Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 31 (2011) 665–671

www.elsevier.com/locate/jeurceramsoc

Dependence of surface porosity on the polishing depth of porcelain stoneware tiles

H.J. Alves *, M.R. Freitas, F.G. Melchiades, A.O. Boschi

Laboratório de Revestimentos Cerâmicos (LaRC), Departamento de Engenharia de Materiais (DEMa), Universidade Federal de São Carlos (UFSCar), Rod. Washington Luiz, Km. 235, 13574-970, São Carlos, SP, Brazil

Received 9 April 2010; received in revised form 15 November 2010; accepted 28 November 2010
Available online 19 December 2010

Abstract

Porcelain stoneware tile polishing is a process that adds value to ceramic tiles due to the high gloss achieved upon reducing surface roughness. However, surface polishing removes a fine layer of the product, revealing numerous "closed" pores initially located inside the material, which may compromise some of its properties such as stain resistance. The literature indicates a possible orientation of pores on surfaces parallel to that of the use of the product. Based on this hypothesis, the present work aimed to evaluate how the thickness of the layer removed by polishing acts upon the profile of exposed surface pores, and hence, on the stain resistance of the product. The results of this study are novel and reveal that the staining tendency of porcelain stoneware tile can be altered significantly by varying the conditions of the surface wear produced by polishing.

Keywords: Porcelain; Porosity; Finishing; Microstructure-final; Stain resistance

1. Introduction

Sintered products are polished in order to reduce their surface roughness and increase their gloss, giving them esthetic characteristics that are highly valued by the consumer. The polishing process consists of using a machine equipped with several high-speed buffer heads composed of abrasive materials that polish the product under controlled speed and in the presence of water.[1,2]

During polishing it is inevitable that the volume of pores that remain on the surface of the finished product will increase. The removal of a fine surface layer, which normally varies from 0.5 to 1.5 mm depending of the tile's characteristics (specially curvature and decoration process), reveals a new surface composed of numerous open pores that were previously "closed" inside the material. These pores appear distributed throughout the surface of the product, and are visible under low magnification microscopy.[3–5]

Some of the variables of the polishing process may alter the characteristics of the final surface of the product, affecting its technical and esthetic performance. Recent studies based on the speed and rate of polishing machines have revealed that the oscillations of the transversal and lateral movements of the buffer heads used in the kinematics of the industrial polishing process modify the area of the product's effectively polished surface and its gloss.[6,7]

Experiments conducted by ARANTES[8] indicated that the pores in porcelain stoneware tile can be oriented in the pressing stage, showing a porosity gradient along the cross section of the product. This information is not supported by other investigations, but if those findings can occur under determined conditions, it can be concluded that another important variable to be considered is the thickness of the surface layer removed by polishing. In this case, variations in the thickness of the removed layer could modify the profile of the pores revealed at the surface, since the volume, size and morphology of pores would differ in each wear situation evaluated. Hence, the product's stain resistance should also undergo changes, for this property is intrinsically dependent on the characteristics of the surface pores.[9–13]

The literature offers diverging opinions about the characteristics of pores responsible for staining. Some authors believe that staining is related to the presence of pores with diameters of 15–60 μm.[13] Other authors are of the opinion that only pores

* Corresponding author. Tel.: +55 16 33617980; fax: +55 16 33615404.
E-mail address: helquimica@yahoo.com.br (H.J. Alves).

0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.11.028

with diameters of less than 10 μm do not contribute to staining.[10] However, the results of some works indicates that the staining is dependent on the diameter of pores on the polished surface of the products, and that to minimize this phenomenon requires the elimination of pores with diameters of 5–20 μm.[9,12,14] In fact, the presence of large pores (>30 μm) facilitates the removal of staining agents by the cleaning processes. In contrast, in the case of very small pores (<5 μm), the penetration of the staining agent is hindered.[10]

The purpose of the present work was to ascertain if the thickness of the layer removed by polishing can modify the superficial porous microstructure and stain resistance of the final surface of porcelain stoneware tile. This study is also expected to contribute to the literature on the theme.[1–14]

2. Materials and methods

A type of commercial polished porcelain stoneware tile called STD was selected as the object of this study. STD is white and is known to be vulnerable to staining.

2.1. Physical characterization of porosity

Test specimens were removed from commercial polished STD tiles by precision cutting with a diamond disc cutter. The test specimens were then subjected to ultrasonic cleaning for 20 min and dried at 110 °C for 24 h. After this preparation, the following values were determined:

- water absorption (AA) by the boiling water method for 2 h, according to the ISO 10545-3 standard[15];
- apparent porosity (ε_A) determined by the Archimedes principle;
- total porosity (ε) and closed porosity (ε_F), determined by the following equations:

$$\varepsilon = 1 - \left(\frac{\rho_C}{\rho_R}\right) \quad (1)$$

$$\varepsilon_F = \varepsilon - \varepsilon_A \quad (2)$$

where ρ_C is the apparent density and ρ_R corresponds to the absolute density (determined by helium pycnometry-Quantachrome Ultrapycnometer 1000). Ten test specimens of the STD sample were used for the porosity tests.

2.2. Characterization of surface and cross-section porosity

Test specimens from each evaluated section (surface and cross section) were removed from randomly selected regions of the unpolished tiles. The test specimens were then sanded and polished to expose the closed pores of the material, using an automatic system with water, composed of a rotary disc and a series of five sanding and polishing pads.[16] On the surface, the polishing was performed to obtain three distinct wear situations: remove a surface layer of 0.5 mm, 1.0 mm and 1.5 mm.

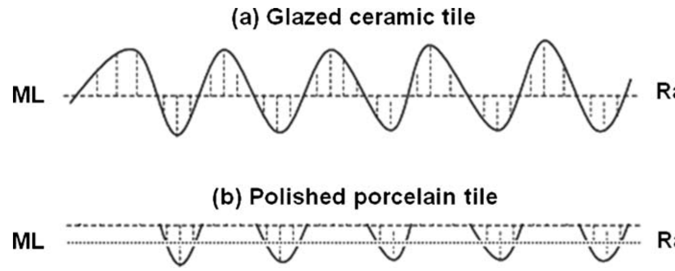

Fig. 1. Mean surface roughness parameter (Ra) of: (a) glazed ceramic tile and (b) polished porcelain stoneware tile.

The porous microstructure of the test specimens was examined in digital images (micrographs) obtained by scanning electron microscopy (SEM, Leo Stereoscan 440).

The digital images were analyzed using Image-Pro 4.5 software, enabling the percentage corresponding to the area covered by pores to be determined in relation to the total area of the images analyzed, as well as their diameter distribution and morphological aspects (aspect ratio).

2.2.1. Analysis of porosity by mechanical profilometry

The mechanical profilometry technique was employed to measure the surface roughness (Ra) and indirectly evaluate the product's pore profile, in view of its magnitude.[17] Mean roughness (Ra), which is the parameter most widely used as an indicator of the roughness of a surface, can be calculated from the arithmetic mean of the absolute values of the heights of the points that make up the profile in relation to the median line (ML), as illustrated in Fig. 1a. The equipment (Perthometer S8P 4.51) has a conical probe with a fine tip with angle of 40° and 2 μm radius.

In the analysis of a glazed ceramic tile, both the peaks and the valleys contribute to the calculation of Ra (Fig. 1a). However, considering that the samples under study are polished, only the valleys determine the Ra value (Fig. 1b). In this work, the valleys were associated with the pores of the polished surface.

In this study, the surface test specimens that were subjected to progressive surface wear were tested in sample lengths of 10 mm, at a probe rate of 1 mm/s. Five measurements were taken of each test specimen.

2.3. Evaluation of stain resistance

The surface test specimens that underwent progressive wear were subjected to the stain resistance test prescribed by the ISO 10545-14 standard.[18] The staining agents used here were chrome green (oily solution containing 40 wt% of Cr_2O_3 – as recommended by the standard) and earth (aqueous solution containing 50 wt% of red earth – simulating conditions found in everyday situations).

The intensity of the stains was evaluated from the difference in color ΔE^*, of the surface prior to staining and after the cleaning steps applied on the region where the staining agents had been applied.[19] The values of ΔE^* were determined by diffuse reflectance spectrophotometry (Konica Minolta CM–2600d), using a standard 10° colorimetric observer and a standard

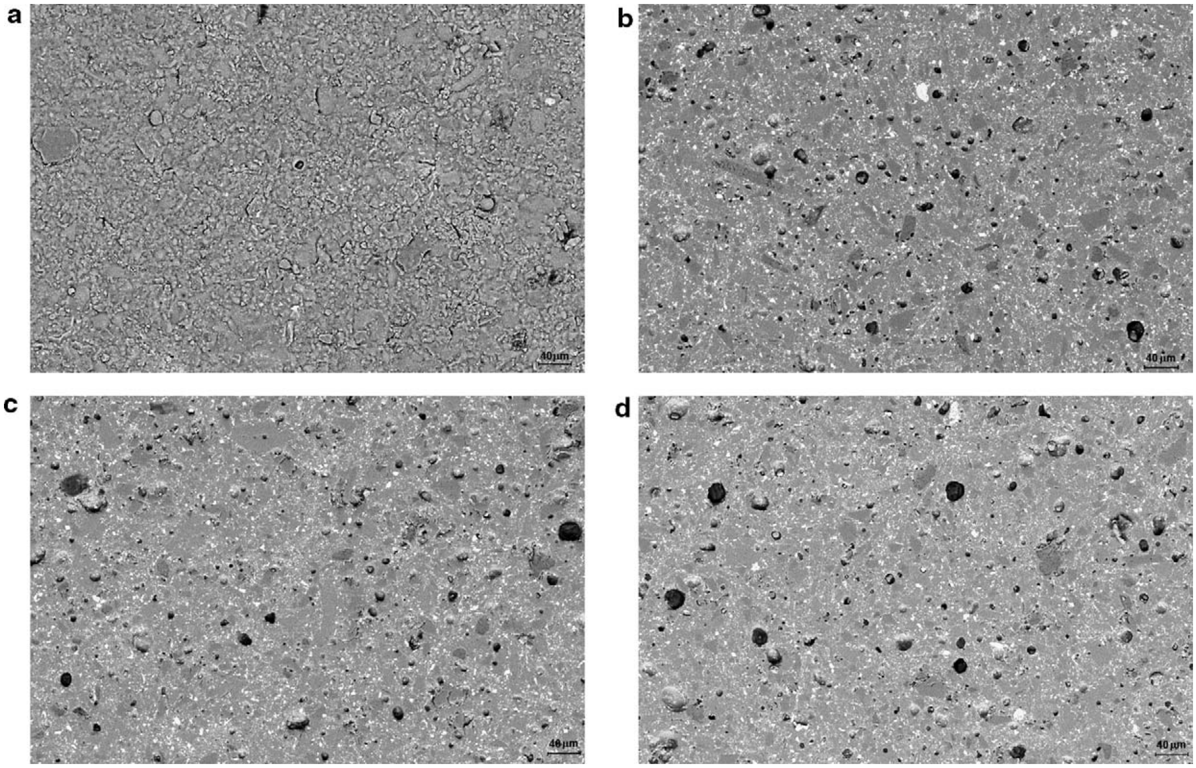

Fig. 2. SEM micrographs of the STD surface: (a) original unpolished surface, (b) wear of 0.5 mm, (c) wear of 1.0 mm, and (d) wear of 1.5 mm.

D65 light source (equivalent to daylight). The higher the value of ΔE^* the more intense the stain observed on the surface.

Determination of stain intensity by spectrophotometry has proved very efficient in the evaluation of the staining tendency of ceramic tiles, according to recent works.[4,19,20]

3. Results and discussion

Table 1 lists the results of the physical characterization of porosity of STD. Note that although the values of AA and ε_A are low, closed porosity ε_F is high, which may impair some of the properties of the polished product.

3.1. Progressive surface wear

The results indicated changes in the porous microstructure of STD in response to variations in the thickness of the layer removed by polishing.

Fig. 2 shows micrographs of the STD surfaces before and after polishing in the laboratory ((a) no polishing; (b) 0.5 mm layer removed; (c) 1.0 mm layer removed; and (d) 1.5 mm layer removed). A comparison of the micrograph in Fig. 2a and the other micrographs in Fig. 2 reveals the opening of the closed pores caused by polishing.

The analysis of the images revealed that the area occupied by the pores did not vary significantly with the increasing thickness of the layer removed by polishing, as indicated by the data in Table 2. However, as the wear advanced into the sample, there was a decrease in the occurrence of pores with critical stain diameters, i.e., between 5 and 20 μm (Fig. 3).[9,12,14] The tendency for spherical shapes also increased with progressive polishing, as indicated in the graph in Fig. 4.

It is important to note that the software Image-Pro 4.5 accurately determines the number total of pores that the image has, but when the pores have diameter below 5 μm the determination of the characteristics such as mean diameter, aspect ratio and area, becomes limited because the accurate definition of the pore is not good. This way, the graphics of the distribution of pore sizes (Fig. 3) and distribution of the aspect ratio (Fig. 4) cannot represent the pores smaller than 5 μm. However, since the total number of pores of the images is accurately determined, it is possible to quantify the percentage of pores with diameters less than 5 μm. As the particles of staining agents have difficulty to penetrate in the pores with diameters smaller than 5 μm, as

Table 1
Characterization of the porosity of STD test specimens.

Sample	*WA* (%)	ε_A (%)	ε_F (%)	ε^a (%)
STD	0.03 ± 0.02	0.08 ± 0.05	10.60 ± 0.08	10.68 ± 0.19

[a] The value of ρ_R obtained for the calculation of ε was 2.750 g/cm^3.

Table 2
Area of surface pores.

Area of coverage of surface pores/total area of the image (%)		
Wear of 0.5 mm	Wear of 1.0 mm	Wear of 1.5 mm
3.3 ± 0.2	3.3 ± 0.2	3.7 ± 0.3

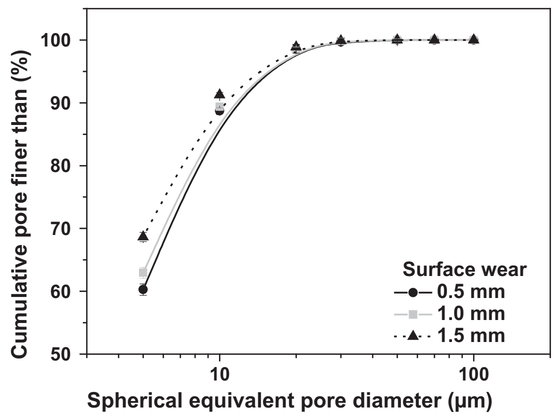

Fig. 3. Distribution of surface pore diameters of STD after progressive wear.

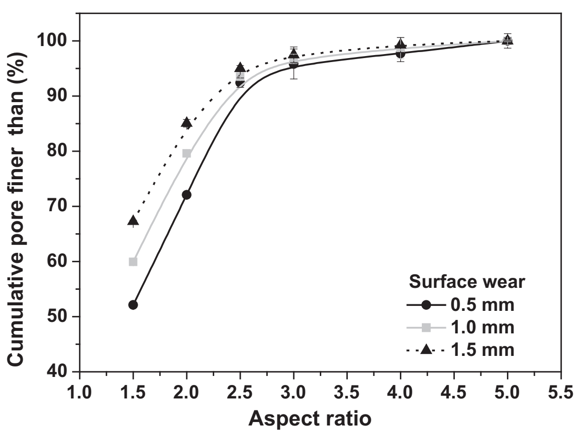

Fig. 4. Aspect ratio distribution of STD surface pores after progressive wear.

discussed in item 1, the inability to evaluate the characteristics of these types of pores does not compromise the results obtained by image analysis.

The data presented in Table 2 indicate that the percentage related to the area of pores of the images analyzed (3–4%) is much lower than the percentage of pores determined by density measurements (about 10%), according to the values in Table 1. This can be explained by the fact that 6–7% of total porosity of the product have a diameter less than 5 μm, and therefore were not determined by image analysis.

3.2. Analysis of the cross section

Fig. 5 shows some micrographs of the cross section: (a) corresponding to the region closest to the original surface of the unpolished product (<0.5 mm); (b) the region below (a) (0.5–1.0 mm); and (c) the region farthest from the original surface, immediately below (c) (1.0–1.5 mm). Figs. 6 and 7 show the results, which represent the mean obtained from the analysis of 16 images of each region, taken from different test specimens.

An analysis of Fig. 6 indicates increasing pore size in the cross section as the distance from the original surface of unpolished product increases. This increase in pore size apparently is accompanied by an increment in the area occupied by the pores in the direction of the center of the tests specimens (Table 3). It is important to note that the figures presented in Table 3 correspond to the sum of the area of pores with diameters larger than 5 μm.

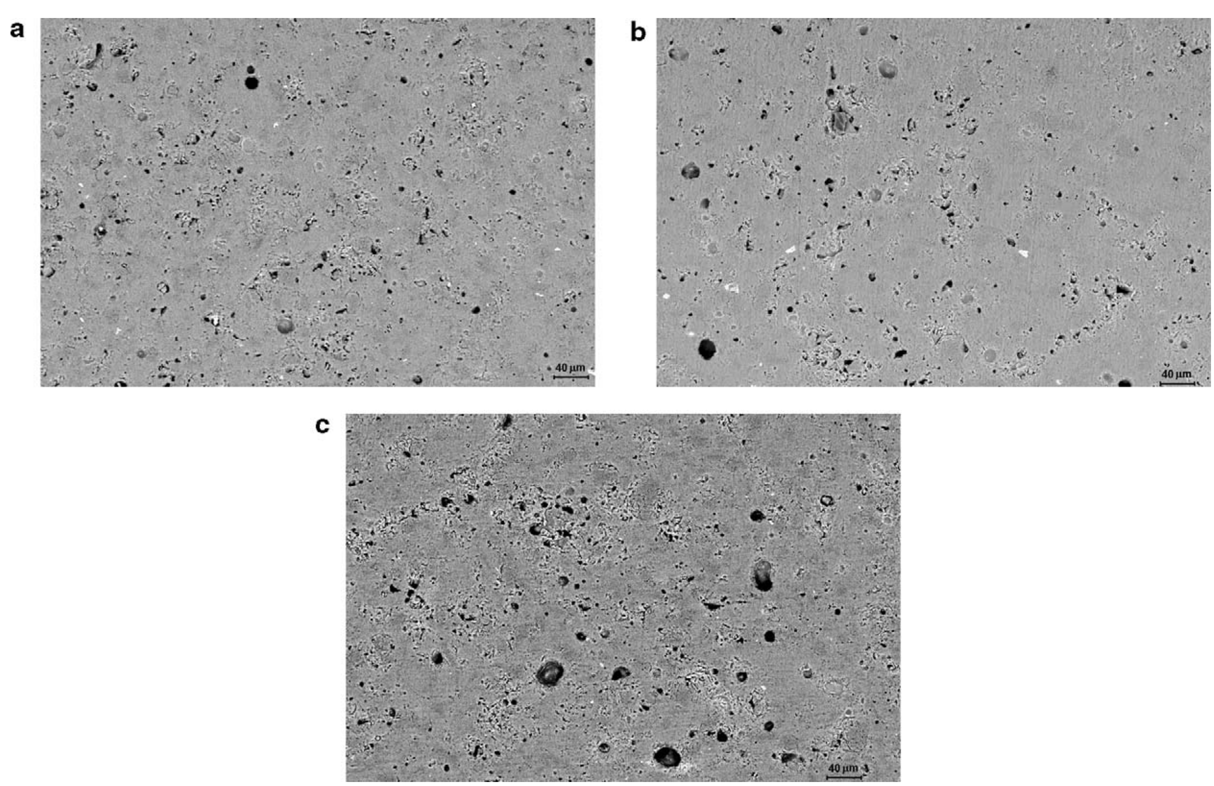

Fig. 5. SEM micrographs of the cross section of STD: (a) region close to the original surface of the unpolished sample (<0.5 mm), (b) intermediary region (0.5–1.0 mm), and (c) internal region of the product, immediately below (b) (1.0–1.5 mm).

Table 3
Area corresponding to the pores in the cross section.

Area of coverage of the pores in the cross section/total area of the image (%)		
Region close to the original surface (<0.5 mm)	Intermediary region (0.5–1.0 mm)	Region most distant from the original surface (1.0–1.5 mm)
2.9 ± 0.2	3.3 ± 0.2	4.3 ± 0.2

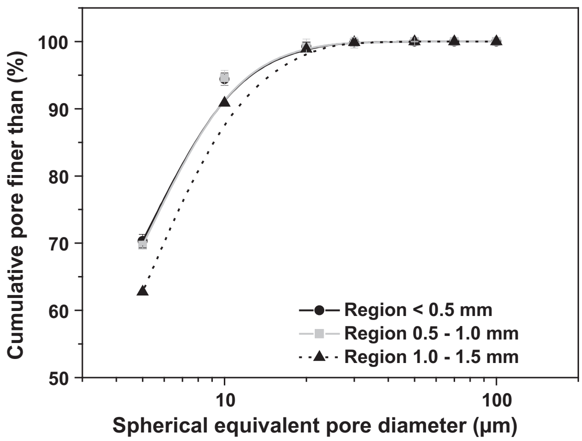

Fig. 6. Pore diameter distribution in the cross section of STD.

In other words, as one advances from the surface into the interior of the ceramic body, the area occupied by the pores may increase by up to 70%, indicating the existence of a kind of "porosity gradient" along the cross section. These data were obtained by image analysis, where errors can be high. However, in this case, the differences are sufficiently high to allow these conclusions. Another important factor is that the area of pores in regions immediately below the polished surface (cross section-region < 0.5 mm) is approximately 25% smaller than the area of pores on the polished surfaces, as can be seen from the data in Tables 3 and 2, respectively.

There is also an increasing tendency for spherical shapes as the distance from the surface increases, with a higher concentration of elongated pores in regions close to the surface (Fig. 7).

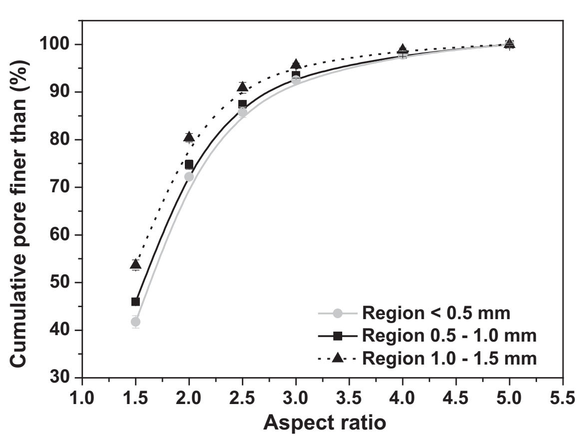

Fig. 7. Distribution of the values of the aspect ratio of pores in the cross section of STD.

The difference between the values of the areas occupied by surface pores and cross section pores, as well as the morphological variations observed, may be related to the orientation (more elongated and flattened) of the pores during the compacting stage.[8,13,20] In this case, pressing of the atomized powder places greater strain on the surface pores, thus subjecting them to greater distortion since they are closest to the areas under mechanical loading. This leads to a buffer effect of the compaction pressure, which cannot so effectively reach the center of the body where the pore shape and size remain closer to what they were when the mold was filled. This explains why the analysis of both the surface (item 3.1) and the cross section indicated that the pores most distant from surface of the product displayed a higher tendency for sphericity. The orientation of the pores also explains their size variation along the ceramic body, since the results indicated that the most oriented pores (close to the surface) presented larger diameters when observed at the surface (Fig. 3) and smaller diameters when observed in the cross section (Fig. 6).

3.3. Determination of pore profiles based on surface roughness measurements

Table 4 lists the values of Ra obtained under the different wear conditions evaluated here. Based on the results found in the analysis, the diameter distribution of surface pores was also determined, as shown in Fig. 8.

The results indicated that an increase in the thickness of the layer removed by polishing (progressive wear) is accompanied by an increase in Ra and a decrease in mean pore diameter. This means that the closer to the original surface of the sample (unpolished) the lower the mean pore depth (lower Ra) and the higher the mean pore diameter, i.e., greater pore orientation. As one advances toward the center of the body, the mean pore depth and diameter decrease, since there is less pore orientation.

Ra is a measure of deviation from the median line (ML) in the vertical direction. Therefore, it has more relation with the displacement of the conical tip down or up through the surface of the product than the number of pores examined. As in polished porcelain the movement is never up, we can say that the

Table 4
Mean roughness (Ra) of the surfaces of STD obtained with different wear conditions.

Surface wear	Ra	Number of pores measured
0.5 mm	0.246 ± 0.004	43 ± 2
1.0 mm	0.286 ± 0.003	42 ± 3
1.5 mm	0.375 ± 0.007	43 ± 2

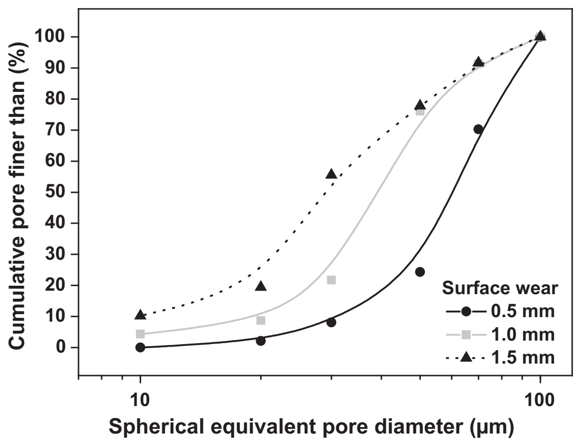

Fig. 8. Pore diameter distribution determined by mechanical profilometry.

increase of Ra is related to increased depth of the pores. Moreover, the number of pores measured in the sections evaluated is similar (inserted column in Table 4), not being a variable to be considered in this case.

These results are consistent with those described in Sections 3.1 and 3.2, and indicate that the image analysis and mechanical profilometry techniques can be used jointly to characterize the porosity of polished ceramic tiles, although the minimum pore size detectable by the techniques is equal to 5 μm and 10 μm, respectively.

3.4. Staining tendency

As can be seen in Fig. 9, the intensity of the stain decreased (decrease of the value of ΔE^*) as the thickness of the layer removed by polishing increased, since there was a significant reduction in the percentage of pores with critical staining diameters, i.e., between 5 and 20 μm.

The results indicated that the thickness of the layer removed by polishing can alter the intensity of the stains visible on the surface. In the case of the analyzed product, the removal of a 1.5 mm layer from the surface by polishing contributed more to reduce the intensity of stains than the removal of 0.5 mm. The variations in stain intensity, in turn, are explained by the distinct distributions of pore diameters and of aspect ratios presented by the different surfaces generated after each wear stage applied. In this case, the situation in which the area of pores remains practically unchanged with progressive surface wear may indicate a kind of pore orientation possibly caused by gradients in the deformation of the atomized granules generated during the compaction of the powder.

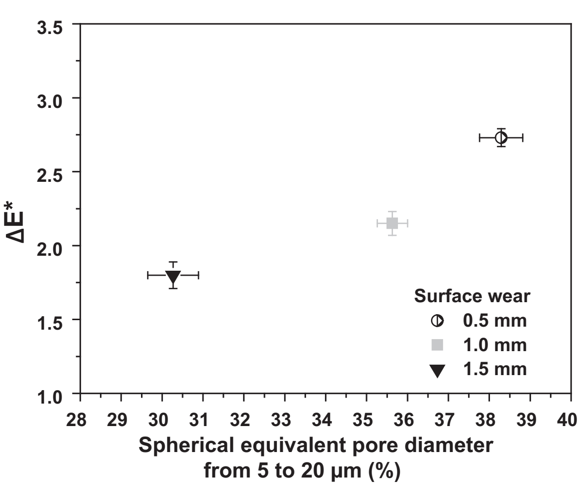

Fig. 9. Variation in stain intensity according to the percentage of pores with critical staining diameters, generated under distinct conditions of surface wear.

4. Conclusions

The following conclusions can be drawn based on the results of this study:

- The thickness of the layer removed by polishing may affect the intensity of the stains observed on the surface of porcelain stoneware tile, since pore size distribution and morphology change from the surface toward the center of the ceramic body. The best condition was one in which there was a removal of a layer of 1.5 mm from the surface by polishing.
- As for the characterization of porosity in the cross section of the samples, the results underpin the following assumptions:
  - The pores closest to the surface of the product undergo orientation (more elongated and flattened), probably caused during the compaction stage. In this case, the lower the thickness of the layer removed by polishing the higher the intensity of visible stains, since this type of porosity more oriented contributes to increase the tendency for staining.
  - There are differences in the characteristics of pores along the thickness of the material, which confirms the pore orientation caused in the compaction stage. In the cross section examined by SEM, the pores in the region closest to the center of the ceramic body occupy a larger area than in the regions closer to the original surface of the unpolished product. This is explained by the gradual decrease in pore orientation from the surface toward the center.

References

1. Bittencourt EL, Benincá E. Aspectos superficiais do produto grês polido. *Cerâmica Industrial, São Paulo, Brasil* 2002;**7**(4):40–6.
2. Wiggers WS, Santos RA, Hotza D. Evolução da superfície do porcelanato ao longo do processo de polimento. *Cerâmica Industrial, São Paulo, Brasil* 2007;**12**(1–2):27–30.
3. Hutchings IM, Xu Y, Sánchez E, Ibáñez MJ, Quereda MF. Porcelain tile microstructure: implications for polishability. *Journal of the European Ceramic Society* 2006;**26**:1035–42.
4. Sánchez E, Ibáñez MJ, García-Ten J, Quereda MF, Hutchings IM, Xu YM. Porcelain tile microstructure: implications for polished tile properties. *Journal of the European Ceramic Society* 2006;**26**:2533–40.
5. Jazayeri SH, Salem A, Timellini G, Rastelli E. A kinetic study on the development of porosity in porcelain stoneware tile sintering. *Boletin de la Sociedad Española de Cerámica y Vidrio* 2007;**46**(1):1–6.
6. Souza FJP, Aurich JC, Weingaertner WL, Alarcon OE. Kinematics of a single abrasive particle during the industrial polishing process of porcelain stoneware tile. *Journal of the European Ceramic Society* 2007;**27**:3183–90.
7. Souza FJP, Aurich JC, Weingaertner WL, Alarcon OE. Analytical determination of the distribution of polishing time over the surface of polished tiles. *Journal of the American Ceramic Society* 2007;**90**(11):3468–77.

8. Arantes FJS, Galesi DF, Quinteiro E, Boschi AO. O manchamento e a porosidade fechada de grês porcelanato. *Cerâmica Industrial, São Paulo, Brasil* 2001;**6**(3):18–25.
9. Alves HJ, Minussi FB, Melchiades FG, Boschi AO. Porosidade susceptível ao manchamento em porcelanato polido. *Cerâmica Industrial, São Paulo, Brasil* 2009;**14**(1):21–6.
10. Dondi M, Raimondo M, Zanelli C. Stain resistance of ceramic tiles. *Ceramic World Review* 2008;**77**:82–9.
11. Cavalcante PMT, Dondi M, Ercolani G, Guarini G, Melandri C, Raimondo M, et al. The influence of microstructure on the performance of white porcelain stoneware. *Ceramics International* 2004;**30**:953–63.
12. Suvaci E, Tamsu N. The role of viscosity on microstructure development and stain resistance in porcelain stoneware tiles. *Journal of the European Ceramic Society*, in press.
13. Beltrán V, Ferrer C, Bagán V, Sánchez E, Garcia J, Mestre S. Influence of pressing powder characteristics and firing temperature on the porous microestructure and stain resistance of porcelain tile. In: *Proceedings of the IV World Congress on Ceramic Tile Quality*. 1996. p. 133–48.
14. Rastelli E, Tucci A, Esposito L, Selli S. Stain resistance of porcelain stoneware tile: mechanisms of penetration of staining agents and quantitative evaluation. *Ceramic Acta* 2002;**14**(1):30–7.
15. International Standard ISO 10545-3, Ceramic Tile—Part 3: determination of water absorption, apparent porosity, apparent relative density and bulk density, 1997.
16. Hutchings IM, Adachi K, Xu Y, Sánchez E, Ibáñez MJ, Quereda MF. Analysis and laboratory simulation of an industrial polishing process for porcelain ceramic tiles. *Journal of the European Ceramic Society* 2005;**25**: 3151–6.
17. Parra BS, Gennari RC, Melchiades FG, Boschi AO. Rugosidade superficial de revestimentos cerâmicos. *Cerâmica Industrial, São Paulo, Brasil* 2006;**11**(2):15–8.
18. International Standard ISO 10545-14, Ceramic Tiles—Part 14: determination of resistance to stains, 1997.
19. Dondi M, Ercolani G, Guarini G, Melandri C, Raimondo M, Rocha e Almendra E, et al. The role of surface microstructure on the resistance to stains of porcelain stoneware tiles. *Journal of the European Ceramic Society* 2005;**25**:357–65.
20. Alves HJ, Melchiades FG, Boschi AO. Effect of spray-dried powder granulometry on the porous microstructure of polished porcelain tile. *Journal of the European Ceramic Society* 2010;**30**:1259–65.