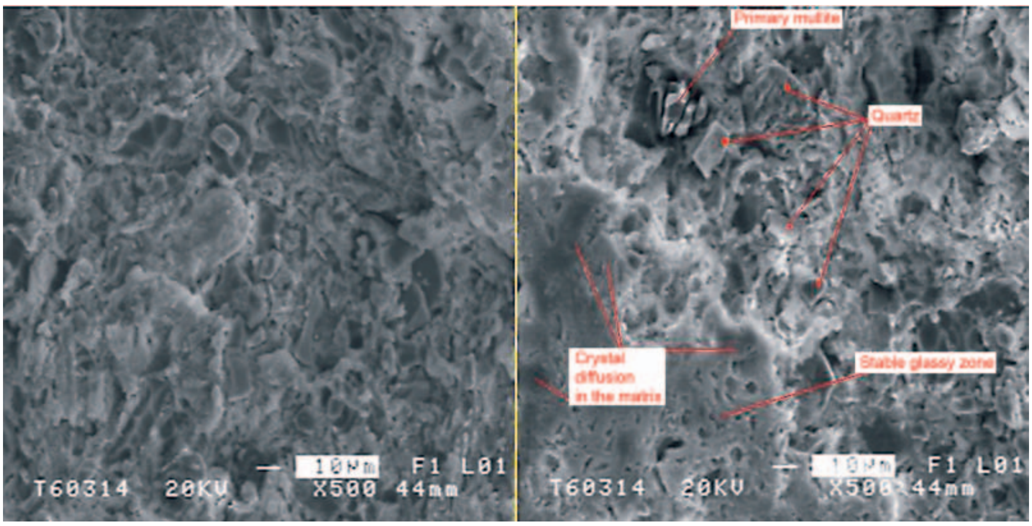
Table 1. Interpreted XRD and XRF results.



Picture 1. Secondary mullite formations in porcelain tile type B.



Picture 2. Typical microstructure of porcelain tile type A.



Picture 3. Typically homogeneous microstructure of porcelain tile type B and stable glassy phase.

3.2. MECHANICAL PROPERTIES.

The study of the different mechanical properties analysed and calculated according to the models and expressions set out in the previous section enables stating that the porcelain tile of the B family displays better mechanical properties than that of A. The mean values of Knoop hardness (HK), impact hardness (LDL), and fracture toughness (K_{IC}) are higher for B (Table 2), while the resistance to abrasive wear, established by means of the CAR, is lower.

PROPERTY	FAMILY	VALUE
Knoop hardness [GPa]	A	4.308±0.848
	B	4.695±0.782
LDL hardness [LDL scale]	A	967±4
	B	976±2
Fracture toughness [$MPa \cdot m^{0.5}$]	A	1.886±0.223
	B	2.197±0.175
CAR [$(GPa \cdot (N/m^{0.5})^{0.25})^{-1}$]	A	0.338±0.106
	B	0.283±0.044

Table 2. Mean values of the studied mechanical properties.

The values found lie within the working ranges reported by other authors who have studied different types of industrial porcelain tile[3][4], and confirm the hypotheses that were formulated in view of the compositional and microstructural study regarding the superiority of the B family, ratifying the critical importance of the firing cycle, together with the nature of the raw materials used and their proportions, in product end quality.

In addition, Table 2 allows drawing important conclusions from an analysis of the data scatter. Although, in the Knoop hardness properties, fracture toughness and abrasion resistance, the scatterings are relatively high, with values typically above 10%, in the case of LDL impact hardness these are below 0.5% in both A and B. This may be understood by observing the dimensional magnitude of the indents made by each of the different tests, and the microstructure examinations of both materials. In this sense, the porcelain tile appears, macroscopically, to be a basically homogeneous material (fundamentally in regard to its properties), which is confirmed by the results of the LDL impact hardness tests, whose scatter is much smaller than that in the other studied mechanical properties measurements (up to 120 times less). On a microscopic scale, confirmed by SEM observation of the samples, porcelain tile is a strongly heterogeneous material, which resembles a doubly reinforced ceramic composite, in which the vitrified glassy phase plays the role of the matrix and the quartz crystals and mullite are the reinforcements, sprinkled throughout the empty interstices formed by the pores and which, depending on the sintering degree and the firing cycle undergone by the material, will develop a positive or negative role in regard to the properties of the material involved, as the following sections will show. This heterogeneity on a microscopic level, in which the dimensions of the different effects can reach the order of magnitude of the indents themselves, produced by the various test microindenters, is responsible for the very high scatterings recorded in the measurements of the other properties, which, moreover, in the case of Knoop hardness, were even greater, as the indentations were made at different loads.

Porcelain tile type A displays typically higher values for these scatterings than type B, which even become 100% higher in the case of the CAR. The remarks made above regarding the detected microstructure and the grain types recorded in each family are consistent with these results, because porcelain tile type A is characterised by a high heterogeneity in crystal size and shape, unlike type B, and this morphology notably affects the dimension of the microindents.

This study phase, besides supplying the mechanical characterisation of both types of porcelain tiles, has enabled observing (when this was complemented with the inspection of the microstructure) that certain characteristic transition lengths between the macroscopic and the microscopic scale can be defined, beyond which the material ceases to behave as a mechanically homogeneous material and starts acting as a heterogeneous material, in terms of the porous model of the composite with double reinforcement and glassy matrix. These transition lengths have been fixed at 350 microns for A and 300 microns for `B.

3.3. STUDY OF SURFACE POROSITY

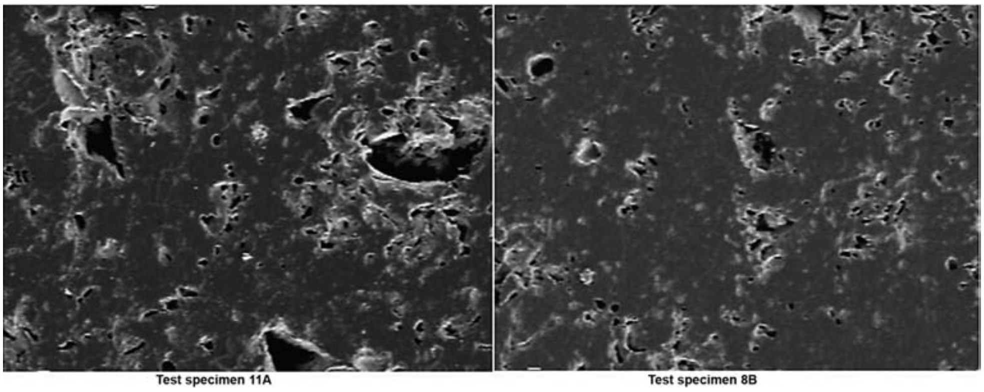
In the studies of surface porosity by quantitative microscopy techniques, two direct mode variables were recorded: the percentage of area occupied by pores (PorI) and the mean area of the pore characteristic of the studied surface, in μm^2 (PorII).

The results obtained in this study are summarised in the following table (Table 3).

PROPERTY	SUBFAMILY	VALUE
PorI [%]	A (LDL)	3.073±0.517
	A (V-K)	2.266±0.595
	B (LDL)	2.474±0.261
	B (V-K)	1.854±0.367
PorII [μm^2]	A (LDL)	10.740±1.314
	A (V-K)	9.574±1.918
	B (LDL)	5.383±0.421
	B (V-K)	4.917±0.758

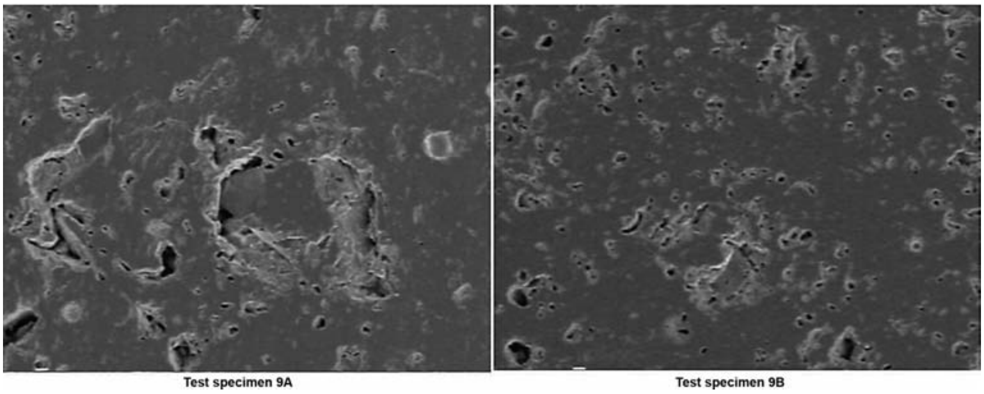
Table 3. Mean values of the surface porosities recorded.

The deviation, both in the values of the percentage area occupied by pores and the mean area of the characteristic pore, which can be observed among the LDL and V-K subfamilies of A and B, with slightly higher values for the LDL subfamilies, can be attributed to differences in the fitting standards of both subfamilies. However, the variations observed are within the ranges of each subfamily, and the fitting standards of the LDL subgroups were verified to be the same, as well as those of V-K (Pictures 5, 6); and since cross relations were not established at any moment between the two subfamilies of the same type of porcelain tile, these changes in reference did not disturb the study of the relation of properties–surface porosity in each subgroup.



Picture 4. Examples of photographs of the surface porosity of test specimens from the LDL subgroups of A and B.

The results set out in the foregoing table are quite explicit: family A displays higher values of porosity than B, both in regard to the percentage area occupied by pores and the mean area of the characteristic pore. Thus, the values of PorI in A are between 20 and 25% higher than those of B, while the values of PorII are about 100% higher. These results are perfectly consistent with the conclusions already drawn above for each type of porcelain tile from the analysis of microstructure and the firing cycle. The high heterogeneity in the grain size present in A originates empty interstices in the green product, which the glassy matrix that develops during vitrification fails to fill, because firing does not last long enough.

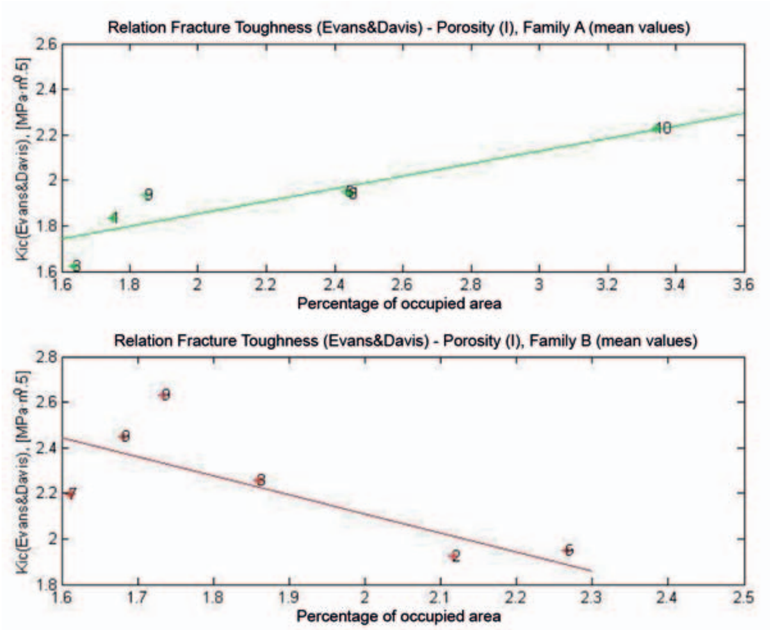


Picture 5. Examples of photographs of surface porosity of test specimens from the V-K subgroups of A and B.

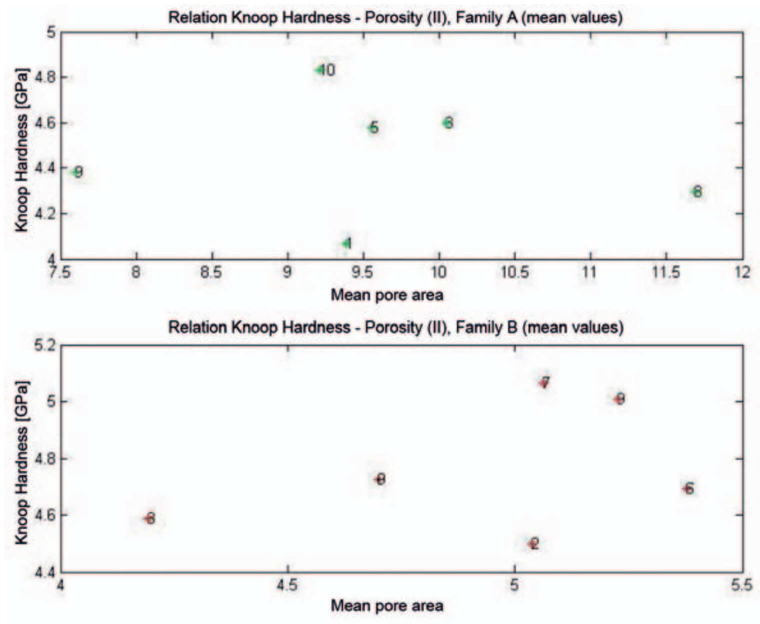
The identified types of surface porosity will condition the behaviour of the different studied types of porcelain tile in regard to staining. Family A, with larger, irregular and more numerous pores, will have a greater tendency to accumulate dirt and dust in the surface, making cleaning difficult and affecting how the floor tile looks after prolonged use.

3.4. RELATIONS OF MECHANICAL BEHAVIOUR–SURFACE POROSITY.

To carry out this study of the relation existing between both parameters, each of the different families and subfamilies was analysed separately and the mean values of the mechanical properties and surface porosities of each test specimen were used as items in the graph. The lines signalling the tendencies observed in the successive mechanical properties–porosity graphs were then analysed. This analysis yielded interesting results: it was observed that, in general, mechanical properties increased in family A (Knoop hardness, fracture toughness and abrasion resistance) as the value of the magnitude PorI of the test specimens of this family rose, whereas in B, the tendency was exactly the opposite one (Graph 1). The evolution of the same mechanical properties with respect to the magnitude PorII was similar in both families, and no type of easily identifiable influence could be appreciated between both parameters in any of the cases (Graph 2).



Graph 1. Examples of the relation mechanical behaviour–PorI



Graph 2. Examples of the relation mechanical behaviour–PorII

The explanation for the different dynamics exhibited by A and B, which might seem contradictory, a priori, lies in the role played by the pores during the firing process of the product. During the first stages of the firing cycle, the pores of the green ceramic piece favour product vitrification, because such voids act as propitious zones for the incipient glassy matrix originating from feldspar fusion to flow into and flood the other crystals in the ceramic piece. When the firing process lasts sufficiently long for the vitrification to become massive, the occluded pores in the material are transformed into pockets of gas under high pressure, which try to escape from the matrix; the pores that cannot migrate to the surface become overtensioned zones, as a result of the effect of the gases trapped inside the pore volume; and these, when the material is cooled, generate residual stresses that end up debilitating the material, particularly when the product is polished; it is this type of pore that then remains cut in the surface. Based on the forgoing, the causes of the different tendencies shown by A and B may be inferred. As the compositional study of the finished product of family A indicated when the significant presence of crystalline albite was detected, the firing cycle of this material lasted less time than suitable for that material, leaving this porcelain tile, from the point of view of porosity, in a state in which the pores have favoured the vitrification and sintering of the product. Porcelain tile B, on the other hand, has undergone a more prolonged firing cycle, as indicated by the detection of secondary mullite formations in the examination of its microstructure; for this reason, in these conditions, the effects of the recorded porosity on the mechanical properties of B have been the opposite to those observed in A.

4. CONCLUSIONS

The present study shows that porcelain tile family A displays a greater number of pores and a larger mean pore size, as well as a much more heterogeneous microstructure that the analogous features of porcelain tile family B, as a result of which A has a greater capacity for permanent soiling and poorer mechanical properties. It has furthermore been found that the raw materials milling process in B lasted until obtaining a smaller mean particle size than in A, and that the firing cycle of B has been more prolonged than that of A.

The analysis of the microstructure and the scatter in the mechanical behaviour measurements have led to the definition of characteristic transition lengths between the macroscopic and the microscopic operation scale of the material, dimensions that are determined by the microstructure of each material and are obviously related to tile formulation and processing; these were fixed at 350 microns for A and 300 microns for B.

The study of the relations between surface porosity and mechanical behaviour of both families has shown the different tendencies displayed by each family. Whereas in porcelain tile A the higher values of PorI were found to correspond to higher values of Knoop hardness, fracture toughness and abrasion resistance, in porcelain tile type B, the higher values of PorI corresponded to worse mechanical properties, both opposing tendencies being explained by the different role of the pores in the firing cycle of the ceramic pieces.

Surface porosity is shown to be a useful parameter for establishing and controlling porcelain tile properties when the different variables involved in product processing are known, and enables integrating artificial vision systems in the last stages of the porcelain tile production process, in porcelain tile quality control and dimensional metrology, as well as providing continuous feedback on the production process in order to optimise this.

5. ACKNOWLEDGEMENTS

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