APPLICATION OF DIFFERENT TEST METHODS TO ASSESS THE WEAR RESISTANCE OF CERAMIC TILES

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ABSTRACT

Over the past decade, ceramic tile production and consumption have experienced significant growth, despite the increasing requirements imposed by the market. This growth is attributed not only to technological advancements and product aesthetics, but also to innovative tile formats (e.g., ceramic slabs). Additionally, enhancements in mechanical, technological, and tribological properties have promoted new applications. Ceramic tiles, largely present in the international market, shall follow classification criteria and test methods outlined in ISO 13006 and ISO 10545 (parts 1-20), respectively. However, among test methods, a specific test to measure wear resistance is still missing. This aspect is of paramount importance, especially for glazed tiles, where the glaze has the main function of preserving the underlying decoration. The aim of this study is to investigate the mechanical and tribological properties of two different glazes applied on porcelain stoneware tiles. With a view to obtaining a clear picture of the mechanical and tribological properties of the glazed surface, different analytical tests were carried out, such as Vickers microhardness indentation, roughness measurement, and microstructural investigation using a scanning electron microscope (FEG-SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Wear resistance was assessed by adopting two different test methods: the abrasion resistance test done according to ISO 10545-7 and the multi-attribute method, a novel approach that allows determination of the intended use of a ceramic tile based on a combination of different tests. Results indicate that the multi-attribute test offers a more accurate assessment of ceramic tile wear resistance, unaffected by the color of the underlying decorations.

1. INTRODUCTION

In the industrial manufacturing sector, technical standards play a pivotal role in establishing test methods to verify product quality and set requirements for its classification. For ceramic tiles, the most important standards for the European and International markets are developed in the frameworks of CEN/TC 67 and ISO/TC 189 "Ceramic Tiles", respectively. Ceramic tiles are classified in accordance with ISO 13006 and/or EN 14411 and are tested using methods outlined in EN ISO 10545 parts 1-20. These test methods encompass a wide number of physical, chemical, and mechanical characterizations. However, they need to be periodically revised and/or updated in order to be able to follow/collect all the improvements promoted by technological changes. Currently, ceramic tiles are still divided into unglazed (UGL) and glazed (GL) tiles. Their wear resistance is determined only on the basis of two different abrasion tests, reported in ISO EN 10545-6 for unglazed tiles and ISO EN 10545-7 for glazed tiles. These two tests differ significantly: ISO EN 10545-6 measures the deep abrasion resistance of UGL tiles by quantifying the volume of material removed after 150 revolutions of a steel disc in the presence of abrasive powder, whereas ISO EN 10545-7 evaluates the surface abrasion resistance of GL tiles through visual observation of the abraded area [1–3].

However, wear resistance usually refers to the capacity of a surface to withstand degradative processes, such as surface abrasion resulting from the relative motion between two contacting surfaces, and its ability to resist mechanical forces that may lead to permanent deformations such as scratches or incisions altering or damaging the surface texture [4]. Wear resistance also depends on mechanical and morphological properties of the surface, such as hardness, roughness, pore size and distribution, and the material surface microstructure (e.g., amount of amorphous and crystalline phase, and size, shape, and typology of crystalline structures) [5]. Furthermore, wear greatly affects the durability of exposed surfaces reducing the service life of the product [4]. The definition of wear resistance for ceramic tiles is currently a topic of discussion within Working Group 1 "Test methods" of ISO/TC 189. The ongoing debates focus on identifying the best methodology to assess wear resistance and to establish a test method suitable for both GL and UGL tiles, which is also able to overcome the limitations exhibited by current methods 10545-6 and 10545-7. One proposal under development is a multi-attribute method that incorporates different tests to evaluate wear resistance. This approach has been described in a work item project WI ISO/CD 10545-22 titled "Determination of resistance to wear with a multi-attribute method", still under discussion [6].

The aim of this work is to evaluate the wear resistance of glazed tiles using the multi-attribute method and compare the results with those obtained on the same samples tested by ISO 10545-7. For this purpose, porcelain stoneware tiles coated with glossy and matte glazes were tested. Moreover, several analytical surface characterizations were also conducted on the ceramic tile samples, including Vickers hardness measurement (HV), and determination of roughness parameters such as average roughness (R_a) and total roughness (R_z). Microstructural analysis was also performed using a scanning electron microscope (FEG-SEM) equipped with energy dispersive X-ray spectroscopy (EDS) on both glazed surfaces, to characterize their microstructure.

2. MATERIALS AND METHOD

2.1 SAMPLE PREPARATION

Two different industrial glazes were prepared according to the recipes provided by Colorobbia. With a view to producing a glossy and a matte glaze (GL-A and GL-B respectively), the mixtures were prepared by appropriately mixing the frits and raw materials. The GL-A mixture is composed of Zinc-based frit (FR-Zn, 30-40 wt% and Calcium-based frit (FR-Ca, 10-20 wt%). Additionally, the GL-A composition contains various raw materials: clay (5-10 wt%), kaolin (10-20 wt%), dolomite (5-10 wt%), feldspar (10-20 wt%), quartz (10-20 wt%), $BaCO_3$ (5-10 wt%), and ZnO (1-5 wt%). The GL-B mixture is composed of FR-Ca (10-20 wt%) and barium-based frits (FR-Ba, 10-20 wt%). Additionally, GL-B contains clay (5-10 wt%), dolomite (5-10 wt%), feldspar (10-20 wt%), nepheline (10-20 wt%), quartz (1-5 wt%), and $BaCO_3$ (5-10 wt%) as raw materials.

Small amounts of sodium tripolyphosphate (STPP, 0.1 wt%) and carboxymethyl cellulose (CMC, 0.3 wt%) were also added together with 40 wt% of distilled water. These mixtures were milled for 45 minutes in a ceramic jar using Al_2O_3 balls. The resulting slurries were sieved using a 200-mesh sieve to remove any unground or coarse particles. Slurry density was verified using a 100 mL pycnometer and adjusted to 1450 g/L by adding distilled water. Glazes were applied in the amount of 44 mg/cm^2 using the airless technique on 30 cm x 30 cm engobed tile bodies. Glazed samples were first dried in a ventilated electric oven at 110°C for 60 minutes and then air-cooled. Subsequently, glazed samples were single-fired in an industrial roller kiln adopting a fast-firing cycle with a heating rate of 30°C/min and a maximum temperature of 1205°C, maintained for 7 minutes, followed by controlled cooling. The ISO 10545-7 abrasion test was carried out on tiles featuring light and dark decorations digitally printed before glaze application.

2.2 SAMPLE CHARACTERIZATION

Wear resistance was assessed through two different tests: the abrasion resistance test carried out following the ISO 10545-7 methodology and the novel multi-attribute test [7]. The results of ISO 10545-7 were classified according to Annex N reported in ISO 13006 [8].

The multi-attribute test is mainly composed of 3 different tests:

I. Determination of Specific Weight Loss (ΔWL_S) after 6000 abrasion cycles carried out with the same equipment described in ISO 10545-7. The ΔWL_S is calculated using Equation (1), where W_i and W_f indicate the initial and final weights, and A represents the abraded area.

a. $$\Delta WL_S = \frac{W_i - W_f}{A} \text{ [g/cm}^2\text{]} \quad (1)$$

II. The assessment of gloss variation (ΔG) after 600 and/or 6000 abrasion cycles, was done using Equation (2), where G_i and G_f indicate the initial and final gloss, respectively. The evaluation of stain resistance is carried out on the abraded area by applying a green chromo solution in accordance with ISO 10545-14 [9].

$$\text{b. } \Delta G = G_i - G_f \qquad (2)$$

III. Scratch resistance measurements are carried out according to the procedure reported in ASTM C1895-20 [10].

The results of the 3 test methods are then compared with the limits reported in Table 1 in order to classify the ceramic tile.

Test Method	Wear resistance class		
	H	HH	HHH
Intended use	Residential application	Low traffic area	Heavy traffic area
ΔWL_S [mg/cm^2] (@ 6000)	$0.035<\Delta W_r<0.045$	$0.028\leq \Delta W_r<0.035$	$\Delta W_r<0.028$
ΔG	@ 600 cycles $36\leq\Delta G\leq50$	@ 600 cycles $6<\Delta G\leq35$	@ 6000 cycles $\Delta G \leq 5$
Stain resistance	Minimum class: 3		
Scratch resistance	hardness point ≤4	hardness point≤5	hardness point≤7

Table 1: *Requirements for wear resistance classification*

Vickers microhardness measurements were carried out along the thin glaze film using a microhardness indenter (Isoscan Galileo microhardness tester) with an applied force of 9.81 N and a dwell time of 15 seconds as specified in ASTM C1327-15 [11]. Five indentations were made for both GL-A and GL-B samples. Microhardness was determined by measuring the indentation diagonals using image analysis software (ISOSCAN). The average roughness (R_a) and total roughness (R_z) were determined in accordance with ISO 4287 by acquiring and analyzing the surface roughness profiles using an optical profilometer (Leica Dual Core Microscope 3D DCM 3D), equipped with image analysis software (Leica Map Premium) [12]. For each glaze, five profiles with a length of 50 mm were acquired with 20X magnification. Microstructural characterization was performed on the gold-plated glaze surface using a scanning electron microscope (FEG-SEM, Tescan Mira 3) equipped with energy-dispersive X-ray spectroscopy (EDS) in order to gather information about the distribution of crystalline structure embedded in the amorphous matrix. Micrographs were acquired by capturing backscattered electrons with a working distance (WD) of 10 mm and an accelerating voltage of 20 kV. Before observation, SEM samples were made conductive by sputtering with gold (Quorum Q150R ES).

3. RESULTS AND DISCUSSION

The abrasion resistance of the GL-A and GL-B samples was determined and visually evaluated according to the methodology outlined in ISO 10545-7 [7]. The outcomes of the test were then classified according to Annex-N reported in ISO 13006, based on 5 classes (from class 1 to class 5, indicating final destinations that are increasingly resistant to abrasion action) [8]. The results highlight a notable distinction in terms of abrasion resistance between the dark-decorated and light-decorated samples. In fact, the abraded area of the dark-decorated samples became visible after 600 cycles, thus resulting in class 2. Conversely, the abraded area of the light-decorated samples was not visible even after 12000 cycles, resulting in class 5, the highest class specified in the ISO 10545-7 [7]. With a view to validating the classification provided for light-decorated samples, the evaluation of the stain resistance was carried out in the abraded area as outlined in ISO 10545-7, following the procedure reported in ISO 10545-14 [7,9]. Stains were effectively removed using a weak agent (acetone) and a non-abrasive sponge, as prescribed in procedure B of ISO 10545-14. The abraded areas of GL-A and GL-B featuring light and dark decorations are shown in Figure 1.

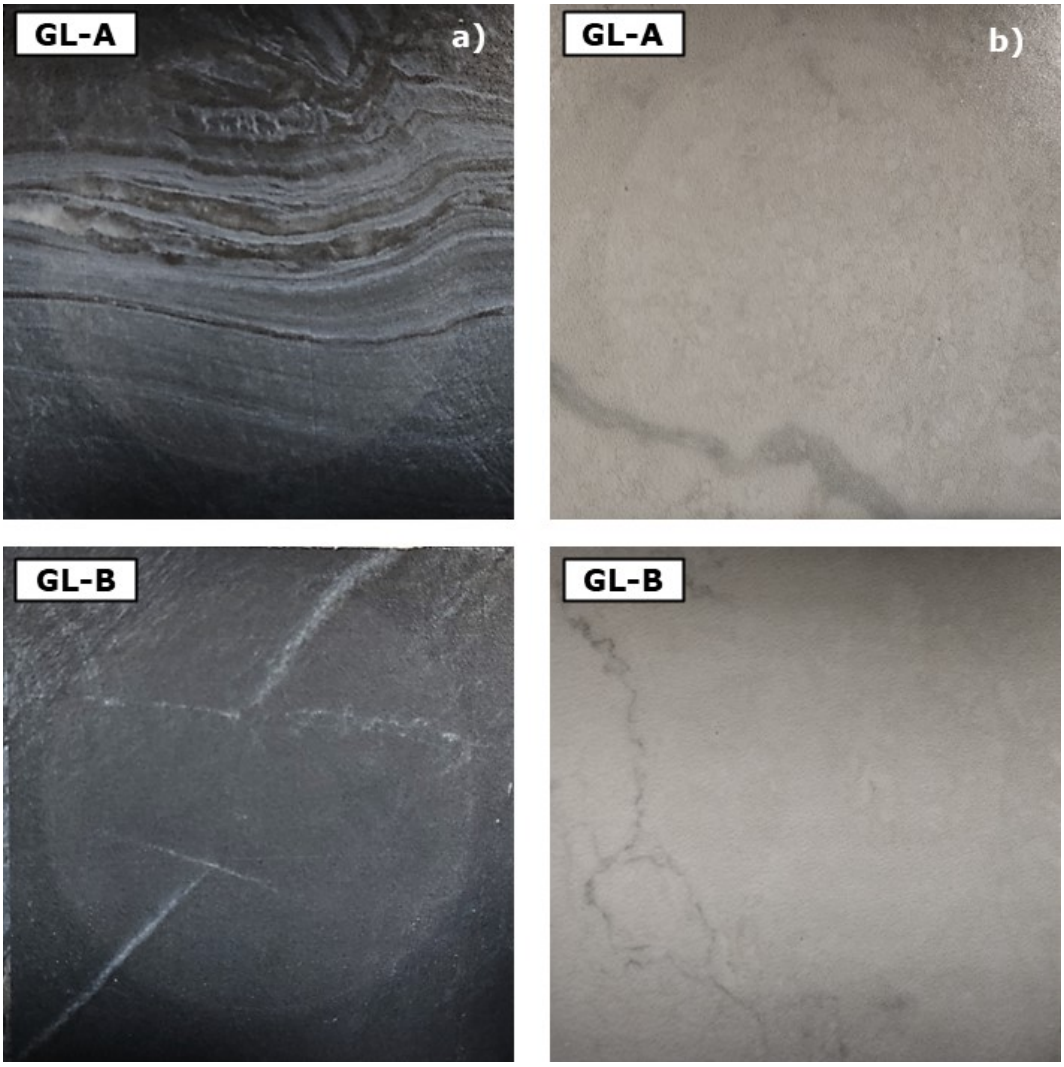

Figure 1: *Abraded areas of GL-A and GL-B glazed tiles. a) Abraded area visible after 600 cycles, b) abraded area after 12000 cycles*

According to the classification outlined in ISO 13006 Annex-N, GL-A and GL-B with dark decoration patterns are suitable for areas with low foot traffic and minimal abrasive dirt (e.g., residential rooms). Conversely, GL-A and GL-B with light decorations are suitable for highly traffic areas prone to scratches, such as shopping centers and airports [8]. Based on the obtained results, it was observed that the abrasion resistance according to ISO 10545-7 is strictly affected by the color of the underlying decoration, leading to different results even when the same glazes are used [1,3]. This happens because a clear contrast between the light decoration and the abraded surface is difficult to observe and may be subjective [1]. To overcome the limitations of ISO 10545-7, wear resistance was assessed using the multi-attribute method, which consists of three different methods. The outcomes of these three tests are reported in Table 2.

Sample	ΔWL_S [g/cm^2]	ΔG (600 cycles)	ΔG (6000 cycles)	Scratch resistance	Class Method
GL-A	0.025±0.001	38.7±0.9	-	6	H
GL-B	0.017±0.001	-	2.5±1.3	7	HHH

***Table 2**: Results obtained by the multi-attribute test*

Based on the ΔWL_S values measured after 6000 abrasion cycles, both GL-A and GL-B would be placed in the HHH class, the highest reported in the method, whereas, after the scratch test, GL-A would result in HH class, while for GL-B the HHH class would be confirmed. However, the absolute gloss variation (ΔG) turned out to be the most critical parameter. In fact, considering the ΔG value, it was observed that GL-A exhibited the highest value, leading to its classification in the H class. Conversely, GL-B displayed the lowest ΔG values, resulting in the HHH class. Additionally, the green chromium stain in the abraded area was removed according to ISO 10545-14 using procedure A, resulting in a stain resistance classification of class 1.

According to the classification provided by the multi-attribute method, GL-A resulted in being classified as H and thus suitable for residential applications, whereas GL-B resulted in being classified as HHH, thus suitable for highly trafficked areas. Comparing these results with those obtained by applying the ISO 10545-7 method, it is clear that this new approach is more sensitive in discriminating the differences between glazes, regardless of the color of the underlying decoration.

To verify the outcomes of the multi-attribute method and demonstrate its effectiveness, some analytical characterizations were carried out. In particular, mechanical and tribological characteristics such as Vickers microhardness (HV), roughness parameters (R_a and R_z) and microstructure analysis were determined. The results of the Vickers microhardness values and roughness parameters are collectively reported in Table 3.

Samples	HV	Ra	Rz
	[GPa]	[mm]	[mm]
GL-A	6.2±0.5	0.43±0.02	1.96±0.11
GL-B	7.5±0.6	0.67±0.02	3.05±0.11

***Table 3:** HV value and R_a and R_z roughness parameters of the analyzed glazes*

GL-A exhibited the lowest HV values as well as the lowest R_a and R_z roughness parameters, indicating a softer and smoother surface compared to GL-B. Literature data suggest that the hardness value of GL-A closely aligns with that of a traditional glaze (HV≈5.9 GPa) [13–15]. Conversely, GL-B displayed HV values comparable to those measured for well-crystallized glass-ceramic glazes [13,14,16]. With a view to obtaining information about glaze microstructure, scanning electron microscopy observations were done on both GL-A and GL-B (Figure 2).

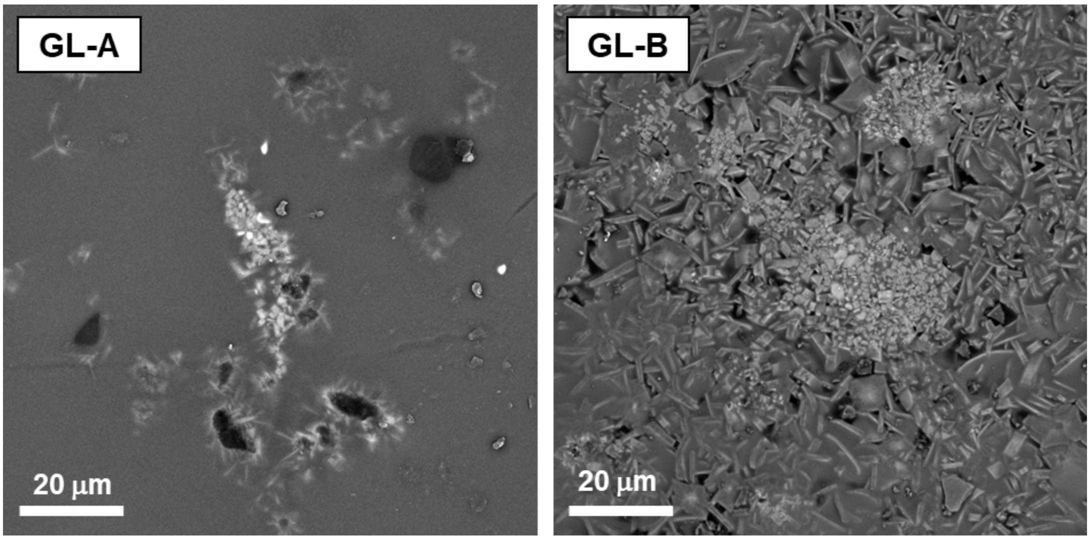

***Figure 2**: Microstructural investigations on the GL-A and GL-B glazes*

Both GL-A and GL-B exhibited a microstructure characterized by flake-like and square-shaped crystalline phases. According to the EDS data (not reported for the sake of brevity) and to the available literature, the bright square crystals corresponded to $BaAl_2Si_2O_8$ crystalline phase, while the flake-like ones corresponded to $CaAl_2Si_2O_8$ crystalline phase [13,16–18]. Furthermore, the microstructure of GL-A was primarily characterized by a small quantity of heterogeneously dispersed crystalline clusters within the amorphous matrix, whereas the microstructure of GL-B was mainly composed of uniformly dispersed crystalline structure within the amorphous matrix. Comparing the microstructural characterization with the HV values, R_a, and R_z parameters, it is possible to observe a relationship between the amount of crystalline phase embedded in the amorphous matrix and the aforementioned parameters. The higher the amount of crystalline phases, the greater the HV value, and the rougher the surface [13,16,19]. According to the obtained results, GL-A is less hard and rough than GL-B due to a lower amount of crystalline phases.

The analytical characterizations allow differentiation of the two different glazes in agreement with the results obtained by the multi-attribute test method, GL-A and GL-B being as classified H and HHH, respectively.

4. CONCLUSION

In conclusion, this study aimed to assess the wear resistance of glazed tiles using two methodologies: the abrasion resistance outlined in ISO EN 10545-7, and a new multi-attribute approach under development (ISO CD 10545-22). To validate the data obtained from the multi-attribute method and demonstrate its effectiveness, various analytical tests were carried out, including Vickers microhardness (HV) measurements, assessment of R_z and R_a roughness parameters, and microstructural investigations.

The evaluation of abrasion resistance, performed in compliance with ISO 10545-7, widely adopted in the ceramic industry, was able to provide a distinction between the two investigated glazes only based on the color of the underlying decoration.

Wear resistance assessed using the multi-attribute method was successful in providing the quantitative data necessary to distinguish the two glazes. The outcomes of the multi-attribute approach were also strongly supported by the analytical tests.

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