PYROPLASTIC BEHAVIOUR OF PORCELAIN STONEWARE TILES: COMPARISON OF THE WET AND DRY MANUFACTURING ROUTES

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1. ABSTRACT

The growing concern for the economic and environmental sustainability of ceramic tile production is drawing attention to the dry manufacturing route as an alternative to the wet cycle conventionally used for porcelain stoneware tiles. At the same time, the control of firing deformations, associated with pyroplasticity, has become be crucial with the development of large size, rectangular shapes, with low thickness, and with use of energetic fluxes and micronized fillers. The present work merges these two issues with a view to comparing the pyroplastic behaviour of industrial-like body compositions processed by both the wet and dry routes. Pyroplasticity is active when sintering acts through viscous flow of an abundant vitreous phase, as typical of porcelain stoneware. It is thought to depend on microstructural variables (amount, size, shape and mutual arrangement of coarse grains) and on the viscosity of the liquid phase formed at high temperature. Six batches were prepared by ball milling (wet) and four by hammer milling (dry) followed by granulation in sieves (wet) or microgranulation (dry). The laboratory simulation of the industrial processing

was carefully carried out in order to obtain every pair of bodies (wet route vs. dry route) with the same chemical and mineralogical composition, and with minimal differences in terms of particle size distribution. Fired samples were characterized by determining the water absorption, bulk density, open and closed porosity, phase composition (XRD-Rietveld) and microstructure (SEM with image analysis). A pyroplasticity index (PI) was determined by the three-point flexural test at maximum densification temperature. Results reveal a conspicuous difference in the pyroplastic behaviour between bodies manufactured by the wet route (PI=7-10·10^{-5} cm^{-1}) and the dry route (PI=4-6·10^{-5} cm^{-1}). The PI values are strongly affected by the volumetric fraction of skeleton grains consisting essentially of quartz. In fact, the amount of coarse-grained quartz is higher in the dry processed tiles (13-20% vol) with respect to the wet manufactured tiles (7-13% vol). No clear correlation emerged between PI and the amount of vitreous phase. The different microstructure obtained by the wet and the dry routes has repercussion on the phase composition, which is expected to affect the pyroplastic behaviour. The PI values correlate almost linearly with the viscosity of the viscous phase at the temperature of the maximum densification rate, but only for the wet route. In conclusion, pyroplasticity appears to involve a complex behaviour depending on both microstructure (particularly number, volume and mean distance of skeleton grains) and vitreous phase features (chemical composition and viscosity at high temperature). The sintering of porcelain stoneware tiles proved to proceed by different paths in the dry and the wet routes, thus originating different microstructures, which in turn affect the firing deformations.

2. INTRODUCTION

The dry manufacturing route is becoming an alternative to the wet cycle conventionally used for porcelain stoneware tiles as a result of the growing concern for the economic and environmental sustainability of ceramic tile production [1-3]. At the same time, the control of firing deformations related to pyroplasticity has become crucial with the development of ceramic tiles with large size, rectangular shape, low thickness, and made using energetic fluxes, particularly when two or more of these factors are combined in the same production [4-7]. Pyroplasticity is active when sintering acts through viscous flow in the presence of abundant vitreous phase, as typical of porcelain stoneware [8]. It is thought to depend on microstructural variables, like amount, size, shape and mutual arrangement of coarse grains (the so-called 'skeleton') and on the viscosity of the liquid phase formed at high temperature [9-11].

The present work merges these two issues with the aim of comparing the pyroplastic behaviour of industrial-like body compositions processed by the wet and the dry routes, following a previous contribution that identified the main variables responsible for pyroplasticity and how to quantitatively express this phenomenon [12].

3. EXPERIMENTAL

A standard formulation for porcelain stoneware (51) was modified by replacing 10% of the coarse-grained feldspars, usually utilized in the ceramic industry. The following replacements were carried out: 10% fine-grained quartz (52), 10% micronized-grained quartz (53), 10% micronized-grained potassium feldspar (54), a combination with 5% micronized-grained potassium feldspar with 5% fine-grained quartz (55) or micronized-grained quartz (56); details on batch formulation are in Melchiades et al. [12]. Samples processed by the wet and dry routes are marked by "W" and "D", respectively.

Bodies were prepared by both wet and dry grinding, taking care to obtain similar particle size distributions, e.g., d_{50} ~2.3 μm (51W) versus ~3.4 μm (51D). Wet grinding was carried out in a ball mill with 50% water and 0.6% sodium silicate (deflocculant) and the residue content was controlled between 0.5% and 2.0% after sieving through an ASTM #325-mesh sieve (45 μm); the slip was dried in electric oven at 110°C, disaggregated and moistened with 6.5% water. Dry grinding was performed in a ball mill up to a residue equivalent to that of the wet route and the resulting powders underwent microgranulation in an Eirich laboratory granulator [13-14] with moisture adjusted to 9%. The 51D body was also prepared with 6.5% moisture content to assess the influence of the decreased deformability of agglomerates.

Prismatic test specimens were prepared by pressing at 450 kgf/cm^2. Bulk density of the unfired compacts was determined by geometric measurements to evaluate the apparent volume of the dried test specimens. Drying was performed in an electric oven at 110ºC.

Sintering curves were obtained by evaluating the water absorption and linear shrinkage after firing to four different maximum temperatures. The heating rate was 60ºC/min and the soaking time at the maximum temperature was 8 minutes. The sintering curves were employed to determine the maximum densification temperature (T_{md}) corresponding to the highest firing shrinkage of the samples. Specimens fired at T_{md} were characterized by measuring: water absorption, open porosity OP, and bulk density, BD (ISO 10545-3); total porosity as TP = 100 x (1 - BD/SW) where the specific weight, SW, was determined by He pycnometry (ASTM C-329); closed porosity as CP = TP – OP.

Firing deformation was determined by the three-point flexural test at T_{md} (8 min soaking time). Results are expressed as the pyroplastic index (PI, cm^{-1})=$(4 \cdot h2 \cdot S) \cdot (3 \cdot L4)^{-1}$, where h is the specimen thickness, S is the sag of the deformed specimen and L is the span length.

The chemical compositions of the bodies were determined by XRF. Loss on ignition was evaluated at 1000ºC. Phase composition was determined by X ray diffraction (Bruker D8 Advance, 10-80º2θ range, scan rate 0.02º, 16 s per step) with full profile interpretation by Rietveld refinement (GSAS-EXPGUI) using corundum as internal standard [15]. The chemical composition of the vitreous phase was derived from the bulk chemical and phase composition of the samples and used to estimate the viscosity at high temperature according to available models [8,16].

Microstructure was observed under SEM (FEI Quanta200) on gold sputtered polished surfaces, previously etched (10 s in a HF aqueous solution 30% V/V). Analysis was performed on the section of specimens used to test pyroplasticity. Several micrographs were randomly taken at 1000 magnifications, which was a compromise between minimum resolution (skeleton particles >5 μm) and analysed area (1 mm^2).

Property	51W	52W	53W	54W	55W	56W	s.d.
Bulk density, unfired ($g \cdot cm^{-3}$)	1.830	1.838	1.801	1.803	1.770	1.829	0.003
Bulk density, fired ($g \cdot cm^{-3}$)	2.475	2.482	2.473	2.465	2.463	2.460	0.003
Water absorption (%wt)	0.01	0.00	0.16	0.08	0.08	0.16	0.02
T_{md} (°C)	1185	1195	1190	1170	1185	1185	5
Pyroplasticity index (10^{-5} cm^{-1})	9.5	8.4	7.8	9.1	8.6	7.4	0.1
Property	**51D6**	**51D9**		**54D**	**55D**	**56D**	**s.d.**
Bulk density, unfired ($g \cdot cm^{-3}$)	2.081	2.090		2.039	2.061	2.051	0.003
Bulk density, fired ($g \cdot cm^{-3}$)	2.458	2.452		2.470	2.465	2.475	0.003
Water absorption (%wt)	0.14	0.26		0.23	0.29	0.13	0.02
T_{md} (°C)	1185	1185		1170	1185	1185	5
Pyroplasticity index (10^{-5} cm^{-1})	6.1	5.8		4.5	4.4	4.4	0.1

Table 1. *Mean physical properties of the unfired and fired test specimens, maximum densification temperature (T_{md}) and pyroplastic index (s.d.= standard deviation).*

4. RESULTS

The difference in compaction between the wet and dry agglomerates, already known in the literature [13,14,17] is confirmed: wet route powders gave rise to dry tiles with a bulk density around 1.8 g·cm^{-3}, while the dry route powders were pressed to bulk density always over 2.0 g·cm^{-3} (Table 1). This implies a systematic difference in porosity of the unfired bodies: on average 33% in wet processing versus 24% in dry processing.

The firing behaviour of the bodies is rather similar in the wet- and dry-processed batches (Fig. 1). This was expected, as the composition is the same and the particle size distribution is very close in the dry and wet ground bodies. As a matter of fact, the maximum densification temperature is the same in every wet-dry pair of bodies (Table 1). However, examining the sintering curves in detail, the main difference concerns the firing shrinkage values that are lower in the case of the dry process, which was expected due to the lower porosity of unfired bodies. Furthermore, it is important to observe that the inversion of the shrinkage curve of the dry route occurs at lower temperatures than the wet route; at this point the bodies have not yet reached their maximum densification, as shown by water absorption. This phenomenon is already known in the literature [13,17]. Comparing the samples sintered at the T_{md}, just small differences arose in terms of water absorption and bulk density (Table 1).

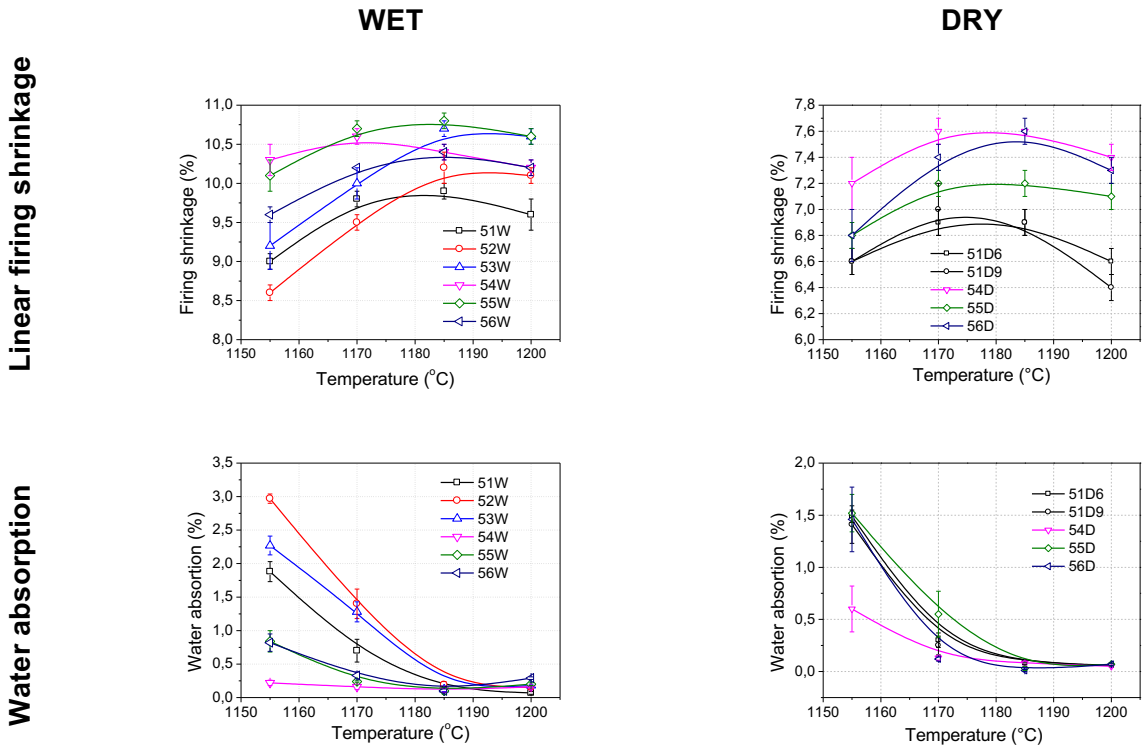

Figure 1. *Sintering curves of porcelain stoneware bodies processed by the wet route and the dry route.*

There is a conspicuous and systematic difference in the pyroplastic behaviour between bodies manufactured by the wet route (PI=7-10·10^{-5} cm^{-1}) and the dry route (4-6·10^{-5} cm^{-1}). This indicates a much larger pyroplastic deformation in the wet-ground batches (Table 1).

Small differences were observed in the phase composition of wet and dry manufactured tiles fired at T_{md}. In the wet route, slightly more quartz and mullite were found, while the dry route is characterized by slightly more vitreous phase and feldspar (Table 2). Such a different phase composition is consistent with slightly higher viscosity at T_{md} and Flow Point of the vitreous phase of the dry-ground bodies (Table 2).

Body	Phase composition (%wt)					Viscosity at T_{md} (kPa·s)	Flow Point (°C)
	Quartz	Mullite	Plagioclase	Zircon	Vitreous phase		
51W	17.0	13.0	2.0	3.0	65.0	4.75	1192
52W	21.0	12.0	2.5	2.0	62.0	4.77	1221
53W	17.0	11.0	2.0	2.0	68.0	4.80	1231
54W	14.0	11.0	2.0	3.0	70.0	4.97	1216
55W	18.0	13.0	2.5	2.5	64.0	4.78	1210
56W	16.0	12.0	3.0	2.0	67.0	4.81	1222
51D6	16.0	10.0	3.5	2.0	68.5	4.90	1221
51D9	16.0	11.0	3.0	2.0	68.0	4.85	1214
54D	13.0	11.0	3.0	2.0	71.0	4.96	1224
55D	14.5	10.0	1.5	2.0	72.0	4.88	1231
56D	15.0	11.0	4.0	2.0	68.0	4.85	1230
s.d.	*0.5*	*0.5*	*0.5*	*0.5*	*0.5*	*0.05*	*3*

Table 2. *Phase composition of porcelain stoneware tiles manufactured by the wet (W) and dry (D) routes. Viscosity and Flow Point of the vitreous phase.*

The microstructural observations reveal a strong difference between the dry and the wet routes, as exemplified by the batch 54 (Fig. 2). The wet processed bodies exhibit a relatively homogeneous texture, where rounded coarse quartz grains appear to be scattered in a matrix consisting of vitreous phase and smaller quartz and mullite crystals. Looking in detail, it can be seen that the HF etching, removing preferentially the vitreous phase, highlighted wavy features that are probably flow lines caused by pyroplastic deformation. In contrast, the texture of dry ground bodies is clearly non-homogeneous with both sharp-edged coarse quartz grains and coarse glass puddles (likely feldspar remnants discernible by the occurrence of dissolution grooves and spherical pores) dispersed in a glass-mullite matrix. These microstructures are visibly different, particularly in the amount, size and shape of skeleton grains (Fig. 2).

The interpretation of SEM micrographs allowed obtaining granulometric curves of the residual skeleton grains (Fig. 3). It may be clearly observed in Figure 3 that the amount of coarse-grained quartz is higher in the dry processed tiles (13-20% vol) with respect to the wet manufactured tiles (7-13% vol). It is plain to see that the dry processed bodies have a coarser skeleton size distribution with many grains over 40 μm, while in the wet processed ones, practically no grains over 40 μm are present. A possible explanation is that the presence of a greater amount of coarse grains in the

dry route can help stabilize the dissolution of the viscous phase reducing mobility and contributing to reduction of the PI.

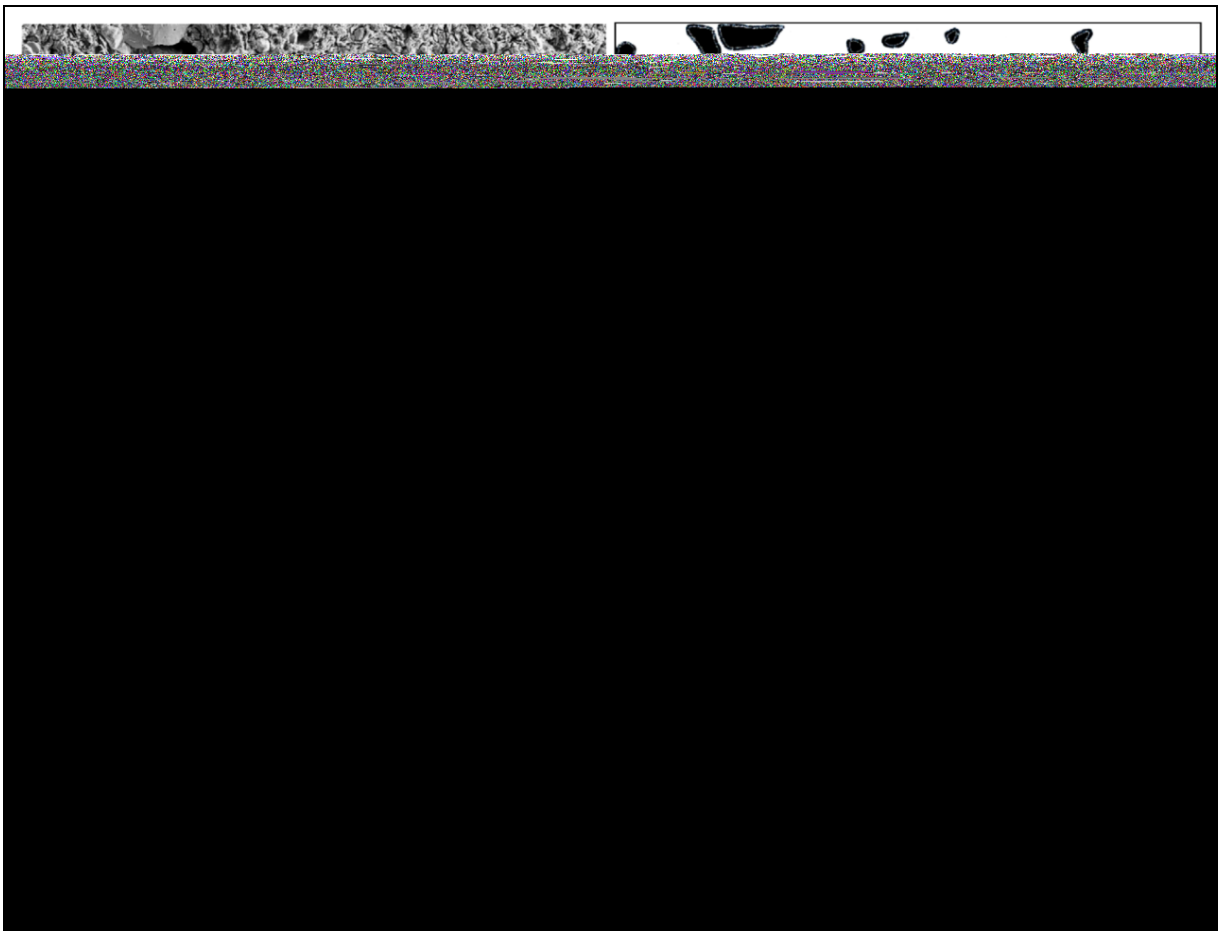

Figure 2. *Comparison of the microstructure obtained by the wet and the dry routes (example of batch 54): SEM micrographs (left) and interpretation of the skeleton grains over 5 μm in size (right). The scale bar is 20 μm.*

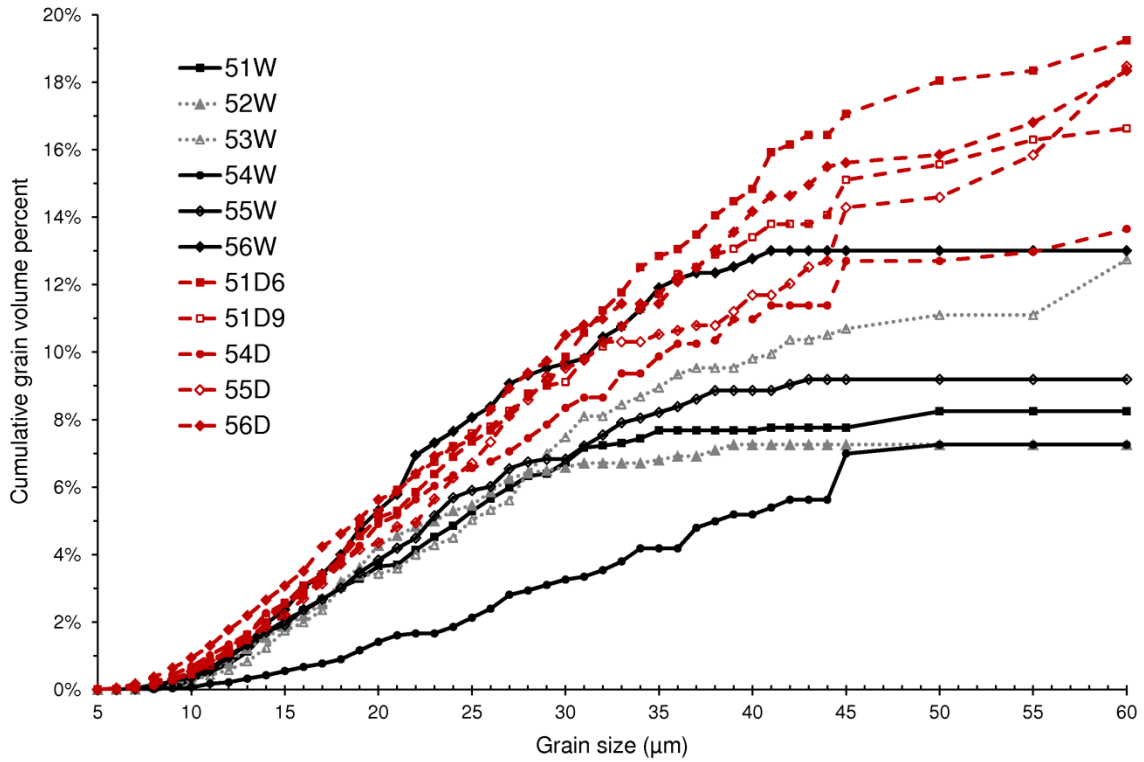

Figure 3. *Comparison of the size distribution of skeleton grains in porcelain stoneware manufactured by the wet and the dry routes.*

5. DISCUSSION

An apparent negative correlation emerged between the PI and the amount of vitreous phase (Fig. 4A). The opposite behaviour was expected: the more abundant the vitreous phase, the stronger the firing deformation. Therefore, interference from other variables need to be checked. The PI is function of the viscosity (Fig. 4B) and the Flow Point (Fig. 4C) of the vitreous phase. Such a correlation is less dispersed in the wet route. The pyroplastic deformation related with the wet route occurs through the viscous flow mechanism (diffusion processes). This phenomenon is evidenced by the highly interdependent relationship between viscosity of the liquid phase at the T_{md} and the PI. However, in the dry route, other mechanisms operate in the deformation process and contribute to damp this phenomenon.

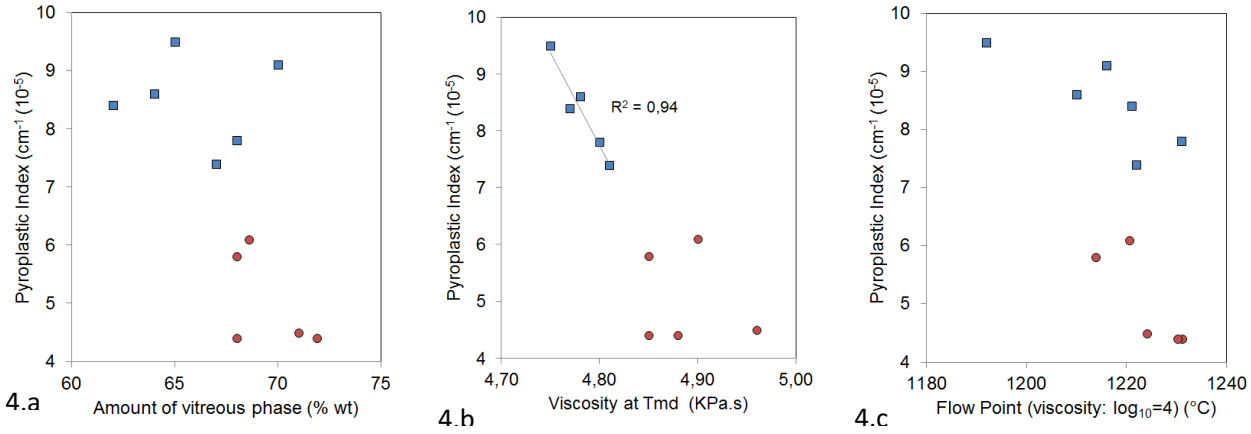

Figure 4. *Pyroplasticity index in function of the amount (A), the viscosity at T_{md} (B) and the Flow Point (C) of the vitreous phase of porcelain stoneware tiles.*

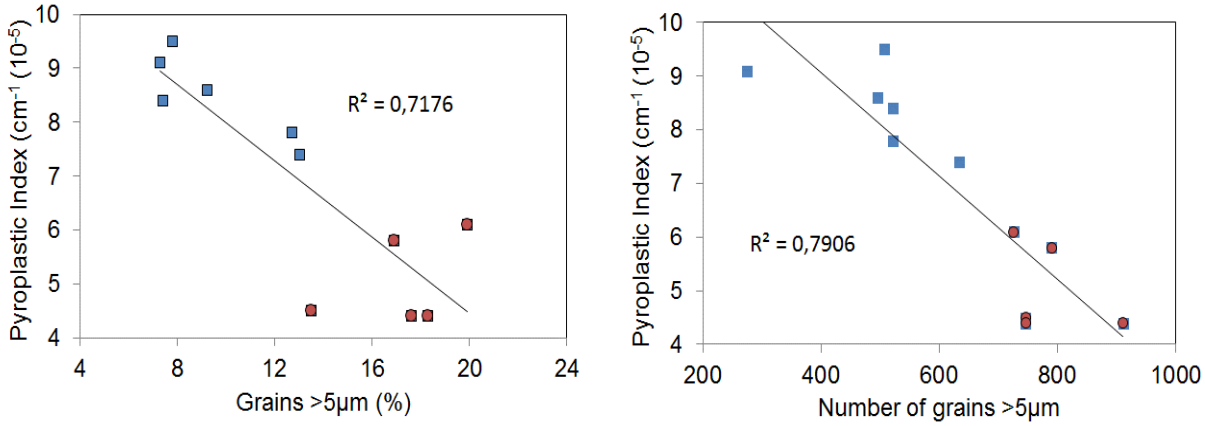

Figure 5. *Pyroplasticity index in function of volume (left) and number (right) of the skeleton grains.*

The pyroplastic index is a function of the microstructural features (Fig. 5). The volume of grains greater than 5 μm showed a clear correlation with PI for both processing routes. These results indicate that the heterogeneity of the microstructure contributes to the reduction of firing deformations.

6. CONCLUSION

Firing deformations indicate a considerably different behaviour between wet and dry processes, wherein the tiles manufactured by dry route showed less tendency to pyroplastic deformation. The different microstructure obtained by the wet and the dry routes has repercussion on the phase composition, which affects the pyroplastic behaviour. No clear correlation emerged between PI and the amount of vitreous phase, whereas the PI values correlate almost linearly with the viscosity of the viscous phase at the temperature of the maximum densification rate, but only for the wet route. The PI values are strongly affected by the volumetric fraction of skeleton grains consisting essentially of quartz. In fact, the amount of coarse-grained quartz is higher in the dry processed tiles with respect to the wet manufactured tiles.

In conclusion, pyroplasticity appears to be a complex behaviour depending on both microstructure (particularly number, volume and mean distance of skeleton grains) and vitreous phase features (chemical composition and viscosity at high temperature).

These observations confirm the key role of the skeleton grains and viscosity of the vitreous phase in the pyroplastic behaviour, already outlined in the literature, but highlight also a different relevance of compositional and microstructural features in the wet and dry routes. Such an in-depth knowledge of firing behaviour allows the design of new batches with improved pyroplastic performance that will be the subject of future work.

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