

Effect of Pore Forming Agents on Geopolymer Porosity and Mechanical Properties

Suresh K. Kaliappan¹, Ahmer A. Siyal¹, Zakaria Man¹, Mark Lay² and Rashid Shamsuddin^{1,3,a)}

¹*Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia.*

²*School of Engineering, Faculty of Science and Engineering, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand.*

³*Center for Biofuel and Biochemical Research (CBBR), Institute for Sustainable Living, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia.*

^{a)}*Corresponding author: mrashids@utp.edu.my*

Abstract. Generation of industrial waste materials such as fly ash and slag in bulk provides an opportunity to convert these wastes into eco-friendly, value-added products. A geopolymer, a strong, porous and environmentally friendly material, was synthesized by mixing fly-ash with an alkaline activator, followed by addition of a pore forming agent (PFA) which created voids of varied pore sizes within the mixture. This polymer has potential applications as an adsorbent or membrane material; however, there is no established technology to regulate the pore size. Corn oil, waste palm oil and starch were investigated as potential organic additives to produce geopolymer materials with pore sizes suitable for water treatment membranes. Geopolymer without additives had a compressive strength of 30.93 MPa. Corn oil induced the highest porosity of up to 26.6 % with a compressive strength of 9.9 MPa, waste palm oil at 21.3 % and 9.0 MPa and starch at 17.9 % and 20.41 MPa. SEM analysis revealed that the voids and tunnels formation increased with increased PFA dosage.

I. INTRODUCTION

A few years ago, the World Board of Commerce for Sustainable Development's (WBCSD), in its initiative into greening the concrete industry, introduced the use of geopolymer adsorbents for reducing volatile gas emissions associated with cement production [1]. Geopolymer adsorbents can also be used for membranes in water filtration to remove impurities, but the porosity of the material must be reproducibly tailored to enable removing contaminants of various sizes and physical states [2]. One potential approach is to introduce organic additives as pore forming agents (PFA) during geo-polymerization to induce pore formation. The objective of this study was to synthesize and characterize geopolymer composites using PFAs.

II. LITERATURE REVIEW

A. Geo-polymerization

Inorganic polymer concrete or geopolymer is a material that is eco-friendly and is formed by alkali activated geopolymerization of industrial waste material such as fly ash or slag with the aid of an alkali activator such as sodium hydroxide. During geo-polymerization, the Si and Al species of the aluminosilicate materials go through condensation, nucleation, oligomerization and polymerization giving an amorphous three-dimensional network. The Si/Al ratio alters the three-dimensional network changing the mechanical strength and porosity of the geopolymer [3].

B. Pore Forming Method Using Foaming Agents

To produce geopolymer materials for adsorption or membranes application, pore forming agents (PFA) are popular as they induce gas formation which generates pores. Pore forming agents such as aluminium, graphite and silica fume have been widely used over the past years [4]. Suitable additives could also enhance the compatibility of the geopolymer material potential end applications. For example, organo-bentonite, produced from absorbing protein on to bentonite clay from meat rendering plant stickwater, was successfully used as a filler material in bioplastics [5], eliminating the need to regenerate the adsorbent.

III. METHODOLOGY

For this project, fly ash was obtained from a coal power plant in Manjung region, Perak. Starch powder, corn oil and palm oil based waste cooking oil were used as pore forming agents. 8M sodium hydroxide solution was used as the alkaline activator for geo-polymerization.

A. Preparation of Pore Forming Agents

The corn oil and waste cooking oil were used as supplied while a 1M starch solution was prepared by mixing starch with water. NaOH solution, fly ash, and PFA were added to water to make a ratio of 30 parts fly ash, 12.5 parts NaOH and 1 part PFA by weight at the concentrations of PFA listed in Table 1

TABLE 1. PFA dosages in geopolymer samples (wt.%)

PFA	Corn Oil	Waste Cooking Oil (Palm Oil)	Starch Solution
Dosage 1	4	4	4
Dosage 2	8	8	8
Dosage 3	12	12	12

B. Synthesis of Fly Ash Based-Geopolymer

The prepared fly ash was mixed with alkaline activator in the ratio of 3:1 respectively. The mixture was stirred until visibly homogeneous. Then, PFA was added into the respective mixture and stirred for about 2 minutes to form a paste. The geopolymer paste was then poured into an iron cast and placed in an oven for 24 hours at 60°C.

C. Characterization of Fly Ash Based Geopolymer

The resulting geopolymer composites were characterised for porosity, mechanical properties, morphology, surface area and pore size.

i) Porosity Test

Bulk density of the geopolymer was measured by immersing a pre-weighed sample into a known volume of water. The change in the volume of water was recorded and divided from the mass of the sample to obtain the bulk density in kg/m³. Powder density was measured using Powder Density Tester AU-300P. Equation 1 was used to calculate the percentage of porosity in the sample [6].

$$\text{Porosity \%} = \frac{\text{Bulk density} - \text{Powder density}}{\text{Bulk density}} \times 100 \quad (1)$$

ii) Compressive Strength Test

The samples were cut into blocks of 5 cm x 5 cm x 5 cm and compression tested using an ADR-Auto compression machine at 3000 kN and compression rate 0.9 s/m. [7].

iii) Scanning Electron Microscopy (SEM) Analysis

The morphology of the crushed specimens after the compression test were examined using SEM following the standard SEM procedure for composite materials [8].

iv) Brunauer–Emmett–Teller (BET) Surface Area Analysis

The surface areas of dry geopolymer samples were determined by nitrogen adsorption using an ASAP Plus 2020 BET analyzer. Powder samples were degassed under vacuum at 80°C for 2 hours and nitrogen adsorption was measured across 35 points of relative pressure (P/P_o) for 6 hours. The mean surface area was determined using the Multi-Point BET method.

IV. RESULTS AND DISCUSSION

Results for bulk and powder density and porosity are summarized in Table 2 below. Using corn oil for the PFA at 12 wt.% loading resulted in the highest porosity at 26.6 % with the lowest bulk and powder density. Waste cooking oil, showed high porosity percentage of about 21.3 % followed by starch at 17.9 %, compared to 4.49 % porosity of the control sample (geopolymer without PFA). SEM showed the control sample contained a high amount of incomplete reaction (during polymerization) of the raw materials compared to samples with PFAs.

A. Density and Porosity

TABLE 2. PFA dosages in geopolymer samples (wt.%)

Sample	Bulk density ($\text{kg/m}^3\text{m}^3$)	Powder density ($\text{kg/m}^3\text{m}^3$)	Porosity (%)
Control	1292	1350	4.49
12 Wt. % Corn Oil	1139	1442	26.6
12 Wt. % Waste Cooking Oil	2304	2795	21.3
2.5 Wt. % Starch	1450	1710	17.9

B. Compressive Strength

The average compressive strength for the control sample was 30.93 MPa. Geopolymers with lower PFA dosages gave the highest compressive strengths for all PFAs (Fig. 1). The highest compressive strength values were recorded for corn oil and waste cooking oil (from palm oil) at 20.71 MPa and 16.98 MPa respectively. SEM analysis showed these samples had lower dispersion and void formation, hence, the mechanical strength of the sample was not compromised as much as the other samples at higher dosages.

Using starch solution at dosages of more than 4 wt.% could not form geopolymers because the resulting slurry become very viscous and dried off during mixing. The condition might be a result of starch hydrolysis in geopolymerization that consumed more water from the starch slurry than normally. In the presence of alkaline activator, further stirring caused the equilibrium to be reached faster and the mixture was gelled into a network of starch and fly ash. This trend was absent in the other two PFAs as they are oil-based and hydrophobic.

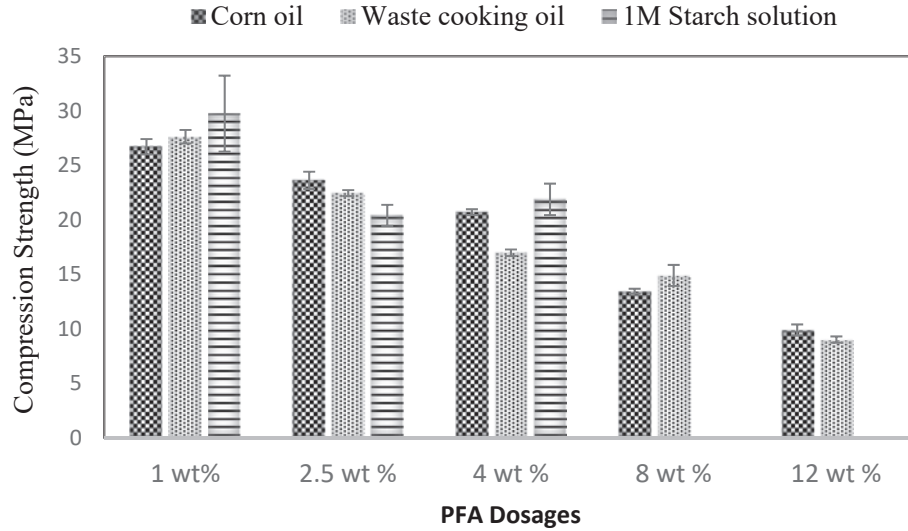


FIGURE 1. Compressive strength comparison of control and PFA-added geopolymers.

C. Scanning Electron Microscopy Analysis (SEM)

From Fig. 2, the presence of irregular pores can easily be seen in both samples resulting from gases released during the geopolymerization reaction. Clumps of fly ash on the surface (Fig. 2a) signify incomplete reaction between the raw materials and the alkaline activator either due to incomplete mixing or excess of fly ash for the amount of NaOH used. From Fig. 2b, the surface of geopolymer with 12 wt.% corn oil seems to be loosely packed with oil residue visible compared to the control sample. This is attributed to the corn oil being immiscible with the mixture. Pore formation and excess of oil weakened the samples explaining the sizeable difference in the compressive strength between the geopolymer and the control. SEM analysis for the rest of samples showed similar trends of highly porous geopolymers with higher dosages of PFAs.

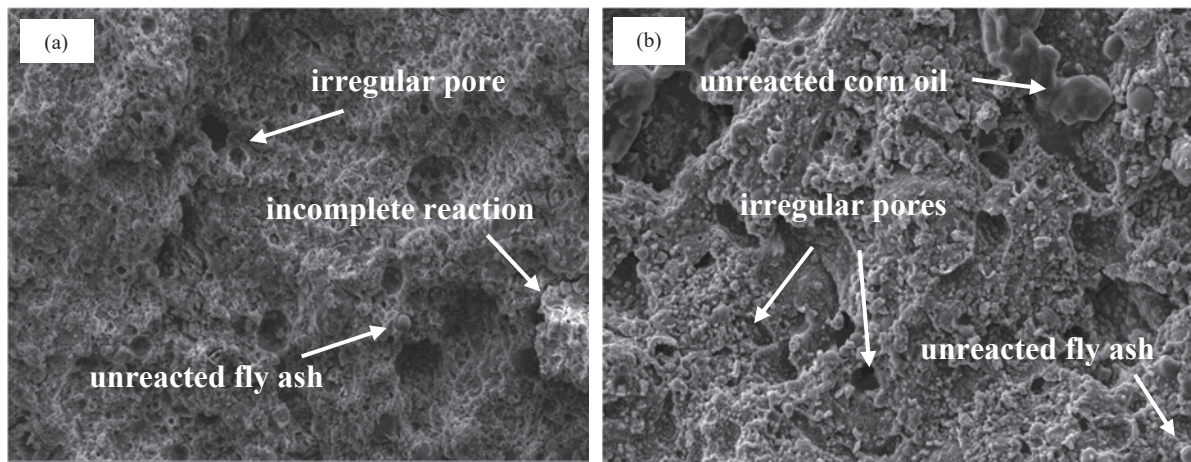


FIGURE 2. SEM images of geopolymer samples at 300X for a) control and b) with 12 wt.% corn oil PFA.

D. BET Surface Area Analysis

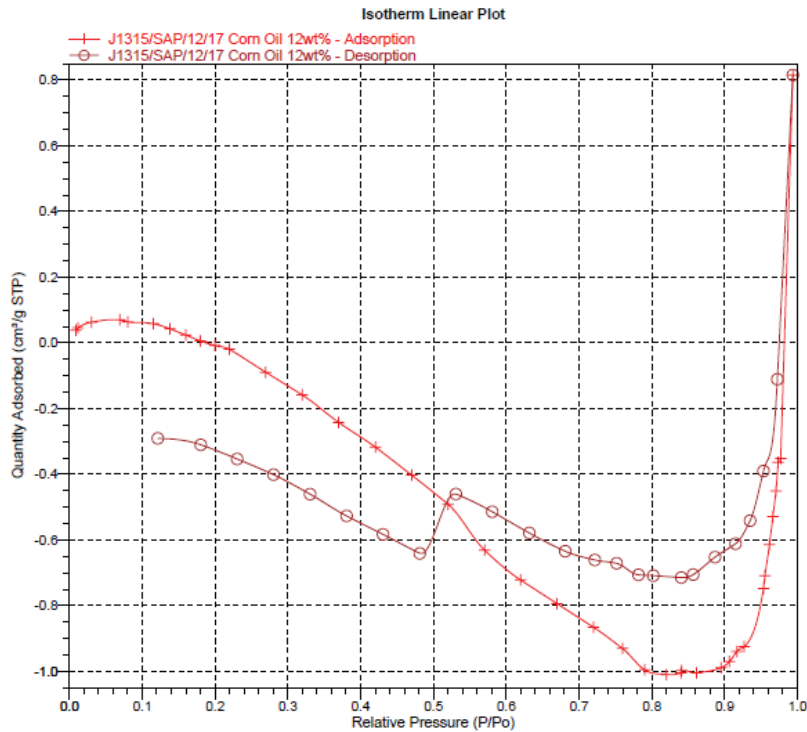


FIGURE 3. BET isotherm plot for geopolymer sample with 12 wt.% corn oil.

The surface area of the control geopolymer was between 50 to 60 m²/g. BET analysis on geopolymer with 12 wt.% corn oil yielded an unusual isotherm with negative adsorption up to relative pressures of 0.8 (Fig. 3), and an unexpectedly low surface area of 0.0307 m²/g. This was despite a high volume of pores recorded from the density test and SEM. It is possible the oil was volatilising during the BET test resulting in the poor result. An accurate isotherm plot of a surface area analysis is expected to follow the typical trend as published by [9]. The oil probably contained a large number of fatty acids and odour compounds that would volatilise while under vacuum. Therefore, BET would need to be repeated with the samples degassing for longer and at higher temperatures for example at smoke point of corn oil at 270°C and above.

V. CONCLUSION

This work has revealed the inverse relationship for geopolymers between porosity and compressive strength. The highest porosity at 26.6% was achieved with the highest PFA addition at 12 wt.% of corn oil, which corresponds to the lowest compression strength of 9.9 MPa. This strength value is considered high for a material with such high percentage of porosity. This finding is consistent with other PFAs used at different dosages. SEM analysis confirmed the initial hypothesis of void and tunnel formation behind the composites porosity. However, the sizes of the pores were not consistent for all PFA loadings. From BET analysis, nitrogen gas was prohibited access to the binding sites on geopolymer surface due to the presence of residual oil, therefore degassing the samples at higher temperature for longer should be investigated.

ACKNOWLEDGMENT

The authors would like to thank Central-Analytical Laboratory (CAL) of UTP for the technical assistance on BET and SEM analysis.

REFERENCES

1. Obonyo, E., Kamseu, E., Melo, U. C., & Leonelli, C. (2011). Advancing the use of secondary inputs in geopolymer binders for sustainable cementitious composites: a review. *Sustainability*, 3(2), 410-423.
2. Föll, H., Carstensen, J., & Frey, S. (2006). Porous and nanoporous semiconductors and emerging applications. *Journal of Nanomaterials*, 2006.
3. Badanoiu, A. I., Al Saadi, T. H. A., Stoleriu, S., & Voicu, G. (2015). Preparation and characterization of foamed geopolymers from waste glass and red mud. *Construction and Building Materials*, 84, 284-293.
4. Obradović, N., Filipović, S., Marković, S., Mitrić, M., Rusmirović, J., Marinković, A., ... & Pavlović, V. (2017). Influence of different pore-forming agents on wollastonite microstructures and adsorption capacities. *Ceramics International*, 43(10), 7461-7468.
5. Shamsuddin, R.M., C.J.R. Verbeek, and M.C. Lay, Protein-Intercalated Bentonite as Nano-Reinforcement in Bloodmeal-Based Bioplastics. *Journal of Polymer Materials*, 2015. 32(4): p. 435-449.
6. Bai, C., & Colombo, P. (2017). High-porosity geopolymer membrane supports by peroxide route with the addition of egg white as surfactant. *Ceramics International*, 43(2), 2267-2273.
7. Rashid, K., & Waqas, R. (2017). Compressive strength evaluation by non-destructive techniques: An automated approach in construction industry. *Journal of Building Engineering*.
8. Krause, F. F., Rosenauer, A., Barthel, J., Mayer, J., Urban, K., Dunin-Borkowski, R. E., ... & Allen, L. J. (2017). Atomic resolution elemental mapping using energy-filtered imaging scanning transmission electron microscopy with chromatic aberration correction. *Ultramicroscopy*.
9. Naderi, M. (2015). Surface Area: Brunauer–Emmett–Teller (BET). In *Progress in filtration and separation* (pp. 585-608).