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Recycling of polishing porcelain stoneware residues in ceramic tiles

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Abstract

The possibility of recycling residues, coming from the industrial polishing process of porcelain stoneware tiles, by their incorporation in a porcelain stoneware body mix, was studied. Starting from a standard body mix, several modified body mixes were prepared by replacing different amounts of the fluxing component, a sodium feldspar sand, with these wastes. The densification behaviour of the different body mixes was investigated by determining water absorption, linear shrinkage and bulk density of the as fired specimens. Phase and microstructural examination, by quantitative X-ray diffractometry and scanning electron microscopy-energy dispersive spectroscopy, made it possible to explain the mechanical behaviour, i.e. flexural strength, Young's modulus and Weibull's modulus. The presence of polishing porcelain stoneware residues, PPR, in particular in a 10 wt% of replacement, made possible a consistent decrease in the maximum temperature of the thermal cycle. That did not cause significant variations in the mechanical strength of the materials, while a slight decrease of the elastic modulus and a remarkable increase of the reliability were registered.

Keywords: Traditional ceramics; Recycling; Firing; Microstructure-final; Mechanical properties

1. Introduction

Porcelain stoneware tiles represent an advanced product developed in the sector of ceramic tiles. The particular mix of raw materials (a typical current composition contains 25–30% of kaolin and ball clays, 50–60% of feldspars and 5–10% of quartz sand) and the high firing temperatures used, make it possible to obtain a dense ceramic, characterised by very high physical–mechanical characteristics. These products can also be surface polished to enhance their aesthetic and performances.[1,2] A significant increase in the production of porcelain stoneware tiles, comprehensive of the polished ones, was observed in the last years. Only in Italy, in 5 years, this production passed from 22.3% to 64.7% of the total tiles production.[3]

Even if the industrial polishing process strongly improves the aesthetic appearance of the product, several problems exist: (i) irreversible surface damage, mainly due to the opening of the bulk closed porosity and the onset of surface machining flaws that decrease the functional properties,[4–8] and (ii) an important environmental aspect, due to the disposal of the polishing porcelain stoneware residues, PPR, in form of mud. This mud contains water and very fine debris, coming from the tiles and the tools bond, prevalently magnesite, and abrasive particles, silicon carbide and diamond, driven out from the tools.

Within the ceramic industries, this kind of residues are collected and temporarily stored in effluent treatment stations that, removing the residual water, produce a mud. Afterwards, it is generally disposed in landfill sites. Since, i.e. in Italy the production is around 20,000 t/year,[9] these residues cause both an environmental impact and an increasing of the industrial running costs.

Nowadays UE policy pays much attention to environmental problems and due to the exponential increasing of wastes in the last years, the new directives do not provide a landfill confinement, but promote a waste prevention or their minimization and recycling, referring to clean technologies and residue management.[10,11] At this purpose, a valid alternative to the landfill confinement, for PPR, could be represented by their direct recycling in the production of porcelain stoneware tiles. The few investigations on this item, conducted in the past when the first polished porcelain stoneware tiles were manufactered,[12,13] reported that the fineness of PPR powder and the relevant amount of silicon carbide prevented the processing of dense ceramics. Regarding this latest aspect, at the usual firing temperatures adopted in the production of ceramic tiles, >1100 °C, silicon carbide (SiC) decomposes and forms silica and carbon

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dioxide, giving rise to porous microstructures. PPR were positively recycled only when incorporated in low density ceramic products.[14]

Recently, many efforts have been addressed to improve the industrial polishing lines in order to reduce the induced damages, the consumption of abrasive and, consequently, the amount of PPR.[15–19] These technological innovations concerned also the partial replacing of the abrasive mainly used in the industrial polishing process, silicon carbide bonded in organic and inorganic matrix, polyester resins and magnesite, respectively,[20,21] with a stronger abrasive material, such as synthetic diamond bonded in polymeric matrix.[22]

Actually, silicon carbide content in PPR is lower than some years ago, opening interesting perspectives of directly reusing these wastes in the production of porcelain stoneware tiles. The recycling of PPR, in the production of porcelain stoneware tiles, could form a closed process that, following a logical chain of events, allows the consumption of the wastes in the same production line of the starting material.

The aim of the research is to assess the possibility to recycle PPR, in the preparation of the body mix for porcelain stoneware tiles, by replacing different amounts of one of the natural raw materials. Their recycling involves at least two environmental aspects: (i) it partly solves the disposal problem, and (ii) it reduces the consumption of natural raw materials. The costs reduction for the ceramic industry is also directly linked to these crucial aspects. Using PPR, industry can dispose of a free secondary raw material that is directly available, by avoiding both the transport and the landfill costs. Moreover, the presence in PPR of calcite, magnesite, in low amounts, and feldspar, could promote the sintering in the ceramic body, allowing also a positive effect on the firing process. The PPR studied in the present work come from a regional landfill site located in Emilia Romagna (Italy) where almost the 90% of the national ceramic tiles production is concentrated.[3] Considering also the rather constant composition of the different porcelain stoneware products, the PPR disposed in this landfill site, coming from all the regional polishing industries, are characterised by an average composition and can be considered representative of this kind of material.

2. Materials and methods

The chemical and mineralogical composition of PPR, coming from a landfill site in Emilia-Romagna (Italy), was determined with the use of inductively coupled plasma emission spectroscopy (ICP-OES Optima 3200 XL, Perkin-Elmer, USA), Table 1, and by X-ray diffraction analysis (PW3830, Philips, NL). The CO_2 amount was determined by using the calcimeter Dietrich-Frühling. The morphology of the powder particles was evaluated with the aid of a scanning electron microscope (Zeiss EVO 40, D) and by determining the particle size distribution (Master-Size 2000, Malvern, UK) and the specific surface analysis BET (Flowsorb II 2300 Micromeritics, USA), Table 2. Differential thermal analysis, DTA (Netzsch STA 409C/CD, D), was carried out on PPR by using a heating rate of 10 °C/min till 1200 °C.

Table 2
Mineralogical composition, specific surface, BET, and particle size distribution (values at 10th, 50th and 90th percentiles) of dried PPR

Crystalline phases	Quartz, zircon, feldspar, mullite, calcite, magnesite, moissanite (SiC)
BET analysis (m^2/g)	23.6
Particle size distribution (μm)	d_{10}, 2.1; d_{50}, 12.3; d_{90}, 41.3

An industrial porcelain stoneware mix was chosen as reference material. It was composed by 10% kaolinitic clay, 33% illitic clay, 31% sodium feldspar sand, 19% potassium feldspar sand and 7% green body scrap, corresponding to fractured and rejected green tiles, that are reused as a raw material for the same product. Three modified body mixes were formulated replacing 5, 10 and 15 wt% of the original fluxing agent, a Na-feldspar sand (Table 1), by the same percentages of dried PPR. The compositions and labelling of the materials are summarised in Table 3.

The different studied mixes were prepared by milling the raw materials in a porcelain jar mill for 1 h, with 33 wt% of water and 0.6 wt% of the deflocculating agent, FLUICER CF907 (Ceramco, Zwischer & Schwarz Group, D). To obtain powders suitable for shaping, the slips were dried overnight in an oven at 110 °C, crushed and sieved to pass at 125 μm screen. The test specimens, in form of disks and bars, were prepared by adding 6 wt% water to the dried powders, followed by uniaxial pressing at 52 MPa. The sintering was performed in a laboratory electric furnace, following four scheduled thermal cycles, reaching four different maximum temperatures, 1120, 1140, 1160 and 1180 °C, adopting a heating rate of ∼5 °C/min and a natural cooling to room temperature. The sintering behaviour of the fired specimens was evaluated on the basis of their linear shrinkage. Water absorption and bulk density were also determined according to the test method recommended for ceramic tiles, reported in the Standard EN ISO 10545-3.[23]

The quantitative mineralogical compositions, of the as fired samples, were determined by X-ray diffraction analysis (PW3830, Philips, NL). Powdered specimens, diluted with 10 wt% of corundum NIST 676 as internal standard, were side loaded to minimize preferred orientation. Data were collected in the angular range 10–80° 2θ with steps of 0.02° and 5 s/step and the Rietveld refinements were performed using GSAS.[24]

Table 1
Chemical composition (wt%) of the polishing porcelain stoneware residues, PPR, and the sodium feldspar sand

	SiO_2	Al_2O_3	TiO_2	Fe_2O_2	CaO	MgO	K_2O	Na_2O	ZrO_2	PF	CO_2
PPR	64.06	16.54	0.48	0.50	1.40	4.63	2.05	4.43	1.10	4.03	0.7
Na feldspar sand	70.11	17.82	0.06	0.30	1.32	0.19	0.59	8.97	0.0	0.64	–

Table 3
Chemical composition (wt%) of the tested body mixes

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	ZrO_2	LI[a]	CO_2
S	72.36	17.15	0.48	0.49	0.68	0.25	1.85	3.53	0.00	3.19	0.00
S5L	72.05	17.09	0.50	0.50	0.69	0.47	1.93	3.30	0.06	3.36	0.04
S10L	71.75	17.02	0.53	0.51	0.69	0.59	2.00	3.08	0.08	3.45	0.07
S15L	71.45	16.96	0.55	0.52	0.70	0.92	2.07	2.85	0.17	3.70	0.11

[a] LI = loss on ignition.

The microstructure of the fired materials was analysed by a scanning electron microscope, SEM (Zeiss EVO 40, D) equipped with an energy dispersion X-ray attachment, EDS (Inca, Oxford Instruments, UK), observing suitable specimens polished to mirror like finish and etched, when appropriate, by using a 5% HF solution for 3 min.

The flexural strength of the as fired specimens in form of bars, 70 mm × 10 mm × 6 mm was measured by using an universal testing machine (10/M, MTS, USA), equipped with a three point bending apparatus, 60 mm roller span, adopting a crosshead speed of 5 mm min^{-1}. The modulus of elasticity was also evaluated, via an extensometer applied in correspondence to the middle of the surface of the bars subjected to the tensile stress. The average flexural strength, σ, was calculated on twenty results of correctly fractured specimen and Weibull's modulus, m, was evaluated via the least squares method and linear regression analysis, adopting, as the probability estimator, $P_n = (i - 0.5)/N$.

3. Results and discussion

The results of the PPR characterisation, Tables 1 and 2 and Fig. 1, indicated as they are constituted by very fine particles, containing both typical constituents of porcelain stoneware, such as quartz, zircon, feldspar, mullite, and the ones of the abrasives, such as magnesite, calcite and silicon carbide, in its crystallographic form of moissanite. The DTA analysis, Fig. 2, confirms these results, showing the endothermic peaks at 577, 755 and 831 °C that indicate the presence of quartz, calcite and magnesite, respectively. At higher temperatures, around 1100 °C, the DTA curve presents an almost straight line with a higher slope, indicating the suddenly fusion of the material, caused by the carbonates. Due to the rather low level of moissanite, no clear evidence of its decomposition was detected.

Because of the presence of carbonates and feldspars, both exerting a fluxing action in a silicate body mix, the PPR powder was used as raw material for an industrial porcelain stoneware body mix formulation, by partially replacing the original fluxing agent, a sodium feldspar sand, Table 1.

The chemical analysis of the unfired batches, reported in Table 3, shows the compositional changes among the standard reference material, S, and the materials containing different amounts of PPR. Because of this substitution, the percentage of magnesium oxide increases, the ones of sodium and silicon oxides decrease, while the calcium oxide content remains constant. To appreciate these differences in composition across broad composition ranges, all the batch constituents were converted to a molar basis, using the unity molecular formula (UMF) approach.[25] In Table 4 are reported the sums of the flux levels, R_2O and RO (Na_2O, K_2O, MgO and CaO), and their comparison with the Al_2O_3 and SiO_2 levels. It is evident that the modified formulations present a higher amount of fluxing agent and a lower amount of alumina and silica.

The firing behaviour of the materials has been studied by evaluating the trend of shrinkage and water absorption, WA, versus temperature, Fig. 3. The S material reaches a value of 0.00% WA, at the firing temperature of 1160 °C. The replacement of the sodium feldspar sand with PPR results in a lowering of the water absorption curves for all the modified compositions. Already at 1140 °C, WA, for S5L, S10L and S15L materials, is

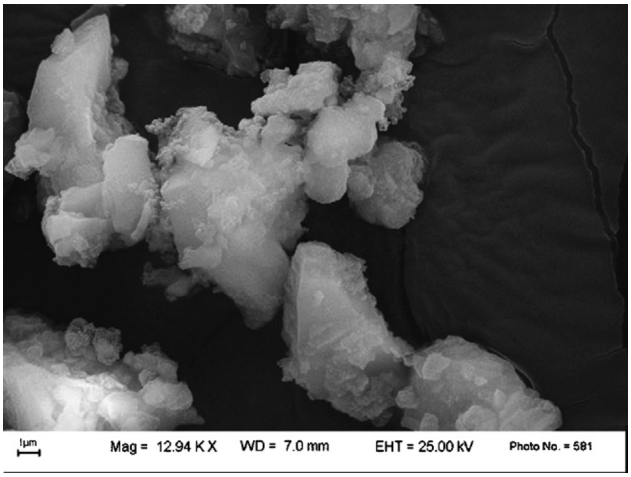

Fig. 1. SEM micrograph of the dried PPR. The submicronic particles on the top of the micrograph are calcite and magnesite.

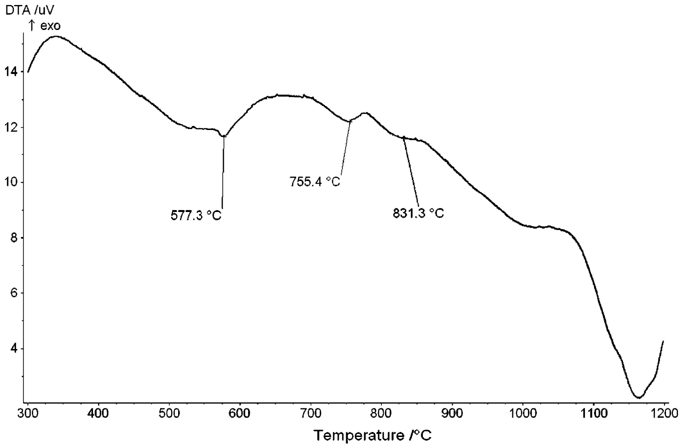

Fig. 2. DTA analysis of PPR.

Table 4
Chemical composition (mol%) and unity molecular formula (UMF) of the body mixes

	CaO	MgO	K_2O	Na_2O	Sum RO + R_2O	Al_2O_3	SiO_2	UMF
S	0.84	0.36	1.37	3.82	6.39	11.63	81.98	1:1.82:12.83
S5L	0.85	0.60	1.37	3.61	6.43	11.60	81.97	1:1.80:12.74
S10L	0.85	0.85	1.45	3.41	6.56	11.58	81.86	1:1.76:12.48
S15L	0.85	1.10	1.54	3.09	6.58	11.58	81.84	1:1.76:12.44

0.27, 0.13 and 0.07 wt%, respectively, while it is 1.31 wt%, for S. According to the Standard EN 14411,[26] tiles can be considered porcelain stoneware only if their WA is ≤0.5 wt%. It is evident as S material, fired at 1140 °C, does not belong to this class of tiles.

The standard mix, S, reaches the maximum shrinkage at 1160 °C, Fig. 3, maintaining a rather constant plateau also at higher temperatures. The mixes modified with PPR, S5L, S10L and S15L, reach the maximum shrinkage at a lower temperature, 1140 °C, with very similar values. Compared to S, S5L and S10L show a rather large dimensional stability range, slightly shifted towards lower temperatures, even if a slight expansion is observed for temperatures >1160 °C. On the contrary, S15L presents a strong dimensional instability with a considerable expansion, already at temperatures >1140 °C, Fig. 3.

These thermal behaviours can be explained taking into account the physical-chemical characteristic of PPR. The data, reported in Tables 3 and 4, show two interesting aspects: (i) the increasing of the total amount of fluxing oxides in the body mixes containing PPR and (ii) the important role played by the different nature of the components present. The larger amount of alkali energetically promotes the sintering. Furthermore, the presence of carbonate particles, of small dimensions, favours the development of a less viscous liquid phase, at lower temperature, able to easily penetrate into inter-particles voids, promoting densification.[27]

The microstructure of S, fired at 1140 °C, Fig. 4a, results to be rather porous, according to its still high open porosity, essentially interconnected. The increase in firing temperature, 1160 °C, causes a larger development of liquid phase, able to decrease porosity and transform interconnected pores into spherical ones, Fig. 4b. The presence of 5 wt% of PPR, sample S5L, makes it possible to obtain a similar compact microstructure, Fig. 5a, but firing it at lower temperature, 1140 °C. By increasing the amount of PPR, S10L and S15L, the total porosity decreases and essentially closed and round pores are still visible, Fig. 5b and c.

Further characterisations, mineralogical and mechanical, were carried out only for those materials that, on the basis of water absorption, were considered belonging to porcelain stoneware material, Fig. 3. As regards, the standard reference material S, fired at 1140 °C, was neglected because of the high water absorption, 1.31 wt%.

Comparing the mineralogical compositions of the standard reference material S, fired at 1160 °C, and the materials containing PPR, S5L, S10L and S15L, fired at 1140 °C, Table 5,

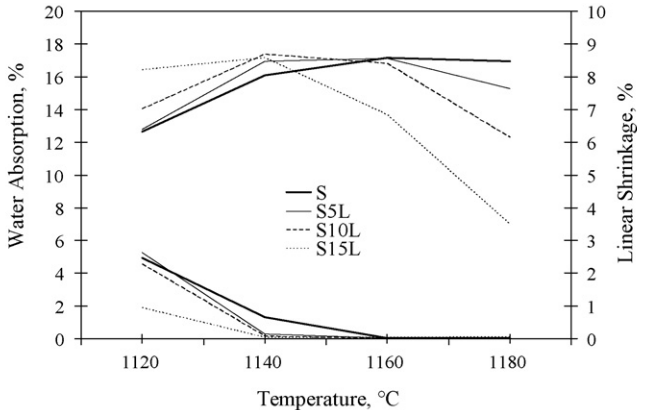

Fig. 3. Water absorption and linear shrinkage as a function of the firing temperature of the materials.

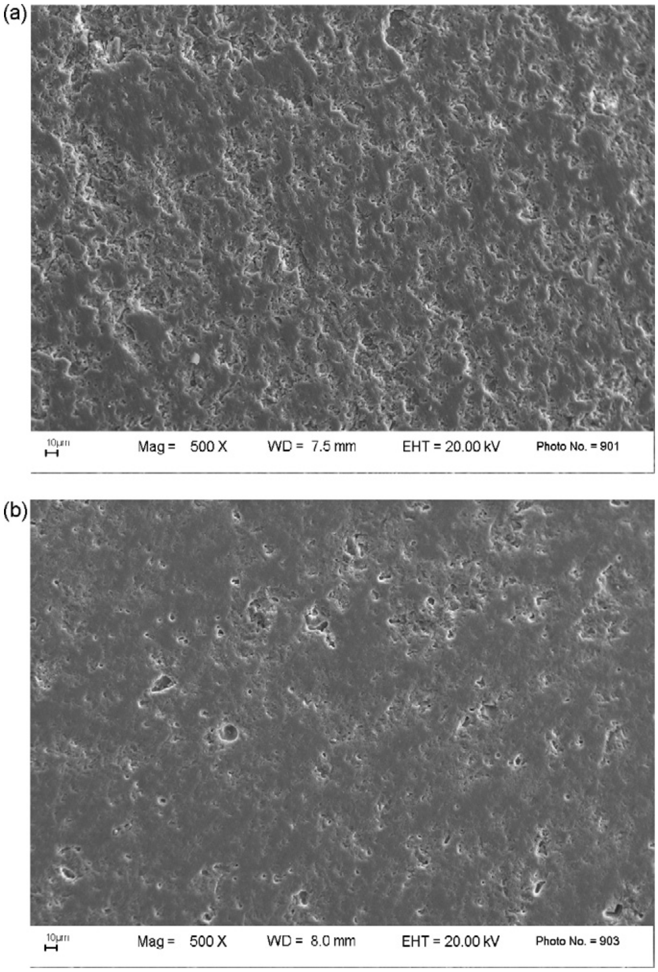

Fig. 4. SEM micrographs of the polished surfaces of S material, firing temperatures 1140 °C (a) and 1160 °C (b).

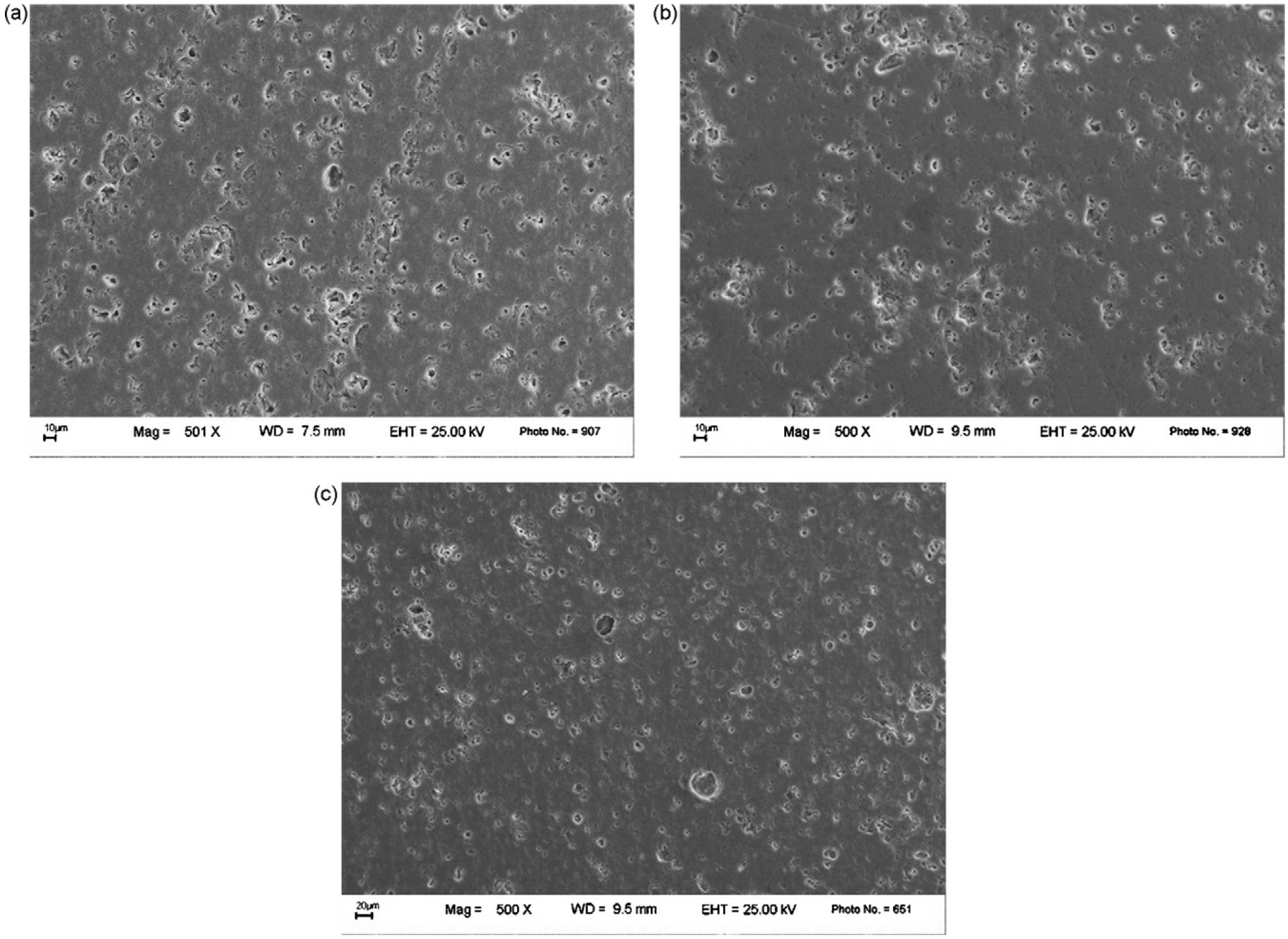

Fig. 5. SEM micrographs of the polished surfaces of S5 (a), S10L (b) and S15L (c), firing temperature 1140 °C.

an increase of the crystalline fraction is evident. Taking into account the mineralogical composition of PPR, Table 2, it is clear how the modified body yields higher amount of quartz, mullite and feldspar (albite). Passing from S5L to S15L, the increase of quartz is also evident, while the amount of feldspar, even if it strongly increases passing from S to S5L, for higher amount of PPR proportionally decreases. The phenomenon can be correlated with the fact that, increasing amounts of PPR implies the presence of higher and stronger fluxing agent in the body mix. These conditions favour both an earlier dissolution of feldspar and the formation of a larger amount of glassy phase. Furthermore, also the crystallisation of rather elongated secondary mullite is favoured in such low viscosity liquid phase, Fig. 6.[28]

The mechanical properties of the materials are reported in Table 6. The presence of PPR makes it possible to obtain materials, characterised by average flexural strength values, σ, not significantly different, while the Young's modulus, E, shows, a slight decreasing trend, if compared with the data of the standard reference material, S. That means a lower stiffness of the materials. However, it has to be noted that the results corresponding to the modified mixes, S5L, S10L and S15L, have

Table 5
Mineralogical composition (wt%) of the fired materials

	Quartz	Mullite	Albite	Glass
S, 1160 °C	21.4 ± 0.1	5.3 ± 0.5	3.4 ± 0.4	69.9 ± 1.2
S5L, 1140 °C	23.7 ± 0.1	5.5 ± 0.5	8.0 ± 0.4	62.8 ± 1.2
S10L, 1140 °C	27.0 ± 0.2	5.5 ± 0.5	6.9 ± 0.4	60.6 ± 1.0
S15L, 1140 °C	25.5 ± 0.1	6.3 ± 0.5	3.9 ± 0.4	64.3 ± 1.2

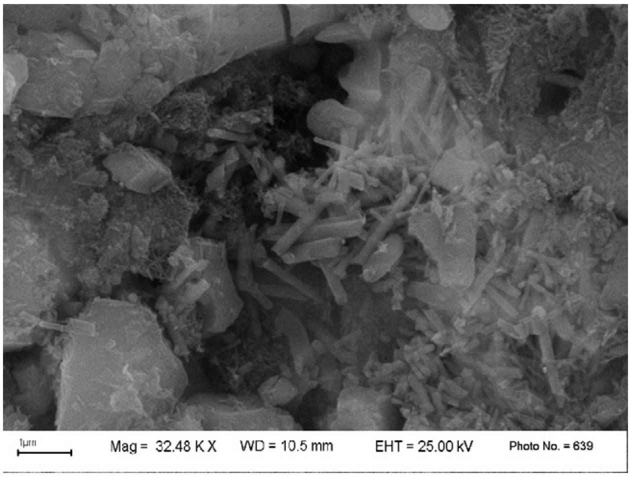

Fig. 6. SEM micrograph of the polished etched surface of S10L material, firing temperature 1140 °C. Needle like mullite crystals is shown.

Table 6
Mechanical and physical characteristics of the fired materials

	σ (MPa)	E (GPa)	m	p_{tot} (%)	p_{open} (%)	ρ_{bulk} (g/cm^3)
S, 1160 °C	94.9 ± 5.0	72.9 ± 1.5	21.9	3.54	0.01	2.43
S5L, 1140 °C	97.2 ± 5.9	64.0 ± 4.1	19.5	4.50	0.41	2.41
S10L, 1140 °C	96.0 ± 4.3	66.4 ± 4.3	26.2	4.09	0.02	2.41
S15L, 1140 °C	97.0 ± 4.1	64.9 ± 5.5	27.9	3.06	0.00	2.40

been obtained by sintering at a maximum temperature, 1140 of 20 °C lower than that adopted for the standard S, 1160 °C. For this reason, the total porosity, p_{tot}, is a little higher in S5L and S10L than in S but, in S15L this value decrease. Besides, the bulk density, ρ of the modified body mixes is slightly lower than the standard reference material, S, and the Weibull's modulus, m, significantly increases with increasing amounts of PPR. These data are only apparently conflicting and can be explained by considering the results of the mineralogical and morphological analysis. For the materials containing PPR, the increased amount of crystalline phases, compared to S, and the presence of a less viscous liquid phase, able to better fill the voids during sintering, make it possible to obtain a more homogeneous microstructure. So, even though the flexural strength results do not show significant variations and the bulk density slightly decreases, the reliability of the materials exhibits a remarkable increase. This latter aspect, directly correlated with a decreased scattering of the data, is for this class of tiles, usually subjected to very severe service conditions, a further positive outcome.

Finally, analysing the results reported in Table 6, significantly changes are not observed between S10L and S15L, even if this latter presents, during firing, a rather low thermal stability. The previous observations make it possible to assert that replacements of PPR, beyond 10 wt%, do not seem to confer beneficial results to this kind of body mix. The excessive amount of stronger fluxing agent, carbonates present in S15L material, compromises the performance.

4. Conclusions

In the present study, the possibility of replacing different percentages of sodium feldspar sand with PPR in a standard porcelain stoneware body mix was investigated.

The replacement in the range 5–15 wt%, made it possible to obtain porcelain stoneware materials with rather good characteristics. The new materials showed a meaningful decrease in the maximum sintering temperature, keeping at the same, the mechanical properties. Furthermore an enhanced microstructural homogeneity favoured a significant increase of the reliability. In particular, the body mix containing 10 wt% of PPR turned out the best material, showing the highest mechanical properties with good thermal stability in a temperature range 1140–1160 °C.

These results outline as the recycling and the exploitation of this kind of wastes can be for ceramic industry a viable procedure. In agreement with the UE policy, the recycling in the production process of PPR, could save both energy and natural resources, avoiding also the economical and environmental problems linked to the disposal in landfill site.

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References

1. Menegazzo, A. P. M., Paschoal, J. O. A., Andrade, A. M., Gouvêa, D. and Carvalho, J. C., Evaluation of the technical properties of porcelain tile and granite. *Proc. Qualicer*, 2002, 211–230.
2. Esposito, L. and Tucci, A., Porcelain stoneware tile surfaces. *Am. Ceram. Soc. Bull.*, 2000, **79**(5), 59–63.
3. *26^a ISN, 2005. Assopiastrelle*, 2006, http://www.assopiastrelle.it.
4. Orts, M. J., Sánchez, E., García-Ten, J., Ibañez, M. J., Sánchez, J., Soler, C. *et al.*, Comportamiento del gres porcelanico durante la operacion de pulido. *Bol. Soc. Esp. Ceram. Vidrio*, 2001, **40**(6), 445–453.
5. Esposito, L., Tucci, A., Rastelli, E., Palmonari, C. and Selli, S., Stain resistance of porcelain stoneware tiles. *Am. Ceram. Soc. Bull.*, 2002, **81**(10), 38–42.
6. Dondi, M., Ercolani, G., Guarini, G., Melandri, C., Raimondo, M., Rocha e Almendra, E. *et al.*, The role of surface microstructure on the resistance to stain of porcelain stoneware tiles. *J. Eur. Ceram. Soc.*, 2005, **25**(4), 357–365.
7. Silva, G., Munõz, A., Feliu, C., Ibañez, M. J., Barbera, J. and Soler, C., Abrasion resistance of ceramic flooring in actual heavy traffic conditions. *Proc. Qualicer*, 2002, 79–82.
8. Tucci, A., Esposito, L., Malmusi, L. and Piccinini, A., Wear resistance and stain resistance of porcelain stoneware tiles. *Key Eng. Mater.*, 2002, **206–213**, 1759–1762.
9. *Private communication*.
10. Report from the commission to the council and the european parliament on implementation of the community waste legislation. *COM*, 2006, 406 [final, Brussels].
11. Communication from the commission to the council, the European parliament, the European economic and social committee and the committee of the regions. Taking sustainable use of resources forward: a thematic strategy on the prevention and recycling of waste. *COM*, 2005, 666 [final, Brussels].
12. Andreola, F. and Barbieri, L., Problematiche e prospettive di recupero ed utilizzo dei fanghi di levigatura del grès porcellanato. *Ceram. Informazione*, 2001, **36**(404), 158–162.
13. Andreola, F., Leonelli, C., Siligardi, C., Bonamartini and Corradi, A., Microwave technology applied to the recycling of fine stoneware tiles polishing sludge compared to conventional firing. *Tile Brick Int.*, 2000, **16**(1), 6–11.
14. Bernardin, A. M., Silva, M. J., Silva, H. G. C. and Riella, H. G., Physical, structural and mechanical characterization of expanded ceramics obtained from polishing residues. *Proc. Qualicer*, 2006, 189–196.

15. Di Ilio, A. and Paoletti, A., A comparison between conventional abrasives and superabrasives in grinding of SiC–aluminium composites. *J. Mach. Tools Manuf.*, 2000, **40**, 173–184.
16. Pollini, W. and Turchetta, S., Force and specific energy in stone cutting by diamond mill. *J. Mach. Tools Manuf.*, 2004, **44**, 1189–1196.
17. Pollini, W. and Turchetta, S., Test protocol for micro-geometric wear of sintered diamond tools. *Wear*, 2004, **257**, 246–256.
18. Tönshoff, H. K., Hillmann-Apmann, H. and Asche, J., Diamond tools in stone and civil engineering industry: cutting principles, wear and applications. *Diamond Relat. Mater.*, 2002, **11**, 736–741.
19. Luo, S. Y., Effect of fillers of resin-bonded composites on diamond retention and wear behaviour. *Wear*, 1999, **236**, 339–349.
20. Sánchez, E., García-Ten, J., Ibáñez, M. J., Orts, M. J. and Cantavella, V., Polishing porcelain tile. Part 1. Wear mechanism. *Am. Ceram. Soc. Bull.*, 2002, **81**(9), 50–54.
21. Hutchings, I. M., Adachi, K., Xu, Y., Sánchez, E., Ibáñez, M. J. and Quereda, M. F., Analysis and laboratory simulation of an industrial polishing process for porcelain ceramic tiles. *J. Eur. Ceram. Soc.*, 2005, **25**(13), 3151–3156.
22. Traversa, L., Marinelli, F., Maye, A. S., Torsi, L., Sabbatini, L., Cioffi, N., Cutrignelli, G., Zambonin, P. G., *Caratterizzazione spettroscopica di materiali innovativi impiegati nella realizzazione di utensili abrasivi ad alte prestazioni*. ISA, 2006 [Bari, I].
23. EN ISO 10545-3, *Ceramic tiles. Part 3. Determination of Water Absorption, Apparent Porosity, Apparent Relative Density and Bulk Density*, 1995.
24. Larson, A. C., Von Dreele, R. B., *GSAS—General Structural Analysis System. Los Alamos National Laboratory Report, LAUR*, 1994, pp. 86–748.
25. Carty, W., Katz, M. and Gill, J., Unity molecular formula approach to glaze development. *Ceram. Eng. Sci. Proc.*, 2000, **21**(2), 95–109.
26. EN 14411, *Ceramic Tile—Definitions, Classification, Characteristics and Marking*, 2003.
27. Peters, T. and Iberg, R., Mineralogical changes during firing of calcium-rich brick clays. *J. Am. Ceram. Soc.*, 1978, **57**, 504.
28. Iqbal, Y. and Lee, W. E., Microstructural evolution in triaxial porcelain. *J. Am. Ceram. Soc.*, 2000, **83**(12), 3121–3127.