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High strength metakaolin-based geopolymer foams with variable macroporous structure

Chengying Bai[a,*], Giorgia Franchin[a], Hamada Elsayed[a], Alberto Conte[a], Paolo Colombo[a,b]

[a] *Department of Industrial Engineering, University of Padova, via Marzolo, 9, Padova, Italy*
[b] *Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States*

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ABSTRACT

Metakaolin-based geopolymer foams were synthesized by mechanical frothing, using hydrogen peroxide as additional foaming agent; three vegetable oils were added in order for the saponification reaction to occur. The combined use of the two foaming techniques (mechanical frothing and H_2O_2 decomposition) led to interconnected porosity: the in-situ formation of the soap molecules generated by the saponification reaction was exploited to generate macro-porosity. This combined route enabled the production of geopolymer foams with a range of total porosity and strength values, with an optimal sample possessing a total porosity of to ~81 vol%, an open porosity of ~79 vol%, and a compressive strength of ~3.1 MPa. Moreover, factors that influence the compressive strength, the porosity, and the pore size distribution were investigated. The results showed that the cell size and cell window size can be controlled by adding different oils and different contents of peroxide.

1. Introduction

Geopolymer foams have been the focus of attention in the field of eco-friendly porous materials because of their favorable mechanical and chemical stability, low shrinkage after forming, high temperature resistance, etc. [1–4]. They have been employed in photocatalytic degradation applications or used as membrane supports, catalyst supports, heavy metals adsorbents and so on [4–9]. Aluminum and silicon and H_2O_2 have been used as pore foaming agents for the fabrication of geopolymer foams [1,10,11], but the pores generated by this foaming technique are typically closed, thereby limiting the range of applications for the components.

Recently, alternative processing routes for the fabrication of porous geopolymers have been proposed. An oil-based emulsion templating route was put forward, which enables to obtain hierarchically porous geopolymers suitable for catalyst applications [9,12]. Other experiments related to the addition of oil to geopolymers, showed that waste oil can be trapped inside the geopolymeric matrix [13]. Geopolymers with a mesoporous matrix and unidirectional lamellar macro-porosity were also produced by the freeze-casting technique [14], and a saponification/peroxide/gelcasting combined method was proposed by Cilla et al. [15]. Although geopolymer foams with an open porosity of ~70 vol% and a total porosity as high as ~85 vol% were successfully produced by the combined techniques, the compression strength of the foams was only ~0.45 MPa, which limited the range of applications for the components.

Despite an increasing number of papers dealing with the fabrication of porous geopolymers using different approaches [1–15], more investigation is still required to improve the process, especially in reference to the amount of open porosity and mechanical strength of the components. In particular, components possessing high strength and a high amount of open porosity, with controlled pore size and distribution, are of interest for several aplications.

In this study, high mechanical strength metakaolin-based geopolymer foams (MGFs) with open porosity were fabricated using the gelcasting/saponification/peroxide combined route. Their porosity, cell and cell window size and mechanical properties were controlled by adding different oils and different contents of peroxide.

2. Experimental procedure

Metakaolin (Argical 1200s, AGS Mineraux) was used to fabricate the MGFs. A 17.6 M KOH solution was prepared by dissolving potassium hydroxide pellets (Sigma-Aldrich) for at least 24 h at room temperature [1,15]. A potassium silicate solution (KSIL 0465,

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[*] Corresponding author.
E-mail addresses: chengyingbai@163.com, baichenying@gmail.com (C. Bai).

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Crosfield Italia srl) and the KOH solution were mixed to provide the alkali activator solution. Three vegetable oils (canola oil (Great Value, Wal-Mart, USA); sunflower oil (Panorama, Pam, Italy); olive oil (Fragrante, Bertolli, Italy)) and a 3 wt% H_2O_2 solution diluted from 30 wt% H_2O_2 (Sigma-Aldrich), were used as chemical foaming agents. A previous study [1] showed that the addition of diluted hydrogen peroxide to the system enabled to obtain uniform, less anisotropic pores.

A suspension (S) with theoretical oxide molar ratios: $SiO_2/Al_2O_3 = 3.53$, $K_2O/SiO_2 = 0.36$ and $H_2O/K_2O = 11.1$ was prepared by mechanical mixing for 30 min at 800 rpm of the alkali activator solution in which metakaolin (MK) was dispersed. The oil and H_2O_2 were then added successively at room temperature, stirring at 1200 rpm for 10 min (frothing) and 600 rpm for 5 min, respectively. The weight fraction of oil in S was defined as x, and the weight fraction of H_2O_2 in S as y.

The geopolymer foams were produced by casting the slurry into a sealed plastic mold and curing for 24 h at room temperature and for another 24 h at 75 °C in an oven. Previous works [1,14] showed that the pre-heat treatment can contribute to improve the physical strength and the rate of geopolymerization. To obtain the final MGFs, an extraction step was carried out by saturating the samples with hot water (renewed every 20 min until it remained clear), to completely evacuate the water-soluble soap and glycerol molecules generated by the saponification. This step also allowed to verify the completion of the geopolymerization reaction, as a non-fully condensed geopolymer structure would disaggregate (undergo dehydroxylation and expansion) in water [4,15]. Prior to characterization, the MGFs were dried at 40 °C for one week.

The relative (bulk) density (ρ_r) of the MGFs was obtained as the ratio between the mass of a parallelepiped-shaped sample cut from a larger foam and its geometrical volume (as measured with a digital caliper). The true (skeleton) density (ρ_0) was measured with a gas pycnometer (Accupyc1330, Micromeritics, USA) at room temperature on finely ground MGFs powders. The total porosity (TP) was calculated based on the relation $TP = 100\ (1 - \rho_r/\rho_0) \times 100\%$ [15,16], and the corresponding open porosity (OP) was determined by the Archimedes' 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 with a $\sim 10 \times \sim 10 \times \sim 15\ mm^3$ dimension, cut from larger samples, were tested. A Brookfield viscometer (DV-II+ Pro EXTRA, spindle R1-4, rpm 12, USA) was used for evaluating the viscosity of the geopolymer slurries at room temperature.

The crystalline phase assemblage was investigated using an X-ray diffractometer (XRD; AXS-D8 advance, Germany), operated at 40 kV, 40 mA, with Cu Kα radiation (step width 0.05°). The morphology of cut surfaces was observed using optical microscopy (AxioCam ERc 5s, Carl Zeiss, Germany) and a Scanning Electron Microscope (SEM; FEI Quanta 200, Netherlands). The cell size and side distribution, as well as the cell windows size, were assessed from SEM images using an image analysis software (Nano Measurer 1.2), and at least 100 pores were measured per sample [17]. The data were converted to three-dimensional values using the stereological equation $D_{sphere} = D_{circle}/0.785$ [2,15].

3. Results and discussion

3.1. Effect of different types of oil

The foaming mechanism when using vegetable oils (mainly hydrophobic triglycerides) [12] can be described as follows: the highly alkaline geopolymer slurry mixed with the oil generates in situ a carboxylate surfactant (soap) and glycerol ($CH_2(OH)–CH(OH)–CH_2(OH)$) molecules, via a saponification reaction. The excess of KOH present in formulation of the slurry ensures that the oil triglycerides convert completely into soap and glycerol. Glycerol is a water soluble molecule which can be extracted by hot water after the curing process leaving behind (meso-)pores. The soap molecules formed in situ stabilize the gas bubbles generated by the mixing and the decomposition of the peroxide, leading to open, interconnected cells [12,15]. It can therefore be expected that the different chemical characteristics of the various oils would affect the morphology, hence the strength, of the MGFs. Considering that the saponification value (i.e. the number of milligrams of potassium hydroxide required to saponify 1 g of triglyceride) of the three oils was about 190, [18,19] the ratio of K_2O/SiO_2 in the geopolymer slurry before and after the addition of the different oils addition was 0.36 and 0.29, respectively.

The SEM images of MGFS produced using different oils (x = 0.2, y = 0.1) are reported in Fig. 1. All samples possessed a cellular structure with a large number of partially open cells, surrounded by relatively thick walls, having a size distribution ranging from ∼150 to ∼450 μm.

The type of oil used was found to have an effect on the pore structure of MGFs. The average cell pore size of the foams, computed by image analysis for each sample, was: 339 ± 136 μm (canola oil, Fig. 1A), 391 ± 151 μm (sunflower oil, Fig. 1B), and 247 ± 89 μm (olive oil, Fig. 1C). The wide distribution of the cell size is typical of foams produced using a direct foaming approach. Moreover, many smaller pores were present in the cell walls and the struts (see Fig. 1(a–c)). They are attributable to oil droplets that were trapped in the geopolymer structure, and removed by the hot water extraction [12,13]. Their presence, particularly in the cell walls, increased the amount of open porosity in the samples (see later), since they increase the permeability of the structure. The average sizes for the pores in the cell walls and struts were 15.0 ± 4.5 μm (canola oil), 22.8 ± 8.3 μm (sunflower oil) and 17.3 ± 5.3 μm (olive oil).

The effect of the type of oil on the compressive strength of MGFs produced using similar processing conditions (x = 0.2, y = 0.1) is reported in Fig. 2.

In order to assess the effect of the addition of different types of oil on the microstructure of the samples, we should consider: (i) the nature of the oils, (ii) the viscosity changes caused by the oils [15,20], and (iii) the emulsion stability [21]. In fact, different oils produce different types of soap molecules (surfactants), and any variation in the viscosity of the mixture would affect the degree of foaming (while the rest of the processing parameters, such as mixing rate and amount of H_2O_2, are kept constant). It should be noted that the amount of surfactant molecules produced was the same for every oils, since they had a similar saponification value and the systems contained enough potassium hydroxide to lead to the completion of the saponification reaction. Concerning the stability of the emulsions, the time scale for our process is typically shorter than that for which flocculation, coalescence and Ostwald ripening can occur in an oil/water emulsion, so we could disregard this complex effect, at least in an initial analysis [21].

Firstly, the viscosity for the different slurries was measured. It is also important to observe that the geopolymer mixtures are reactive, and therefore their viscosity changes with time. The measurements were therefore carried out for a time interval ranging from 30 s to 1 h, to take into account the variation of viscosity during processing. The data concerning the viscosity of the different systems are listed in Table 1. The viscosity of the different pure oils was rather similar (0.067 Pa s for olive oil, 0.058 Pa s for canola oil and 0.050 Pa s for sunflower oil), but lower than that of the oil-free slurry (1.60 Pa s).

The data indicate that the addition of oil increased significantly the viscosity of the system, and this can be explained by the elastic

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