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High-porosity geopolymer membrane supports by peroxide route with the addition of egg white as surfactant

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ABSTRACT

Metakaolin-based geopolymer membrane supports were synthesized by gelcasting using hydrogen peroxide with the addition of albumen powder as surfactant. A geopolymer slurry was prepared using metakaolin and an alkaline medium at room temperature, the obtained viscous paste was expanded by means of the decomposition of peroxide in combination with protein-assisted foaming, and the geopolymerization was conducted in a closed environment at 75 °C. The combination of peroxide and albumen protein enabled the production of geopolymer membrane supports with a total porosity of ~74.29%, open porosity as high as ~65.25%, and possessing a compressive strength of ~4.47 MPa. Moreover, factors that influence the compressive strength, the porosity, and the pore size distribution were investigated. The results showed that the sizes of cell could be controlled by adding different content of peroxide and protein, and by heat-treating at different temperatures.

1. Introduction

Geopolymer foams (GFs), a new class of eco-friendly alkali-bonded porous ceramics, have attracted more and more attention in the recent years because of their interesting combination of good mechanical and thermal properties [1–5], excellent chemical and high temperature stability [5–8], and large internal surface area [9,10]. They have been used as membrane and catalyst supports [11,12], coatings [6,7], adsorbents and filters [13–15], and catalysts [16,17] and so on. Generally, aluminum [5,18,19] and silicon [20–23] powders have been used as pore foaming agent for the fabrication of geopolymer foams, but the pores generated by these foaming technique are typically closed.

Hydrogen peroxide (H_2O_2), as chemical blowing agent for the foaming of the GFs, is currently attracting great interest for the production of high porosity GFs [1,3,9,18,19,24]. Many works have been published concerning the fabrication of porous geopolymer-based components using different processing methods, but more investigations are still required to improve the process. In particular, it is of practical interest to increase the strength as well as the amount of interconnected porosity in a porous body possessing a well controlled pore size and distribution. Previous works showed that combined routes [9,25] or the use of surfactants [19,21] are two simple approaches [26,27] that enable the production of high porosity open-cell foams. In this study, we investigated the effect of a foaming agent (H_2O_2), in combination with protein-assisted foaming, on the porosity, cellular morphology and mechanical properties of geopolymer membrane supports (GMSs).

2. Experimental procedure

Commercial metakaolin (Argical 1200s, AGS Mineraux) was used to fabricate the GFs. 11 M KOH solution (prepared by dissolving potassium hydroxide pellets, from Sigma-Aldrich) and potassium silicate solution (KSIL 0465, Crosfield Italia) were mixed for at least 24 h as reagents (reactive ingredients). 3 wt% of H_2O_2 solution, diluted to 30 wt%, was supplied by Sigma-Aldrich, was used as chemical foaming agent. Previous studies [2,25] showed that diluted hydrogen peroxide was expected to provide less anisotropic pores. Albumin crude protein from chicken egg white (A4344, 80%) was supplied by Panreac AppliChem, Germany.

The original suspension (OS), with a theoretical oxide molar ratios: SiO_2/Al_2O_3=3.53, K_2O/SiO_2=0.29 and H_2O/K_2O=15.1, was prepared by mechanical mixing of metakaolin (MK) and the alkali medium solution for 30 min at 600 rpm. The protein and H_2O_2 were then successively added at room temperature to the suspension, stirring at 1000 rpm for 10 min and then at 600 rpm for 5 min, respectively. We define the weight fraction of protein in OS as x, and the weight fraction of H_2O_2 in OS as y.

The geopolymer foams were prepared by casting the slurry into a

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sealed plastic mold. Finally, the GFs were cured in a laboratory oven in two steps: (1) overnight at room temperature, to prevent cracking due to an abrupt loss of water; (2) at 75 °C for 24 h in an oven, to consolidate. A one step curing procedure (directly to 75 °C for 24 h) was also conducted for comparison (sample labelled SAO).

Prior to the characterization, the specimens were cut into a parallelepiped with ~11×~11×~13 mm^3 dimension; after that, the GFs were dried at 40 °C for one week. Measurements were conducted on samples cured at 75 °C and after firing for 2 h at 600 °C, 800 °C, and 1000 °C in a muffle furnace and static air atmosphere with 3 °C/min heating rate. The high temperature performance and phase transformation characteristics of the samples were evaluated, respectively, by thermogravimetry analysis and differential thermal analysis (DTA/TG, STA409, Netzsch GmbH, Selb, Germany) with a heating rate of 3 °C/min up to 1100 °C in air and by dilatometer (DIL,402 C, Netzsch, Selb, Germany) with a heating rate of 10 °C/min up to 1100 °C in air. The crystalline phase assemblage was identified on ground samples using an X-ray diffractometer (XRD; AXS-D8 advance, Germany), operated at 40 kV, 40 mA, with Cu Kα radiation and at a step width 0.05° and a scanning range of 5–55°.

The relative (bulk) density (ρ_r) of the MGF was obtained as the ratio between the parallelepiped-foam samples and the geometrical volume (as measured with a digital caliper). The true (skeleton) density (ρ_0) was measured with an automatic true density analyzer (Accupyc1330, Micromeritics, USA) at room temperature. The total porosity (TP) was calculated based on the relation: TP=100% ($1-\rho_r/\rho_0$) [24,25], and the corresponding open porosity (OP) was determined by the Achimedes method using distilled water as the immersion medium.

Compressive strength was measured using an Instron 1121 universal material testing machine (Canton, Massachusetts, USA), with a cross-head speed of 1 mm/min, and at least six specimens were tested to obtain the average strength value and standard deviation. Samples were tested parallel to the foaming directions (axial direction), but in one case (sample SAT) also perpendicularly to it (radial direction).

The morphology of porous specimens was observed using an optical microscope (AxioCam ERc 5 s, Carl Zeiss, Germany) and a Scanning Electron Microscope (SEM; FEI Quanta 200, Netherlands). Cut surfaces were examined. The cell size distribution of MGFs was characterized based on digital images (at least 100 cell sizes were measured per image) using the Nano Measurer 1.2 program (Fudan University, China) [25,28,29]. Values computed by the analysis of SEM images were converted to three-dimensional values using the stereological equation: $D_{sphere} = D_{circle}/0.785$ [9,25].

3. Results and discussion

3.1. 1. Effect of curing process

Since the mechanical properties and volume fraction of pores are two important parameters for the performance of membrane supports [30], a preliminary investigation was conducted to investigate the influence of the curing process. The compressive strength (measured on as-cured samples, without any further heat treatment) and the porosity of the GMSs with different curing procedures (one-step and two-step curing) are reported in Table 1. Only sample SAO was subjected to one-step curing; all the other ones were subjected to two-step curing.

The sample (SAO) obtained by one-step curing had a significantly higher open porosity (~74.4%) than the two-step cured sample (SAT, ~65.3%), but a relatively similar total porosity (~78.8 vs ~74.3%). However, its compressive strength was lower than that of the two-step specimen, and in particular lower than expected according to the value of the total porosity (the expected value was ~2.0 MPa, see Fig. 4 later). Previous works [2,27,31] showed that the pre-heat treatment can contribute to improve the physical strength and the degree of geopolymerization; specifically, longer curing leads to better mechanical properties. Therefore, the two-step curing process is to be preferred.

SEM analysis (Fig. 1) was performed to provide a comparison of the morphology of the samples according to the two types of curing procedure (samples SAO and SAT), and between the axial (along the foaming direction) and the radial (perpendicular to the foaming direction) cross-sections (sample SAT).

A well defined cellular structure, comprised of a large amount of spheroidal cells surrounded by relatively thick struts, having a size distribution ranging from ~100 μm to ~600 μm, was observed for all samples. Most cells show the presence of spherical interconnecting cell windows. However, the homogeneity of the cellular structure was reduced in the sample cured by the one-step method (Fig. 1a), probably because the sudden relatively high temperature curing treatment accelerated the decomposition of hydrogen peroxide as well as the curing of the geopolymer, leading to either underdeveloped or to a not stabilized cell structure. The curing process was therefore found to have an effect on both the strength and the cellular morphology.

The different cross-section show a similar pore size distribution, microstructure, and mechanical properties, i.e., the sample appears to possess a very good homogeneity, and therefore it could be used without taking into account the foaming direction. Additionally, some smaller pores, having a size distribution ranging from ~10 to ~70 μm, exist in the cell walls and the struts of all samples. Their presence increase the permeability of the structure [25]. Simultaneously, the thick struts are beneficial to achieve excellent mechanical strength.

3.2. Effect of surfactant content

Fig. 2(a-d) show the morphology of GMSs produced using different amounts of egg protein surfactant, and Table 1 reports the values for their porosity (total and open), relative density, average cell size, and compressive strength. It is obvious that different contents of albumen had a significant effect on the pore characteristics. When the protein content increased from 2.5 to 10 wt%, the total porosity fell from ~77.1 to ~68.1 vol%; this could be explained by the observed increase in viscosity of the slurry [32] and the reduction of its foamability [33] with increasing amount of protein. In fact, while viscous slurries are well suited for retaining the formed gas bubbles and produce foams, the expansion of the gas contained in them (which affects the total porosity generated in the sample at the end of the process) can be hindered when the viscosity of the slurry is too high. The corresponding compressive strength increased from ~2.1 to ~7.0 MPa. The samples were all produced using the same amount (10 wt%) of hydrogen peroxide, and the results indicate that the average cell size gradually decreases with increasing amount of surfactant. This is in accordance with the fact that the surfactant stabilizes the liquid-gas interface, and the more surfactant is present the larger amount of surface per unit volume can be stabilized.

For comparison purposes, a sample (SH0) was produced with no addition of protein. In Fig. 2(a), its cellular structure possessing a limited number of closed cells with a very inhomogeneous cell size can be observed. This confirms that the cellular structure is by the decomposition reaction of hydrogen peroxide, but that the surfactant is necessary to obtain a homogeneous cell size distribution as well as interconnected porosity. Indeed, previous studies [19,21] showed that presence of a surfactant stabilizes the foaming procedure, reducing the pore collapse and coalescence when the foam is still in the liquid state.

The high amount of open porosity (~61.6 vol%) for the foam produced without surfactant can be explained by the presence of intrinsic interconnected meso/macro-pores in the geopolymer matrix, which can be as high as 18 vol%, [9,10,31,34], as measured by N_2 adsorption [34–36] and observed by SEM [31] analyses, as well as of the macro-porosity generated by the decomposition of hydrogen peroxide, that was accessible by the boiling water during the measurement (Archimedes Principle).