TECHNICAL AND MICROSTRUCTURAL PROPERTIES OF MATT GLAZES FOR PORCELAIN TILE

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ABSTRACT

Porcelain tile is the most widely manufactured type of ceramic tile in the world and its use as flooring requires optimisation of sometimes opposing properties. Thus, tile manufacturers are demanding glazes that provide a matt finish with high slip resistance, but which is also simultaneously smooth to the touch and has high stain resistance.

These properties depend, beside the application and firing conditions, on the mixture of raw materials making up the glaze, as well as on their particle size. The mixtures usually consist of frits and different crystalline raw materials, such as feldspar, nepheline, corundum, and wollastonite. During the firing stage, numerous physico-chemical changes take place, which are responsible for the final properties of the glaze. Depending on their chemical composition, frits can devitrify larger or smaller amounts of crystalline species, such as silicates and aluminosilicates; feldspars foster glassy phase formation, while corundum usually acts as an inert material. In addition, in the contact areas between different particles, new crystalline phases can form that also contribute to the final properties of the tiles.

In this study, two types of matt glazes were used, each of whose components was systematically modified to determine the resulting effect on the final properties, in particular tactile feeling, slip and stain resistance, and gloss, which allowed the effect of each raw material to be quantified. The glaze surface was characterised by scanning electron microscopy (SEM) and X-ray diffraction (XRD), a good correlation being found between the surface texture observed by SEM and slip resistance. In contrast, these properties were not entirely related to the crystalline phases present in the surface, owing to the different size and morphology of the crystals that formed, the preferred orientation of some crystals that intensified X-ray reflections, as well as to the apparent viscosity of the glaze.

1. INTRODUCCION

Glazed porcelain tile manufacture has grown very significantly in recent years, mirroring increased porcelain tile applications both indoors and outdoors [1]. Use of these tiles as flooring requires optimisation of tile surface properties in order to adapt these to the technical demands of intended use and to the requirements of the end-users. Thus, glazes are being demanded that provide a matt finish with high slip resistance, but which is also simultaneously smooth to the touch and has high stain resistance.

These properties depend, beside the application and firing conditions, on the mixture of raw materials making up the glaze and on their particle size [2]. The mixtures are usually made up of frits, which define the resulting type of glaze (glossy, matt, opaque, translucent, etc.) and its basic properties [3], in addition to different crystalline raw materials that modify these properties [4, 5].

During the firing stage, numerous physico-chemical changes take place that are responsible for the final properties of the glazes [6,7]. Thus, depending on their chemical composition, frits can devitrify larger or smaller amounts of crystalline species, such as silicates and aluminosilicates; feldspars foster glassy phase formation, while corundum usually acts as an inert material [8, 9]. In addition, in the contact areas between different particles, new crystalline phases can form that also contribute to the final properties of the tiles [10].

The complexity of these systems made up of different frits and crystalline raw materials makes it necessary to use a specific methodology for obtaining all the properties demanded of the glazes. In addition, depending on the frits used, the resulting properties change, as does the effect of each crystalline raw material introduced into the glaze. In this study, the effect of four crystalline raw materials customarily used in these glazes: wollastonite, corundum, sodium feldspar, and clay, has been quantified.

2. EXPERIMENTAL

2.1. MATERIALS

The study was conducted using two base glazes customarily used in porcelain tile manufacture that provided matt finishes. The glazes were formulated with different frits and crystalline raw materials. One glaze contained a frit with barium, while the other was formulated with a mixture of calcium–magnesium frit and a zinc-containing reactive frit. The following table details the composition of the two base glazes.

	PF-026/7	PF-026/9
Barium matt frit	40	
Calcium–magnesium matt frit		30
Zinc reactive frit		10
Wollastonite	13	16
Corundum (d_{90}: 28µm)	6	6
Nepheline	17	
Kaolin	10	10
Sodium feldspar	7	18
Clay	7	8
Zinc oxide		2

Table 1. *Base glazes studied.*

To study the effect of the crystalline raw materials on the final properties of the glaze, both compositions were modified by increasing and reducing each of the raw materials in a range of ± 50%, maintaining the proportion between the rest of the raw materials in each composition. The references assigned to the compositions in which each raw material was modified were as follows:

- Wollastonite (Wo)
- Corundum (Co)
- Sodium feldspar (Fd)
- Clay (Ar)

2.2. EXPERIMENTAL PROCEDURE

2.2.1. PREPARATION OF TEST PIECES

Glazes were prepared from the raw materials by wet milling, at a solids content of 70% by weight, in a laboratory planetary grinding mill with alumina balls, using sodium carboxymethylcellulose as binder and sodium tripolyphosphate as deflocculant, both in a proportion of 0.2% by weight relative to the solid. The mixtures were milled until a residue of about 1% by weight was obtained on a sieve with a mesh opening of 45 µm.

Each glaze was applied on a green engobed industrial porcelain tile body using an applicator with an opening of 450 µm. The glazed pieces were fired in a pilot combustion kiln at a peak temperature of 1210 ºC.

2.2.2. SURFACE CHARACTERISATION

Surface gloss was determined using a reflectometer and the measurements were made at an angle of 85°. The test pieces were then classified according to their degree of asperity by tactile evaluation, carried out by a group of 8 individuals accustomed to making this type of assessment. The classification was performed on the set of 18 test pieces corresponding to the types of glazes and their modifications, assigning number 1 to the least asperous and number 18 to most asperous surface.

Slip resistance was determined in accordance with the method described in standard UNE 41901 EX:2017 "Surfaces for pedestrian transit. Determination of the slip resistance by friction pendulum method. Wet test".

Stain resistance was determined by measuring the chromatic coordinates L*, a*, and b* of the glaze surface and then brushing on a mixture of olive oil and active coal that remained in contact with the glaze for 7 days. This was then cleaned by hand with a cloth dampened in water, and the chromatic coordinates L*, a*, and b* were determined again. Dirt retention was quantified on the basis of the colour difference (ΔE) of the surface, before and after staining.

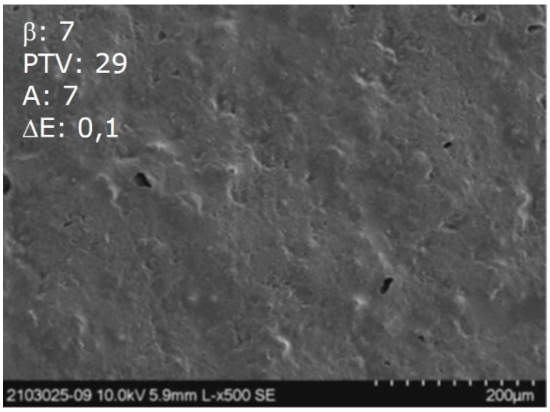
2.2.3. MICROSTRUCTURAL CHARACTERISATION

Observations were carried out of the surface of the samples by scanning electron microscopy (SEM) to evaluate the surface texture of the pieces using the secondary electron signal, and also in cross-section in order to observe the morphology and composition of the crystals using the backscattered electron signal. The crystal structures were identified by X-ray diffraction on the surface of the pieces (Bragg–Brentano geometry), using a BRUKER Theta-Theta D8 Advance diffractometer. To do so, the test conditions established in the powder crystal method were maintained in order to obtain an overview of the crystalline phases that were forming in the glaze surface.

3. RESULTS AND DISCUSSION

3.1. CHARACTERISATION OF THE BASE GLAZES

Figure 1 shows the appearance of the surface of the base glazes by scanning electron microscopy at 1500 magnifications, and includes the gloss values at 85° (β), slip resistance (PTV), asperity (A) and dirt retention (ΔE). Glaze PF-026/7, obtained with the barium frit (Figure 1, left), exhibited lower gloss and higher slip resistance than glaze PF-026/9, obtained with the calcium–magnesium frit (Figure 1, right), but lower asperity and dirt retention. This indicated that, depending on the glaze composition, the same level of slip resistance could be obtained with different tactile feelings. Gloss and slip values were observed to match the visual appearance of the surface, in which the glaze with the barium frit (PF-026/7) exhibited a texture with protuberances.



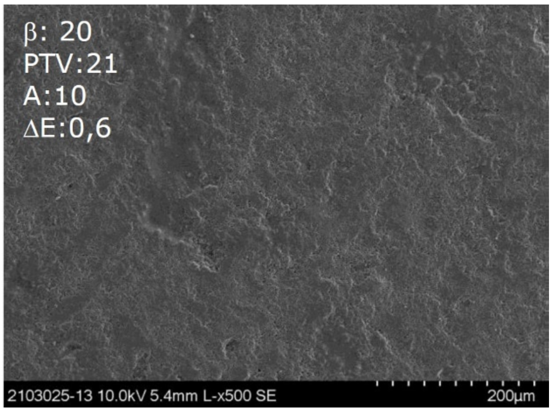


***Figure 1**. Micrographs of the surface of glaze PF-026/7 (left) and PF-026/9 (right).*

To understand the reasons for the different surface properties of the two glazes, the crystalline phases present were determined, whose peak areas are detailed in Table 2, and their cross-section was observed by SEM (Figure 2). The glaze with the barium frit was observed to contain mainly hyalophane ($(K,Ba)Al(Si,Al)_3O_8$) and anorthoclase ($(Na,K)AlSi_3O_8$), whereas the glaze with the calcium–magnesium frit exhibited plagioclase ($(Ca,Na)Al_2Si_2O_8$) and diopside ($MgCaSi_2O_6$). Both glazes contained residual corundum. Hyalophane devitrified in cubic crystals of about 5 µm, whereas anorthoclase did so in the form of acicular crystals of very small thickness (0.5 µm). Plagioclase crystals displayed a variable morphology, ranging from tabular to acicular. Finally, diopside and residual corundum exhibited equidimensional crystals smaller than 15 µm.

Glaze PF-26/7, which exhibited the highest slip resistance and lowest gloss, also contained a larger amount of crystalline phases than glaze PF-026/9.

These crystalline phases could stem from frit devitrification, the presence of very refractory raw materials (such as corundum), or from reaction between different raw materials in the glaze. With a view to determining the importance of the interactions between the raw materials in crystalline phase formation, the crystalline phases of glazes made up only of frit and kaolin were identified. These two new glazes have been referenced by adding the letter “F” to their reference.

The results indicate that, for glaze PF-026/7, hyalophane devitrified exclusively from the frit, as it was the only raw material that contributed barium to the glaze, whereas anorthoclase (which contained Na and K) possibly crystallised from raw materials such as nepheline that already contained orthoclase in its composition.

For glaze PF-026/9, diopside devitrified from the Ca–Mg frit because it was the only raw material that contributed Mg, while plagioclase crystallised both from the frit and from the reaction between the other raw materials in the glaze, which could explain the different crystal morphologies (tabular/acicular).

Glaze	Hyalophane	Anorthoclase	Plagioclase	Diopside	Corundum	Amorphous
PF-026/7-F	80					20
PF-026/7	50	23			5	22
PF-026/9-F			40	30		30
PF-026/9			52	4	5	39

Table 2. *Crystalline phases present in the glazes (% by weight).*

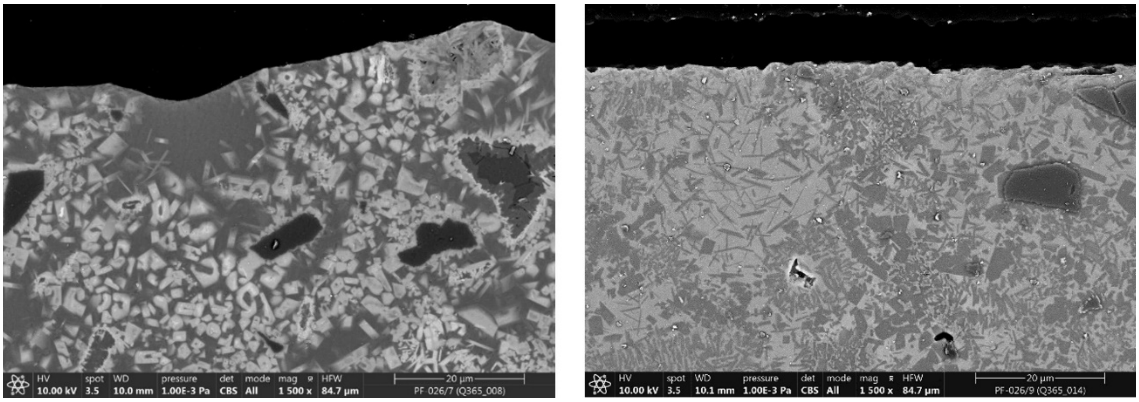


Figure 2.*Micrograph of the cross-section of glaze PF-026/7 (left) and PF-026/9 (right).*

Finally, mappings were made of both base glazes to identify the position of the elements present in the crystalline phases. Figure 3 shows the surface appearance of glaze PF-026/7, together with one of the mappings made displaying the distribution of the elements present in the hyalophane (Ba, K, Si, and Al). More-textured areas (light zones), in addition to areas with a smoother surface (dark zones), may be observed. The image on the right shows the distribution of the elements in the hyalophane, exhibiting a very good correlation between the Ba distribution and the textured areas. Blue areas corresponding to residual corundum and the presence of Si and Al in the dark zones where the glass matrix must be located were also detected. These zones also contained concentrations of Ca and Na, mainly from the wollastonite, feldspar, and nepheline (not included in the mapping shown).

In regard to anorthoclase, the distribution of the elements making up the anorthoclase (Na, K, Si, and Al) provided less information, because these elements were contributed both by the frit and by some raw materials such as nepheline and feldspar. However, it was observed in the corresponding mapping (not included) that, while sodium was mainly concentrated in the dark smooth zones (glass matrix), potassium was mainly found in the textured zones. These zones, besides corresponding to what were initially frit particles, could also be related to nepheline particles, rich in Na and K, especially considering that this raw material already contained orthoclase.

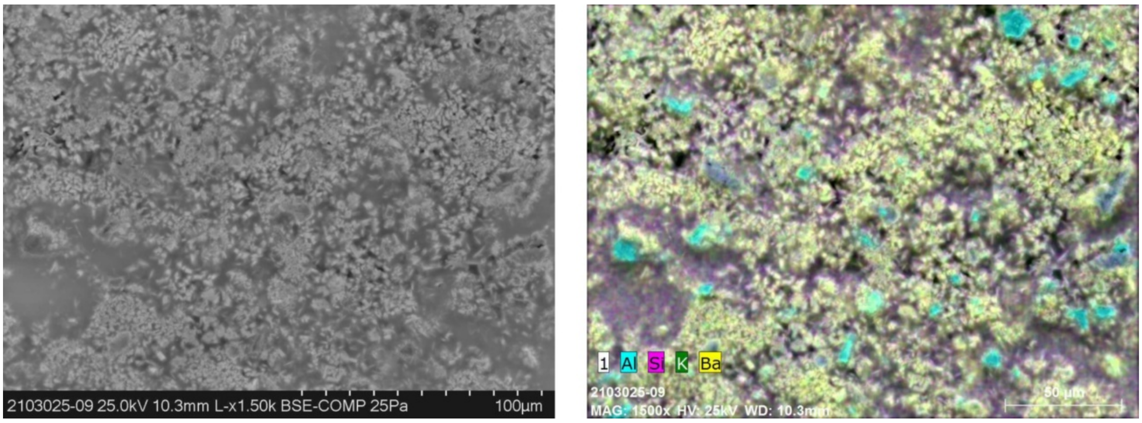


Figure 3. *Micrograph of the surface of glaze PF-026/7 (left) and mapping (right).*

Figure 4 shows the appearance and mapping of glaze PF-026/9 in which Ca was concentrated in the textured area, while Na, K (not included in the image) and Si were concentrated in the smoother zone. A part of the plagioclase crystals devitrified from the frit. However, the presence of raw materials with high Na and Ca contents (Fd and Wo) also facilitated plagioclase formation to the detriment of diopside, given the larger plagioclase and smaller diopside content in the base glaze with respect to the glaze with just the frit.

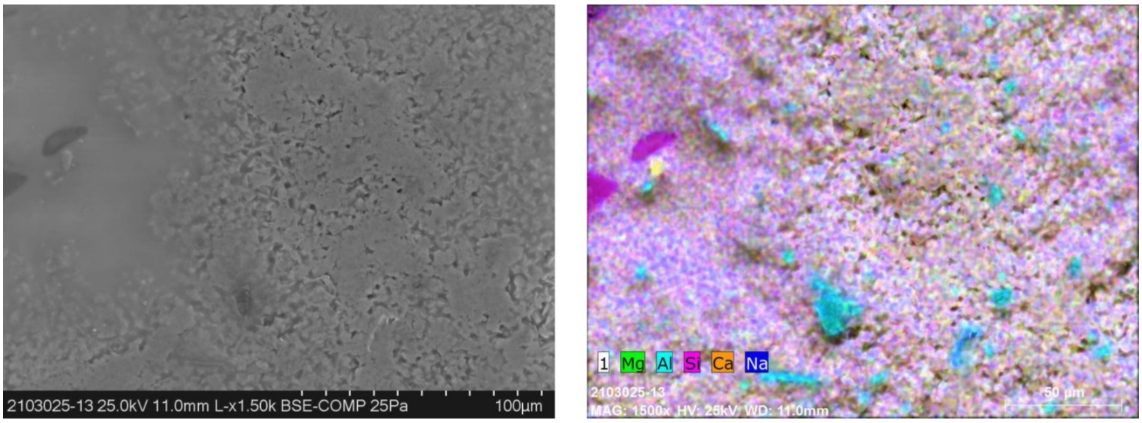


Figure 4. *Micrograph of the surface of glaze PF-026/9 (left) and mapping (right).*

3.2. INFLUENCE OF THE RAW MATERIALS IN THE TEXTURE AND CRYSTALLINE PHASE CONTENT

Figure 5, Table 3, and Table 4 show the appearance of the surface texture of the two base glazes on decreasing (left) and on increasing (right) the content of each raw material, as well as crystalline phase content. The following trends were observed:

- The increase in wollastonite content provided smoother textures in both glazes. For glaze PF-026/9, this greater smoothness could be related to a decrease in crystalline phase content, especially that of plagioclase, which indicates that, although wollastonite contributed a great amount of Ca, it largely fostered glassy phase formation in this glaze. However, for glaze PF-026/7, the increase in wollastonite led to an unexpected increase in hyalophane and decrease in anorthoclase, giving rise to a drop in glassy phase content.
- Corundum raised surface roughness as very refractory particles were involved, which remained after firing, as detected by XRD. Although the other crystalline phases would be expected to decrease proportionally with the increase in corundum, a slight increase in anorthoclase in glaze PF-026/7 and in plagioclase in PF-026/9 was observed. SEM observation of the cross-section of both base glazes (Figure 2) revealed that a significant number of crystals had formed at the boundaries of the corundum particles, which could explain the rise in Al2O3-containing crystalline phases, as has been verified elsewhere [11].
- Raising feldspar content gave rise to surfaces with a slightly smoother texture, particularly for glaze PF-026/9 with a larger feldspar content. This glaze exhibited the only noteworthy change in crystalline phase content, namely a decrease in diopside, which could explain its smoother texture.
- Finally, the increase in clay content generated slightly more-textured surfaces in the SEM images. In this case, the effect of the SiO_2 and Al_2O_3 contribution had a different effect, depending on the type of glaze. Thus, for glaze PF-026/7, crystalline phase formation decreased, whereas no noticeable changes were observed for glaze PF-026/9.

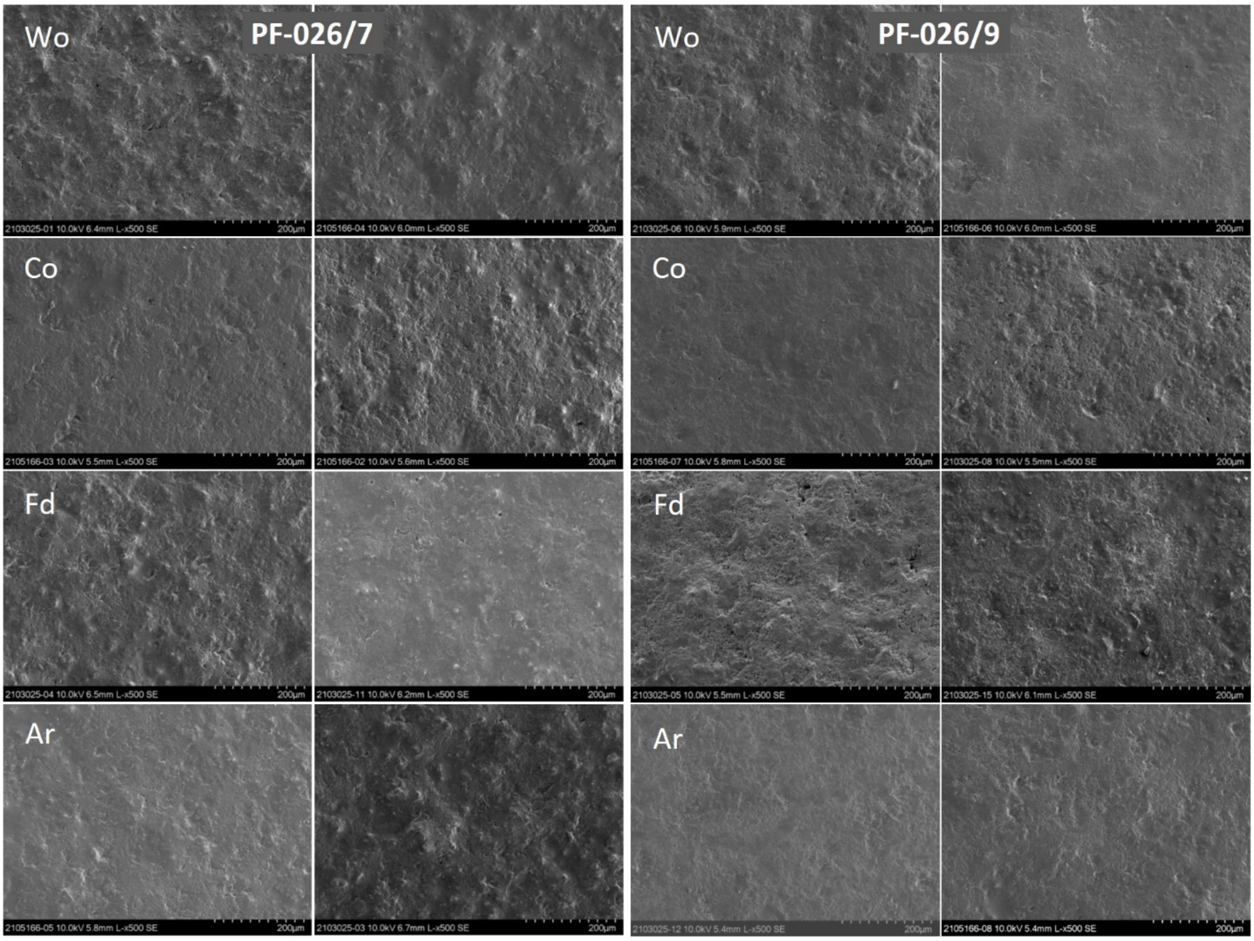


Figure 5. *Micrographs of glaze PF-026/7 and PF-026/9 with a different content (left: decrease and right: increase) of each raw material.*

	Decrease			Increase		
	Hyalophane	Anorthoclase	Corundum	Hyalophane	Anorthoclase	Corundum
Wo	51	20	5	62	15	4
Co	63	17	2	51	22	7
Fd	48	23	5	48	22	5
Ar	56	22	5	45	21	5

Table 3. *Crystalline phases present in the glazes of the PF-026/7 series (% by weight).*

	Decrease			Increase		
	Plagioclase	Diopside	Corundum	Plagioclase	Diopside	Corundum
Wo	78	4	6	49	3	5
Co	50	4	3	60	6	8
Fd	56	14	6	52	3	5
Ar	57	6	5	57	5	6

***Table 3**. Crystalline phases present in the glazes of the PF-026/9 series (% by weight).*

This difference between glaze surface appearance and crystalline phase content detected by XRD could be due to several reasons. On the one hand, to the size and shape of the crystals in each crystalline phase. Thus, for example, in glazes of the zirconium white type, as the devitrified zircon crystals exhibit a small size, they do not generate texture in the glaze surface [12], while in aluminosilicate glazes, in addition to being larger, they can sequester fluxing cations in the glassy phase (alkalis and alkaline earths), increasing glaze viscosity and texture. On the other hand, when addressing the quantification of crystalline phases, one of the specific casuistries to be taken into account is the possibility that some of these phases may develop a preferred orientation, i.e. have a high signal in some of the reflections of their diffraction pattern, which happens more frequently on conducting random surface tests on the powder. In some of the diffractograms obtained, the phenomenon of anomalous intensities at some diffraction angles was noted, so that preferred orientation phenomena were taken into account in quantification. When the corresponding mathematical fits were made, it was noted that, for some samples, the change in intensities at some of these angles was so high that it could not be solely due to crystal orientation, but that it must be related to preferred crystal growth at the surface along one direction. This fact was validated by XRD analysis on polished and on unpolished surfaces. Finally, as the glassy phase composition defined glass viscosity, it also had a certain influence on surface texture.

3.3. INFLUENCE OF THE RAW MATERIALS ON SURFACE PROPERTIES

This section details the results corresponding to the influence of each raw material on gloss and slip resistance. The dirt retention values are not displayed owing to the low value obtained in all glazes ($\Delta E<1$).

3.3.1. GLOSS

Figure 6 shows the evolution of gloss of the two glazes with the content in each of the raw materials. In general terms, the effect of each raw material on gloss was the same for both glazes. However, owing to the different glaze composition and to the different content in each raw material in the glaze, the magnitude of the effect changed. It was thus observed that, while wollastonite and feldspar raised glaze gloss, corundum and clay lowered it. The gloss changes were consistent with the surface texture of the test pieces (Figure 5), as feldspar and particularly wollastonite provided smoother textures while corundum and clay produced greater roughness.

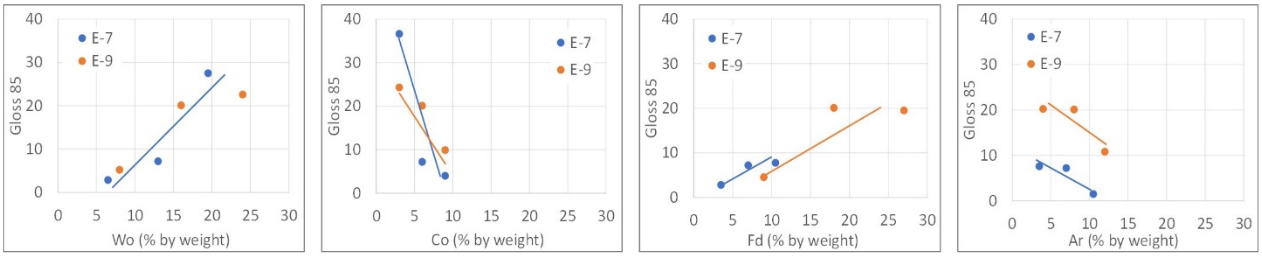


Figure 6. *Influence of the variation of each raw material on gloss.*

3.3.2. SLIP RESISTANCE

The slip resistance results (Figure 7) indicate that wollastonite and feldspar lowered slip resistance, whereas corundum and clay raised it. These trends, as was to be expected, were opposite to the gloss trends and, in general terms, they matched the texture of the pieces observed by SEM.

Figure 7

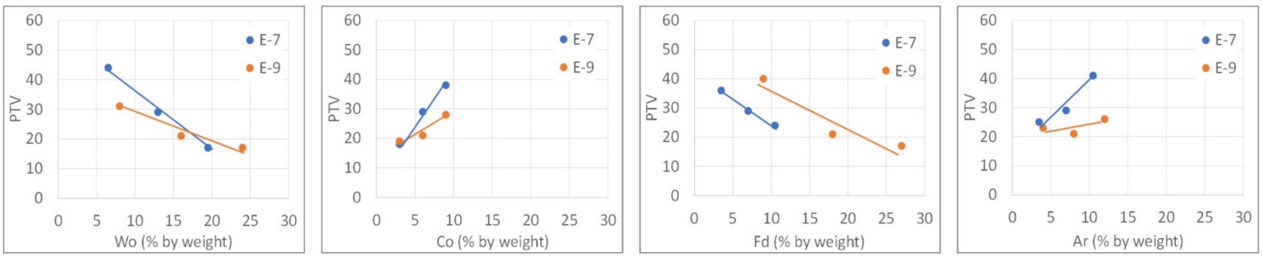


***Figure 7**. Influence of the variation of each raw material on slip resistance.*

3.3.3. TACTILE FEELING AND DIRT RETENTION

The tactile feeling results exhibited a greater scatter, even though the averages of 8 evaluators were used. However, it was clearly observed for both glazes that wollastonite reduced surface asperity, whereas clay and particularly corundum increased it. Feldspar did not give rise to any important changes in glaze asperity.

With regard to dirt retention, the glazes of the PF-026/7 series exhibited very low ΔE values (<0.5), while for those of the PF-026/9 series, though wollastonite had no significant effect, corundum raised dirt retention, feldspar only lowered it at high contents, and clay raised ∆E when clay content was low.

3.3.4 QUANTIFICATION OF THE EFFECT OF EACH RAW MATERIAL ON SURFACE PROPERTIES

A multiparameter fit was carried out using linear equations to parameterise the effect of each raw material on gloss and slip resistance, which allowed the effect of each raw material to be quantified by a coefficient. It was observed that, while the values of the calculated PTV fitted well to the experimental data, the gloss values exhibited a greater scatter as their evolution did not follow such a linear trend as observed for slip resistance.

The raw materials with negative values for the PTV coefficients were wollastonite and feldspar, particularly for glaze PF-026/7, while corundum and clay yielded positive values for the PTV coefficient, especially also for glaze PF-026/7. The effect of the frit was different, depending on the type of glaze. Thus, for glaze PF-026/7, the barium frit provided a negative coefficient that was close to zero, which indicated that the devitrified hyalophane did not contribute significantly to improving slip resistance, which is consistent with glazes containing barium frits providing a smoother texture. For glaze FP-026/9, both frits provided positive coefficients, which meant that devitrified plagioclase contributed to enhancing slip resistance. The values of the gloss coefficients for crystalline raw materials followed the opposite trend to that mentioned previously, given the inverse relationship between both properties.

The results indicate that, for both glazes, corundum was the raw material that most improved slip resistance, followed by clay. With respect to gloss, wollastonite most increased gloss, followed by feldspar.

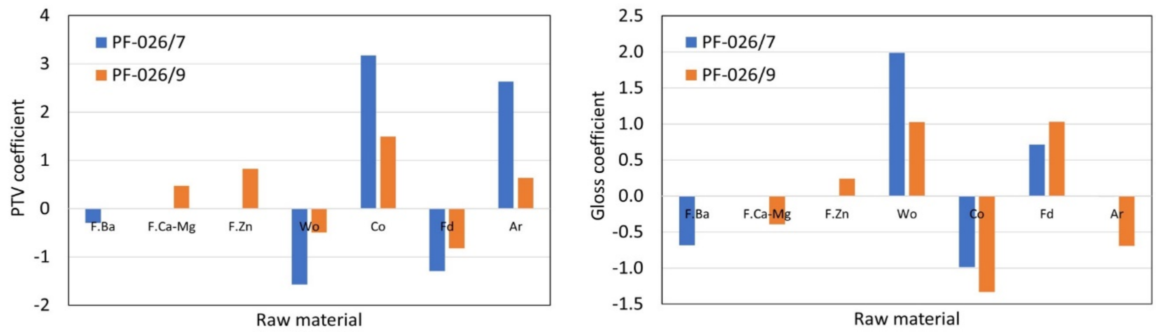


***Figure 8**. Coefficients of the multiparameter fit for PTV (left) and gloss (right).*

3.3. RELATIONSHIP BETWEEN CRYSTALLINE PHASE CONTENT AND SURFACE PROPIERTIES

The size and shape of the crystals in the glaze, as well as glaze apparent viscosity at high temperature significantly affected glaze surface appearance, so that slip resistance and gloss values could not be directly related to crystalline phase content. On the other hand, for glaze PF-026/7, crystal orientation in the surface generated a data bias that made it difficult to establish these relationships, which is why only the results corresponding to glaze PF-026/9 are set out in this section.

A multiparameter fit was carried out again to estimate the effect of each crystalline phase on surface properties, a good fit being obtained for both slip resistance and gloss.

For this glaze (Figure 9Figure 9), diopside was the crystalline phase that most changed its properties, as it exhibited the highest values (positive or negative) for both coefficients. Corundum and plagioclase had a similar albeit lower effect on slip resistance and gloss. Finally, glassy phase did not contribute to improving slip resistance and noticeably increased gloss.

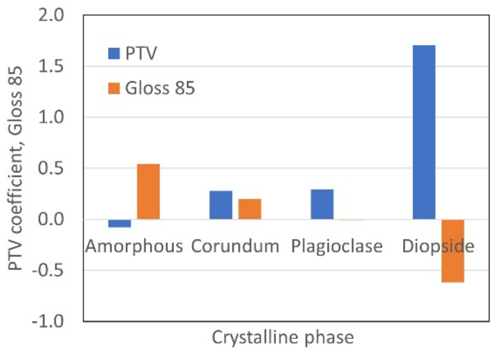


Figure 9. *Fit coefficients for PTV and gloss.*

4. CONCLUSIONS

The main conclusions drawn from this study were as follows:

- The surface texture of glazes observed by SEM correlated quite well with gloss and slip resistance. In contrast, both properties did not relate well to the crystalline phases detected by XRD in the glaze surface. The influence of crystal morphology and size, crystal orientation and growth in a preferred direction, and glaze apparent viscosity at high temperature made it difficult to establish these correlations.
- In the studied glazes, crystalline phases were verified to exist that devitrified exclusively from the frit (hyalophane and diopside), from the crystalline raw materials (anorthoclase), from the frit and raw materials (plagioclase), or that stemmed from the presence of very refractory raw materials that remained after firing (corundum). In addition, when the same crystalline phase had different precursors (frit or crystalline raw material), the crystals exhibited a different morphology, which could affect surface properties.
- The effect of each crystalline raw material on gloss and slip resistance was quantified for the two studied glazes, which allows optimisation of both properties. Thus, wollastonite and feldspar lowered slip resistance and raised gloss on fostering glassy phase formation, while clay and corundum had the opposite effect. The effect of clay must stem from the rise in viscosity of the glassy phase, as it did not foster crystalline phase formation, while the effect of corundum was due to its high refractoriness and its interaction with the glassy phase to form aluminosilicates in the surface.
- The Ba frit used did not contribute to improving slip resistance, whereas the frits containing Ca–Mg and Zn did.
- It was observed that, for glaze PF-026/9, the diopside that devitrified from the frit had a noticeable influence on slip resistance and gloss, followed by plagioclase and corundum.

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