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Processing and properties of large-sized ceramic slabs

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Large-sized ceramic slabs – with dimensions up to 360x120 cm^2 and thickness down to 2 mm – are manufactured through an innovative ceramic process, starting from porcelain stoneware formulations and involving wet ball milling, spray drying, die-less slow-rate pressing, a single stage of fast drying-firing, and finishing (trimming, assembling of ceramic-fiberglass composites). Fired and unfired industrial slabs were selected and characterized from the technological, compositional (XRF, XRD) and microstructural (SEM) viewpoints. Semi-finished products exhibit a remarkable microstructural uniformity and stability in a rather wide window of firing schedules. The phase composition and compact microstructure of fired slabs are very similar to those of porcelain stoneware tiles. The values of water absorption, bulk density, closed porosity, functional performances as well as mechanical and tribological properties conform to the top quality range of porcelain stoneware tiles. However, the large size coupled with low thickness bestow on the slab a certain degree of flexibility, which is emphasized in ceramic-fiberglass composites. These outstanding performances make the large-sized slabs suitable to be used in novel applications: building and construction (new floorings without dismantling the previous paving, ventilated façades, tunnel coverings, insulating panelling), indoor furnitures (table tops, doors), support for photovoltaic ceramic panels.

Keywords: porcelain stoneware slabs, pressing, microstructure-final, structural applications

Procesamiento y propiedades de pavimentos cerámicos de gran formato

Se han fabricado piezas de gran formato, con dimensiones de hasta 360x120 cm, y menos de 2 mm, de espesor, empleando métodos innovadores de fabricación, partiendo de composiciones de gres porcelánico y utilizando, molienda con bolas por vía húmeda, atomización, prensado a baja velocidad sin boquilla de extrusión, secado y cocción rápido en una sola etapa, y un acabado que incluye la adhesión de fibra de vidrio al soporte cerámico y el rectificado de la pieza final. Se han seleccionado piezas en verde y cocidas, caracterizándolas desde el punto de vista tecnológico, composicional (FRZ, DRX) y microestructural (MEB). Los productos semiacabados muestran una destacada uniformidad microestructural y estabilidad dimensional, dentro de un amplio margen de temperaturas de cocción. La composición de las fases y la compacidad de la microestructura, son muy semejantes a las que presentan las baldosas de gres porcelánico convencionales. Los valores de la capacidad de absorción de agua, densidad aparente, porosidad cerrada, propiedades funcionales así como las propiedades tribológicas y mecánicas se sitúan en los mejores valores de las piezas de gres porcelánico. No obstante las grandes dimensiones, unidas al reducido espesor dotan a las piezas de una cierta flexibilidad, que refuerza el empleo de la capa de fibra de vidrio. Estas destacadas propiedades hacen utilizables, a los grandes formatos, en nueva s aplicaciones, construcción y edificación (sin desmontar los pavimentos preexistentes, fachadas ventiladas, revestimiento de túneles, paneles aislantes etc.) muebles (encimeras y puertas), soporte de paneles fotovoltaicos

Palabras clave: grandes formatos, gres porcelánico, prensado, microstuctura, aplicaciones estructurales

1. INTRODUCTION

In the ceramic tile market, the growth rate of porcelain stoneware has considerably increased in the last decade due to excellent technological and functional properties coupled with the even more improved aesthetical appearance [1-8]. The latest market trends go towards large dimensions (e.g. 60x60 cm^2 or 120x60 cm^2) and a reduced thickness of tiles (3-6 mm) [9, 10] However, strong technological hindrances constrain the ceramic process and need to be faced up: role and effect of plasticity-enhancing additives, improved powder processing, better control on behaviour during compaction, drying and firing operations [11, 12]. The existing limits can be overcome by innovative technological solutions, involving a brand new approach to both shaping and thermal treatments, suitable to produce large sized ceramic slabs – i.e. up to 3.6x1.2 m^2 and 3-4 mm of minimum thickness – by a novel process [13, 14].

This work is aimed at characterizing the main compositional, technological and functional properties of such large-sized porcelain stoneware slabs obtained by the industrial manufacturing cycle (hereafter called *Lamina*) comparing their performances with those of conventional porcelain stoneware tiles taken as benchmark [15].

2. EXPERIMENTAL

Lamina slabs (3x1 m^2) were sampled from three different manufacturers in Italy and Spain: both unfired and fired ceramic products were characterized from the technological, functional and microstructural viewpoints. Subsamples were cut from each slab; furthermore, different parts of industrial slabs (i.e. head, middle and tail) were investigated in order to evaluate the product homogeneity. In addition, two ceramic-fiberglass composites were selected and characterized from the mechanical point of view: slab with fiberglass net (L1) and slab-fiberglass-slab multilayer (L2) were compared with the slab without reinforcing element (L0).

Physical and microstructural features of dry slabs were investigated by scanning electron microscopy observations (SEM, Leica Cambridge Stereoscan 360, Au-coated specimens), particle size distribution by photosedimentation (Micromeritics SediGraph 5100, ASTM C958), pore size distribution by mercury intrusion porosimetry (MIP, ThermoFinnegan Pascal 140-240), bulk density by geometrical method (BD), specific weight by He pycnometry (SW, Micromeritics MVP 1305, ASTM C329) and total porosity (TP) calculated as: TP = (1 - BD/SW) x 100.

Technological properties of ceramic slabs were determined (on 5x5 cm^2 specimens cut from the slab, 5 replicates): water absorption, open porosity (OP) and bulk density (ISO 10545-3), specific weight (ASTM C329), total porosity as TP = (1 - BD/SW) x 100, and closed porosity as CP = TP – OP.

Microstructural features were evaluated by scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360, Au-coated polished surface and section) and quantitatively determining the phase composition by X-ray powder diffraction (Bruker, Advance D8) using the Rietveld-RIR method [16].

Mechanical and tribological properties were investigated by measuring Young modulus (ENV 843-2, 8x2 cm^2 specimen), fracture toughness (ENV 843-12, SENB, 4x0.4 cm^2 specimens, 4 replicates), resistance to deep abrasion (ISO 10545-6, 10x10 cm^2 specimens assembled on a rigid wood substrate, 10 replicates), modulus of rupture (MOR) by 3-point bending (ISO 10545-4) on ceramic slabs (20x10 cm^2 specimens, 8 replicates, maximum deflection below the specimen thickness) and on ceramic-fiberglass composites (Zwick Roell, mod. Z050, 30x30 cm^2 specimens, 1 MPa×s^{-1} load rate).

Functional properties were determined to check the compliance with standard requirements for porcelain stoneware tiles (ISO 13006, Group BIa): linear thermal expansion (ISO 10545-8) and resistance to thermal shock (ISO 10545-9), freeze/thaw cycles (ISO 10545-12), chemicals (ISO 10545-13) and stains (ISO 10545-14).

The firing behaviour of a typical Lamina industrial body was assessed by monitoring the main technological properties (water absorption, linear shrinkage, BD, CP, MOR) in function of thermal conditions. Different firing cycles were performed in a laboratory electric roller kiln: from 1190 to 1230°C of maximum temperature and from 37 to 51 minutes cold-to-cold.

3. RESULTS AND DISCUSSION

3.1. Processing

Porcelain stoneware large slabs, manufactured through the innovative ceramic process Lamina, can make use of either conventional raw materials or pre-milled fluxes; as a matter of fact, Lamina bodies consist of typical porcelain stoneware formulations being a mixture of ball clays, sodic-potassic feldspars and quartz-feldspathic sands in slightly variable amounts (Fig. 1) [13, 14].

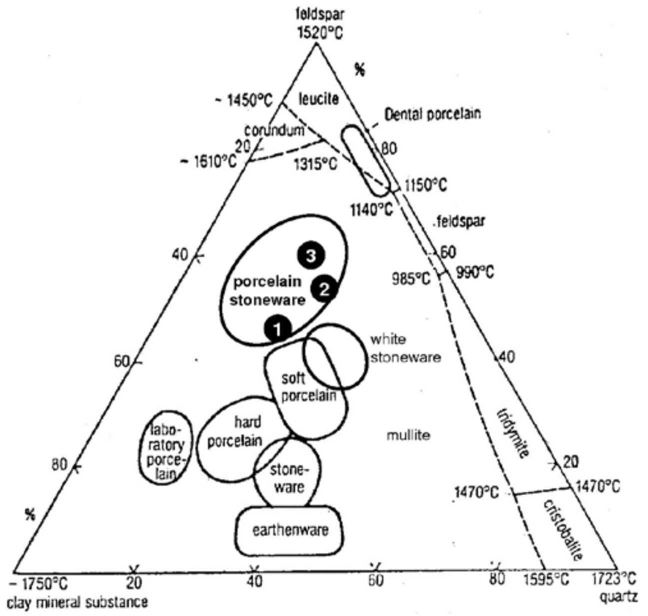

Figure 1. Body formulations of porcelain stoneware large slabs (full circles) in comparison with different ceramic products.

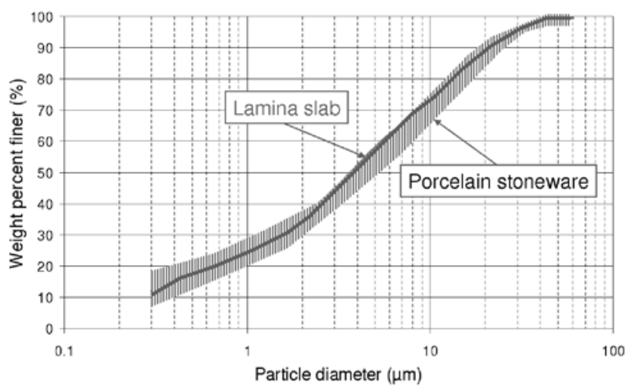

Figure 2. Particle size distribution of porcelain stoneware large slabs bodies compared with that of porcelain stoneware tiles.

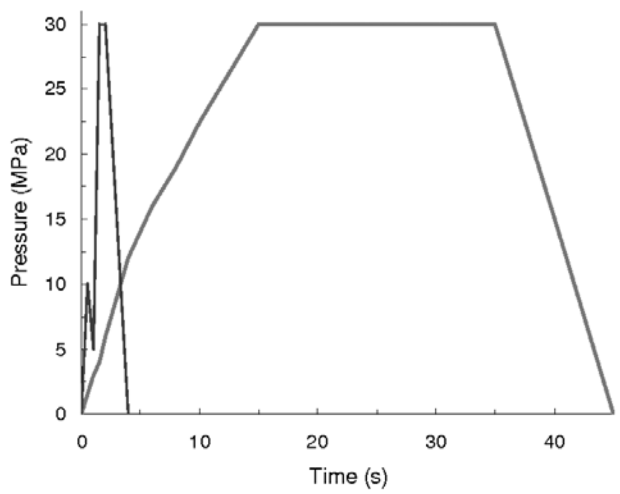

Figure 3. Pressure-time curves of conventional versus Lamina pressing.

The processing route involves wet ball milling to get powders with particle size distribution analogous to that of conventional porcelain stoneware bodies (Fig. 2) [17]. Subsequent powder granulation is carried out by spray drying with a fine-grained distribution of aggregates and a moisture content between 4.5 and 5.5% wt.

A special pressing system has been developed to obtain the ca. 400x160 cm^2 green slab, consisting in a die-less mould by which pressing without lateral constraining is performed. Specific pressures are in the 30-40 MPa range, as in common porcelain stoneware manufacturing, but a slow pressure rate is applied, instead of the "hammer principle" currently utilized in tile pressing (Fig. 3).

Soon after shaping, slabs are dry cut to eliminate 5-10 cm at each edge (i.e. the parts that do not conform the density specifications) prior undergoing an extremely fast, single-step thermal treatment in an electric or hybrid (electric/methane fed) roller kiln, acting as both drier (in the pre-heating ramp) and furnace. Such treatment is carried out at a maximum temperature going from 1200 to 1220°C with a cycle ranging from 30 to 45 minutes cold to cold, depending on the kind of body.

3.1.1. SEMI-FINISHED PRODUCTS

The dieless pressing used to manufacture the large-sized slabs is able to get a remarkable densification: bulk density ranges from 1.88 to 2.02 g/cm^3 at the dry state, depending on the specific pressure (from 30 to 35 MPa) and the characteristics (composition, moisture content, particle size distribution) of spray dried granules (Table 1). Such values are comparable or even higher than those obtained by conventional pressing of porcelain stoneware tiles – typically from 1.90 to 1.98 g/cm^3 – emphasizing the effectiveness of the Lamina compaction technique. The uniformity of pressing is also witnessed by the modest bulk density variations from head to tail (1.88-1.92 g/cm^3) corresponding to a total porosity ranging from 27% to 29% along a total length of over 3 metres (Table 1).

Pore size distribution is almost entirely comprised between 0.01 and 1 μm, with a median value of about 0.1 μm, which are common values in porcelain stoneware manufacturing. Interestingly, no significant change in porosimetric features was observed along the slab (Fig. 5). On the other hand, SEM micrographs show a good microstructural uniformity of unfired slabs, so confirming the high compaction degree without significant textural differences from head to tail (Fig. 6).

TABLE 1. TECHNOLOGICAL PROPERTIES OF SEMI-FINISHED SLABS.

	Properties	Bulk density (g cm^{-3})	Total porosity (% vol.)
Slabs from different factories	Manufacturer #1	1.907 ± 0.003	28.4 ± 0.8
	Manufacturer #2	1.883 ± 0.002	29.5 ± 0.7
	Manufacturer #3	2.022 ± 0.003	27.4 ± 0.5
Manufacturer #1 same slab	Head	1.921 ± 0.002	27.6 ± 0.2
	Middle	1.915 ± 0.003	28.2 ± 0.3
	Tail	1.884 ± 0.001	29.3 ± 0.1
Benchmark	Reference values for porcelain stoneware tiles	1.85 – 1.93	26 – 32

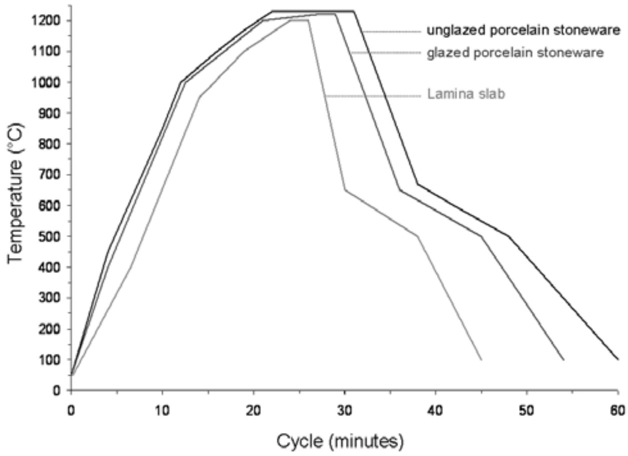

Figure 4. Firing schedule of large-sized ceramic slab compared to those of porcelain stoneware tiles.

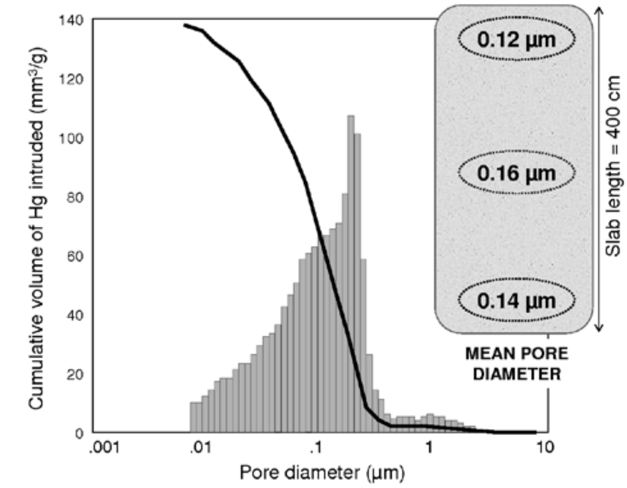

Figure 5. Pore size distribution of the unfired porcelain stoneware large slab.

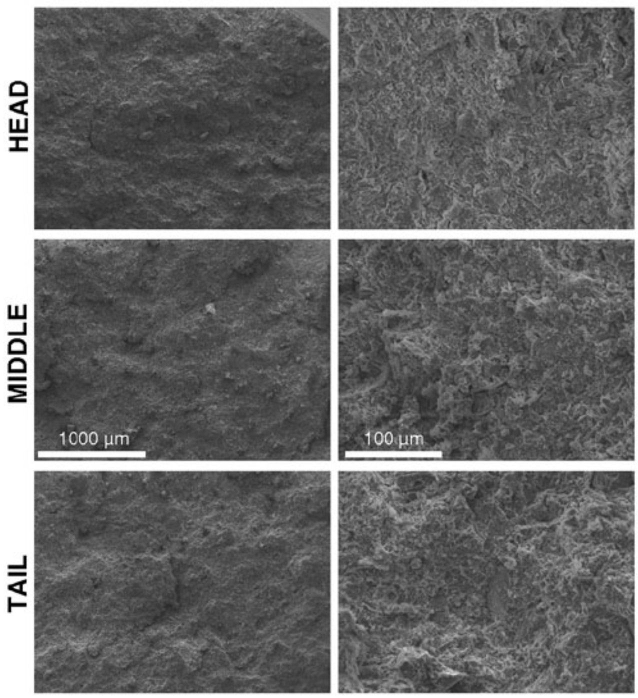

Figure 6. SEM micrographs of unfired Lamina slab.

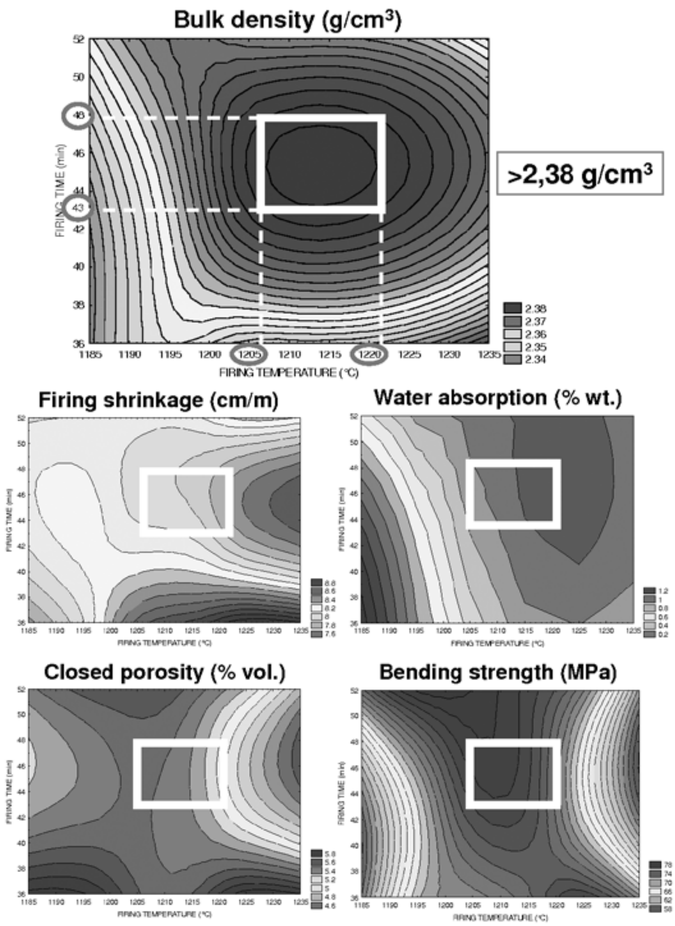

Figure 7. Firing behaviour of porcelain stoneware in the Lamina process.

3.1.1.2. Firing behaviour

Limited deformations occur during the industrial firing of slabs: the deviation from straightness of the long side is usually within 5 mm; taking into account a full slab length of 300 cm, it corresponds to a curvature below 0.2%.

The stability of the main physical and technological characteristics of large-sized slabs was appraised over a wide range of firing conditions. It can be appreciated that a very high degree of sintering (bulk density >2.38 g cm^{-3}) can be achieved in a relatively wide span of firing schedules, from 1205 to 1220°C of maximum temperature and 43 to 48 minutes of total time (Fig. 7). In such a window, water absorption values always meet the standard prescription (<0.5%) with nearly constant closed porosity (5.2-5.4%), while linear shrinkage and bending strength vary in quite narrow ranges (7.6-8.0 cm/m and 74-78 MPa, respectively). This sintering behaviour is fundamental in the case of very large slabs, although common to many porcelain stoneware bodies [7, 8,18-20].

3.1.1.3. Technological and functional properties of ceramic slabs

The values of water absorption, bulk density and closed porosity exhibit very limited fluctuations, even if slabs came from different manufacturing plants. Such variations often correspond to the experimental uncertainty, even when different parts of the same slab are taken into account (Table 2). On the other hand, these values fit well those usually found for porcelain stoneware tiles (Fig. 8): water absorption generally below 0.1%; total porosity between 5 and 8%, mostly being represented by closed porosity (5.0 -7.9%); bulk density in the 2.34-2.42 g·cm^{-3} range [1-8, 17-20].

Large slabs fulfil the standard and market requirements for tiles belonging to the BI_a group, also when functional properties are taken into account. In particular, the linear thermal expansion appears to be acceptable, although lower than common values for porcelain stoneware tiles (Table 3). The resistance to thermal shock and freeze/thaw cycles is excellent, while the resistance to chemicals and stains is well over the required thresholds.

TABLE 2. TECHNOLOGICAL PROPERTIES OF CERAMIC SLABS.

Properties		Water absorption (% wt.)	Open porosity (% vol.)	Closed porosity (% vol.)	Total porosity (% vol.)	Bulk density (g cm^{-3})
Slabs from different factories	Manufacturer #1	0.11 ± 0.02	0.25 ± 0.04	6.5 ± 0.1	6.7 ± 0.1	2.337 ± 0.005
	Manufacturer #2	0.07 ± 0.02	0.16 ± 0.06	7.9 ± 0.2	8.1 ± 0.2	2.338 ± 0.003
	Manufacturer #3	0.06 ± 0.01	0.14 ± 0.03	5.0 ± 0.1	5.1 ± 0.1	2.416 ± 0.014
Manufac-turer #3 same slab	Head	0.05 ± 0.01	0.13 ± 0.04	4.5 ± 0.2	4.6 ± 0.2	2.428 ± 0.006
	Middle	0.06 ± 0.01	0.14 ± 0.04	5.4 ± 0.3	5.5 ± 0.2	2.404 ± 0.008
	Tail	0.07 ± 0.01	0.16 ± 0.01	5.0 ± 0.3	5.2 ± 0.2	2.414 ± 0.009
Benchmark	Reference values for porcelain stoneware tiles	0.01 – 0.80	0.01 – 5.00	1.5 – 9.0	2.0 – 13.0	2.33 – 2.54

TABLE 4. PHASE COMPOSITION OF LARGE SLABS COMPARED WITH THAT OF PORCELAIN STONEWARE TILE

	Properties	Vitreous phase (% wt.)	Quartz (% wt.)	Feldspars (% wt.)	Mullite (% wt.)
Slabs from different factories	Manufacturer #1	71.0 ± 0.5	17.5 ± 0.1	2.5 ± 0.2	8.9 ± 0.2
	Manufacturer #2	79.8 ± 1.5	11.4 ± 0.5	2.0 ± 0.3	6.8 ± 0.7
	Manufacturer #3	62.0 ± 1.1	16.4 ± 0.3	10.7 ± 0.2	8.5 ± 0.5
Benchmark	Reference values for porcelain stoneware tiles	55 – 70	13 – 28	0 – 10	4 – 10

3.1.1.4. Microstructure and phase composition of ceramic slabs

The composition of large slabs consists of an abundant vitreous phase (up to 80%) associated with residual phases (quartz and little feldspars) plus a small quantity of new formed mullite (Table 4). The overall composition is fully comparable with that of typical porcelain stoneware [2, 3, 6-8, 17-20], even if the vitreous phase may be present in larger amounts (and quartz in lower contents) especially when pre-milled body formulations are processed.

Large-sized slabs are characterized by a very compact microstructure, with a limited amount of porosity, mostly represented by irregularly shaped pores showing a maximum size of about 50 μm (Figure 9). Such microstructural features are consistent with those of the best porcelain stoneware tiles, even if the largest pores are coarser than those observed in most compact porcelain stoneware tiles [3-5, 8, 17-20].

3.1.1.5. Mechanical and tribological performance of ceramic slabs

Lamina slabs are characterized by a modulus of rupture around 70 MPa, therefore well over the standard requirement of 35 MPa for BI_a tiles (ISO 13006). Fracture toughness is as high as 1.26 MPa·m$^{1/2}$, and the Young modulus is 68 GPa.

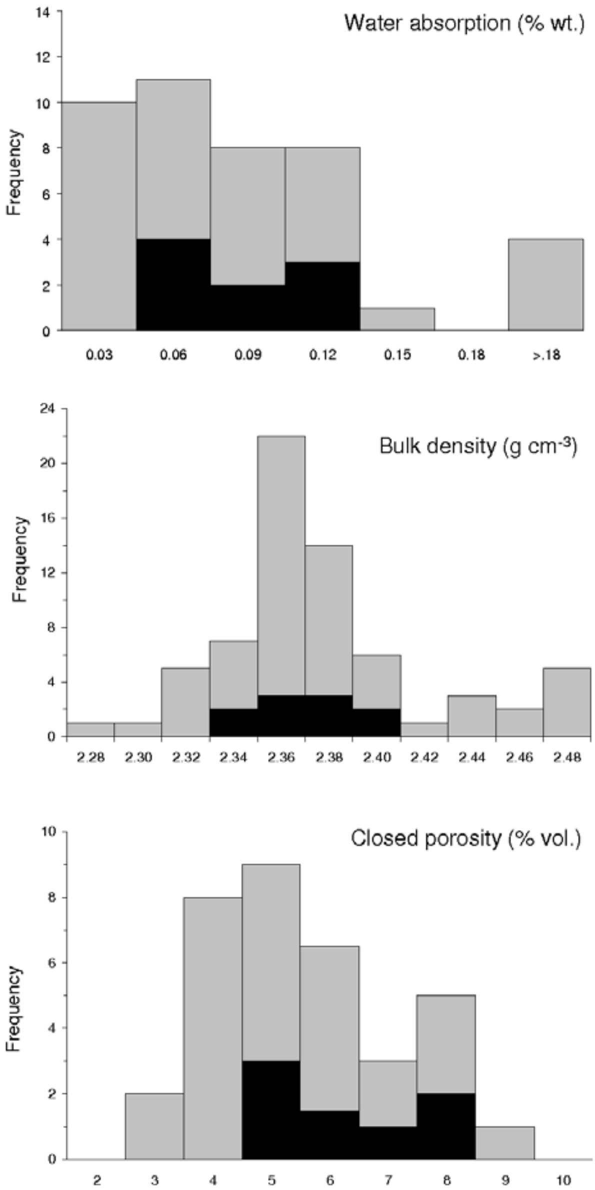

Figure 8. Physical properties of Lamina slabs versus conventional porcelain stoneware tiles.

TABLE 3. TECHNOLOGICAL AND FUNCTIONAL PERFORMANCES OF LARGE SLABS.

Standard method ISO 10545	Unit	ISO 13006 standard value for Group BIa	Benchmark (porcelain stoneware tiles)	Lamina large slabs
Resistance to deep abrasion	volume removed (mm^3)	<175	<150	136 – 167
Linear thermal expansion	coefficient (MK^{-1})	No threshold	≅ 7.0	5.5
Resistance to thermal shock	visible alteration	No threshold	None	None
Moisture expansion	expansion (mm/m)	No threshold	<0.5	0.03
Frost resistance	visible defects	None	None	None
Chemical resistance	minimum class	GB-UB	GB-UB	GA-GLA
Resistance to stains	minimum class	3	3 – 5	5

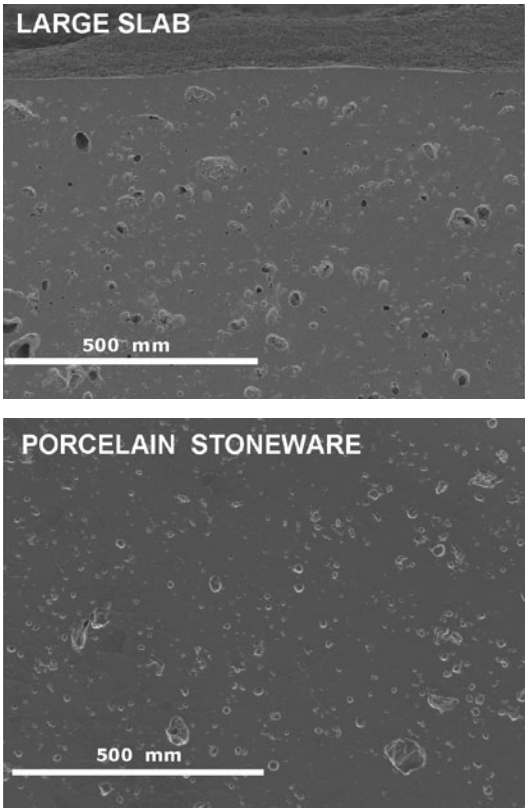

Figure 9. SEM micrographs of large sized slab and porcelain stoneware tile.

The volume of material removed after the deep abrasion test ranges from 136 to 167 mm^3. These values correspond to an excellent mechanical behaviour for ceramic tiles and fall within the field of high strength porcelain stoneware products (Fig. 10) [2, 3, 5-8, 21, 22]. Interestingly, large slabs exhibit a limited sensitivity to the presence of microstructural defects: the critical defect size, calculated on the basis of modulus of rupture and fracture toughness [23], is in the 215-250 μm range, therefore well over the size of coarsest pores (approximately 50 μm) observed under SEM.

The large size coupled with the low thickness bestow a certain degree of flexibility on slabs and particularly in the case of ceramic-fiberglass composites; the value of elastic modulus seems therefore suitable for a flexible, but not stiff slab that can be bent to an estimated curvature radius of about 5 m.

Another important aspect is the strengthening effect due to the fiberglass net applied on the rear of the slab (L1) or between two slabs (L2). While the ceramic slab shows a mechanical behaviour similar to that of porcelain stoneware tile, composite slabs exhibit a prolonged resistance after the rupture of the ceramic component (Fig. 11). Such behaviour is useful especially for applications (e.g. ventilated façades) where, even in case of slab breakdown, no fragment must fall down.

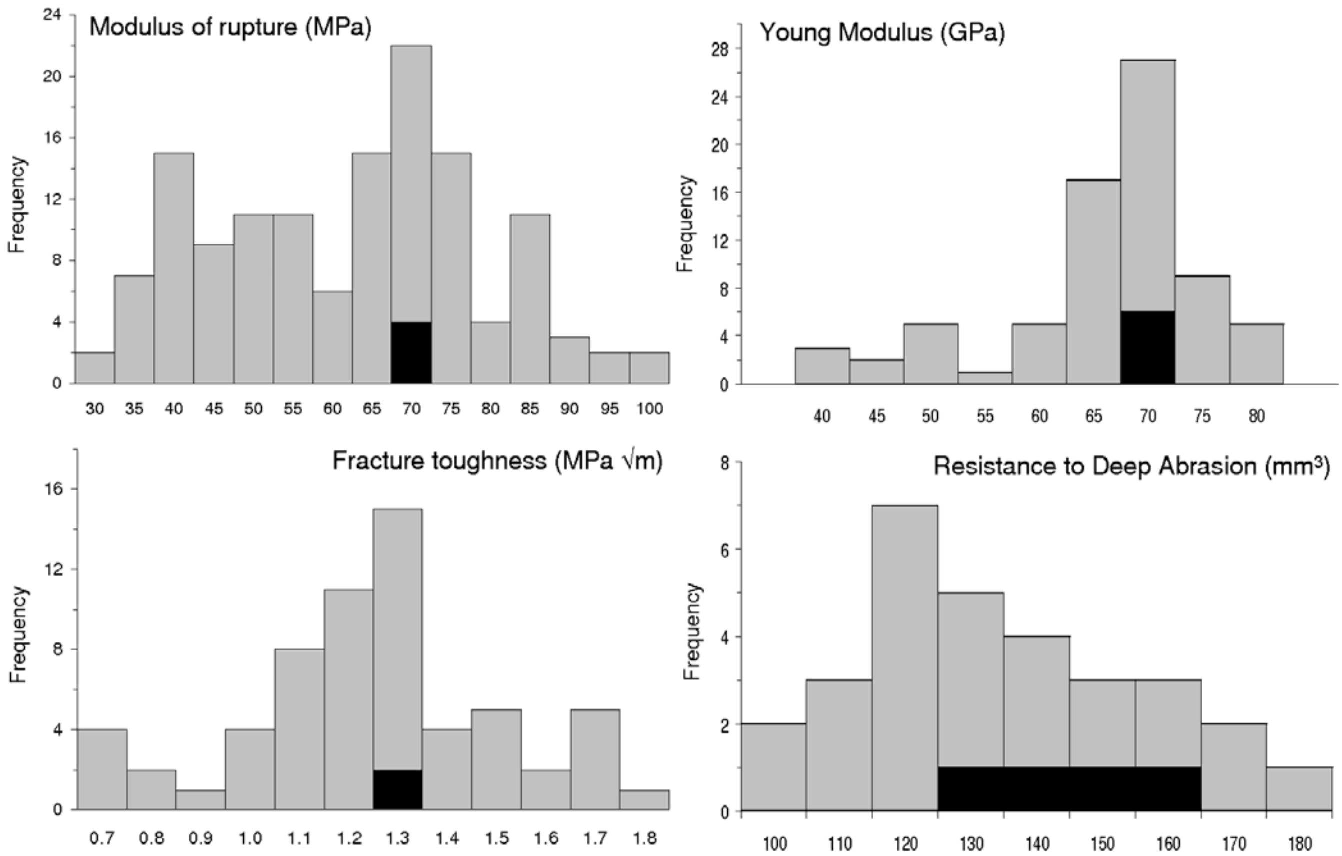

Figure 10. Mechanical and tribological properties of Lamina slabs versus conventional porcelain stoneware tiles.

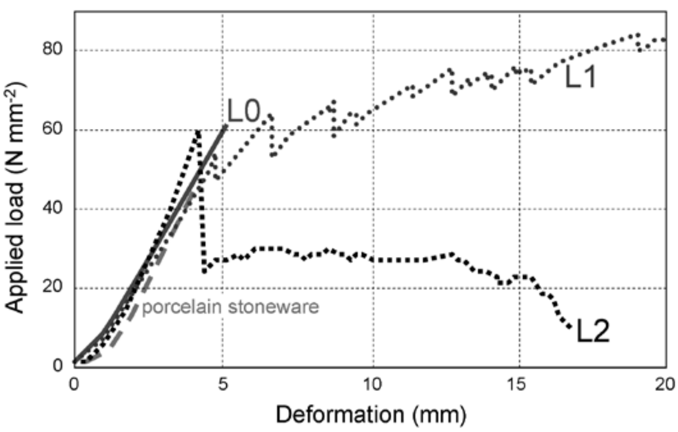

Fig. 11 Mechanical behaviour of ceramic slab (L0), ceramic-fiberglass composite (L1) and slab-fiberglass-slab multilayer (L2).

3.1.1.6. Applications of ceramic slabs

Large-sized slabs are peculiar for combining excellent technological performances with a certain degree of flexibility, which brings about an outstanding potential in novel applications, along with possible extensive use as replacement of old floorings, avoiding to dismantle the existing tiles. A key advantage of these slabs stems from the chance to be customized to the market requirements: for instance, they can be arranged in multilayered composites, by applying reinforcing fiberglass net or interlayer [24]. This ensures an improvement of flexibility and strength, making easier handling and transportation, hence widening the conventional application field of ceramic tiles, as outdoor and indoor building and construction elements (floorings, wall coverings, roofings) to ventilated façades, insulating paneling, tunnel coverings, furniture components (doors, table-tops, panels) [13, 14]. Such applications are favoured by the fact that the slab surface is suitable to be decorated by both traditional and digital techniques.

In addition, slabs can act as support for photovoltaic systems, assembled directly onto the ceramic element, or be treated to get functionalised surfaces (hydrophobic, hydrophilic, photocatalytic, bactericide, etc.) for which work is in progress.

4. CONCLUSIONS

Large-sized ceramic slabs can be considered as a new typology of ceramic product –whose manufacturing requires a redesigned process including ceramic-fiberglass composite assembling – characterized by a size of 4-5 m^2 with a typical thickness of 3 mm, which ensures reduced weight and a certain flexibility. These features, coupled with the excellent technical performances, make them suitable to be used in both conventional and brand new applications for ceramic tiles. Hindrances to the diffusion of low thickness slabs come from the lack of specific standards and regulations.

In perspective, slab surface can be functionalized providing them of outstanding features and an unrivalled versatility among ceramic building materials.

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