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Effect of spray-dried powder granularity on porcelain tile properties

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Porcelain tiles are a ceramic product with high technical and aesthetic performance, whose composition is formulated from a mixture of clay or kaolin, quartz and feldspar. The industrial processing of porcelain tiles consists of various stages such as wet milling, spray-drying, pressing of the spray-dried powder and firing. This paper is a study focusing on determining the influence of the industrially spray-dried powder particle size distribution on technological porcelain tile properties. Five granulometric compositions were prepared artificially with the spray-dried powder: very coarse (VC), coarse (C), medium (M), fine (F), and very fine (VF). The mixtures obtained were formed by pressing at 40 Mpa and fast fired with a maximum temperature of 1220 °C in industrial conditions. The results revealed that the VF composition had better sintering properties, i.e. lower water absorption (0.084%) and porosity, and a higher bending strength (46 N/mm^2) than the other granulometric compositions prepared as a result of a larger amount of spherical regular shaped fine granules in the composition.

Key words: Porcelain tile, Spray drier, Granularity, Porosity.

Introduction

Porcelain tiles are a product with excellent technical characteristics (zero or almost zero apparent porosity, high mechanical strength and frost resistance, high hardness, chemical and stain resistance, etc.) with a broad spectrum of aesthetic possibilities (body coloring with soluble stains, pressed relief, polishing, glazing, etc.) [1]. These technical and aesthetic features have made porcelain tiles a popular product, whose production grows annually [2]. In general, the properties of the product result from its low porosity due to the processing conditions (high degree of milling of raw materials, high force compaction and high sintering temperature), and the potential of the raw materials to form liquid phases during sintering (high densification) [3]. Sanchez et al. [4] reviewed recently the major scientific and technological advances in respect of porcelain tiles, focusing particularly on the developments in raw material compositions, with the introduction of certain key raw materials to enhance the composition quality. Moreover, the interpretation of the unfired body microstructure, and the relation of the unfired tile microstructure to processability and to sintered tile micro-structure and properties have drawn particular attention from the scientific community.

A porcelain tile formulation is based on three major raw materials: clay or kaolin, quartz and feldspar. The clay fraction helps in forming by providing plasticity and dry mechanical strength during processing and forming mullite and a vitreous phase during firing. The feldspar develops a liquid phase at low temperatures and assists the sintering process, allowing a virtually zero (< 0.5%) open porosity and a low level of closed porosity (< 10%). The quartz promotes thermal and dimensional stability thanks to its high melting point [5-8]. Fig. 1 represents compositions of triaxial ceramic products in which a standard composition of a porcelain tile is located [9].

The industrial processing of porcelain tiles covers three main stages: (1) wet milling and homogenization of raw materials, followed by spray-drying of the resulting suspension; (2) uniaxial pressing at 40-50 MPa of the spray-dried powder with a moisture content between 5 and 7%; (3) fast firing for 40-60 minutes at 1180-1220 °C to obtain the maximum densification [5].

Often, the ceramic powders prepared need to be converted into soft agglomerates by spraying a slurry of the powder through the nozzle of an atomizer into a conical chamber

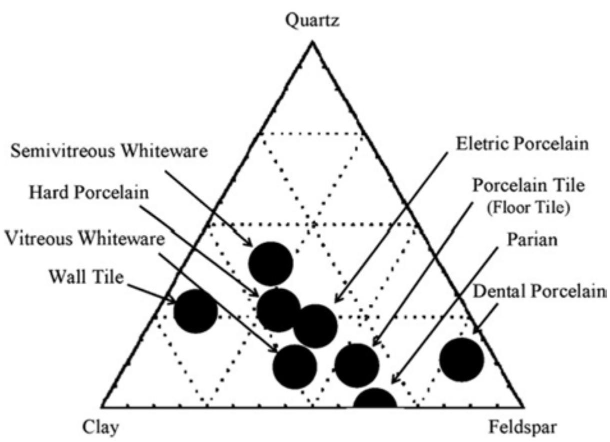

Fig. 1. Composition diagram of triaxial ceramic products including porcelain tile [9].

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(spray dryer) in the presence of hot air. The liquid part of the slurry readily evaporates leaving spherical soft agglomerates having 5-7% moisture and about 30-250 μm diameter [10]. This process leads to the formation of uniform soft agglomerates that flow into the dies used for powder compaction. A slurry of 1 m^3 could be sprayed into billions of droplets with an enormous surface area of 10.000 m^2 [11]. The size of the droplets is controlled by equipment variables such as the nozzle diameter and gas/slurry feed rate, and material variables such as the slurry viscosity and solid content. The resulting powder ideally consists of solid spheres, but if the processing variables are not carefully controlled, hollow spheres or doughnut-shaped particles may result [10]. The typical spray drying system for ceramic applications includes a feed system for pumping the feed slurry to the atomizer, an inlet air system with a heater, a drying chamber with a product discharge, a cyclone collector for fines recovery, a bag filter for air pollution control and an exhaust fan for controlling the air flow through the spray drying system. The mechanisms of types of spray drying equipments are well described in the literature [10-13].

The present work evaluated how the size distribution of spray-dried granules obtained from an industrial scale ceramic plant acts upon the technological properties of porcelain tiles such as bending strength, water absorption, linear shrinkage, and apparent, sealed and total porosities.

Materials and Methods

An adequate amount of the industrial spray-dried product was obtained from Hitit Ceramic Factory situated in Usak, Turkey, which is currently used in the manufacturing of porcelain tiles. A part of the product was dried at 110 °C for 24 h, and then separated by sieving into three granulometric fractions of < 125 μm, 125-250 μm, and > 250 μm. The morphology of the particles comprising these fractions was evaluated in a digital optical microscope using an Olympus BX 60M apparatus.

Five granulometric compositions were then prepared with the spray-dried powder: very coarse (VC), coarse (C), medium (M), fine (F), and very fine (VF). These artificially prepared porcelain compositions contained different percentages of preselected granules, as shown in Table 1.

Table 1. Granulometric porcelain tile compositions studied

Composition	Spray-dried powder (mass%)		
	> 250 μm	125-250 μm	< 125 μm
VC	80	15	5
C	50	25	25
M	35	35	30
F	25	25	50
VF	5	15	80
STD	59.8	32.3	7.9

For the purposes of comparison, a standard (STD) granulometric composition was also evaluated.

The crystalline phase compositions of STD were qualitatively determined by X-ray powder diffraction (XRD) using a Rigaku Rint-2200 diffractometer operating at a tube voltage and current 40 kV and 30 mA, respectively, using monochromatic Cu-Kα_1 radiation (λ = 1.5406 Å). Diffraction patterns were recorded between 5 and 70° 2θ with a scanning rate of 2°/minute. Quantification of different phases was carried out using the computer program MAUD 1.9 [14], which is based on the Rietveld method combined with a Fourier analysis [15]. The chemical composition of the STD samples was determined by X-ray fluorescence (XRF) in a Spectro IQ instrument.

Several 80 × 35 × 7 mm^3 test specimens of each granulometric composition containing 6 mass% moisture content were prepared using a Gabbrielli Titan, Italy mark press under a uniaxial pressure of 40 MPa. The pressed green specimens were dried at 110 °C for 24 h until a constant mass was achieved. The firing of the compositions was carried out in a commercial kiln at the plant within a total firing cycle of 50 minutes (cold-to-cold). During firing, the heating and cooling rates were kept at 50 C.minute^{-1} and at 60 C.minute^{-1}, respectively. The specimens were maintained at a peak temperature of 1220 °C for 6 minutes. After sintering, the firing characteristics (linear shrinkage, water absorption, bending strength, apparent porosity, and total porosity) of each composition were measured. Linear shrinkage (LS%) values were obtained for all samples using the following equation (1):

$$LS(\%) = \frac{L_g - L_f}{L_f} x100 \tag{1}$$

L_g and L_f being the diameter of the green and fired specimens, respectively. The water absorption (WA%) values were determined by a routine procedure involving measuring mass differences between the as-fired (D) and water saturated (M) samples (immersed in boiling water for 2 h, cooling for 3 h and sweeping of their surface with a wet towel) following the Turkish Standards [16].

$$WA(\%) = \frac{M - D}{D} x100 \tag{2}$$

The bending strength (BS) was measured using a three-point bending test (Nannetti Faenza, Italy), following the Turkish Standards [17], and calculated by (3):

$$BS = \frac{3.F.L}{2.b.h^2} \tag{3}$$

in which F = breaking load (kg), L = distance between supports (mm), b = sample width (mm) and h = sample thickness (mm).

Apparent porosity (ε_A) was determined by Archimedes principle using the following equation (4):

$$\varepsilon_A = \frac{M - D}{M - S} x100 \tag{4}$$

Table 2. Chemical composition and quantitative analyses of STD composition (wt.%)

	Chemical composition										
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	LOI*
STD	71.05	17.16	0.66	0.36	0.51	0.81	3.91	2.17	0.10	0.14	3.13
Quantitative analysis											
Quartz : 29.08 ± 0.29			Illite : 35.64 ± 0.93			Kaolinite : 4.26 ± 0.18			Albite : 31.02 ± 0.38		

*LOI = loss on ignition

where M: weight of the saturated specimens with water; D: weight of the dry specimens; and S: weight of the saturated specimens suspended in water.

Total porosity (ε_T) and sealed porosity (ε_S) were determined based on the following equations (5, 6):

$$\varepsilon_T = 1 - \left(\frac{\rho_C}{\rho_R}\right) \quad (5)$$

$$\varepsilon_S = \varepsilon_T - \varepsilon_A \quad (6)$$

where ρ_C is the apparent density ($\rho_C = D/M{-}S$) and ρ_R corresponds to the absolute density determined by helium gas pycnometry.

Results and Discussion

Table 2 shows the results of the chemical and quantitative analyses of the STD spray-dried powder. Fig. 2 presents the mineralogical composition of the STD mixture determined by XRD. The crystalline phases present in the STD mixture are kaolinite, illite, albite and quartz. Kaolinite was identified by the reflections at d = 7.1584 Å, 4.3618 Å and 3.5762 Å, while illite at d = 9.9104 Å, and 4.9975 Å, and albite at d = 3.1848 Å, 3.7642 Å and 6.3444 Å. The STD spray-dried powder consisted mainly of SiO_2 and Al_2O_3 which correspond to about 88% in agreement with the quantitative XRD analysis (Table 2).

Fig. 3 indicates that the morphology of the STD granules varies according to their size. As shown in Fig. 3, the fine granules (Fig. 3(c)) have a regular morphology with a grater tendency to be spherical, while the coarse grains (Fig. 3(a)) show an irregular morphology. Nevertheless, it was recognized that the resulting spray-dried powder ideally consisted of solid spheres according as the carefully controlled spray-drier processing variables at the plant.

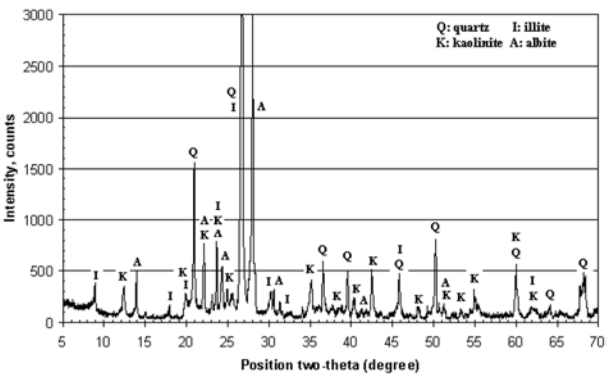

Fig 2. X-ray diffraction pattern (XRD) of STD composition.

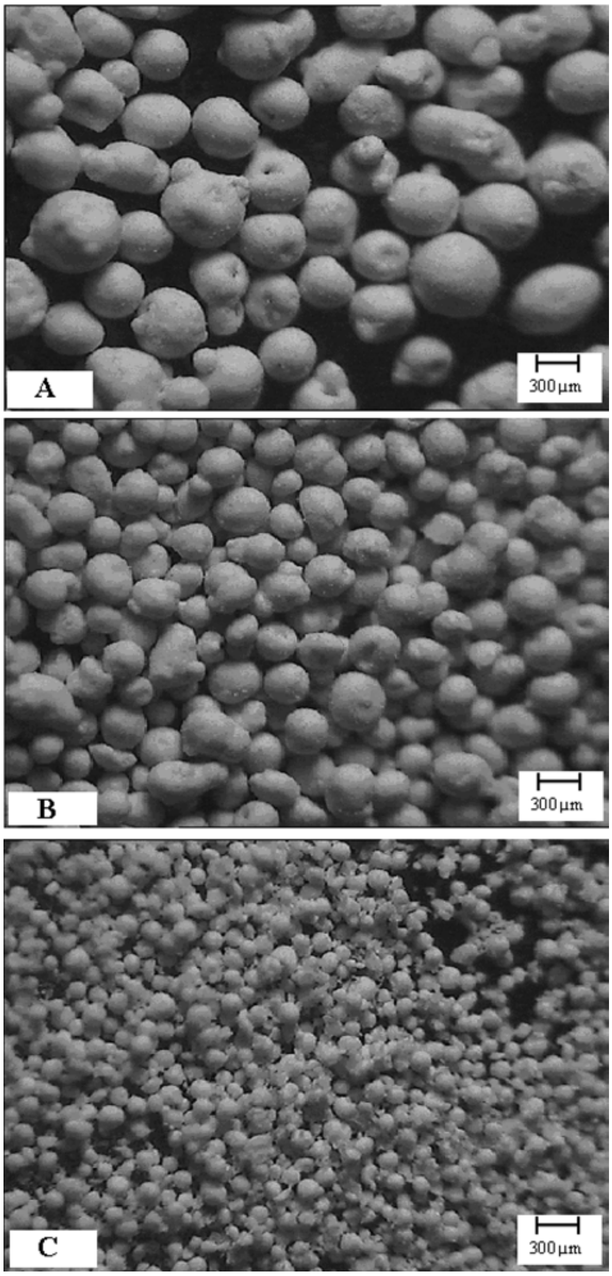

Fig. 3. Micrographs of distinct granulometric fractions of the STD spray-dried powder (A : > 250 μm, B : 125-250 μm, C : < 125 μm).

After pressing, apparent density (ρ_C) values of the green test specimens revealed that the granulometric compositions evaluated showed very similar degrees of compaction as seen from Table 3. This indicates that the total volume of pores generated in the green compact is the same, independent of the initial granule size distribution. This outcome is in agreement with the literature [3] and confirms that the grain size distribution did not affect the characteristics of the porous microstructure of the green compact.

Table 4 shows the mechanical properties of artificially-prepared porcelain tile compositions containing different percentages of preselected granules. Note that the values of linear shrinkage (LS%) are very similar. As can be seen, the result of a higher total porosity and water absorption values, VC has a lower bending strength (BS) value, which may be associated with the higher percentage of coarse granules (> 250 μm) used in this composition. On the other hand, the maximum BS value obtained from the VF composition was increased from 44 N/mm^2 to 46 N/mm^2 compared with STD granulometric composition. The VF composition also had low total, apparent and sealed porosity values. Sealed pores are the result of incomplete densification of the material during sintering, and depend basically on the microstructure of the green compact and on the thermal cycle adopted. With respect to the green compact, the main variables that may interfere in the characteristics of the porous microstructure are the particle and grain size distribution, morphology, humidity and pressing pressure [2]. The VF had more fine granules (< 125 μm) than other composition. As a consequence of the fine granules and regular morphology with a grater tendency to be spherical (Fig. 3(c)), VF showed better sintering properties.

Table 3. Apparent density of the pressed green test specimens

Granulometric composition	ρ_C (g/cm^3)
VC	1.87
C	1.86
M	1.86
F	1.88
VF	1.85
STD	1.87

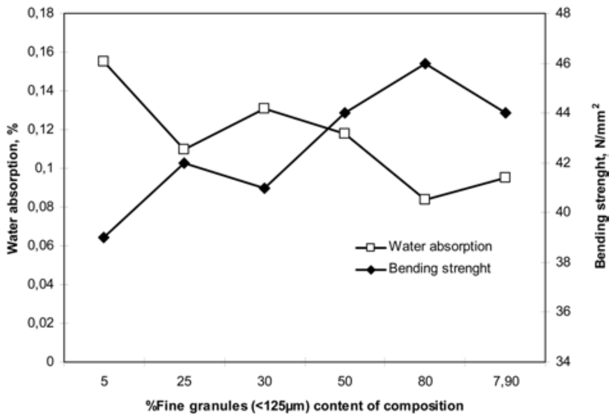

Fig. 4. The variation of bending strength and water absorption values as function of fine granules (< 125 μm) content.

Fig. 4 shows the variation of bending strength and water absorption values as function of fine granules (< 125 μm) content of the granulometric porcelain tile compositions. As can be seen from the figure, BS values increased whereas WA values decreased generally in parallel with an increasing amount of fine granules content of the composition.

Conclusions

The results of this study led to the following conclusions:

- as a consequence of the regular morphology with a grater tendency to be spherical of the spray-drier product, it can be pointed out that spray-drier processing variables such as slurry viscosity, solid content, nozzle diameter, and gas/slurry feed rate are controlled carefully at the plant,
- the grain size distribution of the spray dried product do not affect the characteristics of the porous micro-structure of the green compact since apparent density (ρ_C) values of the green test specimens showed very similar values,
- the very fine (VF) granulometric composition which had 80% fine granules (< 125 μm) had better sintering properties, i.e. lower water absorption and higher

Table 4. Mechanical properties of granulometric porcelain tile composition

Granulometric composition	LS %	WA %	BS N/mm^2	Total Porosity %	Apparent porosity %	Sealed porosity %
VC	9,7	0,155	39	10,02	0,48	9,54
C	10,1	0,110	42	8,87	0,45	8,42
M	9,9	0,131	41	9,52	0,36	9,16
F	10,5	0,118	44	8,54	0,32	8,22
VF	10,2	0,084	46	7,77	0,24	7,53
STD	10,5	0,095	44	8,24	0,32	7,92

bending strength than the other artificially prepared compositions,

- an increasing amount of the fine granules content in the composition improves generally the technological sintering properties of porcelain tiles. This may be the result of the regular morphology of fine granules with a grater tendency to be spherical.

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