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The influence of particle size distribution on the surface appearance of glazed tiles

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ABSTRACT

Matte glaze was milled in for different times (15–50 min) and the glazes obtained were applied over ceramic bodies which were then fired using an industrial cycle and the final surfaces were analyzed using a glossmeter. The same glazes were also uniaxially pressed, forming cylindrical samples; the specimens were placed on engobe surfaces and fired at 1100 °C in a laboratory oven. The contact angles between the melted specimens and the ceramic surfaces were measured to determine their wettability. The results showed a correlation between the glaze particle size distribution and the surface aspect of the final product.

1. Introduction

Among the rheological properties of glass, viscosity is the most important [1–5]. Viscosity is very sensitive to minor differences in composition, allowing for theoretical studies in glass structure or the evaluation of important glass properties, such as bubble retention, flow over ceramic bodies, quality control, glaze preparation and manufacturing [5,6]. Viscosity controls several processes at different temperatures in tile manufacturing. Its magnitude during firing determines the glaze flow over the ceramic body, forming a uniform layer without draining off the surfaces [6]. Viscosity also determines the facility of gas bubble elimination during glaze formation. Thus, the glaze firing interval is related to the magnitude of viscosity variation with temperature. This variation directly influences the workability, elaboration and relaxation of glasses and glazes [1–5].

Another important property related to glass processing is surface tension. Glaze flow during firing – and its wettability – is strongly influenced by its surface tension [1–4]. Some works exist regarding this matter and current knowledge is comparative and empirical [7–17]. Glass manufacturers have analyzed the influence of surface tension in reactions between glass components and the disappearance of heterogeneities in glass fluids.

A low surface tension favors the elimination of gaseous bubbles during glass melting and prevents non-homogeneities, while a high surface tension favors the reabsorption of these bubbles during glass cooling. In a cast glaze with low surface tension, the glaze surface will be smoother, bubbles and craters will be eliminated easily and the solid surface will be brighter; on the other hand, a very high surface tension favors the reabsorption of bubbles during cooling, causing glaze roughness (like “wrinkles”) [1–4,7–17].

Measuring the surface tension of a matte glaze is quite difficult because the glaze is composed of a melt and crystals. In the bibliography there are methods that are used in order to measure the surface tension of a glass. These methods are mainly three: the drop-weight method, the bubble pressure method and the fiber method [18]. Surface tension of glass can also be estimated using the heating microscope [19], this method being more appropriate in order to estimate the surface tension of a glaze. So, in this work the contact angle is being measured in order to determine the wettability of the glaze.

An industrial property related to surface glazes is their gloss, the property of a surface to directly reflect light [20–23]. Gloss depends basically on surface roughness and absorbance. When gloss is high, it is easy to identify surface defects (flaws); with low surface gloss the defects can be dissimulated and remain hidden. The degree of

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Table 1
Chemical analysis of the glaze composition

Oxide	SiO_2	CaO	Al_2O_3	BaO	B_2O_3	Na_2O	K_2O	LOI
Composition (in wt.%)	58.9	10.0	9.8	7.2	6.5	5.3	2.0	0.3

surface gloss can be measured by observing the light reflection behavior of surfaces using a glossmeter. The numerical values obtained from these instruments correspond to the surface reflection when a light with a defined incidence angle strikes this surface. To obtain good measuring results the surface must be plain, uniform and free from flaws [24,25].

This work shows the influence of particle size distribution on the surface appearance of glazed tiles by the measurement of the surface gloss and the contact angle between the glaze and the tile surface instead of glaze viscosity or surface tension. The contact angle was measured for samples fired in an electric furnace after quenching in air, using a digital camera to take photographs of the fired samples' profile. It is a simple way to obtain information about glaze processing, relating its particle size distribution with its surface quality.

2. Materials and methods

The chemical analysis of the glaze formulation is given in Table 1. The formulation was prepared in an eccentric jar mill, mixed with water (30vol.%) and additives (carboxy methyl cellulose and sodium tripolyphosphate) and milled at eight predefined times: 15–50 min, with 5 min intervals between millings, forming eight particle size distributions (PSD).

The glaze particle size distributions were analyzed using a laser diffractometer (0.5 μm resolution). The glaze suspensions were applied over single fired engobed tiles (grés tiles), with 0.4 mm glaze coat thickness. The samples (the grés tile with engobe and glaze coats) were fired at 1100 °C for 5 min in a laboratory electric furnace. The heating rate was 30 °C/min and the samples were quenched in air. Finally, the specular reflection index of each sample was measured using a glossmeter instrument (60°).

In addition, the eight glaze suspensions were dried forming glaze powders; the powders were uniaxially pressed (50 bar, 5% water, 1 cm diameter and 1 cm height) into cylindrical samples, forming compact specimens placed over single fired engobed tiles (grés tiles) used as substrate material. The specimens were dried at 110 °C for 24 h and fired at the same temperature and condition mentioned above (heating to 1100 °C for 5 min at a heating rate of 30 °C/min in the same laboratory electric furnace and air quenching). The purpose of this step was to compare the glaze melting interval as particle size distribution was altered, measuring the wetting (contact) angle variation.

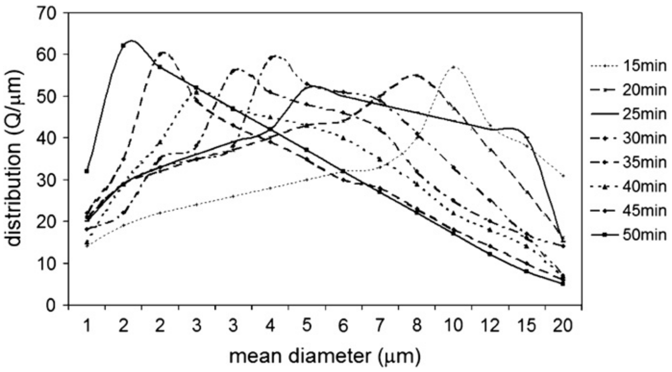

Fig. 1. Glaze particle size cumulative distributions after milling.

After fast cooling (quenching) the profile of the samples was photographed using a digital camera (2 M pixels) and the contact angle was measured on the photographs for a clearer comprehension of the influence of milling (particle size distribution) on the measured internal contact angle θ (wetting angle). As the heat treatment and the substrate used for both the cylindrical samples and the glaze coats were the same, it was assumed that the indirect method of measuring the contact angle correlates with the high temperature values of the surface appearance.

3. Results and discussion

On observing the particle size distribution curves (Fig. 1), all curves present a particle size distribution between 0.9 μm and

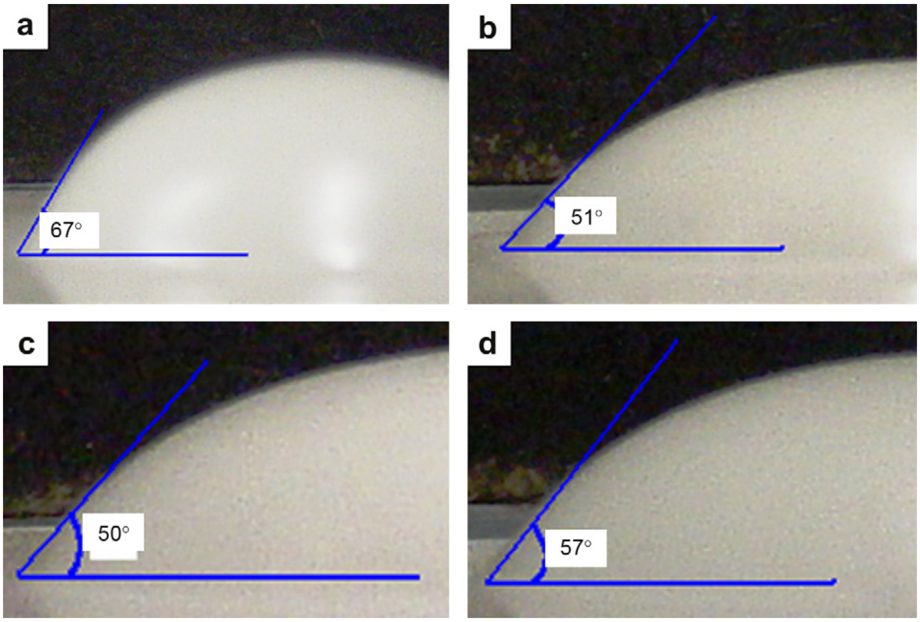

Fig. 2. Contact angles measured for the studied glaze (fired at 1100 °C): (a) 15 min, (b) 30 min, (c) 40 min and (d) 50 min milling.

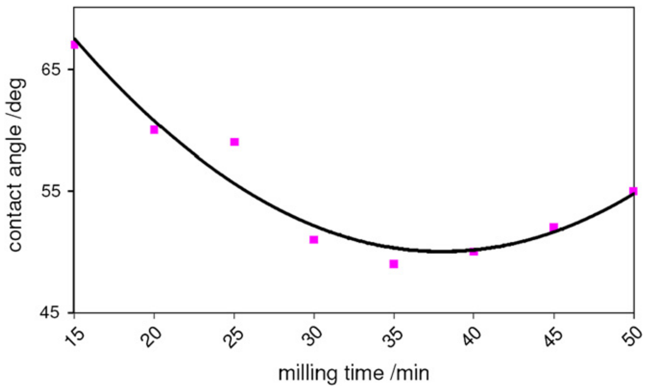

Fig. 3. Glaze wetting angle as a function of its milling time.

20.5 μm; the mean size varies from 2.1 μm to 10.9 μm (average spherical diameter) (Fig. 1).

Particle size clearly influences glaze surface appearance. Excessively milled glazes present an intense shrinkage and crawl when applied to a ceramic body. When a glaze is not sufficiently milled its particles are very large and can segregate during firing, causing defects like surface roughness.

Regarding the contact angle, photographs were taken using a digital camera to measure the wetting angle of the drop at 1100 °C (Fig. 2). The contact angle of the drop diminishes with an increasing glaze milling time up to 35 min. Longer milling times (40 min, 45 min and 50 min) result in an increase of the drop wetting angle. Beginning at 35 min milling time ($D_{50} \sim 3$ μm) the fired samples had presented an increase in the contact angle between the glaze and the tile surface, probably due to a greater interaction of the melted glaze with air during heat treatment [3,6,15–17,25]. This is the reason why the contact angle increased with longer milling times (Fig. 3).

When a glaze is applied to a ceramic body it forms a coat with thousands of drops in contact with each other before firing. During firing if the surface tension between the glaze and the tile surface increases (due to the extreme particle size reduction and glaze composition) a strong interaction between the glaze and air occurs, resulting in air encapsulation by the glaze [3,6,15–17,25]. The glaze coat is filled with air bubbles. Thus, a strong relation between milling time and glaze wetting angle can be observed (Fig. 3).

Finally, each sample was analyzed regarding its gloss. The surface reflection was measured using glossmeter equipment; 10 readings per sample were taken and the average was used to quantify surface gloss (Fig. 4). Analysis of the results showed that specular reflection was directly proportional to milling time; therefore, increased glaze milling time produced a greater magnitude of specular reflection.

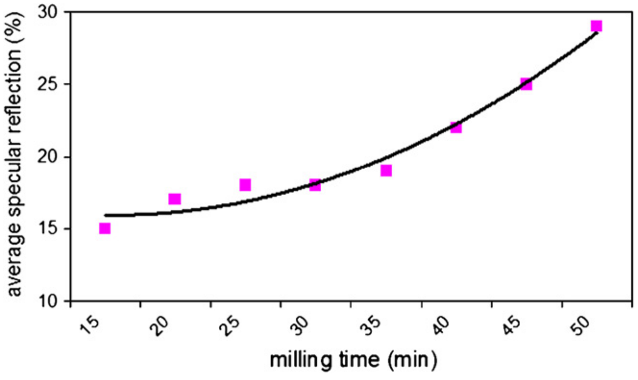

Fig. 4. Glaze specular reflection as a function of its milling time.

As the glaze in question was a glossy matte, the magnitude of the specular reflection was low. Since the particle size has diminished with increased milling time, its surface area increased, thus increasing the contact area between particles. When applied over a ceramic body its surface became smoother and presented small roughness, being stretched. Regardless of the measurement angle used, as the particle size diminished the glaze surface gradually stretched, increasing glaze reflection (Fig. 4).

4. Conclusions

Particle size directly influences the surface appearance of ceramic glazes. The contact angle between the glaze and the ceramic tile was influenced by the particle size of the glaze, probably because the surface tension between the glaze and the ceramic body changed with the milling time. Increased milling times caused significant changes in the wetting angle, due to the increased affinity between the melted glaze and air, which tended to increase the contact angle between the drop (melted glaze) and the ceramic body.

As a result, the glaze coat formed from the smallest particle size can absorb atmospheric air more easily, forming bubbles inside the glaze, probably due to the increase in surface tension between the melt and air. The increase in specular reflection was correlated with diminished glaze particle size, resulting in the reduction of glaze viscosity with temperature, causing greater spreading and uniformity in the glass layer and producing a glaze without roughness.

It must be observed that glaze gloss depends on the surface roughness, which depends on the glaze viscosity and the crystals that are present in the surface of most matte glazes. If a glaze contains crystals, glaze particle size can influence the characteristics of the crystals and thus the glaze gloss [25].

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