DEEP ABRASION RESISTANCE OF PORCELAIN STONEWARE TILES

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ABSTRACT

In this study, the resistance of porcelain stoneware tiles to deep abrasion was investigated. Chemical, physical and microstructural analyses were accomplished in order to determine the relationship between the abrasion resistance and technical characteristics of commercially available tiles. The specimens were characterized by Vickers Microhardness (VHN), X-ray Diffraction (XRD), Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM). The statistical nature in measurements of technical features for porcelain tiles made it difficult to determine well a correlation between abrasion resistance and other physical/chemical characteristics. It seems that by increasing the mean pore size, the abrasion resistance decreases. XRD analysis revealed that the abrasion resistances of the samples in which the amorphous phase was dominant, were greater than of those with lower glassy phase content or a higher amount of non-melted Na-feldspar. It seems that the glassy phase relieves residual stresses during firing and enhances interfacial cohesion between quartz particles and amorphous matrix, reducing material removal during abrasion.

1. INTRODUCTION

Porcelain stoneware tiles are well-known technical ceramics which are extensively used for wall cladding and/or outdoor flooring. Their outstanding properties, such as frost, thermal and abrasion resistance along with low porosity and aesthetic appearance, distinguish them from traditional and porous tiles. They are generally categorized into the two groups, glazed and unglazed porcelain [1,2]. The stringent standards should be considered for porcelains, because they have been designed for use in harsh environments such as high traffic areas and bad weather conditions. Furthermore, the worldwide annual turnover of tile production, which is worth noting (~ 80,000 million € in 2008), encourages the ceramic technicians in industry to satisfy all customer requirements beyond the standard limits and in an innovative way [3].

Porcelain tiles are characterized by their low water absorption (≤ 0.5%), high modulus of rupture (≥ 35 MPa) and resistance to deep abrasion (< 175 mm3). The glazed tiles present higher resistance to staining and household chemicals due to the presence of vitreous and impervious glazes. However, the unglazed ones, which are usually subjected to subsequent polishing, are susceptible to staining and abrasion [4].

Polishing by SiC abrasive, preceded by high energy grinding and levelling, brings closed porosity to the surface and results in the formation of complex texture. The characterization and modification of the resultant surface is vital to improve mechanical and surface properties, specifically stain and abrasion resistances [5].

It has been shown that the pore morphology and surface roughness are main factors which strongly control the stain resistance [6]. Numerous attempts have been made to improve resistance to staining by applying polymer coatings on the surface or increasing the vitreous phase through double charging [7,8]. Additionally, selective crystallization of hard phases like Zircon and/or Zirconia may improve abrasion resistance [9]. It can be also imagined that the resistance to abrasion depends on surface microstructure and characteristics, such as pore size, chemical analysis, mineral phases, degree of vitrification etc., which may have an influence on abrasion resistance.

The purpose of this research was to better understand the relationship between above-mentioned features and deep abrasion resistance. This can help us to employ appropriate methods for improving abrasion resistance. Therefore, ten commercial unglazed porcelain tiles were thoroughly characterized and so correlations between identified features and deep abrasion resistance were explored.

2. EXPERIMENTAL PROCEDURE

Ten various kinds of industrially manufactured polished tiles were selected in order to demonstrate the wide range of technology and decoration techniques currently available in the market. Table 1 presents the name and typology of the samples. The tiles were named in an order such that P1 demonstrates the maximum resistance to abrasion. Resistances to abrasion as well as surface and bulk properties of all samples were then characterized. At least five samples (10×10 cm) cut from original tiles (60×60 cm) were tested for each kind of analysis.

Deep abrasion of samples was performed (Gabrielli test machine Model CAP) according to ISO 10545-6. Deep abrasion was determined through the measure of the volume loss of material after testing. The test was conducted using a steel disc (Fe 360 A) with a diameter of 200 mm and thickness of 10 mm rotating over the sample with 75 rpm for 150 revolutions. The Al_2O_3 powder was employed as abrasive media. Hereafter, further analyses were performed on abraded samples.

A Vickers micro-hardness tester with a diamond pyramid indenter (Buehler, Micromet I) was used to measure microhardness. The load was 500 g and the loading time was 20 s. Data of hardness were determined using at least ten indentations on each specimen and near the abraded area.

Bulk density, apparent porosity and water absorption were determined by water saturation under vacuum and Archimedes' principle (ISO 10545-3). The powder density was measured by pycnometry, which allowed closed porosity to be calculated along with relative density. Pore size distribution estimated by mercury intrusion porosimetry (ThermoFinnigan Pascal 140) on tile fragments with an apparent area of around 3 cm^2.

The chemical composition of powdered samples was determined by wet chemical analysis method. The samples were then subjected to XRD analysis using a powder diffractometer (Philips XPert, Co K_α radiation at 40 kV). Silicon powder (10 wt.%) was used as the standard for semi-quantitative measurements. J. Martín-Márquez et al. have been shown that qualitative mineralogical analysis, based on the intensity of a particular diffraction peak for each crystalline phase, is a suitable methodology to obtain preliminary knowledge about the quantity of mineral phases that forms in porcelain stoneware [10]. Therefore, the peak intensity of existing phases was determined using OriginPro 8.5 SR0 software. The intensity of peaks was then compared with intensity of Si in order to minimize any possible systematic errors. The microstructural studies were done by scanning electron microscope working in secondary electron mode (SEM, Philips XL30).

3. RESULTS AND DISCUSSION

The abrasion resistance and other technical characteristics of the specimens are summarized in Tables 1 and 2, respectively.

Sample	Technology & Decoration Techniques	Abrasion Resistance (mm^3)
P1	Full White Body + Soluble Salts	61 ± 9.7
P2	Non-coloured Body	65 ± 5.1
P3	Double Charged + Micronized Granule	72 ± 6.3
P4	Full Beige Body + Flaked Granule	75.2 ± 5.3
P5	Full Dark Body + Double Charged + Soluble Salts	76.6 ± 8.7
P6	Non-coloured Body	117.2 ± 23.4
P7	Non-coloured Body + Soluble Salts	119.6 ± 17.9
P8	Non-coloured Body	125.4 ± 15.2
P9	Super White Body + Double Charged + Micronized White Granule	127.8 ± 3.9
P10	Non-coloured Body	134.2 ± 3.9

Table 1. Sample names, typology and abrasion resistance.

Sample	Abrasion Resistance (mm^3)	Hardness (GPa)	Apparent Porosity (%)	Bulk Density (gr/cm^3)	Closed Porosity (%)	Mean Pore Size (μm)
P1	61 ± 9.7	4.61 ± 0.67	0 ± 0.0	2.28 ± 0.01	9.50 ± 0.14	46.5 ± 5.2
P2	65 ± 5.1	4.68 ± 0.71	1.55 ± 0.5	2.31 ± 0.01	8.30 ± 0.17	4.6 ± 1.2
P3	72 ± 6.3	5.43 ± 0.80	0.39 ± 0.18	2.36 ± 0.01	5.60 ± 0.12	3.4 ± 0.7
P4	75.2 ± 5.3	4.65 ± 0.89	1.34 ± 0.55	2.32 ± 0.01	8.30 ± 0.10	12.4 ± 3.1
P5	76.6 ± 8.7	5.59 ± 0.55	0.36 ± 0.17	2.37 ± 0.02	5.60 ± 0.21	6.3 ± 1.5
P6	117.2 ± 23.4	6.13 ± 0.78	0 ± 0.0	2.32 ± 0.03	8.3 ± 0.13	14.2 ± 2.1
P7	119.6 ± 17.9	3.94 ± 0.91	1.17 ± 0.41	2.27 ± 0.02	10.3 ± 0.41	36.6 ± 9.6
P8	125.4 ± 15.2	5.39 ± 0.97	0.80 ± 0.4	2.34 ± 0.01	7.5 ± 0.19	12.1 ± 2.2
P9	127.8 ± 3.9	5.34 ± 0.85	0.74 ± 0.39	2.41 ± 0.02	6.6 ± 0.14	68.7 ± 10.2
P10	134.2 ± 3.9	5.05 ± 1.08	0.73 ± 0.32	2.31 ± 0.01	7.9 ± 0.17	28.9 ± 4.5

Table 2. Abrasion resistance and technical characteristics of the samples.

The correlations between abrasion resistance and hardness, apparent porosity, bulk density, closed porosity and mean pore size are also shown in Figs. 1 (a)-(e), respectively. Additionally, the correlation factors of related lines (R^2) are illustrated in the figures. The maximum and minimum resistance to abrasion correspond to the sample P1

(61 mm^3) and P10 (134.2 mm^3), respectively. In addition, the abrasion resistances can be generally divided into the two ranges of 60-80 mm^3 for samples P1-P5 and 115-135 mm^3 for P6-P10.

The very poor relationships between abrasion resistance and other characteristics of the samples can be deduced from Fig. 1 (a)-(e). Even no correlation factor representing a positive or negative trend was attributed to relationship between abrasion resistance and apparent porosity. This might arise from the statistical nature of measurements for ceramic products which usually presented considerable scattering. The only noteworthy and logical correlation factor was related to the relationship between abrasion resistance and mean pore size in which the abrasion was increased by increasing the mean pore sizes. In other words, the resistance to abrasion was decreased by increasing the mean pore size (Fig. 1e).

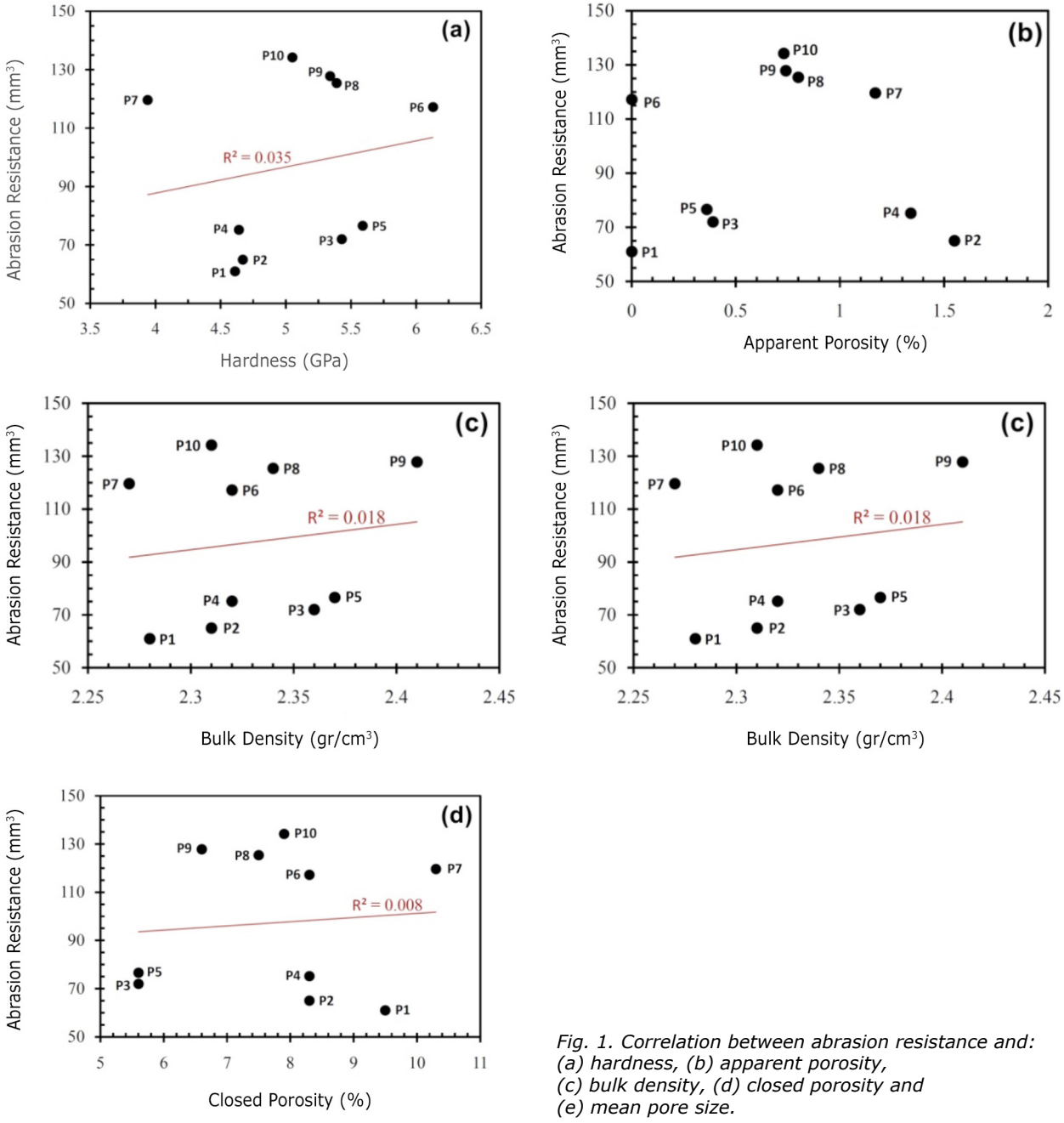

Fig. 1. Correlation between abrasion resistance and: (a) hardness, (b) apparent porosity, (c) bulk density, (d) closed porosity and (e) mean pore size.

The chemical composition of the samples is summarized in Fig. 2. The main constituents of the samples, which are SiO_2, Al_2O_3, Na_2O and K_2O, may be supplied from Quartz, Kaolinite Clays (Kaolin or Ball Clays) sand Na/K-Feldspars [1]. The clay fraction provides plasticity and dry mechanical strength during processing, and promotes mullite formation. Feldspars form glassy phase at relatively low temperatures (sodium feldspar being mainly used), facilitating the sintering process, and achieving to the virtually zero (<0.5%) open porosity and a low level of closed porosity (<10%). Quartz promotes thermal and dimensional stability thanks to its high melting point. At times, quartz is also considered as a reinforcing particle embedded in the glassy matrix [2]. Stress and micro-pore formation near the quartz particles strongly influence the mechanical and surface properties. This results from thermal expansion coefficient mismatch between quartz particles and glassy matrix. Additionally, viscosity and the amount of amorphous phase at firing temperature play a key role to enhance densification and reduce defects [7,8]. In this research, no logical relationship between chemical composition and abrasion resistances could be established (0.02 < correlation factor (R2) < 0.14). Although, high content of Al_2O_3 and SiO_2 would increase abrasion resistance, specimens with low content of those elements presented high resistance to abrasion (samples P3 and P5 in Fig. 2).

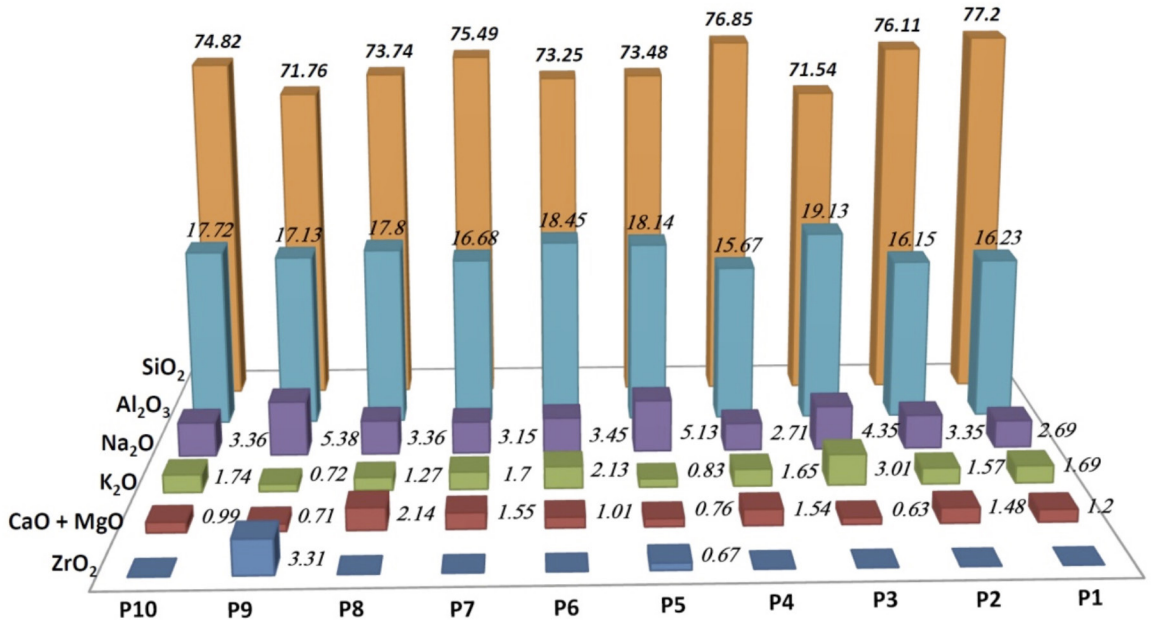

Fig. 2. Chemical analysis (wt.%) of the samples (Fe_2O_3 + TiO_2 < 1.4 % for all samples).

XRD graphs of samples P1-P5 and P6-P10 are shown in Fig 3 (a) and (b), respectively. The identified phases are also summarized in Table 3. As can be observed, samples P1-P5 mainly contain quartz, mullite, amorphous phase and minor amount of Na-feldspar. However, the Na-feldspar becomes the dominant phase in samples P6-P10. In addition, sample P9 as a super white tile contains zircon. It seems that samples P6-P10, which have low abrasion resistance, are not well vitrified at firing temperature and Na-feldspar is not completely melted in these samples.

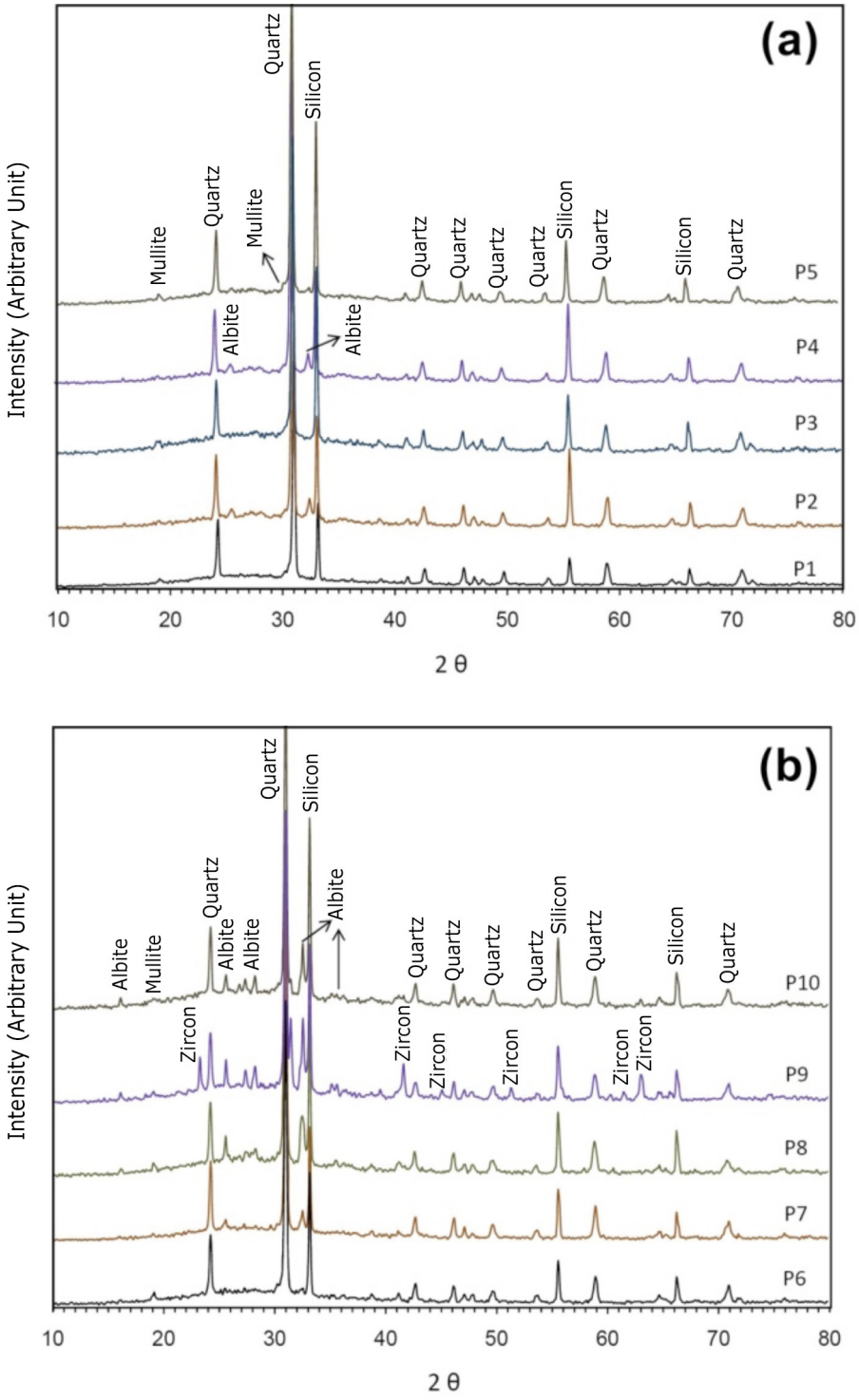

Fig. 3. XRD analysis of samples: (a) Samples P1-P5 and (b) samples P6-P10.

In order to semi-quantify the amount of phases in the samples, the main peak intensity of each phase was compared with the Si peak intensity ($I_{Si(111)}$). Intensity of base line was considered as a criterion for the amount of amorphous phase. The results are summarized in Table 3. The correlations between abrasion resistance and the amount of identified phases are also drawn in Fig. 4 (a)-(d). The best correlations with abrasion resistance were attributed to the albite, quartz and amorphous phase contents.

Sample	Phases	$I_{Quartz(101)}$ / $I_{Si(111)}$	$I_{Mullite(110)}$ / $I_{Si(111)}$	$I_{Albite(002)}$ / $I_{Si(111)}$	$I_{BaseLine}$ / $I_{Si(111)}$
P1	Quartz + Mullite	2.07	0.2	0	0.46
P2	Quartz + Mullite* + Albite	1.85	0.1	0.37	0.37
P3	Quartz + Mullite	1.38	0.14	0	0.34
P4	Quartz + Mullite* + Albite	1.71	0.1	0.24	0.44
P5	Quartz + Mullite + Albite*	1.31	0.13	0.1	0.34
P6	Quartz + Mullite + Albite	1.6	0.18	0.12	0.43
P7	Quartz + Mullite* + Albite	1.75	0.08	0.34	0.4
P8	Quartz + Mullite + Albite	1.44	0.14	0.46	0.35
P9	Quartz + Mullite + Albite + Zircon	1.41	0.12	0.62	0.34
P10	Quartz + Mullite* + Albite	1.32	0.1	0.47	0.32

* Minor Phases

Table 3. Identified phases by XRD analysis..

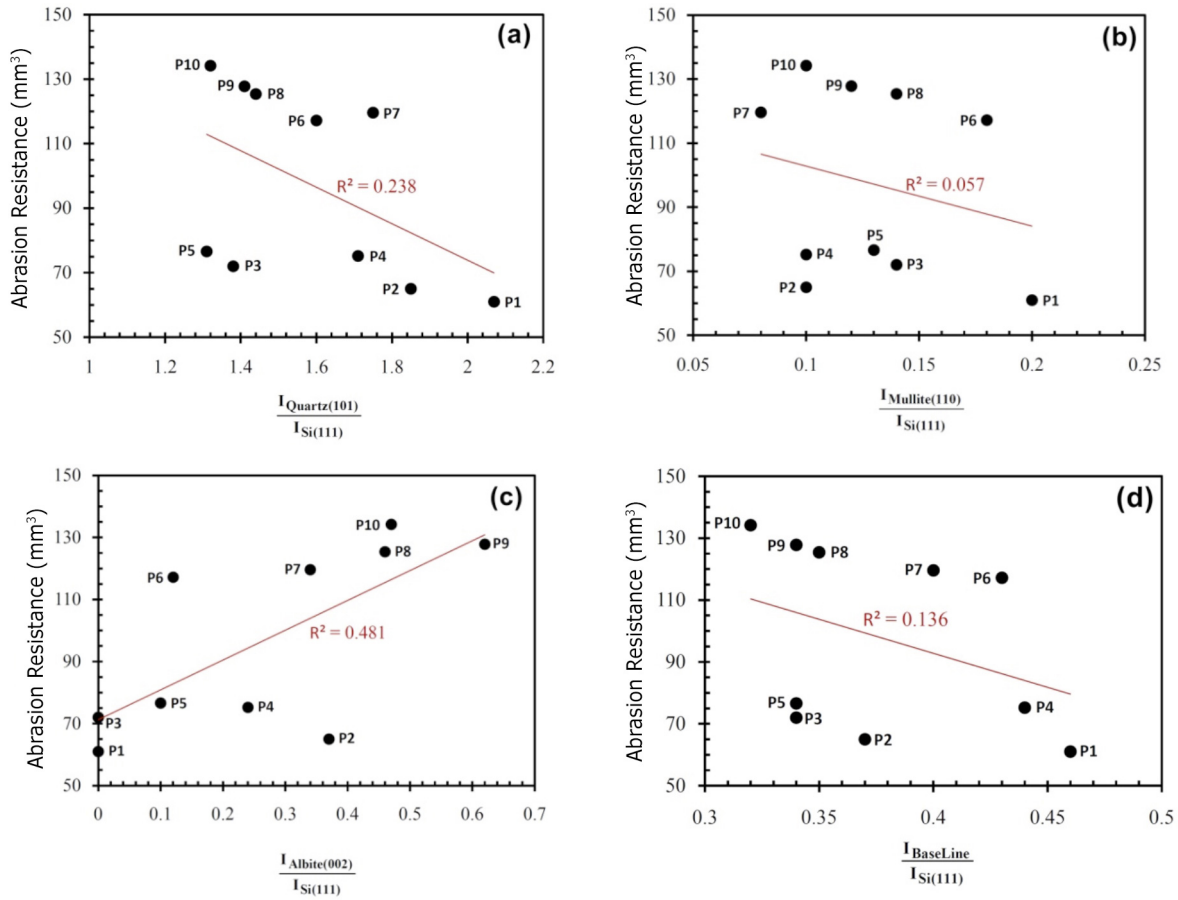

Fig. 4. Correlation between abrasion resistance and the amount of identified phases. Abrasion resistance versus (a) Quartz, (b) Mullite, (C) Albite and (d) amorphous phase.

It seems that by increasing the amount of albite or reducing the glassy phase content in the fired tiles, abrasion resistance significantly decreases. It has been reported that porcelain tiles with high content of amorphous phase demonstrate an ability to promote densification and also relieve residual stress during firing cycle, resulting in the improved mechanical properties such as toughness and strength [5,8]. This can be achieved by employing higher firing temperature during the process or using fluxing agents in the body composition. In recent years, companies prefer to use fluxing agents such as frits, nepheline syenite, Li-Feldspar etc. to enhance the glassy phase and finally improve mechanical properties and actually resistance to staining [11,12]. In this study, samples P1-P5 displayed a well-vitrified surface resulting from high firing temperature or using fluxes in second charge. Furthermore, samples P6-P10 had a high content of residual Na-Feldspar, which was not melted during firing, and low amount of glassy phase. Therefore, they were more sensitive to material removal than samples P1-P5.

SEM micrographs of samples P1, P5 and P8 are shown in Figs. 5 (a)-(c), respectively. The well-vitrified surface of samples P1 and P5 can be observed in Figs. 5 (a) and (b). However, sample P8 exhibits a complex microstructure containing various sizes of micro pores and also quartz particles, which are not well embedded in the matrix. Fig. 5 (d) shows quartz particles surrounded by pores and glassy phase. The quartz particles exhibiting lack of cohesion with the matrix are easily removed during abrasion. Therefore, tailor-made vitrified surface is highly recommended for improving resistance to abrasion..

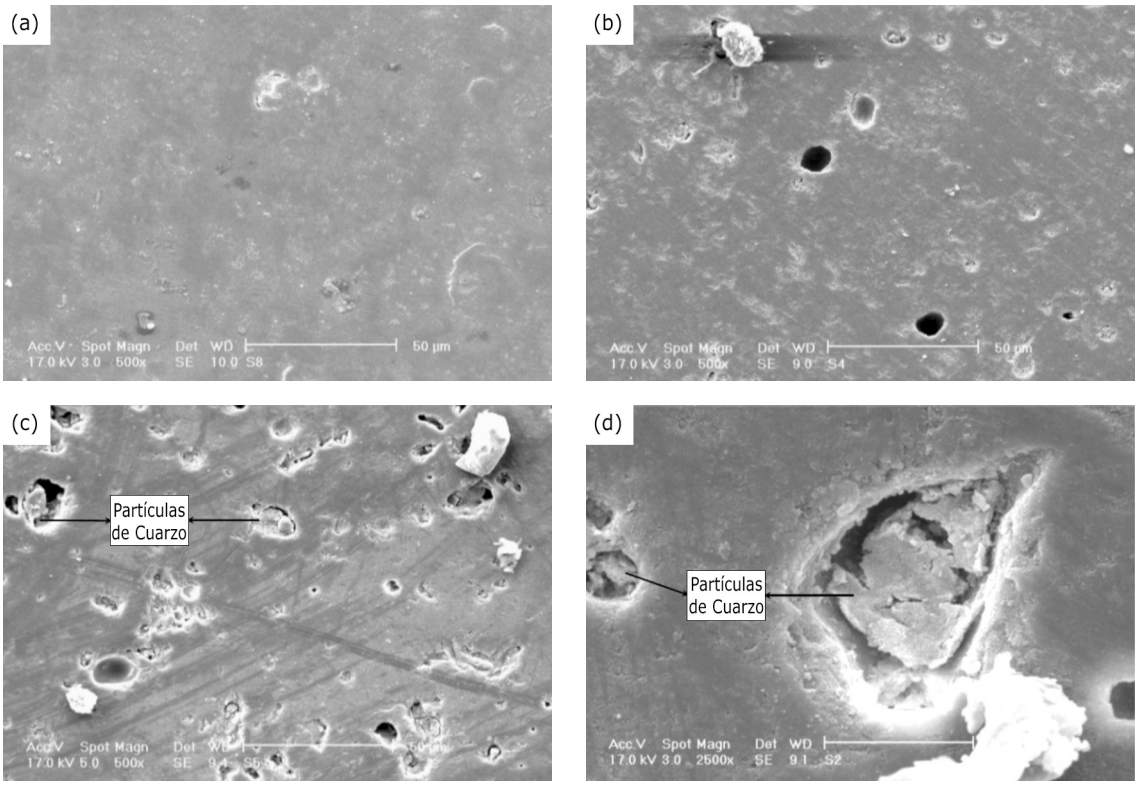

Fig. 5. SEM micrograph of samples (a) P1, (b) P5 and (C & d) P8 (Mag. ×500 for a, b and c & Mag. ×2500 for d).

4. CONCLUSIONS

The statistical nature in measurements of technical features for porcelain tiles made it difficult to determine well a correlation between abrasion resistance and other physical/chemical characteristics. It seems that by increasing the mean pore size, the abrasion resistance decreases.

Semi-quantitative XRD analysis revealed that high resistance to abrasion was displayed by samples with a high glassy phase content and low amount of non-melted Na-feldspar.

Surface textures with a high micro-pore content and not well-embedded quartz particles were much sensitive to abrasion. Therefore, developing a well-vitrified surface may help us to improve abrasion resistance.

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