DETERMINATION OF THE WEAR CHARACTERISTICS OF CERAMIC GLAZES SUBJECTED TO PIN-ON-DISC TRIBOLOGY TESTING

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1. ABSTRACT

This study focuses on the tribological performance (friction and wear behaviour) of two different glazes manufactured for the vitreous china sanitary ware and ceramic tile industries with different compositions, processes and applications, and of a glaze coated with a silicon layer deposited by the sol-gel technique. The surfaces were subjected to pin-on-disc testing in the presence of an alumina-rich abrasive medium, with a view to evaluating the behaviour of frictional forces and the mechanisms and severity of wear on the glazed surfaces. The results showed variations in tribological performance depending on the type of glaze analysed, it being observed that the glazes with a greater presence of crystalline phases exhibited higher friction coefficients and greater wear resistance. The deposited coatings can be considered protective coatings and, depending on the severity of abrasion, sacrificial coatings of the glaze layer.

2. INTRODUCTION

In the ceramic tile industry, the glaze is considered one of the most important layers. It contributes aesthetic attributes as well as mechanical properties that provide resistance to normal and shear stresses, present during friction, which result in surface wear, the loss of attributes such as gloss, colour and material, and subsequent rejection of the product by the client.

The glaze, understood as an intentional mix of metallic oxides in a silicon matrix exhibits variations as a result of the amounts of these oxides, the thermal fusion process and solidification, which can nucleate crystals in the microstructure and vary the final properties of the solid. With regard to the glazed layer, the thermal fusion process and interaction with the substrate body can create unfavourable conditions, resulting in the formation of defects that affect the quality of the surface and promote early surface wear.

Previous studies have shown that the progressive loss of gloss and other aesthetic attributes are associated with wear of the glaze surface as a result of abrasion [1-4]. Likewise, the severity of the abrasion depends on other factors of a tribo-system, such as: particle size, shape and hardness, sliding speed, normal load, glaze porosity, glaze roughness, glaze hardness and phases present in the glaze [5].

Generally, PEI surface abrasion resistance tests are used in industrial plants for determining faults in glaze surface appearance (texture and gloss), based on the cycles to which pieces are subjected when put in contact with alumina balls, corundum and even stainless steel. However, this test can be catalogued as qualitative and some authors state drawbacks as a result [1-3].

Among the tribology tests, pin-on-disc tests allow a more detailed approach, by determining dynamic conditions of the frictional force during a sliding test which shows the effects of the variables of the tribo-system, such as load, speed, pin material, and lubrication condition [6, 7].

This study was conducted with the aim of analysing the response of tribological behaviour (friction and wear) in a pin-on-disc test in the presence of an abrasive medium, as well as the determination of the wear mechanisms that are present in three different glazes, on one of which a layer of silicon had been deposited using the sol-gel technique. The parameters to be evaluated included the variation of the frictional force over time, impact of wear on the surface, identification of the wear mechanisms based on evaluation of the abraded surfaces using the scanning electron microscopy technique.

3. EXPERIMENTAL

3.1. MATERIALS

For this study three glazed surfaces were analysed: SE, EU and SG. Glazes SE and EU were kindly supplied by companies SENCO and EUROCERÁMICA, respectively. Detailed information on their processing was not supplied in order to preserve industry secrets of both companies' glazes. The glazes were analysed using X-ray fluorescence with the following equipment: MagixPro PW - 2440 Philips and X-ray diffraction in a diffractometer, reference XPert PANalytical Empyrean Series II.

Some of the EU glazes were given an additional coating with a layer of silicon using the sol-gel technique (SG glazes) with the aim of increasing hardness and evaluating their tribological performance. The coating was deposited using a solution of 25% tetraethyl orthosilicate (TEOS) along with 65% Ethanol and 10% Water. The process was carried out under acidic conditions to favour hydrolysis in the reaction. The coating was deposited using a Spin Coater VTC-50 at a speed of 2400 RPM. The piece with the deposited coating was dried in an oven by convection at 65 °C for 1 hour. It was then subjected to thermal treatment in a muffle kiln for 4 hours at 600 °C.

Type of glaze	Raw material	Composition (%)	°C	Firing cycle time	Mohs hardness	Resistance to wear by pedestrian traffic (RPM and use) UNE 138001:2008 IN
EU	Transparent frits	88	1130/1150	31 min	4	250 (RM)
	Kaolin	7				
	Sodium feldspar	5				
SE	Sodium-potassium feldspar	59	1200	750 min	4	125 (P)
	Calcium carbonate	12				
	Opaque frit	8				
	Kaolin	8				
	Silica	13				

Table 1. *Composition of test glazes*

3.2. EXPERIMENTAL METHODS:

For the pin-on-disc tribology evaluation, cylindrical pins 6 mm in diameter were made of a composite material of epoxy resin and silicon carbide. The glazed surfaces were cut into square sizes of 50 x 50 mm in order to be put into the pin-on-disc tribometer of the Universidad Pontificia Bolivariana, described elsewhere by Correa et al. [8]. For the analysis, sliding tests were carried out under a normal load of 9.81 N, with a linear speed of 3.76 m/s for 50, 100, 150, 200 and 250 seconds. The tests were carried out under an abrasive environment of aqueous alumina solution (5 µm) 50 to 1 p/p (50 parts water to 1 part abrasive) at an average solution flow rate of 2 ml/min. During the tests, the frictional force generated was evaluated and it was assessed as coefficient of friction (COF) vs time, using equation (1).

$$COF = \frac{\text{Frictional force}}{\text{Normal load}} \qquad \text{Equation (1)}$$

Once the tribology testing was completed each surface was cleaned with water to remove the excess abrasive medium and dried with a soft cloth. A photographic record of the wear tracks was made using a CANON EOS T3I Rebel camera. The images were later processed and digitally analysed with the IMAGE J software in order to determine the level of wear of the surfaces. The severity of the wear tracks was determined using the quantification of the percentage of colour phases (black: wear; white: without wear). Bearing in mind that, under the conditions used (magnifications and image sizes), the fully developed track corresponded to 27% of the image; the severity was evaluated and tabulated using equation (2).

$$\text{Severity of wear} = \frac{\text{\% of worn phase}}{27\%} \qquad \text{Equation (2)}$$

A microscopic observation was then carried out with a scanning electron microscope using a JEOL JCM-6000PLUS NeoScope instrument, with which a more detailed identification was achieved of the wear mechanism in each type of glaze.

4. RESULTS

4.1. GLAZE ANALYSIS

Table 2 shows the results obtained using X-ray fluorescence of the glazes after firing. Glaze EU has lower silicon and alumina contents than glaze SE. However, it presents greater percentages of alkaline and alkaline-earth elements, which allow rapid melting and forming of the glaze layer in the semi-stoneware body. In turn, glaze SE has a greater percentage content of SiO2 and alumina, enabling this glaze to withstand the extensive firing cycle to which it is subjected to fit the porcelain tile body.

Type of glaze	Oxide (%)							
	SiO2	Al2O3	Na2O	K2O	MgO	CaO	SrO	BaO
EU	59.21	10.00	15.52	0.98	2.88	8.17	0.02	0.08
SE	70.79	15.00	4.54	2.48	1.53	4.25	0.02	0.05
Type of glaze	**Oxide (%)**							
	ZnO	**TiO2**	**ZrO2**	**Cr2O3**	**Fe2O3**	**CoO**	**NiO**	**L.O.I.**
EU	2.29	0.08	0.39	0.01	0.27	0.01	0.00	0.68
SE	0.32	0.06	0.72	0.01	0.32	0.49	0.02	0.15

Table 2. *Elemental oxide composition of the test glazes.*

In the glazes, crystalline fractions of silicon (quartz, cristobalite) and of zirconium oxide (zircon) may be recognised, which formed during firing, as shown in the X-ray diffractograms carried out for both glazes. The phases identified are detailed in Table 3. Both crystalline phases are of high hardness and contribute hardness to the glaze.

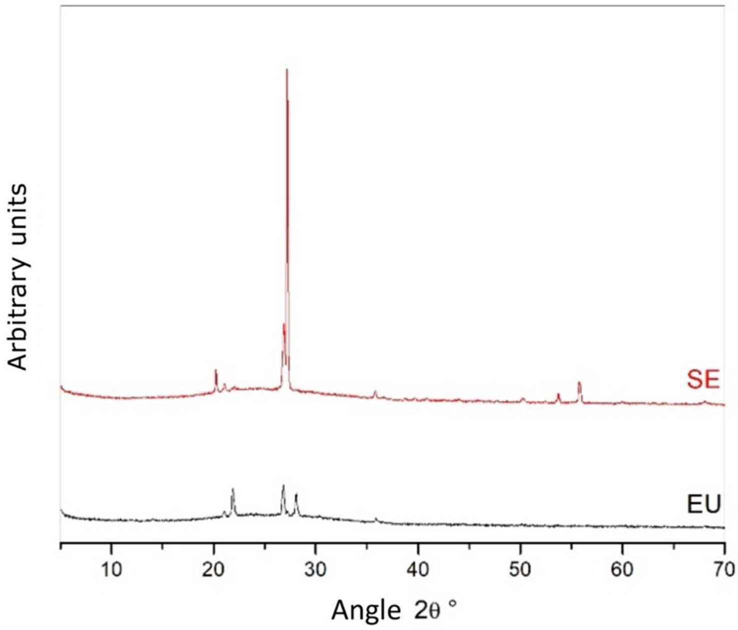


Figure 1. *XRD curve of the studied glazes.*

Type of glaze	Identified crystalline phases - Angle 2θ
EU	Quartz (21.03)
	Cristobalite (21.87, 28.07)
	Zircon (20.23, 26.90,27.19)
SE	Quartz (21.03, 36.65, 42.51, 50.26)
	Zircon (20.23, 26.90, 27.19, 55.73)

Table 3. *Identified crystalline phases in the test glazes.*

4.2. FRICTION ANALYSIS

Figure 2 shows the typical results for the coefficient of friction as a function of the distance travelled. The glazes show variations in friction, evidencing two types of changes: the first is the momentary increase in friction between the bodies in motion, which is observed in glaze SE between 200 and 300 metres of sliding and, in a less pronounced manner, in sample SG between 700 and 800 metres of sliding. These increases can be attributed to a mechanical interference given the accumulation of micro-debris, that is, particles coming from the glaze, the pin, the abrasive medium or a combination of all these.

The second type of change is that recorded in sample EU after 650 metres of sliding. In this case, a considerable increase is observed: the coefficient of friction doubles, which can be attributed to the severe deterioration of the glaze surface, as has been reported by other authors in pin-on-disc studies [9, 10].

In accordance with the results, from the point of view of friction it can be stated that, apart from the changes analysed above, wear occurs without significant increases in friction (under constant friction conditions) and the silicon coating present on glaze SG protects the surface and acts as a friction stabiliser in the tested range.

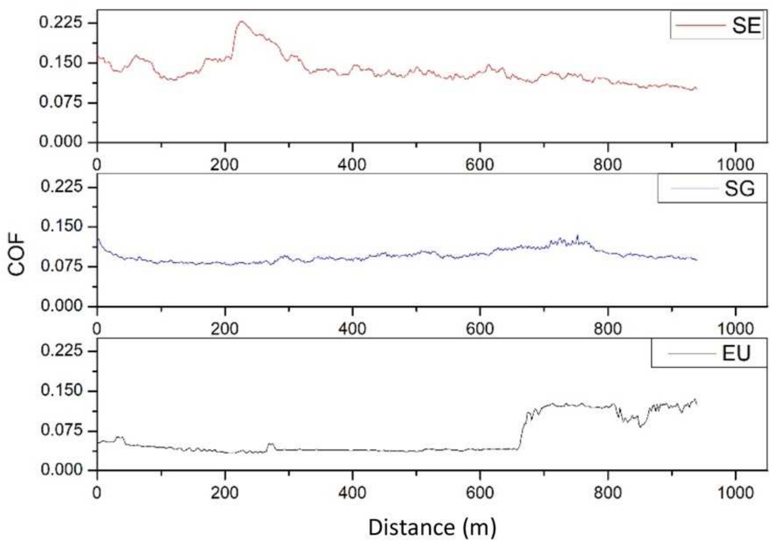


Figure 2. *Curve of the coefficient of friction versus distance for the test glazes.*

4.3. WEAR ANALYSIS

Table 4 shows the typical images of the glazes after being subjected to the tribology testing at different study times. The images obtained were subjected to rigorous digital image processing, which ensures the dimensions, scales and proper conversion of each of the images to binary images (black and white). The images presented in Table 4 correspond to sample SG and show the evolution of wear with time. The images show that wear is not homogeneous and there are areas with greater wear at shorter evaluation times as a result of topographic variations. As the evaluation time increases, wear appears all over the surface and increases. At 100 seconds, marks are observed on the surface forming abrasion grooves until a fully abraded surface develops, forming a circular ring of the width of the pin at 250 S.

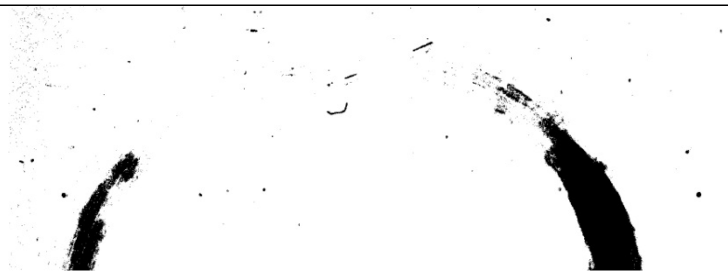
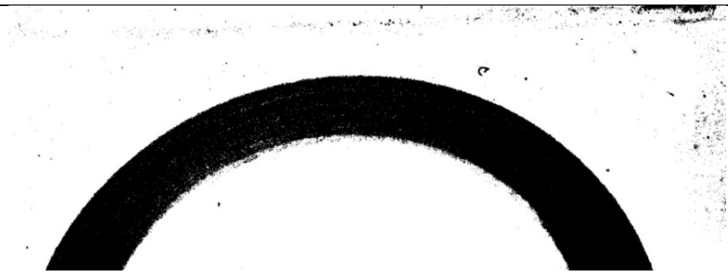
50 S (~188m)	
100 S (~376 m)	
250S (~942 m)	

Table 4. *Evolution of the wear track versus test time. SG samples*

Based on digital image processing and evaluation of the phases identified in the binary images (black and white), it was possible to quantify the severity of the wear as a function of the evaluation time of the samples. In Figure 3 the results are presented for each of the glazes at each of the evaluated test times. They show an incremental tendency in the severity of wear of the glazes as the time of each test increases, even when each value corresponds to an exclusive experimental run, which increases the likelihood of data scattering. The SE glazes exhibit less severity of wear compared to the EU glazes. One possible explanation for this phenomenon is the composition of the glazes and the manufacturing characteristics (thermal cycle), which favour formation of harder crystalline forms as evidenced in the diffractogram of Figure 1. The severity of the wear values of the SG glazes is interesting when compared with the EU and SE glazes in the first 100 seconds of the test. This indicates that the silicon-rich SG coating reduces the severity of wear.

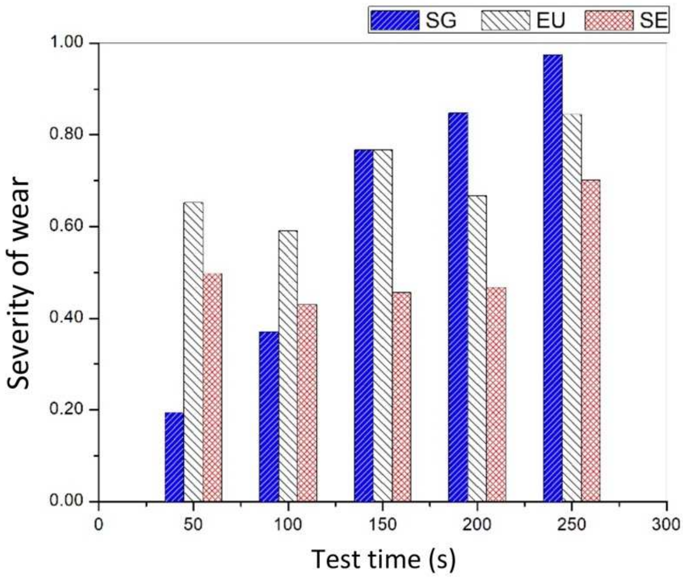
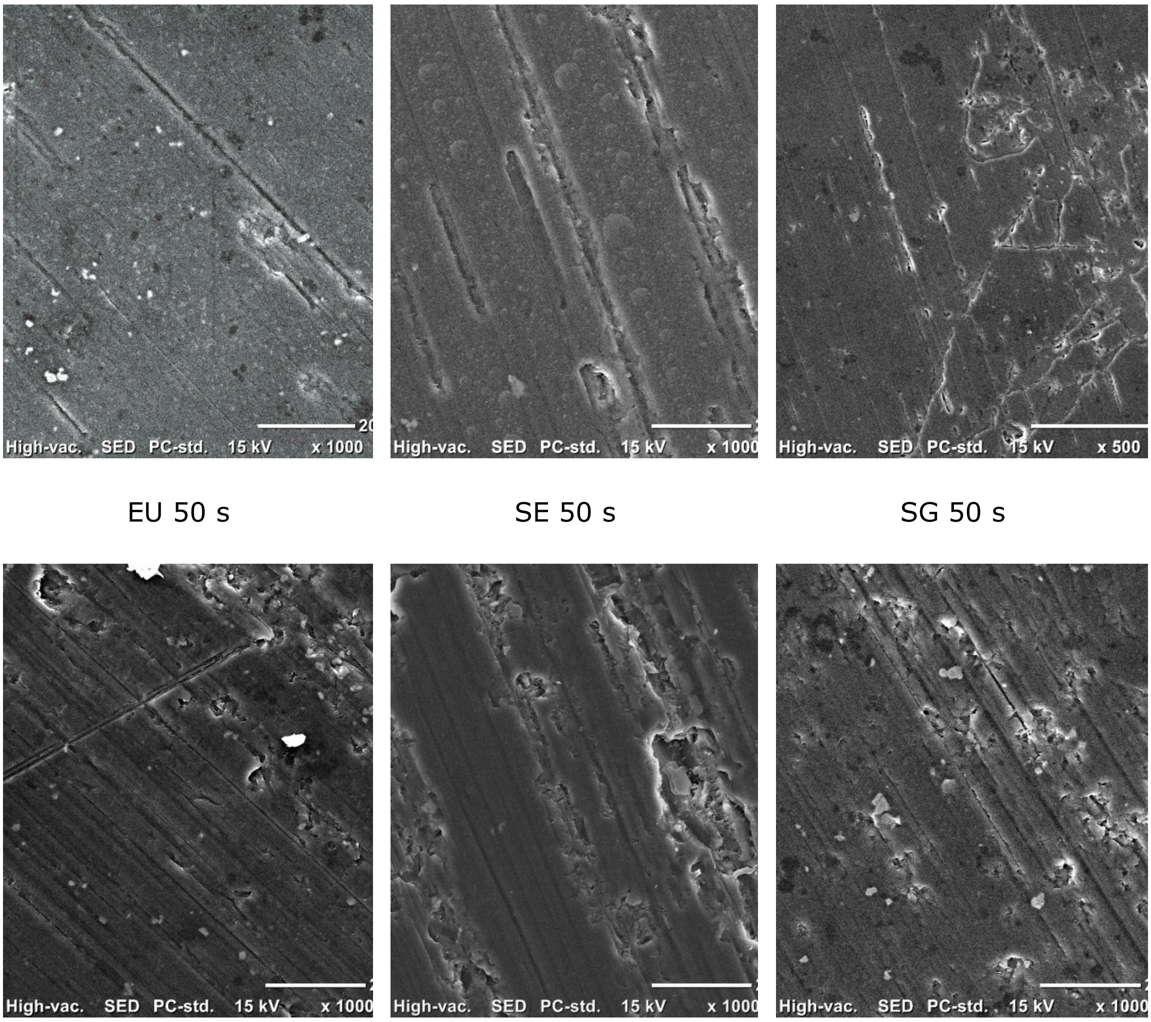


Figure 3. *Severity of wear versus test time in the test glazes.*

Scanning electron microscopy analysis of the glazes abraded at 50 and 100 seconds shows the characteristics of the wear mechanisms. Abrasion lines are observed in the same direction as the movement. In all images, it is possible to identify fine lines coming from the alumina abrasive medium and thick lines resulting from contact with the composite pin of epoxy resin/silicon carbide.

In images SE 50 s and 100 s, deterioration is identified of apparently less depth and lower severity. There are also fractures in the layer and transverse cracks.



EU 50 s | SE 50 s | SG 50 s

EU 100 s | SE 100 s | SG 100 s

Figure 4. *Scanning electron microscopy images for the test glazes. Evolution of the severity of wear for samples at 50 and 100 seconds.*

5. CONCLUSIONS

Variations were observed in tribological performance due to the type of glaze analysed, it being noted that the glazes with greater silicon or alumina contents, more energy during their thermal cycle and greater presence of crystalline phases exhibited higher coefficients of friction and greater wear resistance.

It was found that for the glazes with silicon coatings obtained using the sol-gel technique, the severity of wear decreased at short testing distances. The type of coatings assessed can be considered protective coatings and, depending on the severity of abrasion, sacrificial coatings of the glaze layer.

The wear mechanisms and the characteristics of damages to the glaze surfaces were identified, abrasion being the main wear mechanism generating fractures in the glaze and detachment of layers in the coating.

6. ACKNOWLEDGMENTS

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