

Porous Geopolymer Production And Characterisation

Cansu Demir, Ferhat Kara, ıđdem Pala

Anadolu University, Materials Science and Engineering Department

Kale Ceramic

cansudemir@anadolu.edu.tr

fkara@anadolu.edu.tr

cigdempala@kale.com.tr

ABSTRACT

Porous geopolymers can find application in various areas including heat insulation as well as filtration and catalysis. They are environmentally friendly materials as no substantial energy is needed in order to produce them. In this study, porous geopolymers were produced by using vegetable oil and hydrogen peroxide.. Process conditions including the geopolymer composition, the amount of oil and hydrogen peroxide and geopolymerization temperature were examined in order to see their effect on pore amount, size and morphology. We found that porous geopolymers with density values $< 0.2 \text{ g/cm}^3$ and with total porosity of $> 80\%$ can be prepared by this method. Interesting pore morphology were resulted and will be reported.

Key words: Geopolymer, Foam, Porosity, Oil, Peroxide

1. INTRODUCTION

For structural applications of brittle ceramic materials, pores are generally what to be eliminated because they act as fracture defects and degrade the structural reliability, and therefore, ceramic engineers tried to sinter ceramics to full density to attain high mechanical strength. On the other hand, there have been various industrial applications where pores are taken advantage of positively, from filtration, absorption, catalysts and catalyst supports to lightweight structural components and thermal insulator. In these decades, a great deal of research efforts have been devoted for tailoring deliberately sizes, amounts, shapes, locations and connectivity of distributed pores, which have brought improved or unique properties and functions of porous ceramics [1, 2]. The merits in using porous ceramics for these applications

are generally combination of intrinsic properties of ceramics themselves and advantages of dispersing pores into them [3, 4]. The former include heat and corrosion resistances, wear and erosion resistance, unique electronic properties, good bioaffinity, low density, and high specific strength, and the latter are low density, low thermal conductivity, controlled permeability, high surface area, low dielectric constant, and improved piezoelectric properties [5, 6].

These properties can be tailored for each specific application by controlling the composition and microstructure of the porous ceramic. Changes in open and closed porosity, pore size distribution, and pore morphology can have a major effect on a material's properties. All of these microstructural features are in turn highly influenced by the processing route used for the production of the porous material [7].

Several ways to produce macroporous ceramics have been reported [7], including sacrificial template [8, 9, 10], replica [11, 12] and direct foaming methods [13]. Regardless of the technique used, ceramic foams are usually treated at high temperature for the burnout of fugitive additives or templates and for consolidation (i.e. sintering) in order to achieve specific mechanical and functional properties. However, these processes are really difficult and expensive. For that reason new processes must be developed.

Inorganic polymers, first developed by Davidovits [14], are made by mixing some aluminosilicate minerals with an alkaline activating solution to produce a dense, three-dimensionally Si–O–Al networked microstructure. For instance, calcined clays and industrial waste solids, such as metakaolin, fly ash, and blast furnace slag powders, can be used as raw materials and are typically mixed at room temperature with an alkaline activating solution of alkali metal hydroxide and sodium silicate [15, 16]. In the alkali-activation reaction of inorganic polymers, the dissolution of Si and Al ions and subsequent polycondensation reaction occur in a short period of time, leading to high early compressive strength. In producing low-density foams, high early compressive strength of inorganic polymers not only limits the coalescence of preformed air bubbles but also reduces the formation of ruptured cell walls, resulting in better cell microstructure and mechanical properties. Inorganic polymers with the characteristics of high early strength, low-energy consumption and CO₂ emissions, and good fire resistance and thermal insulation used to produce lightweight foams.

In direct foaming methods, porous materials are produced by incorporating air into a suspension or liquid media, which is subsequently set in order to keep the structure of air bubbles created. The total porosity of directly foamed ceramics is proportional to the amount of gas incorporated into the suspension or liquid medium during the foaming process. Wet foams are thermodynamically unstable systems which undergo continuous Ostwald ripening

and coalescence processes in order to decrease the foam overall free energy. The most critical issue on direct foaming methods is the approach used to stabilize the air bubbles incorporated within the initial suspension or liquid media. Several long-chain amphiphilic molecules and biomolecules such as lipids and proteins can be used as surface-active agents to stabilize wet aqueous foams. These molecules slow down the coalescence and disproportionation of bubbles by adsorbing at the air bubble surface and reducing the air–water interfacial energy [7]. According to studies of Seo et al. and Colombo et al., they used vegetable oil as a surfactant. It has been found their work that the oil in the droplets continues to saponification reaction during the curing of the mixture which turns the originally hydrophobic triglycerides all into soap and glyceride. Those molecules are soluble in water and thus can be extracted by water from the cured solid material, resulting in a porous geopolymer material [17, 18].

In this communication, we demonstrate that a simple reactive emulsion templating with vegetable oil (at 50°C and 80°C) can produce hierarchically porous geopolymer materials with coexisting controllable mesopores and spherical macropores, without a need of significantly modifying the conventional geopolymer synthetic process.

2. MATERIALS AND METHODS

2.1. Materials

Metakaolin powder used to prepare the suspensions (MEFISTO L05) with an average particle size 5 μ m. vegetable oil (Komili Riviera Olive oil) selected to in situ modify particles in a gel with a saponification reaction. Further chemicals used in the present study were hydrogen peroxide (%35), NaOH and sodium silicate (42 Baume).

2.2. Suspension Preparation

In the first step of the synthesis, solution was prepared by dissolving an appropriate amount of NaOH pellets in sodium silicate in a polypropylene cup in a sodium silicate bath. The geopolymer resins were then prepared by mechanically mixing metakaolinite into the alkaline solution to form a homogenous fluidic liquid. The geopolymer mixture was prepared considering the three molar ratios as follows: $\text{SiO}_2/\text{Al}_2\text{O}_3=4,4$, $\text{Na}_2\text{O}/\text{SiO}_2=0.349$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}=11$. The pH of the resins was about 14 for all the compositions. Vegetable oil was then added together with hydrogen peroxide to the resin and mixed for an additional 10 min at 1000 rpm to give a homogeneous emulsion. The emulsion was transferred to a polypropylene

closed cup and cured in a laboratory oven at 80°C for 24 h. After curing operation thermal conductivity and density and amount of porosity values of samples determined.

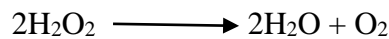
2.3. Analysis and Tests

Apparent density of the foams was determined by measuring the weight of specimens and by measuring their dimensions with electronic caliper. The thermal conductivity was measured with the thermal conductivity analyser (C-Therm TCI) utilizing the modified transient plane source technique.

3. Results and Discussion

3.1. Effect of Hydrogen Peroxide

Hydrogen peroxide is a well-known blowing agent [19], while the redox reaction of Al in alkaline solution induces porosity by H₂ evolution [20]. H₂O₂ is thermodynamically unstable and therefore can be easily decomposed to water and oxygen gas with the latter playing the role of the geopolymeric paste blowing agent [21]:



The decomposition of hydrogen peroxide liberates oxygen creating initially very small bubbles inside the mass of the very viscous paste. The pressure exerted on the bubbles' wall plays the role of the shear stress for the viscous paste which is deformed causing the bubble's expansion and the foaming of the paste. The bubbles' expansion causes a decrease of the oxygen pressure under constant temperature eliminating gradually the shear stress and therefore stopping the bubbles' expansion and the paste's foaming. When the oxygen volume per paste volume is low enough, the spherical bubbles are discernible and they have low population density in the geopolymeric paste. As the H₂O₂ content increases, the bubbles' population density increases as well as the amount of oxygen in each bubble do due to the increased local oxygen concentration. Therefore, the bubble size increases, the thickness of the cells as well as the apparent density of foams decrease and the cell volume increases [21].

In this study effect of peroxide amount on the foaming process is observed. The microstructure of foamy materials is presented in Fig. 1. The cells are generally closed and almost spherical when the % content of H₂O₂ in the paste is low. Aggregation among cells takes place as the % content of H₂O₂ increases changing the cell's geometrical shape from spherical

to oval, creating network of interconnecting cells and affecting the mean cell size as seen in Fig.1. This study gives same results as with the study of Gauckler et al [7].

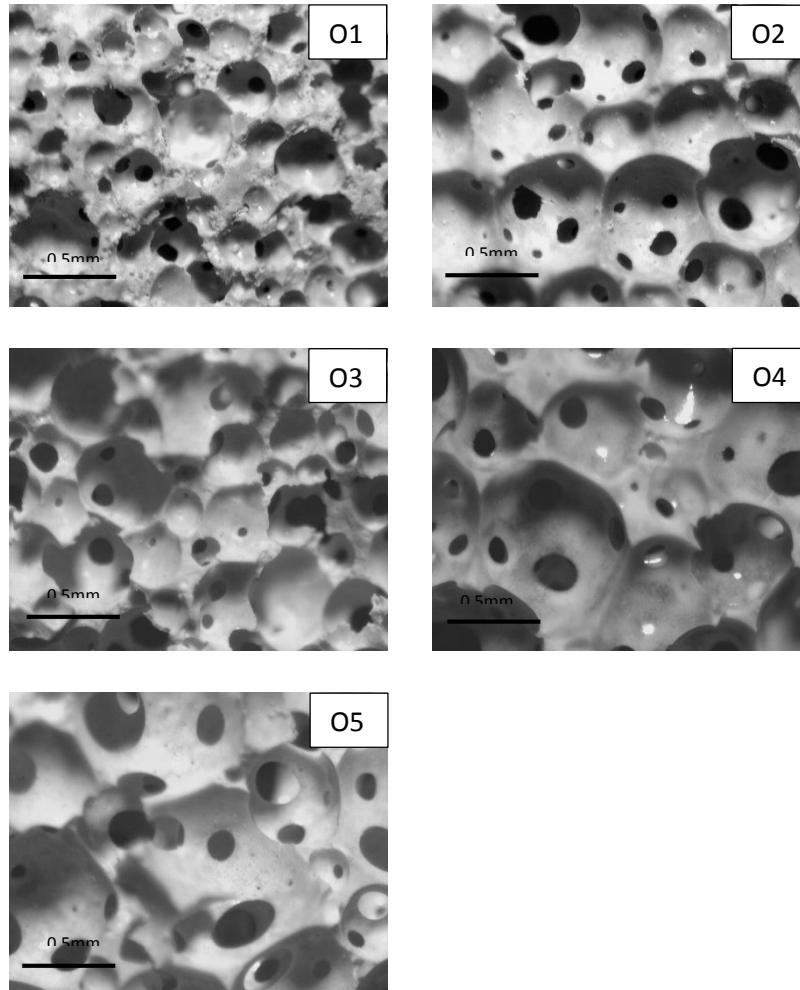


Fig. 1. Stereo microscope photos of geopolymer foam samples (2X Magnification). All samples contains same amount of vegetable oil which is %2v/v and different amounts of peroxide a)%0,5v/v, b) %1v/v, c) %2v/v, d)%4v/v, e)%5v/v

Table 1. Density, thermal conductivity and cell volume values of samples

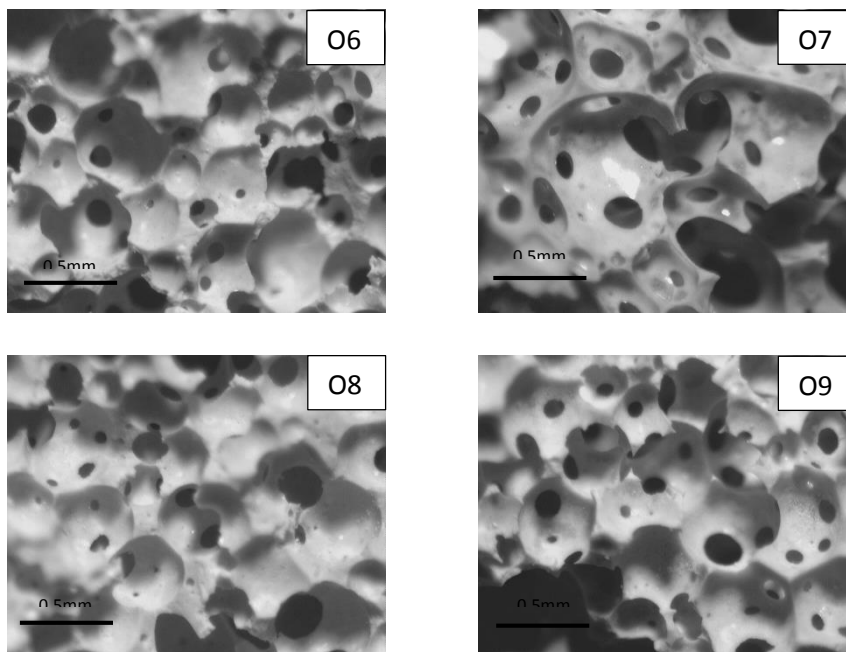
Samples	Density (g/cm³)	Thermal Conductivity (W/mK)	Cell Volume (%)
O1	0,53	0,067	36,15
O2	0,33	0,048	51,53
O3	0,39	0,041	46,92
O4	0,31	0,042	53,07
O5	0,19	0,035	62,30

3.2.Effect of Vegetable Oil

When the vegetable oil is added to the highly alkaline geopolymer suspension, it generates in situ carboxylate surfactants (soap molecules) through the saponification reaction, which consists of the hydrolysis of the triglycerides found in oils or fats, plus glyceride, a water soluble molecule(glycerol) which can be extracted by water after the curing process [17].

In the study of Gauckler at all by controlling the foam stability and the setting kinetics, pore sizes within the range of 35 μ m to 1.2 mm have been achieved using the above surfactant-based direct foaming methods. The pores obtained with this method are typically spherical and can be either closed or opened depending on the foam wet processing. Closed pores, are typically achieved when the particles are distributed uniformly around the gas bubbles upon setting. Open pores, on the other hand, exhibiting interconnecting windows are obtained if particles segregate at the plateau borders of the foam because of bubble disproportionation [7].

In this study effect of vegetable oil amount on the foaming process is observed. The microstructure of foamy materials is presented in Fig. 2. Amount of open pores and their dimensions are increases when the % content of oil high. The samples which are shown in Fig.2. were prepared with same amount of peroxide and different amounts of vegetable oil.



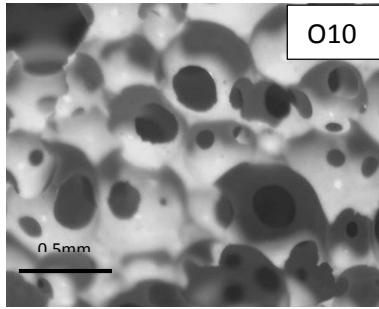


Fig. 2. Stereo microscope photos of geopolymer foam samples (2X Magnification). All samples contains same hydrogen peroxide which is %2v/v and different amounts of vegetable oil a)%2v/v, b) %4v/v, c) %6v/v, d)%8v/v, e)%10v/v

Table 2. Density, thermal conductivity and cell volume values of samples

Samples	Density (g/cm³)	Thermal Conductivity (W/mK)	Cell Volume (%)
O6	0,39	0,041	46,9
O7	0,42	0,040	44,6
O8	0,45	0,045	42,3
O9	0,25	0,043	57,69
O10	0,175	0,037	63,46

3.3.Effect of Oil Type

To observe the effect of oil two type oil was used which are olive oil and sunflower oil. Although the geopolymer compositions prepared in the same manner and pore size and variations of density changes observed in Table3. The microstructure of foamy materials is presented in Fig. 3.

O11 and O12 were prepared by using olive oil and S1 and S2 were prepared by using sunflower oil. All of them prepared same manner which are oxide ratios, curing temperatures, mixing durations are same. The only difference between the samples are oil types. Because of oil type, difference of density values were observed. On the other hand samples which were prepared by using sunflower oil have disordered microstructure in Fig.3.

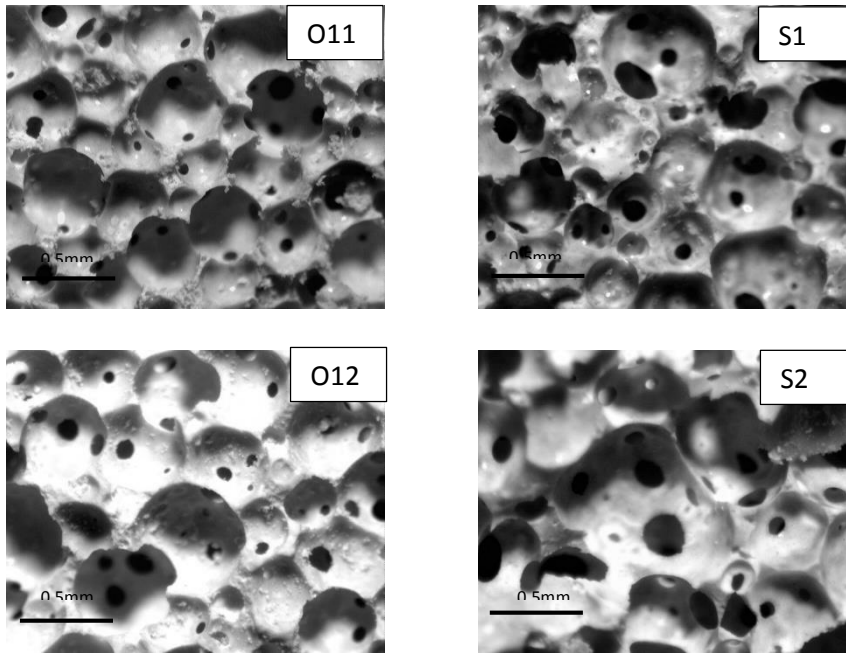


Fig.3. Stereo microscope photos of geopolymer foam samples (2X Magnification). a) O11-S1 %0,5v/v oil and peroxide b) O12-S2 % 1v/v oil and peroxide.

Table 3. Density, thermal conductivity and cell volume values of samples

Samples	Density (g/cm³)	Thermal Conductivity (W/mK)	Cell Volume (%)
O11	0,47	0,056	40,76
S1	0,76	0,05	18,46
O12	0,38	0,044	47,69
S2	0,53	0,049	36,15

3.4.Effect of Temperature

Saponification degree... The microstructure and properties of a mechanically foamed material depend on the stability of air bubbles and workability of geopolymer paste. The workability of paste is related to temperature. Because geopolymerization occurs faster when the temperature increases, and inhibit foaming process due to solidification when the deficiency of vegetable oil. On the other hand, when we add vegetable oil as a surfactant, it needs enough

temperature for saponification reaction (Krafft Temperature [22], then higher temperature degrees gives lower density and thermal conductivity values in Table 3.

S1 and S3 samples were prepared by using %0.5v/v peroxide and %0.5v/v sunflower oil, and S2 and S4 samples prepared by using %0.1v/v peroxide and %0.5v/v sunflower oil. The only difference between S1-S3 and S3-S4 is temperature. S1 and S2 were prepared at 80°C and S3-S4 were prepared at 50°C. Density and thermal conductivity values are given in Table 4. As seen from the data (Table4), 30 degrees temperature increase, doubles of the amount of porosity and density is decreased.

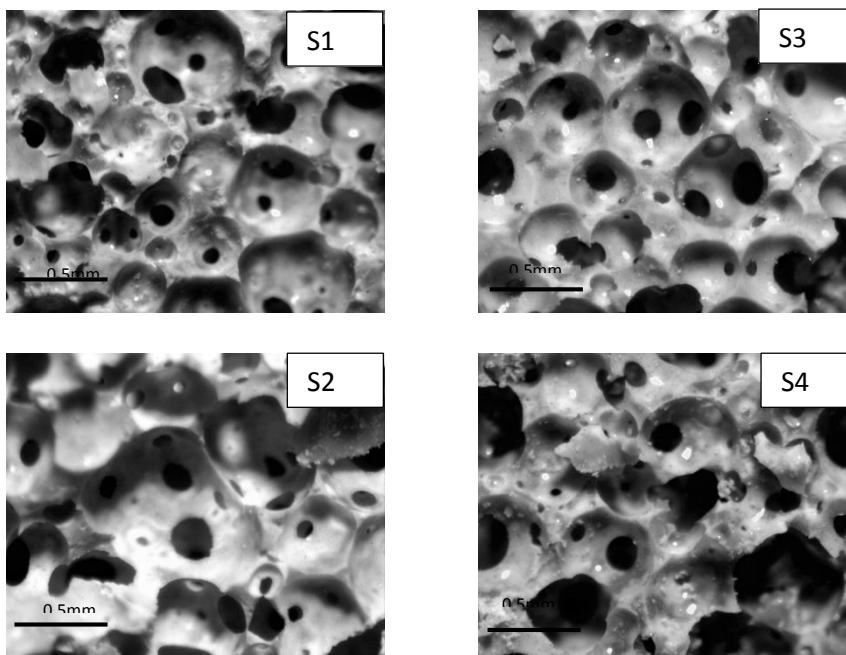


Fig.4. Stereo microscope photos of geopolymer foam samples (2X Magnification). a) S1-S3 %0.5v/v peroxide and b) S2-24 %0.1v/v peroxide and %0.5v/v sunflower oil. Also S1-S2 was prepared at 80°C and S3-S4 was prepared at 50°C.

Table 4. Density, thermal conductivity and cell volume values of samples

Samples	Density (g/cm³)	Thermal Conductivity (W/mK)	Cell Volume (%)
S1	0,76	0,05	18,46
S2	0,53	0,049	36,15
S3	1,08	0,05	6,15
S4	0,83	0,037	13,07

However, at higher temperature degrees peroxide amount is restricted because of excessive amount of H₂ outbreak and network is broken off. For that reason, to use higher amount of peroxide lower temperature degrees appropriate. When the amount of peroxide is increased at 50°C, network structure and thin walls can be observed easily in Fig5. S5 and S6 samples contains same amount of vegetable oil inside which is %1v/v and amount of peroxide inside S5 is %6v/v and inside S6 is %7v/v. In this study density values decreased up to the 0,086g/cm³ (Table 5.). Because of densities are low, thermal conductivity values could not measured.

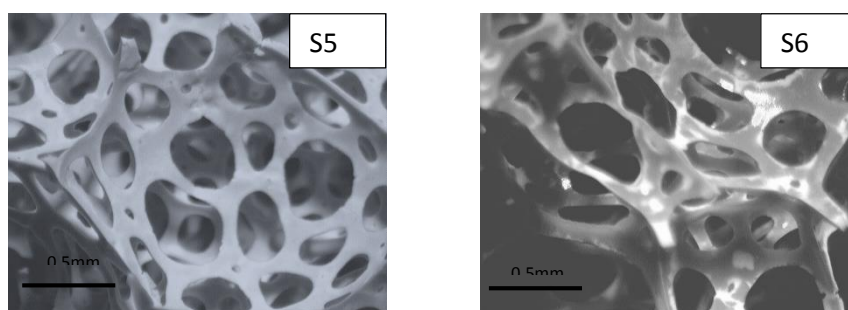


Fig.5. Stereo microscope photos of geopolymer foam samples (1X Magnification).

Table 5. Density, thermal conductivity and cell volume values of samples

Samples	Density (g/cm³)	Thermal Conductivity (W/mK)	Cell Volume (%)
S5	0,12	-	62,30
S6	0,086	-	70,30

4. Conclusion

Self-setting foams with average densities ranging from 0,086-1 g/cm³ and total open cell volume from %6,15 to %70,30 which means total porosities range from % 17 to %93,4 can be produced by combining surfactant stabilized foams with geopolymerization. The foam porosity and pore size can be controlled by changing temperature, oil type and also amount of vegetable oil and peroxide.

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