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Effects of Quartz on Wall Tile Mechanical Properties and Microstructure

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Abstract

The processing of seven typical single fast-firing wall tile (monoporosa) compositions was reproduced in laboratory scale to investigate quartz effects on reducing mechanical properties in fired products. Phases quantities other than quartz were kept constant, varying only quartz quantity and its particle size distribution. Processing parameters like humidity, apparent density after drying and firing temperature were compatible with the ones adopted industrially. Post-sintering characterization involved three-point bending test for modulus of rupture determination, besides thermal, mineralogical and microstructural analysis through Dilatometry, X-ray Diffraction and Optical and Scanning Electron Microscopy. A more evident effect of quartz quantities rather than quartz particle size on thermal expansion coefficient and modulus of rupture was observed.

Keywords: quartz, wall tile, microcracking

Introduction

Quartz is a silica mineral phase naturally found in raw materials used in wall tile production, ranging from few percents to more than half of these materials mineralogical composition. Due to its high melting temperature, quartz is the main structural agent on tiles during firing, where vitreous phase develops. It contributes to mechanical strength on finished product and is used as a controller of ceramic substrate thermal variation coefficient (1), allowing a proper match between substrate and glass thermal variation coefficients. Quartz presence in wall tiles, however, may exert a damaging effect on finished products.

During the cooling of tiles, at about 574°C, β-quartz goes through a reversible polymorphic transformation to α phase, with higher density. Thus, β-quartz particles suffer a sudden shrinkage, which is not followed by surrounding vitreous matrix and particles of other phases. Since quartz possesses anisotropy in thermal variation coefficients (δ) (4) and the highest δ among phases found in the product after firing (1), differential shrinkage arises in the substrate. During firing of ceramic tiles, internal stresses are generated and relieved when microcracks arise associated with quartz, presenting a potential risk when excessive thermal gradients are present in the products.

Raw materials for wall tile are usually minerals that occur naturally (1), like:

- clays containing phases like illite and kaolinite, which are responsible for the necessary plasticity during shaping and for mechanical strength in the green state. Both minerals dehydroxilate during heating above 450°C, loosing structural water and, at temperatures higher than 900°C, decompose originating spinel, α-Al_2O_3 and vitreous phase (1), and spinel, mullite and SiO_2-rich vitreous phase (2), respectively;
- fluxing agents, like Na- and K-feldspar. Feldspars improve densification through viscous liquid formation above 1050°C, allowing relatively low temperatures on firing;
- chalks, usually calcite and dolomite. In wall tiles, where water absorption must be > 10%, these carbonates, which decompose at temperatures higher than 600°C with CO_2 evolution, are extensively used as an aid to reach the desired porosity;
- talc, that reduces friction among particles during pressing and also acts as a flux. Talc dehydroxilates in the 870-1050°C range (5), originating SiO_2-rich vitreous phase and enstatite; and
- quartz.

In the last few decades, firing of ceramic tiles experienced two severe transformations: firing schedules, lasting a whole day, were reduced to half an hour, and double-firing (firing of substrate and subsequent firing of deposited glass) was replaced by single-firing (simultaneous firing of substrate and glass). Compositions were adapted to these transformations mainly with an increase in flux content, but excessive vitreous phase formed in tiles after firing makes products more prone to effects of quartz inversion.

This work analyses quartz influence after firing on wall tiles. Utilizing a ceramic composition adequate to single fast-firing wall tile (monoporosa) production, quartz additions in different sizes and quantities were made to this composition. Compositions were processed in laboratory scale under industrially-compatible parameters. In fired samples, mechanical strength, thermal variation coefficient, mineralogical composition and microstructure were evaluated.

Materials and Methods

A monoporosa composition, named M0 (Table 1), containing two clays, chalk and talc, was utilized as a standard composition (10). The ceramic mass was wet milled in ball mill (50% water and 0.7% sodium silicate, to dry mass) finer than 45µm, dried and powdered in mortar and pestle. The quantity of quartz was also analyzed through Quantitative X-Ray Diffractometry (3).

Table 1: Semi-Quantitative Mineralogical Composition of M0

Phase	Wt. %
α-Quartz	27
Kaolinite	29
Illite	10
Microcline	6
Albite	6
Calcite	7
Dolomite	7
Talc	3
Magnetite	2
Others	3

Quartz sand (98.76% SiO_2) additions, in three narrow ranges of particle size and in two quantities, were made to M0, originating six new masses (Table 2).

Table 2: Particle Size and Quantities of Added Quartz on Investigated Compositions

Composition	Mean particle size of added quartz (µm)	Quartz (wt. %)
M0	-	27
M33L	33	32
M33H	33	37
M48L	48	32
M48H	48	37
M96L	96	32
M96H	96	37

The analyzed masses were humidified to 7% (dry basis) and uniaxially pressed as tiles with about 70g, 12.50mm length, 5.50mm width and variable thickness. Apparent density after drying was standardized to 1.96g/cm^3, and it was measured using a mercury densitometer (Novabelluno). Firing was carried out in a Nannetti fast-firing laboratory kiln (90 minutes schedule, 1140°C max. temperature, soaked for 4 minutes).

Characterization of fired samples involved the determination of the modulus of rupture (MOR) through three-point bending test (Gabbrielli Crometer) and thermal variation coefficient analysis during cooling (Netzsch DIL 402C Dilatometer, -10°C/min.). Comparisons of MOR values were done with Dunnett and Duncan tests (6). Mineralogical analysis through X-Ray Diffraction utilized a Philips X'Pert Diffractometer (CuKα radiation, at 40kV and 30mA, 10-60° 2θ range, 0.02° step, 1s/step).

Microstructural analysis used a Zeiss Neophot 30 Optical Microscope (OM) and a Philips XL 30 Scanning Electron Microscope (SEM) coupled with an EDAX Energy Dispersive Spectroscope (EDS). Samples were transversally cut, mounted on epoxy resin under low vacuum (9) and polished to 0.3µm superficial finish.

Results and Discussion

Qualitative mineralogical analysis after firing indicated the presence of the same phases in all samples: quartz, mullite, enstatite, diopside and anorthite. Taking into consideration that quartz has little contribution to reactions below 1200°C and that the relative proportion among all phases initially present (excluding quartz) were kept constant, only these phases effectively participated on reactions.

The average values of modulus of rupture are presented in Table 3. Comparisons of M0 with other compositions were done with Dunnett's test for analysis of variance (ANOVA). Critical difference $d_{0,05}(6,42)=1.99$ indicated that compositions with quartz additions were significantly different from M0. To compositions with quartz additions, all the possible pairs of MOR means were compared with Duncan's test. The following remarks were done:

- MOR means of samples with 32% initial quartz differ from 37% quartz samples, evidencing the influence of quartz quantities on mechanical strength;
- MOR means of M33L, M48L and M96L are similar, suggesting that increasing the size of quartz that is added does not affect MOR significantly;
- comparing M33H, M48H and M96H, only the two latter do not differ, M33H differing from both. This result shows a greater effect on the decrease of mechanical strength of these samples with increasing the size of the quartz that is added.

Table 3: Average Values of MOR and Thermal Variation Coefficients (δ) in the 650-500°C Range

Composition	MOR (MPa)[a]	$\delta_{650\text{-}500°C} .10^{-6}$ (°C^{-1})
M0	26.1	9.84
M33L	23.8	11.23
M33H	21.9	12.41
M48L	23.3	11.75
M48H	20.6	14.01
M96L	23.3	12.00
M96H	19.9	14.28

n= 7 samples

Dilatometric behavior of all samples showed the same tendency, being almost linear in the ranges 1000-650°C and 500-250°C, with greater dimensional variation occurring between 650°C and 500°C. In this range, linear thermal variation coefficients (Table 3) showed good agreement with MOR (R^2=0.9761), making this region the most critical during cooling (8).

Optical microscopy observation of samples showed rough quartz particles (labeled "Q") embedded in a heterogeneous matrix (M) with round pores (P) (Figure 1). Most quartz particles had their presence associated with peripheral and/or internal cracks.

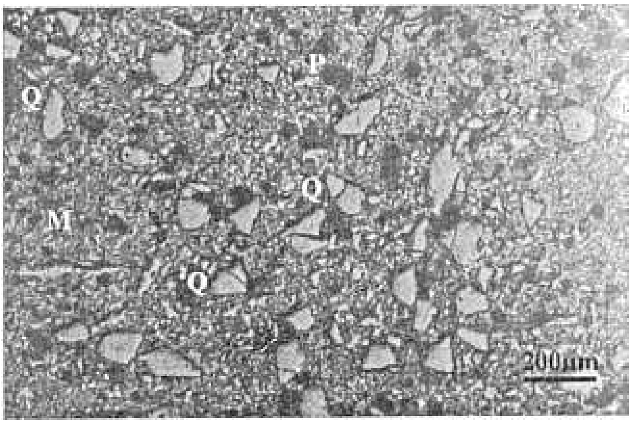

Figure 1: OM micrograph from M96H, showing quartz grains ("Q"), heterogeneous matrix ("M") and pores ("P").

Through SEM, large particles with internal pores (Figure 2) were observed, possibly vitreous regions from clay relicts. EDS detected a composition similar to illite.

In Figure 3, quartz grains are surrounded by a matrix with extensive microcracking. Chemical analysis of region "A" indicates formation of coronytic anorthite on quartz vicinity by compositional variations (7).

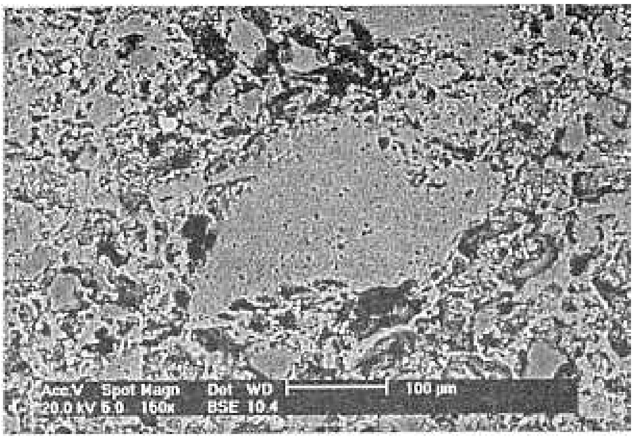

Figure 2: Particle in M0 with internal porosity, associated with external pores.

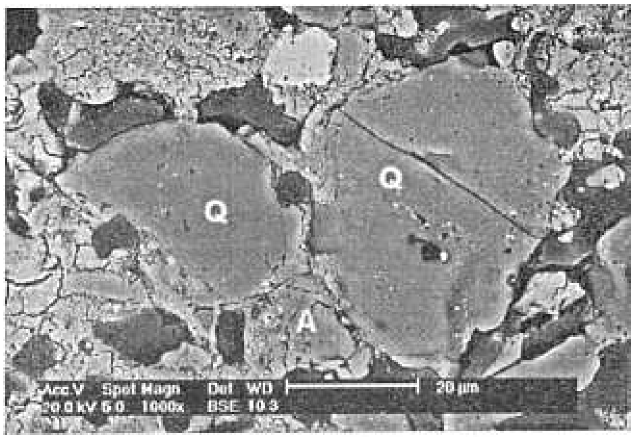

Figure 3: Coronytic anorthite (A) around quartz grains (Q) in M0

Figures 4 and 5 show crystals formed by nucleation and growth (modal reaction), approaching the enstatite and diopside composition, respectively.

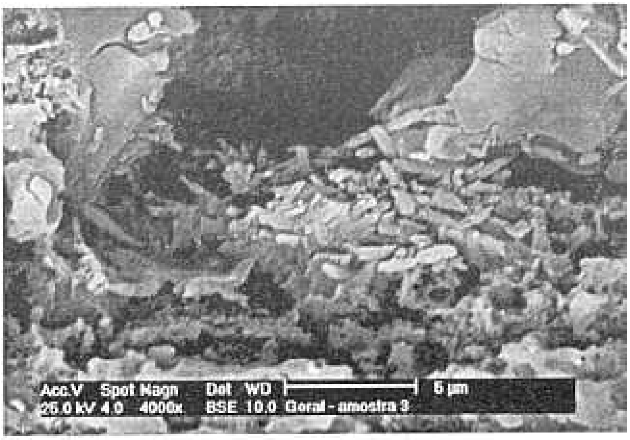

Figure 4: Massive crystals approaching enstatite composition M33H.

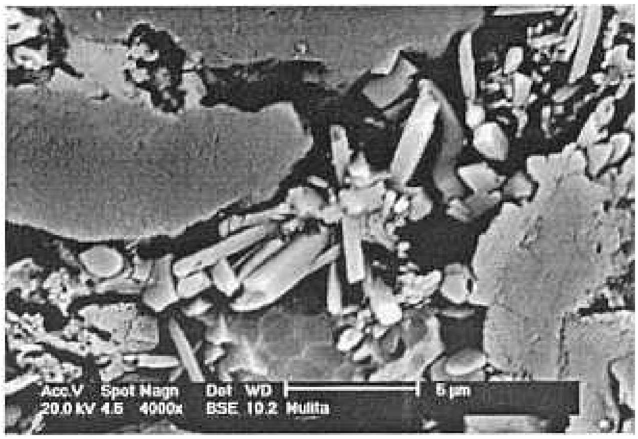

Figure 5: Prismatic diopside occurrence, M33H

Phases like diopside and enstatite present high values of δ, minimizing shrinkage gradient between quartz and the matrix. On the other hand, anorthite possesses the lowest value of δ among the phases formed during firing, being the presence of anorthite on quartz boundaries frequently accompanied by extensive microcracking (Figure 3).

Three crack patterns (in the matrix, inside and around quartz grains) occurred in all samples, even associated with quartz particles smaller than 20µm.

Conclusions

Based on the results obtained, wall tiles are more prone to mechanical strength reduction when quartz is present in higher quantities than when present as rough particles. In this manner, discarding slurry larger particles after milling (a common industry practice) is not always necessary. This fact emphasizes the importance of a parameter that commonly is not yet controlled during the production of wall tiles, the routine mineralogical analysis of raw materials. Due to the necessity of low costs in the production, these materials are utilized *in natura*, i.e., without washing, sieving or blending, being subjected to natural variations of quantities of quartz and other minerals. Also, substitution of calcite by dolomite (decreasing Ca content) would possibly be an interesting choice, minimizing anorthite (Ca-rich phase) and favoring enstatite and diopside formation.

Acknowledgments

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