

Açık Hücreli Poröz Jeopolimer Üretimi

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Öz

Gözenekli jeopolimerler, ısı yalıtımı, filtrasyon ve kataliz gibi çeşitli alanlarda uygulama alanı bulabilmektedirler. Üretmek için önemli bir enerjiye ihtiyaç duyulmadığından dolayı çevre dostu malzemelerdir. Bu çalışmada, bitkisel yağ ve hidrojen peroksit kullanılarak gözenekli jeopolimerler üretilmiştir. Jeopolimer bileşimi, bitkisel yağ miktarı, hidrojen peroksit miktarı ve jeopolimerizasyon sıcaklığı da dahil olmak üzere proses koşullarının gözenek miktarı, büyüklüğü ve morfolojisi üzerindeki etkileri incelenmiştir. Ayrıca açık hücre oluşum mekanizmasını açıklamaya çalışılmıştır. Çalışmamızda yoğunluk değerleri 0.2 g/cm³'ten düşük ve toplam gözenekliliğin % 80'den daha yüksek olduğu gözenekli jeopolimerlerin bu yöntemle hazırlanabileceğini gözlemlenmiştir. İlginç gözenek morfolojisi gözlemlenmiştir ve raporlanacaktır.

Anahtar kelimeler

Köpük, Jeopolimer,
Açık hücre, Peroksit,
Bitkisel yağ

Open Cell Porous Geopolymer Production

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, hydrogen peroxide and geopolymerization temperature were examined in order to see their effect on pore amount, size and morphology. Also formation mechanism of open porosities were tried to explain. In our study we found that porous geopolymers with density values lower than 0.2 g/cm³ and with total porosity of greater than 80% can be prepared by this method. Interesting pore morphology were resulted and will be reported.

Keywords

Foam, Geopolymer,
Open cell, Peroxide,
Vegetable oil.

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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 effectively, 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 ceramic. 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 (Ohji and Fukushima 2012).

Several ways to produce macroporous ceramics have been reported (Gonzenbach et al. 2006a), including sacrificial template replica and direct foaming methods (Gonzenbach et al. 2006b). Regardless of the techniques 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.

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. Several long-chain amphiphilic molecules and biomolecules such as lipids and proteins can be used as surface-active agents to stabilize wet aqueous foams by emulsification. These molecules slow down the coalescence and disproportionation of bubbles by adsorbing at the air bubble surface and reducing the air–water interfacial energy. According to studies of (Cilla, Morelli, and Colombo 2014) 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.

In general, the selection of the proper emulsifier, detergent, or surfactant for every application requires prior knowledge of some basic parameters. The most important technological parameters for surfactants in general are probably the values hydrophilic lipophilic balance (HLB), critical micelle concentration (CMC) and Krafft point. HLB is exceptionally useful and constitutes a general guide to the use of a surfactant based on its hydrophilicity and hydrophobicity. Hydrophobic surfactants are potentially good emulsifiers for water-in-oil emulsions, while hydrophilic emulsifiers are most suitable for oil-in-water emulsions. In the majority of cases, micelles are created spontaneously when the concentration of the surfactant passes a CMC. At this concentration a sudden change in the macroscopic parameters of a surfactant solution is observed. Its value for surfactant depends on the length of the hydrophobic part of the molecule, the chemical structure, charge and size of hydrophilic part. The Krafft phenomenon has to do with the sudden change in solubility of surfactants at a particular temperature that is called Krafft point. At temperatures below the Krafft point, the surfactant minimally soluble in water. As soon as the temperature passes the Krafft point, its solubility increases dramatically (Ritzoulis and Rhoades 2013).

Surfactant chain lengths and area of head groups effects structures and also behaviours of surfactants. Vegetable oil produces soap by saponification reaction and produces planar structure at liquid vapor interface (Holmberg, Bo, and Kronberg 2002). It is generally accepted that the volume fraction of dispersed gas phase in a reasonably stable can be increased relatively easily up to a certain critical value, above which the emulsion tend to break and invert. The analysis

predict the shape of such drops as a function according to volume fraction. When the critical value exceeded, each droplet is deformed and thin flat films of continuous phase are formed at each point where bubbles touch. As amount of gas bubbles increased further and further, the areas of, and the compressive forces on, the films keep increasing; and it is plausible that a stage is reached where the disjoining pressure can no longer balance the compressive forces being exerted, at which point the emulsion is expected to start breaking down (Princen 1979). Thickness, contact angle between films and the adjacent free drop interface changes according to volume fraction. (Fig 1).

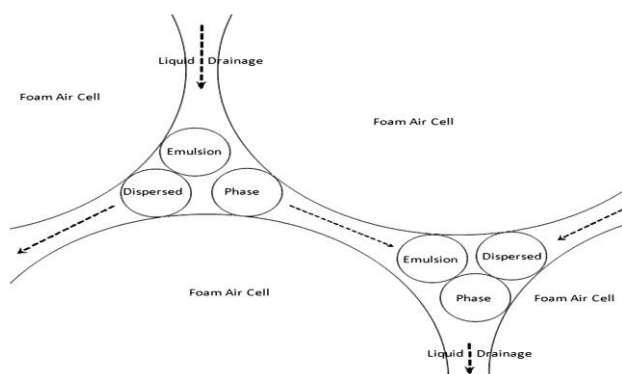


Fig 1. A diagram of the drainage from liquid between foam the air cells (Green et al. 2013)

As surfactant adsorbs at an interface the interfacial tension decreases, a phenomenon termed the Gibbs effect. If a surfactant stabilized film undergoes a sudden expansion, the immediately expanded portion of the films must have a lower degree of surfactant adsorption than unexpanded portions because the surface area has increased. This causes an increased local surface tension which produces immediately contraction of the surface. The surface is coupled, by viscous forces, to the underlying liquid layers. Thus, the contraction of the surface induces liquid flow, in the near surface region, from the low tension region to the high tension region. The transport of bulk liquid due to surface tension gradients is termed the Marangoni effect. In foams Gibbs-Marangoni effect provides a resisting force to the thinning of liquid films (Tauer n.d.) (Fig 2.).

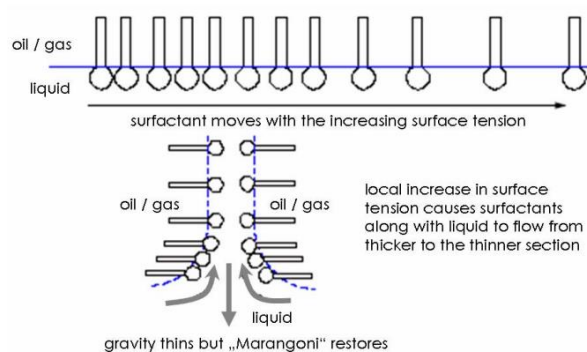


Fig 2. Gibbs-Marangoni Effect on Liquid Films (Tauer, n.d.)

In this communication, we demonstrate that a simple reactive emulsion templating with vegetable oil can produce hierarchically porous geopolymer materials with coexisting controllable mesopores and spherical macropores, without a need of significantly modifying the conventional geopolymer synthetic process. Also, production steps of open porosity were discussed.

2. Materials and Methods

Metakaolin powder used to prepare the suspensions (MEFISTO L05) with an average particle size of 5 μ m. Vegetable oil (Komili Riviera Olive oil) was 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).

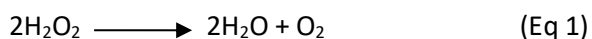
In the first step of the synthesis, solution was prepared by dissolving an appropriate amount of NaOH pellets in sodium silicate in a polypropylene cup in a sodium silicate bath. The geopolymer resins were then prepared by mechanically mixing metakaolinite into the alkaline solution to form a homogenous 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 density and amount of porosity values of samples determined.

3. Results and Discussion

3.1. Effect of Hydrogen Peroxide

Hydrogen peroxide is a well-known blowing agent (Van Bonin, Nehen, and Von Gizycki 1975), while the redox reaction of Al in alkaline solution induces porosity by O₂ evolution (Kriven, Gordon, and Bell 2004). 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 (Eq 1) (Vaou and Panias 2010):



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 an increase of the oxygen pressure under constant temperature. 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 (Vaou and Panias 2010).

In this study effect of peroxide amount on the foaming process is observed. The microstructure of foamy materials is presented in Fig. 3. 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.3. Composition which contains much more peroxide (O5) has thinner walls, much more open porosity and lower density compared to other foams. The reason for increasing amount of open porosity explained as an increase of internal pressure of gas because of higher amount of decomposition reaction of hydrogen peroxide. Then, increased local tension causes to formation of interconnectional porosity.

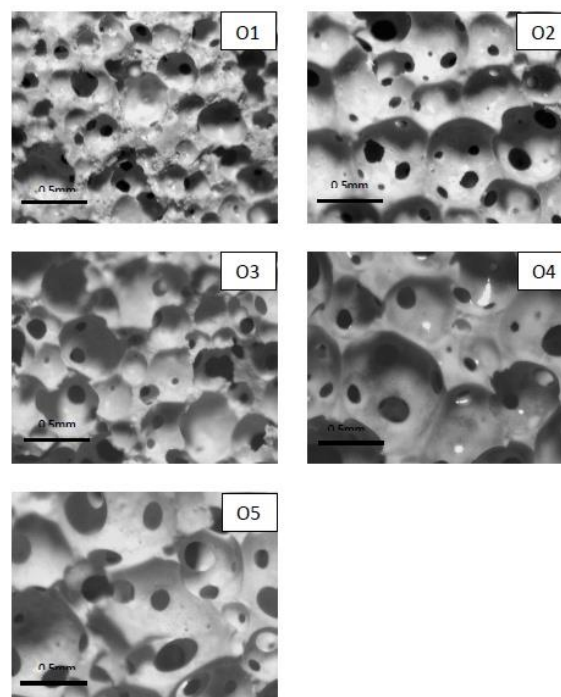


Fig. 3. Stereo microscope images of geopolymer foam samples (2X Magnification). All samples contains same amount of vegetable oil which is %1.5 and different amounts of peroxide a)%0.35, b) %0.70, c) %1.50, d)%3.00, e)%4.00

Table 1. Density and cell volume values of samples.

Samples	Density (g/cm ³)	Cell Volume(%)
O1	0,53	36,15
O2	0,33	51,53
O3	0,39	46,92
O4	0,31	53,07
O5	0,19	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 (Medpelli, Seo, and Seo 2014).

In the study of Gauckler et al. by controlling the foam stability and the setting kinetics, pore sizes within the range of 35 μm 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 (Stuart et al. 2006).

In this study effect of vegetable oil amount on the foaming process was observed. The microstructure of foamy materials are presented in Fig. 4. Amount of open pores and their apertures are increases when the amount of oil increases. This situation was connected to the formation of increasing amount of cells inside geopolymer paste by depending on amount of vegetable oil. It is observed that foam which contains higher amount of vegetable oil has bigger apertures and also thinner wall thicknesses and lower density. The samples which are shown in Fig.4. were prepared with same amount of peroxide and different amounts of vegetable oil.

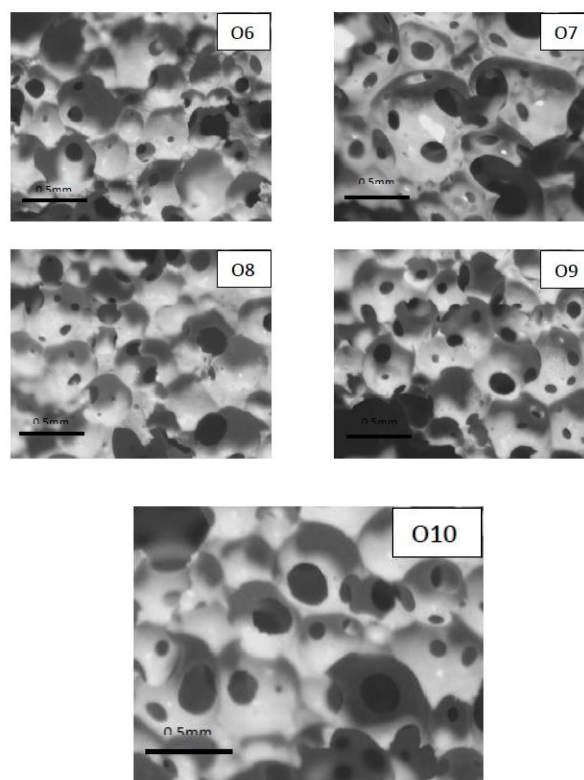


Fig4. Stereo microscope images of geopolymer foam samples (2X Magnification). All samples contains same hydrogen peroxide which is %2 and different amounts of vegetable oil a) %1.2, b) %2.4, c) %3.6, d) %4.8, e) %6.

Table 2. Density and cell volume values of samples.

Samples	Density (g/cm^3)	Cell Volume(%)
O6	0,39	36,15
O7	0,45	51,53
O8	0,42	46,92
O9	0,25	53,07
O10	0,175	62,30

4. Conclusion

Self-setting foams with average densities ranging from 0,175-0,53 g/cm³ and total open cell volume from % 36,15 to % 62,30 which means total porosities range from % 17 to %93,4 can be produced by combining surfactant stabilized foams with geopolymerization method. The foam porosity and pore size can be controlled by changing amount of vegetable oil and peroxide. According to experimental results it can be seen that increasing amount of peroxide enlarges the bubbles, at the point that which is the bubbles touch each other, because of internal pressure surfactant perched. In addition, increasing amount of vegetable oil produces high amount of cells inside geopolymer paste and this also makes closer the cells. Approaching cells makes thinner the walls and this causes the formation of interconnecting porosity.

5. References

- Bonin, Wulf Van, Ulrich Nehen, and Ulrich Von Gizycki. 1975. "Hydrogen Peroxide Blowing Agent for Silicate Foams," February. <http://www.freepatentsonline.com/3864137.html>
- Cilla, Marcelo Strozi, Márcio Raymundo Morelli, and Paolo Colombo. 2014. "Open Cell Geopolymer Foams by a Novel Saponification/peroxide/gelcasting Combined Route." *Journal of the European Ceramic Society* 34 (12). Elsevier: 3133–37. <https://doi.org/10.1016/J.JEURCERAMSOC.2014.04.001>.
- Gonzenbach, Urs T., André R. Studart, Elena Tervoort, and Ludwig J. Gauckler. 2006a. "Stabilization of Foams with Inorganic Colloidal Particles." *Langmuir* 22 (26): 10983–88. <https://doi.org/10.1021/la061825a>.
- Gonzenbach, Urs T., André R. Studart, Elena Tervoort, and Ludwig J. Gauckler. 2006b. "Ultrastable Particle-Stabilized Foams." *Angewandte Chemie - International Edition* 45 (21): 3526–30. <https://doi.org/10.1002/anie.200503676>.
- Green, Ali J., Karen A. Littlejohn, Paul Hooley, and Philip W. Cox. 2013. "Formation and Stability of Food Foams and Aerated Emulsions: Hydrophobins as Novel Functional Ingredients." *Current Opinion in Colloid and Interface Science* 18 (4). The Authors: 292–301. <https://doi.org/10.1016/j.cocis.2013.04.008>.
- Holmberg, Krister, J Bo, and Bengt Kronberg. 2002. *Solution and Polymers in Aqueous*. <https://doi.org/10.1002/0470856424>.
- Kriven, W. M., M. Gordon, and J. L. Bell. 2004. "Geopolymers: Nanoparticulate, Nanoporous Ceramics Made Under Ambient Conditions." *Microscopy and Microanalysis* 10 (S02). Cambridge University Press: 404–5. <https://doi.org/10.1017/S1431927604886719>.
- Medpelli, Dinesh, Jung Min Seo, and Dong Kyun Seo. 2014. "Geopolymer with Hierarchically Meso-/macroporous Structures from Reactive Emulsion Templating." *Journal of the American Ceramic Society* 97 (1): 70–73. <https://doi.org/10.1111/jace.12724>.
- Ohji, T, and M Fukushima. 2012. "Macro-Porous Ceramics: Processing and Properties." *International Materials Reviews* 57 (2): 115–31. <https://doi.org/10.1179/1743280411Y.0000000006>.
- Princen, H.M. 1979. "Highly Concentrated Emulsions. I. Cylindrical Systems." *Journal of Colloid and Interface Science* 71 (1). Academic Press: 55–66. [https://doi.org/10.1016/0021-9797\(79\)90221-2](https://doi.org/10.1016/0021-9797(79)90221-2).
- Ritzoulis, Christos., and Jonathan. Rhoades. 2013. *Introduction to the Physical Chemistry of Foods*. Taylor & Francis.
- Studart, André R., Urs T. Gonzenbach, Elena Tervoort, and Ludwig J. Gauckler. 2006. "Processing Routes to Macroporous Ceramics: A Review." *Journal of the American Ceramic Society* 89 (6): 1771–89. <https://doi.org/10.1111/j.1551-2916.2006.01044.x>.
- Tauer, Klaus. n.d. "A Little (Theory): Emulsion Stability Emulsions-Part 2." Accessed February 12, 2019. https://www.mpikg.mpg.de/886743/Emulsions_2.pdf.
- Tauer, Klaus. n.d. "Emulsions – Part 3 Remarks to : Microemulsions Miniemulsions Micro and Miniemulsion – Why Special Emphasis?" *Interfaces*.

Vaou, V., and D. Parias. 2010. "Thermal Insulating Foamy Geopolymers from Perlite." *Minerals Engineering* 23 (14). Elsevier Ltd: 1146–51. <https://doi.org/10.1016/j.mineng.2010.07.015>.