INFLUENCE OF THE NATURE OF THE GRANULES ON PORCELAIN TILE MANUFACTURE

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ABSTRACT

Porcelain tiles have traditionally been manufactured by pressing granules prepared in spray driers. However, in recent years, several studies have investigated the possibility of using the dry route process as a new alternative for porcelain tile manufacture. In this case, granules with different characteristics – shapes, sizes, bulk densities, etc. – can be obtained during the granulation operation.

The work reported here evaluated the influence of granular bulk density on the behaviour of porcelain tiles during the different manufacturing stages. Two granulated powders were used, having the same chemical composition and similar shapes and sizes but significantly different bulk densities.

An industrial spray-dried composition and a dry route microgranulated powder were employed in this study. The granules prepared from an industrial porcelain tile composition and granulated by different processes presented differences in their bulk densities in the order of 25%. The study began with an evaluation of the size distribution, shape, bulk density and flowability of the granules. Prismatic

samples were then prepared and the behaviour of the powders produced by different granulation processes in response to pressing, drying and firing was examined.

The results indicate that the granules with higher bulk density prepared by the dry route were less deformable during pressing. As a result, the microstructure of the green bodies prepared with this powder presented a significant volume of intergranular pores even after pressing at higher pressures. However, the intragranular porosity of this powder was lower than that of the others due to particle packing inside the granules resulting from the granulation process. Due to these characteristics in the green bodies, their behaviour during drying and firing differed significantly from that of bodies produced with spray-dried powders.

In this context, it is found that the bulk density of granules serves as an important variable in porcelain tile manufacture, particularly in view of the increasing tendency towards dry route processing in the ceramic sector in coming years.

1. INTRODUCTION

The preparation of ceramic bodies for pressing involves two basic stages: grinding and granulation.

The purpose of grinding is to increase the specific surface area of the raw materials [1], increase the homogeneity of the mixture of their constituents and, in the case of ceramic bodies obtained from natural raw materials, reduce the grain size distribution of the impurities. Granulation, in turn, is aimed at promoting the particle agglomeration of the body in order to obtain granules of sizes and morphologies that are suitable for filling press punches. In the granulation operation, it is also normal procedure to simultaneously adjust the moisture content of the bodies, which acts as a plasticizer, to ensure the success of the compaction operation during pressing.

Porcelain tiles are traditionally made from granules prepared by spray drying. However, in recent years the literature [2] has pointed out the possibility of using dry route processes to manufacture porcelain tiles. In this case, granules with characteristics unlike those of spray-dried granules can be obtained through granulation processes.

Spray-dried granules are characterized by their spherical morphologies and large pores in their central portions, resulting from the elimination of the water involved in spray drying. The characteristics of the suspensions utilized affect the properties of the granules obtained in spray driers. According to Bertrand *et al*. [3], the tendency for sedimentation of the suspension, as well as the state of dispersion of the particles and the nature of the binders employed, affects the shape of the granules obtained through the granulation process. The results obtained by these authors indicate that the state of particle deflocculation may lead to the formation of hollow or solid granules.

The literature [4, 5] describes two main granulation methods to granulate dry-ground ceramic bodies: granulation through the application of compressive forces, and granulation in the presence of water. In the second case, water or another added liquid is responsible for bringing the particles together, initially forming a nucleus of agglomerated particles [1]. The capillary forces that are generated keep the agglomerate cohesive and new layers of particles or particle agglomerates become incorporated into the original nucleus, causing the size of the agglomerates to increase. The very movement of the agglomerates during the granulation process may break the granules that come into direct contact with the granulator or that collide with each other. However, the mechanical strength of the granules can be increased in several ways, e.g. by using binders, and by soluble compounds mixed in the body, which cause crystalline bridges to form between granules after the water evaporates [4].

Considering the differences between the mechanisms involved in the preparation of granules for pressing, using ceramic bodies ground by the wet and

dry routes, the objective of this study was to evaluate the influence of the use of granules prepared by the two processes on the manufacture of porcelain tiles. The granules under study exhibited important differences in their densities as a function of their different methods of preparation.

2. MATERIALS AND METHODS

The composition used in this study was a standard ceramic body for the manufacture of glazed porcelain tiles, whose chemical composition was previously determined by X-ray fluorescence. The granules of this body were prepared by the two procedures described below:

- Spray drying: the body was previously wet ground in a ball mill and sieved until less than 2.0% of residue was left on a sieve with 63 μm openings, after which it was spray dried in an industrial spray drier. The spray-dried granules were produced with 6.0% moisture.
- Micrograniulation: the body was dry-milled in a hammer mill and a ball mill in order to reproduce the residue and particle size distribution of the wet-milled body. The resulting material was disaggregated in a hammer mill and granulated with the addition of 12% water in an EIRICH R-type Intensive Mixer microgranulator. The resulting granules were air-dried until their moisture content was reduced to 6.0%.

The granules prepared by these two procedures were then characterized to determine their individual characteristics and their behaviour during pressing. The properties of the compacts obtained were evaluated before and after sintering.

The properties of the granules were evaluated based on the following analyses:

- Size distributions: evaluated by sieving through a battery of sieves with mesh openings of 500, 250, 125 and 63 μm. Sieving was carried out for ten minutes with the aid of an eccentric sieve shaker.
- Morphologies: by observation under optical and scanning electron microscopes. The analyses performed in the scanning electron microscope (SEM) were carried out on granules embedded in acrylic resin, which was polished to enable the analysis of internal sections of the granules.
- Flowability: analysed based on the Hausner ratios [6] of the granulometric compositions, determined by freely filling and then packing the granules in a graduated test tube with a volume of 250 mL.
- Density: using the chamber of a mercury porosimeter, without applying pressure, to identify the apparent volume occupied by the granules.

The behaviours of the granules during compaction and of the resulting compacts were then evaluated based on the following characterizations:

- Compaction curves: identification of the effects of variations in the compaction pressure (103, 132, 169, 221, 302, 419 and 596 kgf/cm^2) on the bulk density of the green compacts.
- Creep pressure: determined in a universal testing machine to identify the pressure required to deform the granules in the initial stages of pressing.
- Pore size distribution: evaluated in green compacts by mercury porosimetry. The compacts were formed by applying a compaction pressure of 370 kgf/cm^2.
- Flexural rupture modulus after drying, linear drying shrinkage and gresification curves: evaluated in bodies pressed under 370 kgf/cm^2 and then fired at different temperatures, at heating rates of 70°C/min and 5 minutes of dwell time at the firing maximum temperature.
- Microstructural evaluation: performed by X-ray diffraction and scanning electron microscopy of the bodies fired at different temperatures, applying the aforementioned firing cycles.

3. RESULTS AND DISCUSSION

Table I presents the chemical composition of the body, which corresponds to the typical chemical composition of a body used for the manufacture of glazed porcelain tiles.

Figure 1 depicts the granulometric distribution curves of the two bodies employed in this study. Note that the two bodies present very similar size distributions. The mean diameter of the spray-dried granules is 420 μm, while that of the granules prepared by dry microgranulation is 460 μm. The two granulometric compositions exhibit only a minor participation of fines (fraction lower than 125 μm < 5.0%), which should also give them high flowability.

Figures 2 to 4 show micrographs of the morphologies of the granules. The images in Figures 2 and 3, obtained by optical microscopy, confirm the results of the size distribution of the granules, since they indicate that the granules are of very similar sizes. However, these images also indicate that the spray-dried granules have more spherical morphologies. Although the granules prepared by microgranulation have more irregular morphologies, their sphericities are very high, considering the morphologies usually found in granules prepared by dry route processes [2]. The SEM micrographs in Figure 4 show the internal sections of granules. Note that the granules prepared by microgranulation are solid, while the spray-dried granules contain large pores. According to the literature [4, 6], these pores are more evident in larger size granules.

Oxides	Porcelain body
L.O.I. (%)	5.59
SiO_2 (%)	68.02
Al_2O_3 (%)	17.72
Fe_2O_3 (%)	1.24
TiO_2 (%)	0.42
CaO (%)	1.05
MgO (%)	1.50
Na_2O (%)	2.20
K_2O (%)	2.02
MnO (%)	-
P_2O_5 (%)	0.02

Table I – Chemical composition of the porcelain body used in this study

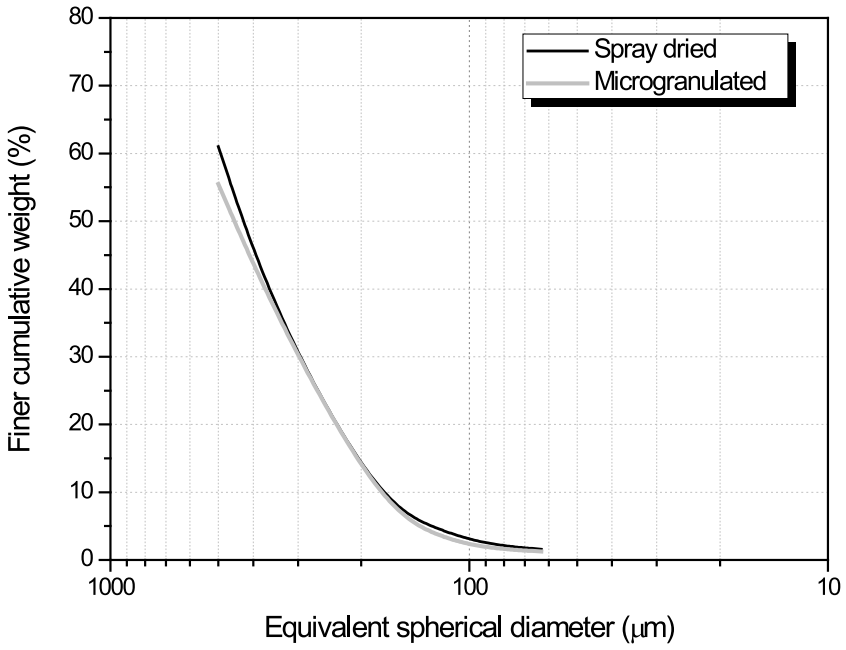

Figure 1 – Grain size distributions of the granulometric compositions

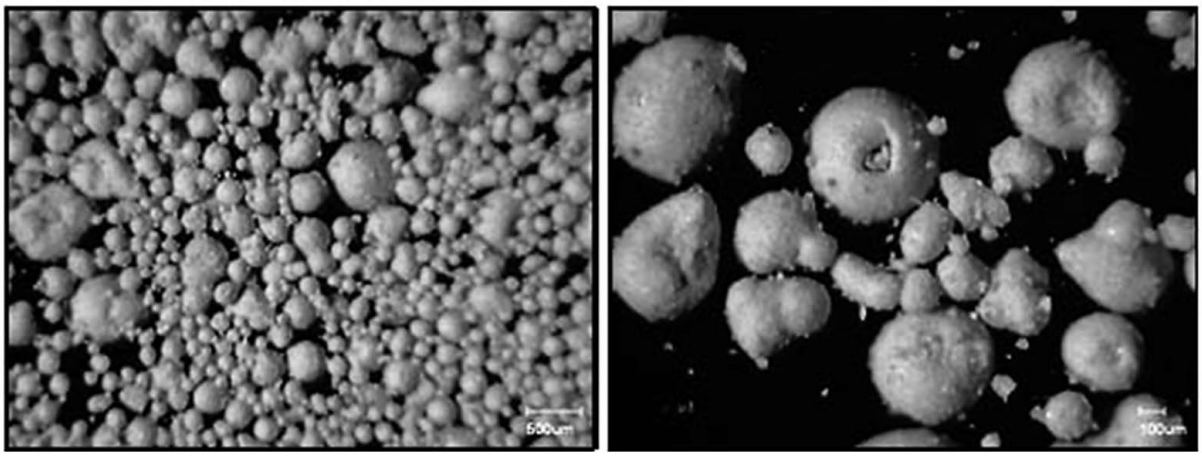

Figure 2 – SEM micrographs of spray-dried granules

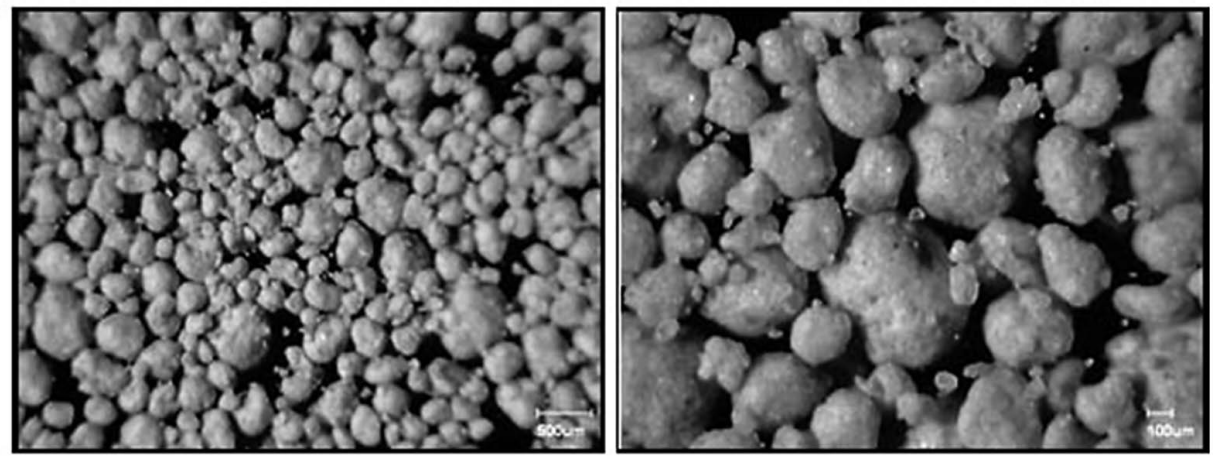

Figure 3 – SEM micrographs of granules prepared by microgranulation

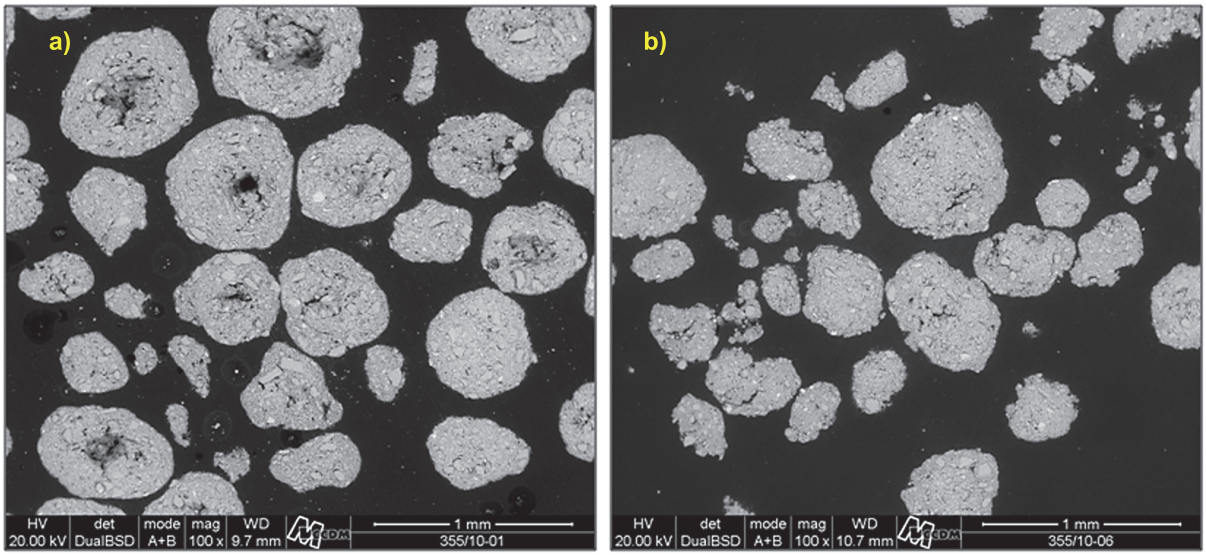

Figure 4 – SEM micrographs of the internal section of granules: a) Spray dried; b) Microgranulated

The similarities between the size distributions and morphologies of the granules prepared by the two methods employed in this study (spray drying and microgranulation) explain the similarities in the flowability of the granulometric compositions, as indicated by the Hausner ratios (H.R.) presented in Table II. However, this same table shows that the granules present significantly different bulk densities (Dap). These differences result from the methods employed for the preparation of the dos granules. The movement generated in the microgranulation process is responsible for the higher particle packing inside the granules prepared by the dry route. In the case of the spray-dried granules, in addition to the lower particle packing, the pores inside large granules contribute to reducing the bulk density.

Granules	H.R.	Dap (g/cm³)	cP (kgf/cm²)
Spray dried	1.140	1.700	2.2
Micrograniulated	1.152	2.197	5.7

Table II – Characteristics of the granules

The differences in the bulk density of the granules prepared by the two methods strongly affect their compaction behaviour. As Figure 5 indicates, significantly dissimilar densities are obtained by the green compacts prepared from the two granulometric compositions. The bulk densities of the compacts prepared from granules produced by the dry route after pressing under the lower compaction pressures were consistently higher than the bulk density of the test samples prepared from spray-dried body, even under the higher pressures.

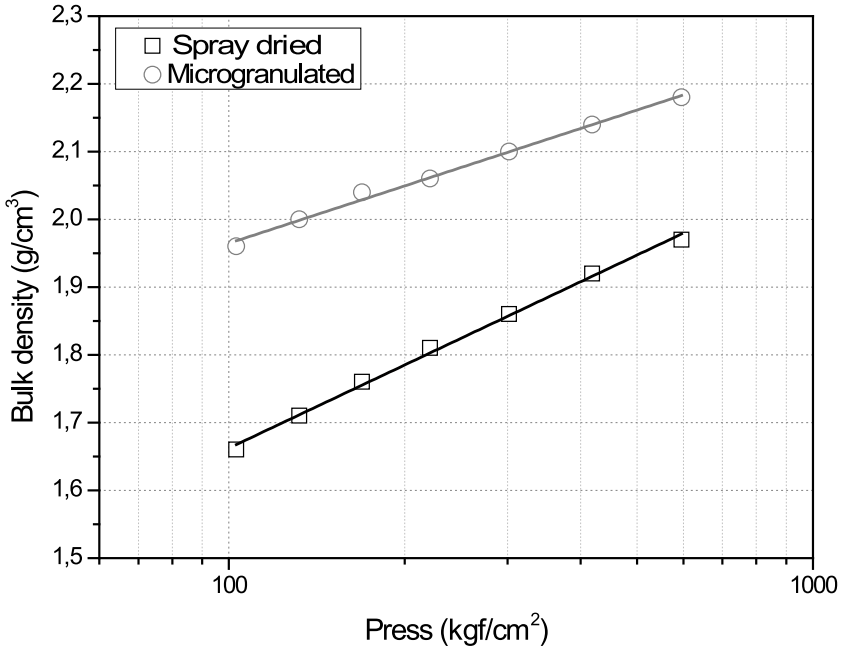

Figure 5 – Effects of compaction pressure on the bulk density of the green compacts

The analysis of Figure 5 also indicates that the spray-dried granules present higher densification rates under increased compaction pressure than the granules prepared by dry granulation. These results indicate that spray-dried granules are more deformable, probably due to their lower densities. These findings are confirmed by the lower creep pressure (cP) of the spray-dried granules, as indicated in Table II, which is consistent with data on the subject reported in the literature [7, 8].

Figure 6 shows the pore size distribution curves of the green compacts prepared from the two granulometric compositions. The total volume of mercury intruded in the samples indicates that the bodies prepared from micrograniulated

granules are significantly less porous. Conversely, however, they present a significant fraction of larger pores. Pores with intrusion diameters larger than 0.5% represent 22% of the total porosity of the compacts prepared by the dry route, while the pores in the compacts prepared from spray-dried body represent only 8% of the total porosity.

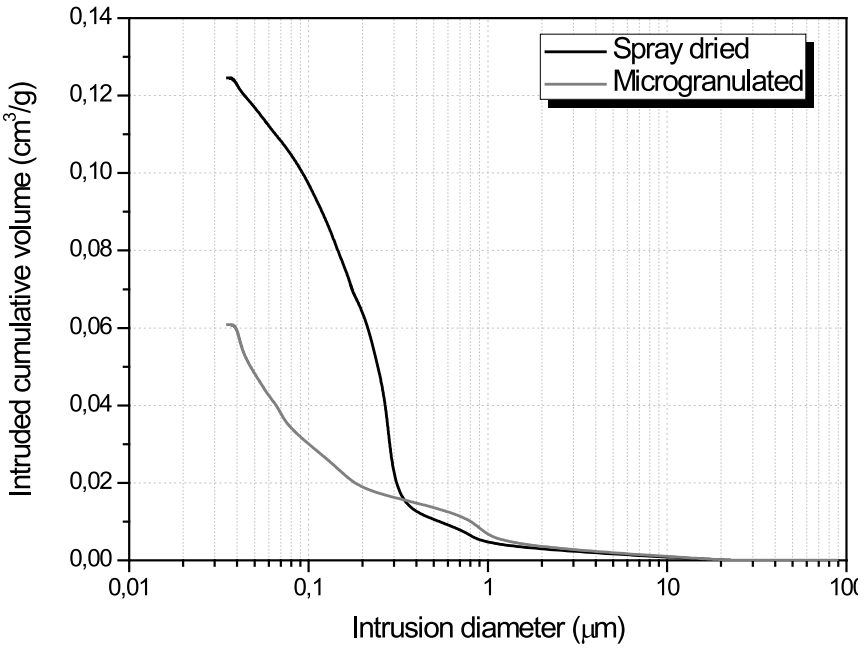

Figure 6 – Pore size distributions of the green compacts

The overall results indicate that the compacts prepared from spray-dried granules generally exhibit lower residual intergranular porosity after compaction. In contrast, the compacts prepared from granules produced by microgranulation exhibit low intragranular porosity and a significant fraction of residual intergranular pores, although their total porosity is lower than that of the compacts made of spray-dried granules.

These differences in the microstructures of the green bodies due to the nature of the granules used here directly affect the behaviour of the compacts during the other manufacturing stages. As can be seen in Table III, the drying shrinkage rates (DSr) and flexural modulus of rupture (FMR) of the green bodies after drying are different. The drying shrinkage is significantly higher in the bodies of the dry-granulated body due to the greater participation of intergranular pores in these compacts. However, their lower total porosity ensures their higher mechanical strength.

Granules	Dap (g/cm³)	DSr (%)	FMR (MPa)
Spray dried	1.935	0.03	2.6
Micrograniulated	2.090	0.22	3.5

Table II – Characteristics of the green compacts

During firing, important differences are also detected in the speed of densification and total shrinkage of the porcelain tiles obtained (Figure 7). The compacts produced from microgranulated body reach maximum densification with low linear firing shrinkage rates (approximately 5.5%), in view of the lower total volume of pores in the green bodies. Moreover, the bodies prepared with this body present a lower densification speed than those prepared with spray-dried body, although their porosities before firing are lower and their maximum densification is reached at similar temperatures.

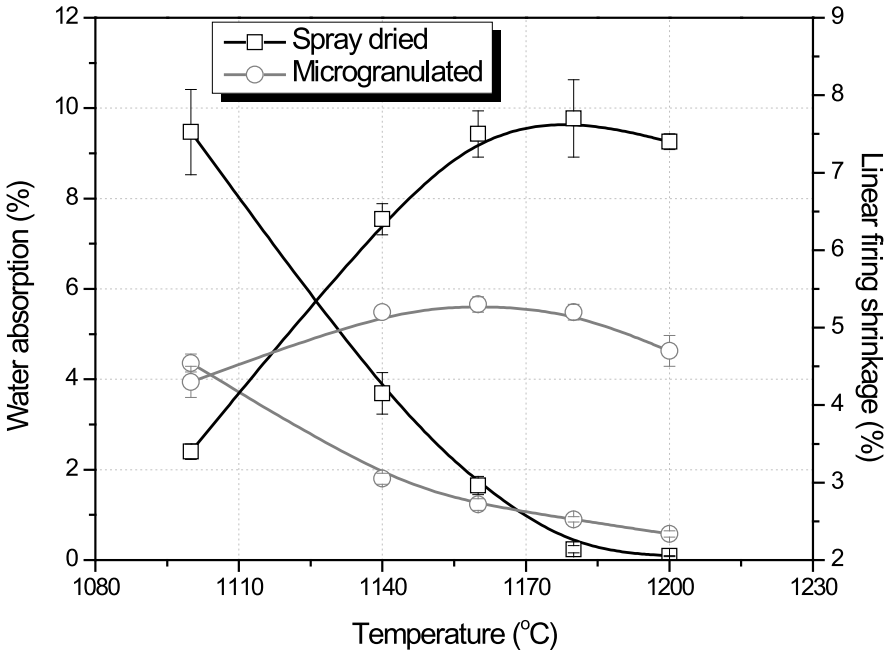

Figure 7 – Gresification curves

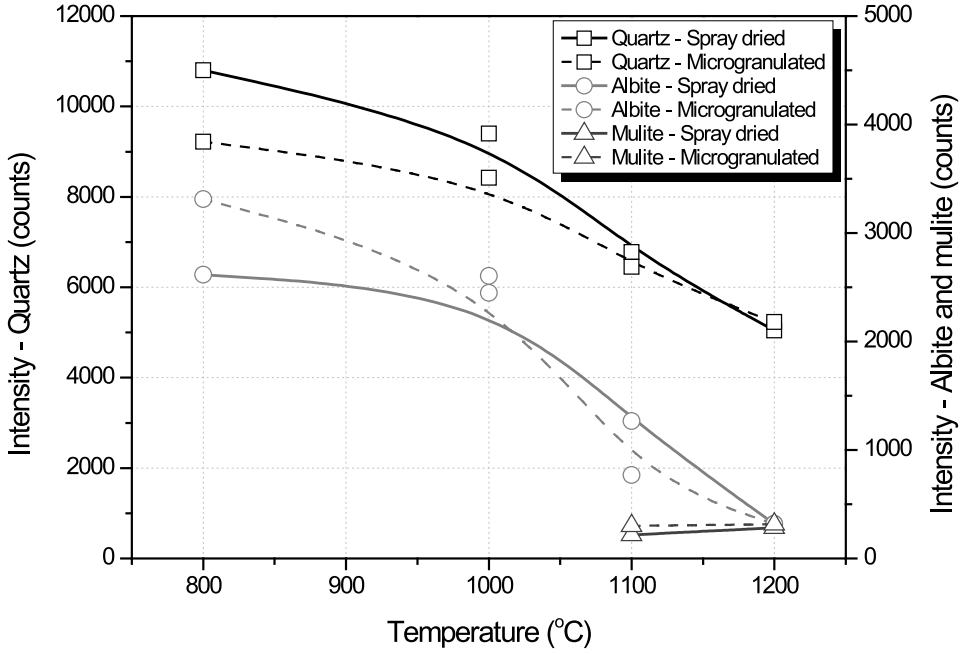

Figure 8 – Effects of firing temperature on the intensity of the main peaks of the crystalline phases in the microstructure

Again, this phenomenon can be explained by the difference in porosity of the green compacts as a result of the granules used here. The green bodies of the microgranulated body presented low intragranular porosity and high intergranular porosity. During sintering, the difficulty in eliminating pores is greater in the body prepared by dry microgranulation, although the glassy phases formed have the same characteristics as those formed in the compacts prepared with the spray-dried body. These results are confirmed by the microstructural analysis of the bodies fired at distinct temperatures, which indicates that the crystalline phases in the two bodies are the same, and that apparently their proportions also vary similarly in response to increasing firing temperatures. This finding is illustrated in Figure 8, which illustrates the variation in the intensity of the main peak of the crystalline phases identified in the XRD analysis as a function of firing temperature. Figure 9 reveals the existence of residual pores in the microstructure of the fired bodies of the dry-granulated body, resulting from the low deformability of these granules during compaction.

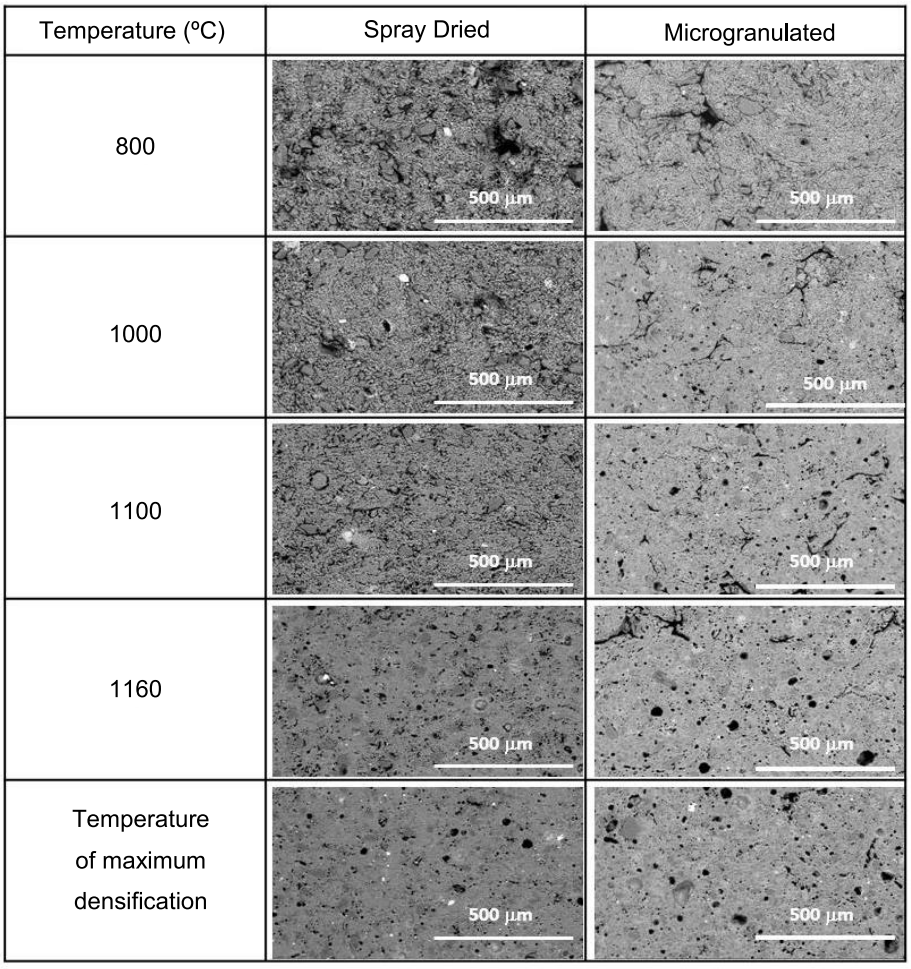

Figure 9 – SEM micrographs of the microstructure of the bodies of the two bodies after firing at different temperatures

4. CONCLUSIONS

The results obtained in this study indicate that the nature of the granules utilized in the manufacture of porcelain tiles can significantly alter the behaviour of a given body during manufacture.

Based on the analyses, it can be stated that granules produced by microgranulation are considerably denser and less deformable than those produced by spray drying, although the two types of granules present similar sizes and morphologies.

These differences strongly affect the behaviour of the body during compaction, producing significantly different green compacts according to the granulation method employed. Due to the higher density and lower deformability of the granules prepared by microgranulation, the green compacts produced with these granules present significant residual intergranular porosities and low volumes of intragranular pores. During the subsequent processing stages, these compacts present high drying shrinkage, high mechanical strength before firing, lower firing shrinkage, and lower vitrification speed during firing.

Considering that many of these characteristics may be favourable for the manufacture of porcelain tiles, it is emphasized that the properties of the granules utilized should be seen as highly relevant variables in the manufacture of porcelain tiles by dry processing.

REFERENCES

[1] REED, J.S. **Principles of ceramics processing**. John Wiley & Sons, Inc. Second Edition, Nueva York, EE.UU., 1995, 658 p.

[2] MELCHIADES, F.G.; BOSCHI, A.O. Study of the feasibility of producing porcelain tiles by the dry route. **Ceramic Forum International**, v.87, n.1-2, p. 43-49, 2010.

[3] BERTRAND G. *et al*. Spray-dried ceramic powders: A quantitative correlation between slurry characteristics and shapes of the granules. **Chemical Engineering Science,** v**.** 60, p.95-102, 2005.

[4] STANLEY-WOOD, N.G. **Enlargement and compaction of particulate solids**. Butterworth & Co Ltd, 1ª Edición, Cambridge, UK, 1983, 294 p.

[5] NASSETI, G.; TENAGLIA, A.; TIMELLINI, G. **La granulazione nell'industria delle piastrelle ceramiche**. Ed. Int. Centro Ceramico, Bolonia, 1987, 263 p.

[6] QUINTEIRO, E. **Efeito das características de pós atomizados sobre as características e qualidade de revestimentos cerâmicos.** Dissertação de mestrado, UFSCar, São Carlos, 1996.

[7] ECKHARD, S.; NEBELUNG, M. Investigations of the correlation between granule structure and deformation behavior. **Powder Technology**. n.206, p.79-87, 2011.

[8] AMORÓS, J.L. *et al*. Fracture properties of spray-dried powder compacts: Effect of granule size. **Journal of the European Ceramic Society**, 28 p. 2823–2834, 2008.