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Ceramic tiles with controlled porosity and low thermal conductivity by using pore-forming agents

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Abstract

This work reports the influence of pore forming agents, their incorporation content and particle size distribution on the bi-layered ceramics porosity, mechanical resistance and thermal conductivity.

The results demonstrate that the porosity level on the bi-layered ceramics bottom layer can be easily controlled by the porogen amount, while porogen particle size affects both the number and size distribution of the pores. Two different pore forming agents were evaluated, namely polypropylene (PP) and polymethyl methacrylate (PMMA). The nature of the pore forming agent, however, did not affect the bi-layered ceramics' properties.

The incorporation of porosity into the bi-layered ceramics promotes thermal conductivity attenuation (up to 79%) in comparison with conventional porcelain stoneware ceramics, yet maintaining suitable mechanical strength. Thermal conductivity decrease is adjustable as a function of the volume and size of the generated pores, thus enabling materials to be tailored for the envisaged applications.

Keywords: A. Pressing; B. Porosity; C. Thermal conductivity; D. Traditional ceramics; E. Functional applications

1. Introduction

Porous ceramic materials have uses in numerous applications, including ceramic filters and membranes [1,2], fuel cell electrodes [3,4], catalyst supports for biomaterials [5], piezoelectric materials [6,7] and thermally or acoustically insulating bulk materials [8].

Several processing routes to produce porous ceramics have been reported [9,10]. In particular, pore-forming agents have shown potential to produce high porosity levels. The principle is that organic particles are burnt out during heating to the firing temperature, leaving voids in the ceramic body. The morphology of these voids will depend on the selected pore-forming agent, and thus can be controlled through suitable incorporation content and particle size distribution.

Numerous pore-forming agents have been investigated, including starch [11–17], graphite [18–22], lycopodium [23–25], sucrose [18,26,27] and polymethyl methacrylate [6,28,29], amongst others [30–32]. Even though starch is the most frequently used pore-forming agent, possibly due to its biological origin and availability, the difficulties in maintaining the pore structure formed by the starch burn out, and the narrow size range of commercially available starch types (typically between 5 and 50 μm) limits its application when large pores are desirable [8].

Polymers emerged as an effective alternative to starch as pore-forming agents. They exhibit defect-free burn out at relatively low temperatures, they are usually environmentally friendly and relatively cheap. In addition, they are easily mixed with ceramic powders or suspensions.

Porcelain stoneware is endowed with high bending strength (ISO 10545/4), virtually null water permeability ($<0.5\%$), excellent frost and chemical resistance and optimal abrasion resistance. These outstanding properties make porcelain stoneware particularly suitable as a material for floor and wall tiles. The investigation of lighter and less thermally conductive floor pavements is an emerging area, partly due to the expected lower production costs associated with the materials' weight

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reduction. Furthermore, the growing concern regarding energy rationalization inside buildings requires the development of smart materials that would limit the energy loss, and therefore increase the thermal comfort inside buildings, while simultaneously reducing energy consumption.

Recently, the production of dense/porous bi-layered ceramics through a simple, fast and flexible procedure was reported [33]. The ceramic tiles were designed to obtain a dense top-layer and a porous bottom-layer. The produced ceramics were lighter than the fully dense product, enabling weight reduction, thus presenting potential as floor and wall tile materials. Colombo et al. [34] produced a hybrid glass–ceramic using double pressing. A glass–ceramic frit was employed as a glaze forming a dense layer on the surface of a brown-colored body derived from natural and waste raw materials.

In this work, following a previously described procedure [33], the influence of pore forming agent type, their incorporation content and particle size distribution on the porosity, mechanical resistance and thermal conductivity of the produced ceramics was investigated.

Two different pore-forming agents were used, namely polypropylene (PP) and polymethyl methacrylate (PMMA). PP was selected due to its large scale production and low price, which makes it economically attractive for industrial applications [35]. Previous studies concerning the thermal degradation of PP had shown that it decomposes into a large number of aliphatic compounds, in a very fast way and without lasting residue [36,37]. For PP no hazardous gaseous emissions are reported [38,39]. PMMA is widely used as a pore-forming agent in ceramics [6,18,22,28,29] presenting a good balance of thermal properties suitable for the application proposed. PMMA decomposes almost exclusively to its monomer [40,41] and burns at a very high and steady rate.

It should be noted that the prepared ceramic tiles possess the potential to increase the thermal comfort inside buildings, as well as reducing energy consumption, not only due to their low thermal conductivity, but also because the porous layer offers the possibility for further modification, such as by the impregnation of phase change materials. This topic will be addressed in future work.

2. Experimental

2.1. Materials

The investigation was performed with an industrial spray-dried powder normally used for the production of porcelain tiles.

The PP was produced by ICORENE PP CO14RM from ICO POLYMERS®, with a melt flow index of 13 g/10 min (2.16 kg at 190 °C) and 0.9 g cm^{-3} density. Altuglas® VSE UVT PMMA with a melt flow index of 27 g/10 min (3.8 kg at 230 °C) and 1.18 g cm^{-3} density was obtained from Arkema.

2.2. Sample preparation

Bi-layered ceramic discs, with 25 mm diameter and 0.8 mm thickness, were produced by a two-step uniaxial pressing technique at room temperature, without the addition of binders or plasticizers, following a procedure described elsewhere [33]. The discs were prepared by double pressing action using a stainless steel die (diameter: 25 mm). The ceramic discs were designed to obtain a dense top-layer, 4 mm thick, and a porous bottom-layer with a similar thickness. The content of pore forming agent in the bottom layer of the disc ranged from 2.5 to 25 wt%.

Two distinct particle size distributions were used for the pore forming agents, namely particles smaller than 250 µm and in the range of 250–425 µm.

2.3. Materials characterization

Thermogravimetric analysis (TGA) was performed on SETSYS Evolution 1750 equipment from Setaram. The samples were heated at 10 °C/min under a constant flow of N_2 (g).

Scanning electron microscopy (SEM, Hitachi S4100) was used to characterize the as-received materials and to investigate the microstructural properties of the fractured surfaces of sintered samples.

Optical analysis (Leica EZ4HD microscope) and mercury intrusion porosimetry (AutoPore IV, Micromeritics) were the techniques used to study the porous morphology. For the optical analysis, samples were cut from the sintered discs using a Struers Secotom-10 table-top cutting machine. At least five specimens were prepared for each analysis. The images were acquired with a digital camera coupled to the microscope. Infinity Analyze software was used to measure pore size and number, providing the porous area distribution for each composition, and the pore area ratio, defined as the sum of all pore areas divided by the total sample area analyzed. Mercury intrusion porosimetry experiments were performed on pieces cut from the sintered discs.

Archimedes method (using ethylene glycol as immersion fluid) was employed to measure the specimens' open porosity, water absorption and bulk density.

Thermal conductivity was measured with the C-Therm TCI™ Thermal conductivity analyzer. Tests were performed at room temperature on sintered discs with 2.5 mm diameter.

Three-point bending strength measurements were selected to evaluate the mechanical resistance. Tests were performed on rectified parallelepiped bars of sintered samples (Shimadzu Autograph AG 25TA) using a 0.5 mm min^{-1} displacement speed. Results were obtained from eight to ten individual samples.

3. Results and discussion

3.1. Particle characteristics and thermal analysis of the pore-forming agents

The SEM micrographs in Fig.1 illustrate the morphology of the ceramic powder and of the pore forming agents. Fig. 1c–f show that PMMA particles present an asymmetric shape distribution, as opposed to the spherical character of the spray-dried ceramic powder (Fig. 1a and b). The inhomogeneous particle shape was also observed for PP particles (Fig. 1g–j), and can be associated with the milling process for the pore formers.

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