STUDY OF THE ADDITION OF ALUMINA AND SILICA NANOPARTICLES TO A GLAZE FORMULATION FOR POLISHED BRAZILIAN PORCELAIN TILE

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ABSTRACT

This paper assesses the effect of adding alumina and silica nanoparticles to a glaze formulation for polished glazed Brazilian porcelain tiles with the intention of achieving improved stain resistance by reducing surface porosity. In the first phase of the study, ten formulations were prepared - one standard and nine test formulations - , which were subjected to a post-polishing selection process, the main criterion for which was the assessed improvement in surface stain resistance. In surface porosity analysis with an optical microscope, it was observed that adding silica nanoparticles reduced the surface porosity of the glaze and consequently improved the end product's stain resistance. The results of adding alumina nanoparticles revealed an increase in porosity, worsening the end product's stain resistance. The three formulations with the lowest surface porosity together with the standard one were selected for supplementary tests, involving: X-ray diffractometry, differential scanning calorimetry, thermogravimetry, dilatometric analysis and scanning electron microscopy. Through thermal expansion and half-sphere temperature tests, it was possible to obtain measurements of theoretical viscosity by using the Vogel-Fulcher-Tammann formula and to demonstrate dilatometric softening, Littleton softening and flow point at lower temperatures in materials when silica nanoparticles are added. The formulation that returned the best value for money, mainly relating to the reduction in glaze porosity and other physico-chemical characteristics (formula with 5% silica nanoparticles) was subsequently selected for factory-scale production, where the results obtained in the laboratory were confirmed, i.e., the surface porosity of the polished glazed porcelain stoneware tiles was reduced.

1. INTRODUCTION

One handicap in terms of commercial success that polished porcelain stoneware tiles suffer has always been their poor rating in what is popularly known in the industry as "stain resistance". This problem is mainly due to the polishing that takes place in the final stage of the industrial process. Abrasive polish removes a thin layer of glaze, thus exposing pores left closed after sintering. When they come into contact with the environment, these pores retain dirt that is difficult to remove [1,2,3]. The number and size of the pores depends on different factors, such as particle packing in the glaze layer, glaze reactivity with the substrate, possible devitrification during firing, or the retention of gases, among others. Therefore, efforts to minimise porosity can provide a considerable competitive edge and are to be encouraged [4,5]. To that end, the ceramic glaze used for polished porcelain stoneware plays an important role in end product quality, as its characteristics, such as stain resistance, abrasion resistance and chemical resistance, define the porosity and therefore the quality of the final surface after polishing [6].

Research on nanomaterials added to ceramics shows that it is possible to improve the physical and chemical properties of the materials in which they are included [7,8,9]. Given the significant benefits that nanoparticles can provide to the characteristics of the finished ceramic tile, this study aims to assess how adding nanoparticles of alumina and silica affects the stain resistance of a glaze formulation for polished Brazilian porcelain tile [7,8,9].

2. MATERIALS AND METHODS

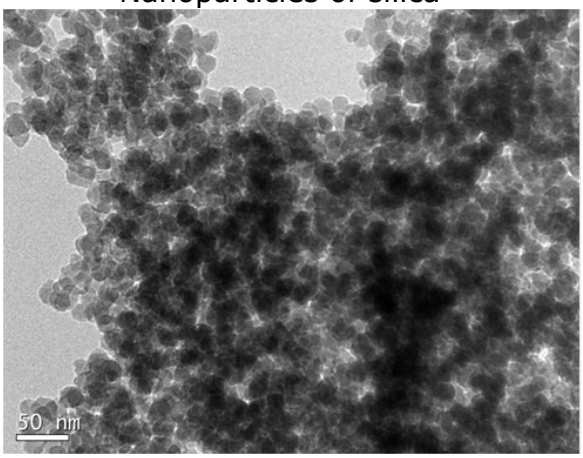
Initially, a floor tile glaze was prepared by wet milling from commercial grade raw materials. The oxide composition of the prepared glaze is shown in Table 1.

SiO_2	Al_2O_3	CaO	ZnO	Na_2O	P_2O_5	MgO	K_2O
58.19	17.28	10.1	6.53	3.8	1.51	1.26	0.92

Table 1. *Chemical composition in oxides of the tested glaze (% by weight).*

The nanometric materials (nano silica and nano alumina) were already dispersed in an aqueous medium when supplied, with a total solids percentage of 40% for nano silica and 20% for nano alumina. Figure 1 illustrates the sizes of the silica and alumina nanoparticles obtained with the transmission electron microscope (TEM), where the predominant particle size was below 50 nm, i.e., within the nanometric size range.

Nanoparticles of silica



Nanoparticles of alumina

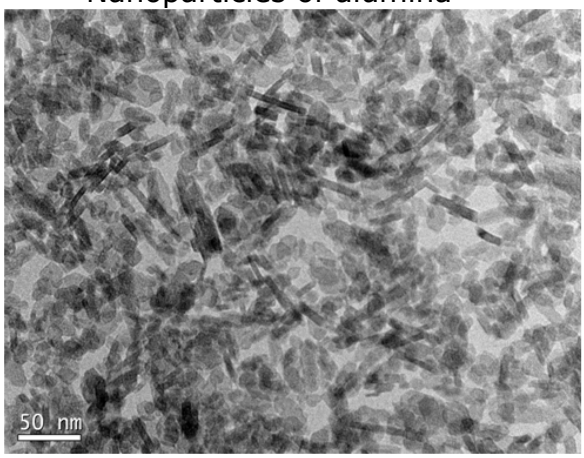


Figure 1. *Transmission electron microscopy of the silica and alumina nanoparticles.*

Ten formulations were then prepared, as shown in Table 2, following a ternary diagram model (glaze-silica-alumina), with the ceramic glaze vertex ranging between 90% and 100%, while the silica and alumina nanoparticle vertices ranged between a minimum value of 0% and a maximum value of 10%.

Formulations	1	2	3	4	5	6	7	8	9	10
Glaze	100	90	90	95	95	90	93.3	91.6	91.6	96.7
Silica nanoparticles	0	10	0	5	0	5	3.3	6.7	1.65	1.6
Alumina nanoparticles	0	0	10	0	5	5	3.3	1.6	6.7	1.6

Table 2. *Ceramic glaze compositions with added nanoparticles of silica and alumina.*

Once the formulations had been prepared in the form of ceramic suspensions, they were applied on a compacted ceramic substrate. Green workpieces were removed from the production line coated with a layer of engobe. The glaze was applied using a metal container with two compartments, one for the standard sample (without nanomaterials, formulation 1) and one for the other formulations containing the nano-material additives. The workpieces were fired in an industrial roller kiln, in accordance with standard firing practice for the type of product. A 41-minute firing cycle was used with a residence time of 5 minutes at a maximum temperature of 1225 °C. After firing, the pieces were industrially polished in accordance with the standard polishing process for glazed porcelain stoneware in terms of abrasive composition, speed and other configurations.

The following steps and tests were then carried out:

a) Characterisation of the test specimens after polishing.

b) Selection of the top 3 formulations, mainly as regards porosity and performance relating to the properties under assessment: stain resistance test, impregnation test, porosity counts using Image J software, and gloss determination.

c) The following tests were then performed on the top 3 formulations and the standard formulation: thermal expansion, optical dilatometry, X-ray diffraction (XRD), and scanning electron microscopy (SEM).

d) Finally, the best formulation was selected, based mainly on stain resistance and other physical and chemical characteristics of the glaze.

3. RESULTS AND DISCUSSION

Phase 1:

In an initial analysis, all ten formulations were subjected to an impregnation test to highlight their surface porosity. The specimens whose surface porosity was impregnated with black dye were analysed with an optical microscope. *Image J* software was used to process the images for the binary system, which enabled a pore count to be carried out and the percentage area with porosity to be calculated (Figure 2 and Table 3). The outcome made it possible to define the formulations with the best results.

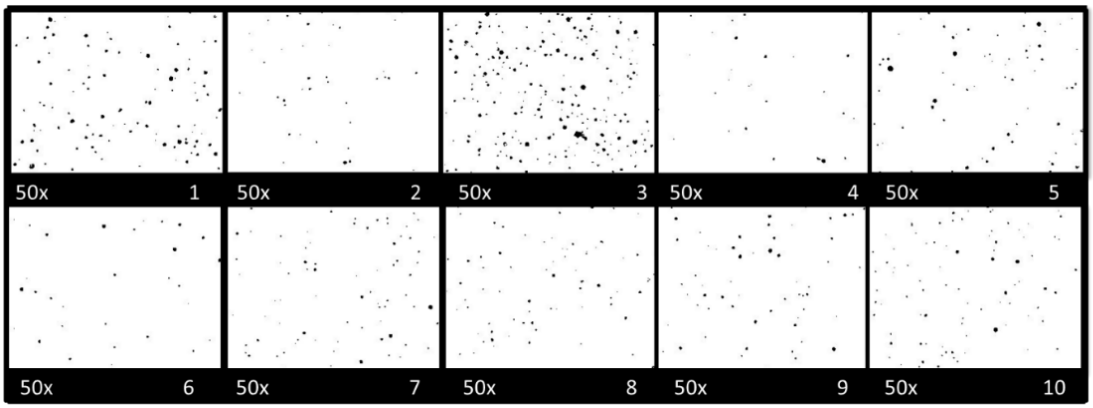


Figure 2. *Testing Surface porosity with Image J software.*

Formulations	1	2	3	4	5	6	7	8	9	10
Area with porosity (%))	1.44	0.26	2.27	0.19	0.57	0.32	0.44	0.44	0.59	0.57
Standard deviation:	± 0.22	± 0.04	± 0.29	± 0.03	± 0.11	± 0.01	± 0.06	± 0.05	± 0.05	± 0.05

Table 3. *Relative surface area with porosity in each of the formulations under study*

From the results obtained, Formulations 2, 4 and 7 were seen to display the greatest reductions in terms of glaze porosity, lower impregnation, and increased gloss.

It is significant that, in all these formulations, nanoparticles of silica were added to the composition. The formulations where only nanoparticles of alumina were added to their compositions - Formulations 3 and 5 with 10% and 5%, respectively, of added alumina nanoparticles – performed the worst in practically all the tests conducted thus far.

In order to understand why alumina nanoparticles induced worse results in terms of the glaze's internal porosity, a density test on the sintered glaze was performed. The formulations used in the test were Formulation 1 (standard), Formulation 4 (5% nano silica) and Formulation 5 (5% nano alumina). Table 4 shows the results of relative density testing after firing, where the formula with added silica nanoparticles revealed an increase in density and a decrease in internal porosity (higher relative density). On the other hand, density in the material with alumina nanoparticles was diminished. The lower porosity achieved by the glazes with added silica nanoparticles (4.8% surface porosity) demonstrates that these nanoparticles do in fact decrease porosity, allowing for a reduction in the end product's tendency to stain. Silica nanoparticles are known to be small in size but with high surface area and surface energy, so that a liquid or vitrification stage is more easily generated during the sintering process, a factor that contributes to the densification of the ceramic glaze. Therefore, adding silica nanoparticles encourages viscous flow during sintering, which contributes to densification [9], thus explaining why shrinkage and bulk density increase in the glaze after sintering when nanoparticles of silica are added.

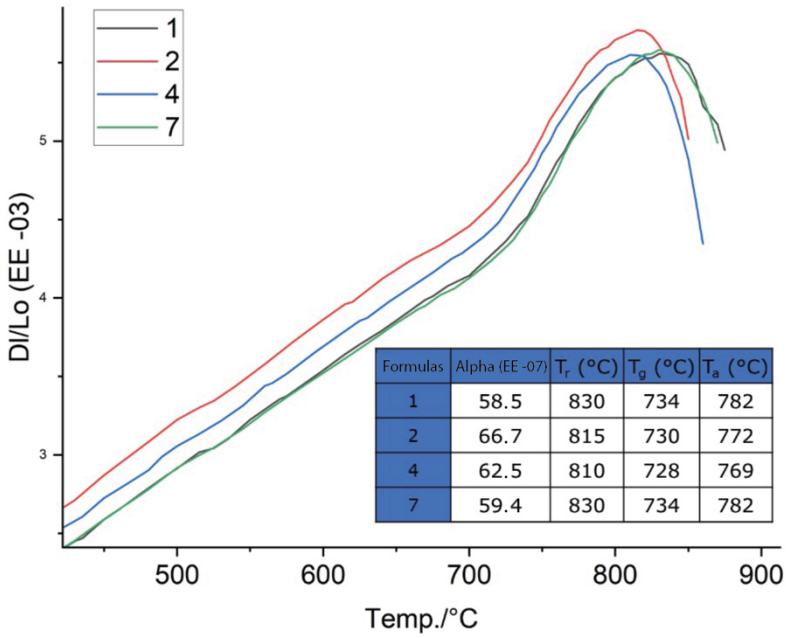
Formulations	Description	Relative density after firing at 1210 °C
1	STD	93.97%
4	5% silica nanoparticles	95.19%
5	5% alumina nanoparticles	93.06%

Table 4. *Results for relative density after firing glazes 1, 4 & 5.*

Phase 2:

In order to optimise work in a second phase, the 3 best formulations in terms of reduced porosity in the glaze, reduced dirt impregnation, and increased gloss were selected. The formulations chosen to pass onto the next stage of comparative analysis with the STD formulation were Formulations 2 (10% nano silica), 4 (5% nano silica) and 7 (3.33% nano silica / 3.33% nano alumina).

Figure 3 shows the dilatometric curves of the glazes in the chosen formulations analysed in comparison with the STD formulation (1), with the results for thermal expansion coefficient (alpha) and the working temperatures to reach the softening point (T_r), glass transition point (T_g), and fit point (T_a) in each formulation.



Formulas	Alpha (EE -07)	T_r (°C)	T_g (°C)	T_a (°C)
1	58.5	830	734	782
2	66.7	815	730	772
4	62.5	810	728	769
7	59.4	830	734	782

Figure 3. *Results of the dilatometric curves for the formulations studied in Phase 2.*

An examination of Figure 3 shows that the glass transition temperature (Tg) decreases in the formulations with added silica nanoparticles. This is in line with what is to be expected regarding the behaviour of glasses with higher silica content in their formulations. As for softening point (Tr), a reduction in the formulations with added silica nanoparticles was also noted. The largest temperature differences were observed at the fit point (Ta) in Formulation 2 (10% nano silica) and Formulation 4 (5% nano silica). This fact demonstrates that these materials acquire a "solid" form at lower temperatures, a phenomenon that leads to easier packing for the glaze particles, which therefore results in greater densification.

Analysing the results for the coefficient of thermal expansion (CTE), it was found that the addition of silica nanoparticles leads to an increase in CTE. The results for Formulations 4 (62.5×10^{-7} °C^{-1}) and 7 (59.4×10^{-7} °C^{-1}) are within the working range, which seeks a smaller coefficient of expansion for the glaze than that of the substrate (66×10^{-7} °C^{-1}), because that property involves a compression effect that increases the end product's crack resistance [10]. In this sense, Formulation 2 (66.7×10^{-7} °C^{-1}) displayed a hint of concave curvature and cracking in the finished product, which indicates that there is a limit to the amount of silica nanoparticles added to ensure no other characteristics in the end product are altered.

Further significant data can be observed from the results of the optical dilatometry using the half-sphere temperature test (Figure 4). From the point of view of surface tension and its correlation with glaze characteristics, Formulation 4 can be said to present greater wettability, which makes working at lower firing temperatures possible. It should be noted that the low shrinkage obtained mainly at higher temperatures worsens the densification of a glaze, which may explain the increase in porosity seen in formulations with alumina nanoparticles. At a working temperature of 1220 °C, Glaze 4 is seen to be the one that densifies best with sintering, as the results presented in Figure 4 show.

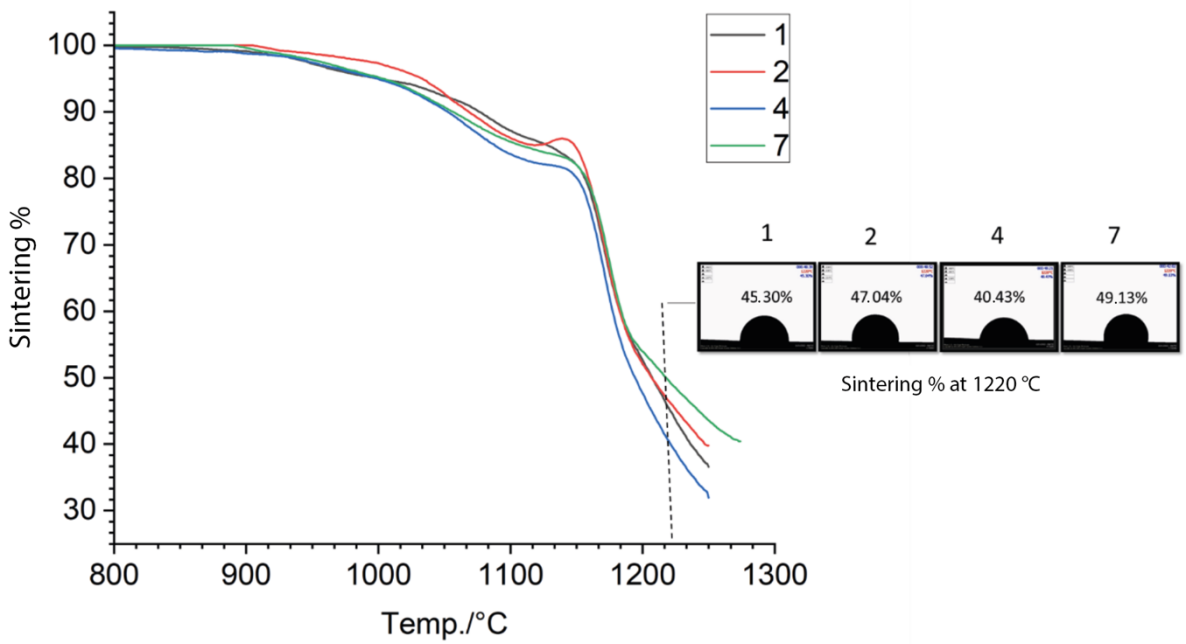


Figure 4. *Sintering curve versus temperature in the formulations selected for Phase 2.*

From the results obtained in the optical microscopy and dilatometry tests, it was possible to calculate the viscosity of the fired glazes using VFT equations. The results are presented in Figure 5.

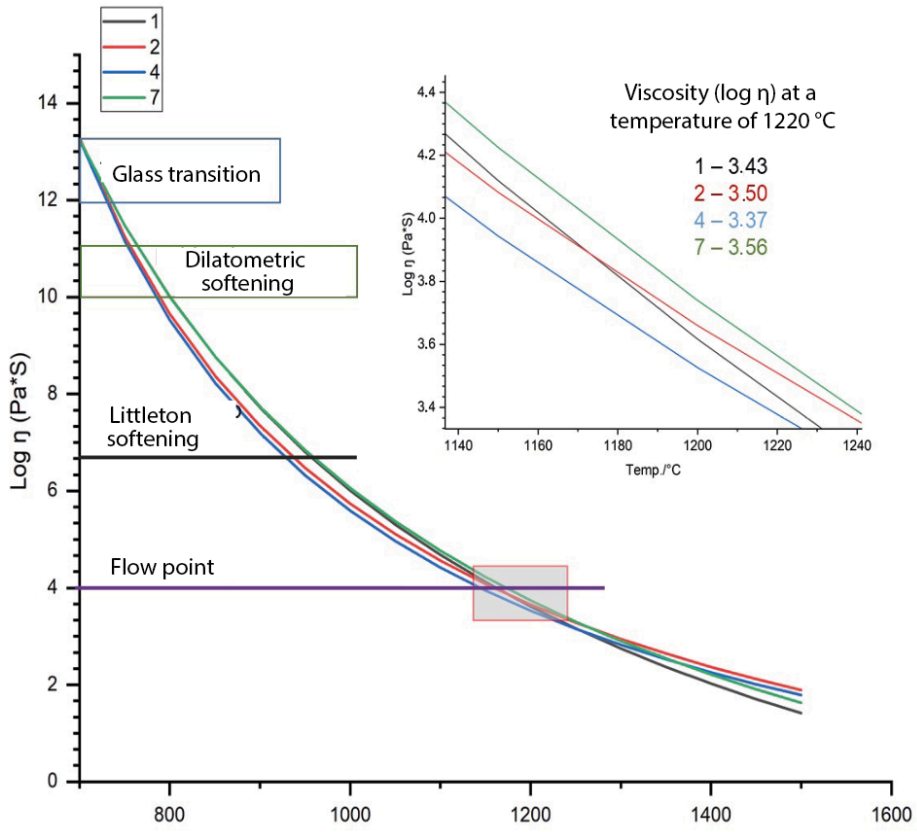


Figure 5. Viscosity in the glazes studied in Phase 2 using the Vogel-Fulcher-Tammann (VFT) formula.

Figure 5 shows the behaviour of flow and Littleton softening temperature following the addition of nanomaterials. Both temperatures decrease when silica nanoparticles are added. In the case of flow temperature, a difference was seen between the standard (1) and silica nanoparticle formulations (2 and 4). This reading is important because flow temperature can be considered as the optimum firing temperature in the kiln, i.e., the temperature at which the glaze reaches the lowest viscosity and thus starts to seal the entire surface of the ceramic substrate. Prior to that point, all gases produced by the reactions in the ceramic substrate and in the glaze need to have been removed via the porosity as the kiln heats up [11]. Littleton softening occurs at an intermediate viscosity between the flow point and dilatometric softening. That point coincides with the glaze maturing temperature, because, as the temperature increases, the glaze starts its viscous deformation due to gravity, i.e., the glaze deforms under the action of its own weight [12,13]. In this case, there was a decrease in Littleton's softening temperature when silica nanoparticles were added to the formulation. The temperature variation between the standard formulation and the 5% and 10% silica nanoparticles formulation was 29 °C and 20 °C respectively. On the other hand, at the working temperature of 1220 °C, lower viscosity was seen in Formulation 4 (Log η = 3.37). The literature cites a log η of between 2.5 and 4.3 as the ideal working range for a glaze and log η = 3.38 as the optimum average value [14]. Values higher than 4.3 do not favour the escape of gas bubbles from the glaze layer, as their mobility is hindered, and values lower than 2.5 allow new bubbles to form due to the excess fluidity of the glaze [15].

The results of the X-ray diffractograms of the formulations presented in Figure 6 demonstrate a quantitative increase in silica in the form of cristobalite and quartz in the formulations, compared to the STD formulation. This increase can be easily understood and correlated with the addition of SiO_2 nanoparticles in the formulations. To identify the peaks, cards 01-070-2517 (Quartz) and 00-027-0605 (Cristobalite) were used.

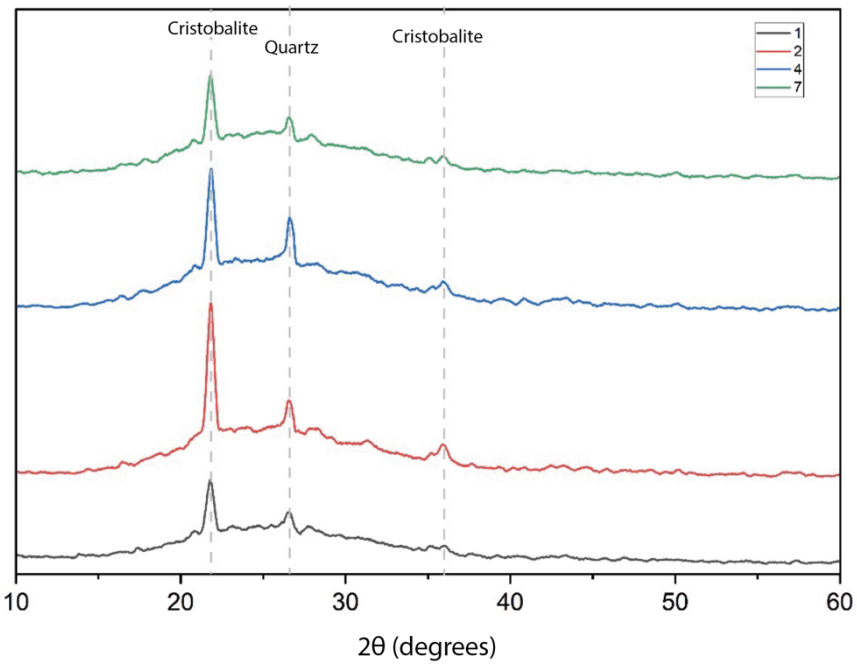


Figure 6. *X-ray diffraction results for the formulations studied in Phase 2.*

It is worth noting from Figure 6 that an increase in silica nanoparticle content led to a significant increase in the maximum intensity of the cristobalite phase, indicating that the amorphous silica nanoparticles crystallised to form cristobalite during firing [9]. The presence of quartz is crucial, as it is one of the components responsible for controlling thermal expansion and adjusting the viscosity of the liquid phase formed during sintering, as well as for facilitating drying and gas release [16]. Therefore, the increase in the amount of cristobalite and quartz phases contributed to the decrease in porosity in the heat-treated glaze.

Apart from the amount of porous area, ceramic tile staining is highly dependent on the average diameter of the open pores present at the surface of the product. In this regard, the critical pore diameter is between 5 and 20 μm. The dye finds it difficult to fill pores with a diameter of less than 5 μm while stains are easily removed from pores with diameters of over 20 μm [17]. It was possible to measure the pore diameter of the formulations using scanning electron microscopy (SEM). Figure 7 analyses the percentage and average diameter of the surface pores. When silica nanoparticles were added, the proportion of pores >20 μm and between 5 μm and 20 μm gradually decreased. On the other hand, the proportion of pores <5 μm gradually increased. This shows that the pore diameters considered to be of critical size decreased in the materials with the addition of silica nanoparticles, thus improving glaze stain resistance. In Formulation 7, an increase in the percentage of critical diameter pores was observed, a fact that relates to the alumina nanoparticles in its composition.

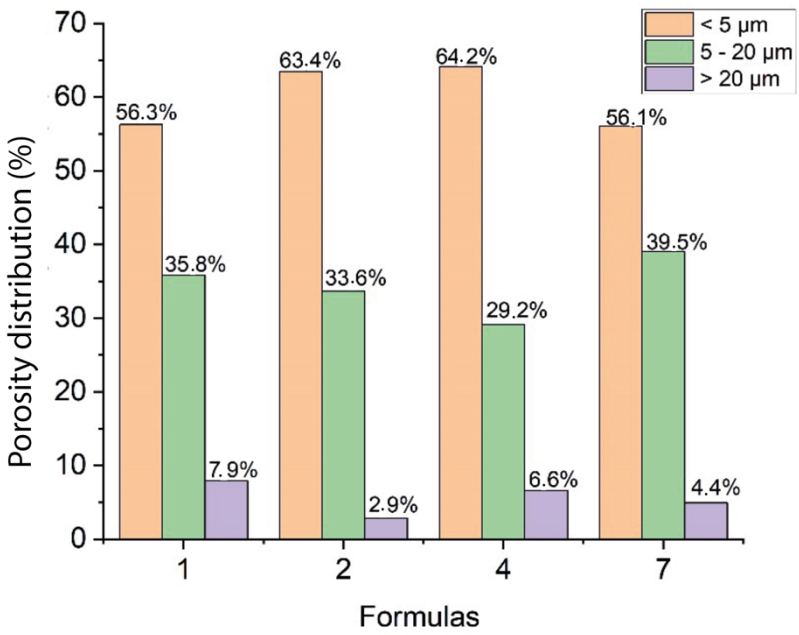


Figure 7. *Percentage and average diameter of surface pores in the glazes in Phase 2.*

4. CONCLUSIONS

On the basis of the results obtained, it can be concluded that:

- The addition of silica nanoparticles influences the sintering and densification of ceramic glaze. When silica nanoparticles were added to the glaze, open porosity and pore size gradually decreased as silica nanoparticle content and bulk density increased. This demonstrates that adding the nanomaterial, which has a high surface energy, promotes viscous flow and volume shrinkage during sintering. In addition, as the nanoparticles group together, they fill the voids between the component particles in the ceramic glaze.
- The amorphous silica nanoparticles crystallised into cristobalite crystals during firing, increasing in quantity as the silica nanoparticle content increased. This crystallisation reduces the viscosity of the quartz glass at high temperatures, thus improving stability.
- The viscosity readings in the experiment at high temperatures for the formulations fit well the VFT viscosity versus temperature equation. Thus, it was possible to determine the temperatures of important characteristic viscosities, which are difficult to measure in the laboratory. This study showed that the flow point and Littleton softening temperatures decreased with the addition of silica nanoparticles, which contributes to better viscous flow at lower temperatures.
- As a supplement to our study, an industrial test was carried out. Standard tests carried out at industrial scale on polished porcelain stoneware with the addition of 5% silica nanoparticles in the glaze show that the glaze meets and improves requirements for these ceramic tiles when tested for crack, stain and acid resistance. The results of these tests show that a glaze with 5% addition of silica nanoparticles performs better than the commercial glaze used as reference.

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