Conversion of palm oil fuel ash (POFA) into foamy geopolymer for lightweight building material application by aluminum powder addition

E Kusumastuti1*, R Desita1, A T Prasetya1, T Sulistyaniingsih1, M Sulistyan2
1 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Central Java, 50229, Indonesia
2 Inorganic Chemistry Laboratory, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Central Java, 50229, Indonesia

*Corresponding author: ella.kusuma@mail.unnes.ac.id

Abstract. Palm Oil Fuel Ash (POFA) is produced from the burning of palm oil solid waste biomass. POFA is abundant in Indonesia considering that Indonesia is one of the world's largest producers of Crude Palm Oil (CPO) and has the largest palm oil plantation. The main content of POFA is SiO$_2$ around 60%, Al$_2$O$_3$ around 3-10% and CaO around 5-15% so that POFA has the potential to be developed as aluminosilicate inorganic polymers. The high SiO$_2$/Al$_2$O$_3$ ratio in POFA needs to be reduced for the formation of Si-O-Al chains in geopolymers. Therefore, two stages of research were carried out. Preliminary research was conducted to obtain optimum Solid/Liquid ratio. Aluminum powder was then added with certain variations to get a certain SiO$_2$/Al$_2$O$_3$ ratio as well as a foaming agent so that the product can later be used as a porous building material. The preliminary results showed that the optimum Solid/Liquid ratio obtained was 0.83. The addition of aluminum powder was optimum at 2% w/w with a compressive strength of 5.4233 MPa, a density of 1339.2175 kg/m$^3$, and a thermal conductivity of 0.6233 Watt/m$^0$K. This geopolymer product can be categorized as a lightweight building material with criteria: a compressive strength of 0.5-10 MPa, densities between 600-1800 Kg/m$^3$, and a thermal conductivity of 0.1-0.7 Watt/m$^0$K which can be used as panels in buildings, casting walls, and ornaments in parks.

1. Introduction
The world's demand for construction materials from year to year always shows an increase along with the many developments. As a consequence, the need for cement as a binding component is also increasing. In the cement production process, CO$_2$ emissions into the air are almost proportional to 1: 1, which means that the production of 1 ton of cement will produce 0.97 tons of CO$_2$ emissions into the atmosphere [1]. One of the efforts to reduce the use of cement is by synthesizing construction materials without using cement. Geopolymers are one of the materials that have been synthesized for this purpose because there is no CO$_2$ production in the geopolymerisation process [2].

Geopolymers are inorganic polymers consisting of SiO$_4^{+}$ and AlO$_4^{+}$ tetrahedra-tetrahedra chains. Geopolymers are made by reacting the aluminosilicate source with an alkaline solution. The main
basic material in the manufacture of geopolymers is a material that contains a lot of silica and alumina elements [3].

Various types of aluminosilicate materials such as metakaolin [3-6], kaolin and dam sludge waste [7], fly ash [8-10], volcanic ash [11], and slag [12] have been applied as starting materials for making geopolymers. Another aluminosilicate source material that is suitable for geopolymer synthesis is Palm Oil Fuel Ash (POFA) [2,13-15]. POFA is produced from burning palm oil solid waste (palm oil fiber, shell, and empty palm fruit bunches) at a temperature that reaches up 1,000°C [1]. In addition to reducing CO$_2$ gas emissions, the use of POFA as the main material for geopolymers can overcome the accumulation of palm oil fuel ash that pollutes the environment.

The combination of their properties and synthesis methods gives geopolymers a variety of promising applications in several industries including civil engineering. Gopolymers possess properties comparable or even better than conventional building materials, such as rapid strength development, improved mechanical properties, resistance to corrosive environments and high temperatures [16]. In recent decades, lightweight building materials have been popular because they are lighter but stronger, thus minimizing fatal injuries in the event of a building collapse. Geopolymers that can be applied to lightweight construction materials are foamy [17]. Foamy geopolymers are geopolymers that are added with a foaming agent, intending to form pores in the geopolymer material [17, 18]. Foamy geopolymers have potential to become a heat-insulating material [17] that does not cause environmental pollution but can even overcome the effects of global warming.

Various foaming agents have been used to produce gas in geopolymers such as using silica fume [19], H$_2$O$_2$ [17], metal powders such as aluminum powder or materials containing elemental silicon (silica powder, FeSi or SiC) [20] or zinc [21] and using organic foaming agents such as sunflower seed oil [14] which produces foam through a saponification reaction. In industry, aluminum powder is generally used as a gas producer [20]. One of the advantages of using aluminum powder as a foaming agent is that the foam produced is more stable at high temperatures so that it does not cause cracks in the resulting geopolymer.

Previous research conducted by Kusumastuti and Widiarti [22] synthesized a lightweight geopolymer from fly ash and hydrogen peroxide as foaming agent to produce a geopolymer with a large compressive strength of 21.28 MPa, a low thermal conductivity 0.0611 Watt/m$^3$°K but still have a high density 1800.83 kg/m$^3$. In another study, the use of POFA as a mixture in geopolymer concrete from fly ash was carried out by [23] which resulted in a drastic reduction in its density from 1840 kg/m$^3$ to 1291 kg/m$^3$ in the addition of Sika AER-50/50 as a foaming agent. So, in this research, a foamy geopolymer made from palm oil fuel ash. Aluminum powder is used as a foaming agent in line with the high SiO$_2$/Al$_2$O$_3$ ratio in POFA [1,13, 23] so that the addition of aluminum powder is not only aimed at forming closed pores but also at the same time decreasing the SiO$_2$/Al$_2$O$_3$ ratio for geopolymer Si-O-Al chains formation. The foamed geopolymer was then identified its physical properties and chemical structure. The purpose of this study is to investigate the physical, mechanical and structural properties of geopolymer from POFA as a starting material and aluminum powder as a foaming agent.

2. Methods

The materials used in this research included palm oil fuel ash (POFA) taken from PT. Karya Teknik Plantation, technical sodium silicate (Na$_2$SiO$_3$), sodium hydroxide (NaOH 99%, Merck), aqua dest (H$_2$O), and aluminum powder. Instruments needed for geopolymer characterization included a compressive strength testing machine (Universal Testing Machine), XRF JSX-3211, Thermal Conductivity Analyzer.

For POFA preparation, palm oil fuel ash was dried in an oven at 110° C for 24 hours [13] to remove the moisture content in it. It was then sieved using a 100-mesh sieve to remove large particles
and incomplete combustion residue. Palm oil fuel ash was analyzed for its chemical composition using XRF (X-Ray Fluorescence).

Geopolymer synthesis was carried out by mixing palm oil fuel ash with activator solutions (NaOH and H$_2$O). Previously the activator solution had been mixed with sodium silicate or Na$_2$SiO$_3$ as a binder. Mixing was done for 5 minutes at 550 rpm [24]. The mixture was poured into a plastic cylinder mold with a diameter: height = 1:2 [25]. The mixture in the mold was allowed to stand for 1 hour at room temperature followed by curing process, which was put in an oven at 60°C for 24 hours [26]. In this study, a preliminary study had been conducted to determine the optimal solid/liquid (S/L) ratio by varying the solid/liquid ratio by 0.66; 0.7025; 0.745; 0.7875; 0.83 and 0.8725. The results of the optimal solid/liquid composition were used for foamy geopolymers synthesis with the addition of aluminum powder foaming agent; 1.0; 1.5; 2.0 and 2.5% w/w. Characterization of the materials was carried out at 28 days of age. The foamy geopolymer products formed were characterized in the form of compressive strength, density, and thermal conductivity.

3. Result and Discussion

3.1. Preparation and characterization of POFA
Palm oil fuel ash (POFA) samples were obtained from PT Karya Teknik Plantation, Sebulu, Kutai Kartanegara, East Kalimantan. The characterization of palm oil fuel ash included the chemical composition using XRF (Table 1).

| Compounds | Percentage (%) | Compounds | Percentage (%) |
|-----------|----------------|-----------|----------------|
| SiO$_2$   | 65.583         | Nd$_2$O$_3$ | 0.155          |
| CaO       | 14.915         | CuO       | 0.124          |
| K$_2$O    | 10.992         | SrO       | 0.043          |
| Fe$_2$O$_3$| 4.275         | Na$_2$O   | 0.037          |
| Al$_2$O$_3$| 1.539         | ZrO$_2$   | 0.019          |
| MgO       | 1.030          | Rb$_2$O   | 0.018          |
| MnO       | 0.379          | P$_2$O$_5$ | 0.002          |
| TiO$_2$   | 0.195          | Y$_2$O$_3$ | 0.002          |

Physically, the ash appearance of oil palm biomass was in the form of fine powder with a blackish gray color. The results of the analysis of the chemical composition of palm oil fuel ash are in Table 1. Palm oil fuel ash contains 65.583% SiO$_2$ and 1.539% Al$_2$O$_3$. The SiO$_2$/Al$_2$O$_3$ weight ratio of palm oil fuel ash was 42.614 when converted into a SiO$_2$/Al$_2$O$_3$ mole ratio of 72.775. Palm oil fuel ash showed a very high SiO$_2$/Al$_2$O$_3$ value as reported by some research [1, 13, 23].

3.2. Solid/Liquid (S/L) ratio optimization
Preliminary research was carried out to obtain the optimum S/L ratio to obtain a geopolymer with high compressive strength and easy workability. In the synthesis carried out, the geopolymer was prepared from palm oil fuel ash, sodium silicate, NaOH, and water. A sodium silicate or Na$_2$SiO$_3$ was used as a binder in geopolymerization and NaOH as an activator solution. POFA as a solid component, while the other materials as a liquid component. The synthesized geopolymer was tested for compressive strength using a universal testing machine at the age of 28 days as shown in Figure 1.
Figure 1. Compressive strength data of Solid/Liquid (S/L) ratio POFA geopolymers

Figure 2. Compressive strength data of POFA geopolymers with aluminum powder addition (S/L=0.83)

Figure 1 shows that the compressive strength continued to increase until the S/L was 0.83 but the compressive strength decreased in the S/L variation of 0.87. The more solid added, the smaller the water content in the geopolymer. The increase of ratio S/L will produce the greater compressive strength of geopolymer [27]. However, the ratio S/L was too large that can cause difficulties in the process [8,11]. Evaporation of a little water leaves a few empty voids (pores) so that the compressive strength increases. The compressive strength will decrease when the amount of water was no longer able to balance the amount of solid material added [8]. The optimum compressive strength was achieved at an S/L ratio of 0.83, which was 9.6374 MPa. The optimum S/L ratio of 0.83 was used as a standard for the further synthesis of foamy geopolymers by adding variations of aluminum powder of 0.5-2.5% by weight of palm oil fuel ash.

3.3. Synthesis and characterization of foamy geopolymers with aluminum powder addition

Figure 2 is a compressive strength graph of foamy geopolymer with aluminum powder addition. The compressive strength of the geopolymer has increased from the aluminum powder addition of 0.5% w/w of 4.9830 MPa to the addition of 2% aluminum powder of 5.4210 MPa. The compressive strength decreased after the addition of aluminum powder by 2.5% with a compressive strength of 5.0925 MPa. This was because the aluminum powder addition of 0.5-2% increased the aluminum content. With the addition of aluminum powder and sufficient alkaline conditions, the formation of [Al(OH)₄]⁻ species will increase as well, thus contributing to the formation of Si-O-Al chains and strengthening the geopolymer matrix [26]. In this range of aluminum addition, the pores generated from the hydrogen gas produced did not cause a decrease in compressive strength because the effect of the aluminate species on the polymer chain was more significant. Whereas in the addition of 2.5% aluminum powder, OH⁻ from the alkaline solution has completely reacted with the aluminum from aluminum powder addition. The aluminate dissolution was not optimal if the OH⁻ was not sufficient to dissolve high aluminum, because metallic aluminum powder is very reactive in alkaline environments [18]. The lack of monomers formed result in the inability to form optimum Si-O-Al polymer chains which decreased the compressive strength value. At this point, the effect of the pores due to gas formation on the geopolymer matrix will cause a decrease in the compressive strength [8].
Figure 3. Density data of POFA geopolymers with aluminum powder addition

Figure 4. Thermal conductivity of POFA geopolymers with aluminum powder addition

Figure 3 is the relationship between density and aluminum powder addition. Before adding aluminum powder, the geopolymer density value was still high, namely 2299.8258 kg/m³. With the addition of 0.5% aluminum powder, the value of the geopolymer density decreased to 1474.8042 kg/m³, then the density value decreased to the lowest of 1339.2175 kg/m³ in the addition of 2% aluminum powder. The density of the geopolymer increased again with the addition of 2.5% aluminum powder of 1345.1519 kg/m³. All foamy geopolymer has a lower density value. Density and compressive strength are directly proportional, that is, the lower the density, the lower the compressive strength. The more the addition of aluminum powder, the smaller the density value of the foamy geopolymer. This was because the pores contained in the geopolymer originating from the reaction of aluminum which reacted with water and hydroxide to form H₂ gas [18, 21]. A geopolymer for lightweight brick application was expected to have a small density but still had a high compressive strength. Geopolymers with high compressive strength and low density were also obtained by adding 2% aluminum powder.

Figure 4 is the result of measuring the thermal conductivity of foamy geopolymers with the addition of aluminum powder. The initial value of thermal conductivity after adding 0.5% aluminum powder is 0.7219 Watt/mºK. The thermal conductivity value continued to decline until the addition of 2.5% aluminum powder to 0.6148 Watt/mºK. The thermal conductivity value was determined by the pore fraction of the most porous specimen that will have the lowest thermal conductivity [15]. The addition of aluminum powder as a foaming agent creates pores in the geopolymer. The more aluminum powder addition, the more pores produced, up to the addition of 2.5% w/w. The trapped air (hydrogen gas) in this pore inhibited the rate of heat being transferred to the geopolymer so that the thermal conductivity value continues to decline [8]. Materials that have low thermal conductivity are good materials for heat insulation. The best materials for lightweight brick applications and heat insulation are materials that have low thermal conductivity and low density, but still have high compressive strength [22, 14]. The geopolymer with high compressive strength and at a time had a low thermal conductivity value was obtained by adding 2% aluminum powder.

4. Conclusion

POFA with a high SiO₂/Al₂O₃ composition can be converted into geopolymers with a character for lightweight building materials. Aluminum powder addition was one from many methods to reduce the SiO₂/Al₂O₃ ratio. Based on the characterization results, the Aluminum powder addition reached the optimum character at 2% (w/w) with a strength of 5.4233 MPa, density 1339.2175 kg/m³ and the thermal conductivity 0.6233 Watt/mºK. Based on this study, geopolymer product can be said to have the potential as lightweight building materials for low strength construction applications.
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