

# Effect of Palm Oil Fuel Ash Treated with Citric Acid to Physico-Mechanical Properties of Cement Paste

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Palm Oil Fuel Ash (POFA), Concrete, Heat Treatment, Acid Treatment, Citric Acid, UPOFA, TPOFA.

## Abstract

The utilization of waste materials in construction materials has gained considerable attention as a sustainable and environmentally friendly practice. This study investigates the application of Palm Oil Fuel Ash treated with citric acid (TPOFA) as a supplementary cementitious material in cement paste. The untreated POFA (UPOFA) undergoes several processes such as sieving, grinding and heat treatment at 800°C for 1.5 hours and citric acid treatment. The highest density for UPOFA, TPOFA and TPOFA mixed with sand is obtained at 20% of POFA both for 7 days and 14 days curing period. The water absorption for TPOFA mixed with sand is the lowest compared to UPOFA and TPOFA. The highest compressive strength of the samples at 7 days curing period for UPOFA (32.40MPa), TPOFA (34.41MPa) and TPOFA mixed with sand (38.62MPa). Meanwhile for 14 days curing period for UPOFA (34.80MPa), TPOFA (36.82MPa) and TPOFA mixed with sand (40.25MPa). The incorporation of treated POFA into cement paste is a promising material that can be used because it improved workability and enhanced the physical and mechanical properties, attributed to enhanced pozzolanic activity. Therefore, the best sample to be used is TPOFA mixed with sand as it has the highest compressive strength and lower water absorption compared to UPOFA and TPOFA mixed with cement.

## 1. Introduction

Concrete, being the most essential construction material, accounts for a substantial portion of this impact. Every year, over 10 billion tons of concrete are produced worldwide. When produced properly, concrete exhibits excellent mechanical strength and durability. However, it also has a significant environmental footprint. To enhance sustainability in the concrete sector, research efforts should focus on utilizing alternative renewable resources, such as palm oil waste, in concrete production [1]. Additionally, utilizing POFA in concrete production helps to conserve natural resources by reducing the reliance on traditional cement, which has a significant carbon footprint. In terms of concrete performance, studies have shown that the addition of POFA can improve various properties [2]. The construction industry, particularly during concrete preparation, has shown a growing interest in utilizing industrial and agricultural waste materials, as highlighted by [3],[4].

POFA is waste products produced from palm oil tree. Consequently, to conserve energy and fuel resources, these waste materials are often incinerated and utilized to heat boilers for power generation in palm oil production facilities. The residue from the burning process, consisting of ash derived from fibers and shells, is commonly referred to as POFA. Subsequent investigation by various researchers have focused on examining the impact of different sizes of the same admixture in concrete or mortar. As highlighted in the work of [5], it has

been established that the fineness of pozzolan plays a pivotal role in influencing concrete properties, primarily by enhancing packing efficiency and pozzolanic activity. This phenomenon contributes to the improvement of concrete durability by refining pore structure and decreasing the presence of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ). Supporting this notion, findings from a study [6] underscore the variability in chemical composition between ground palm oil fuel ash (POFA) and ultra-fine POFA. Notably, as the fineness of POFA increases, there is a corresponding elevation in the  $\text{SiO}_2$  content.

The augmentation in POFA fineness is achieved through additional processes, including further burning and grinding. The extended burning process, in particular leads to an increase in silica content. These collective observations accentuate the intricate relationship between the fineness of POFA and its chemical composition, providing valuable insights for optimizing the performance of concrete in construction applications. The aim of this research is to evaluate the density, water absorption and compressive strength of cement paste incorporating various compositions of citric acid-treated palm oil fuel ash (POFA), assess the performance of citric acid-treated POFA in cement paste mixed with sand, and compare the resulting physical and mechanical characteristics with those of untreated POFA, thereby contributing valuable insights to enhance the utilization of POFA in sustainable concrete formulations. Unraveling the potential improvements in material properties through citric acid treatment presents an intriguing avenue for optimizing the sustainable and durable aspects of concrete structures.

## 2. Methodology

POFA undergoes few processes which are grinding, sieving, heat treatment, acid treatment, drying and mixing. POFA undergoes grinding process to make sure the size of POFA become small and fine. The ratio of POFA powder with the ball mills was 3:1. Next, sieving process by using 50  $\mu\text{m}$  micro sieve to optimize the particle size distribution of POFA and to enhance homogeneity in the composite. The process continued with the heat treatment of POFA. Using the Electronic Box Furnace Protherm PLF 110-130, POFA was heated at a rate of 2  $^\circ\text{C}/\text{min}$ , and the cooling rate was 5  $^\circ\text{C}/\text{min}$ . The heating treatment occurred at 800  $^\circ\text{C}$  with a soaking time of 1.5 hours. After that the POFA that went through heat treatment undergoes acid treatment by using citric acid. Then the TPOFA dried in the oven and mixed with cement using a Kakuhunter. Meanwhile as for the sample preparation it involves mixing, moulding, curing and testing.

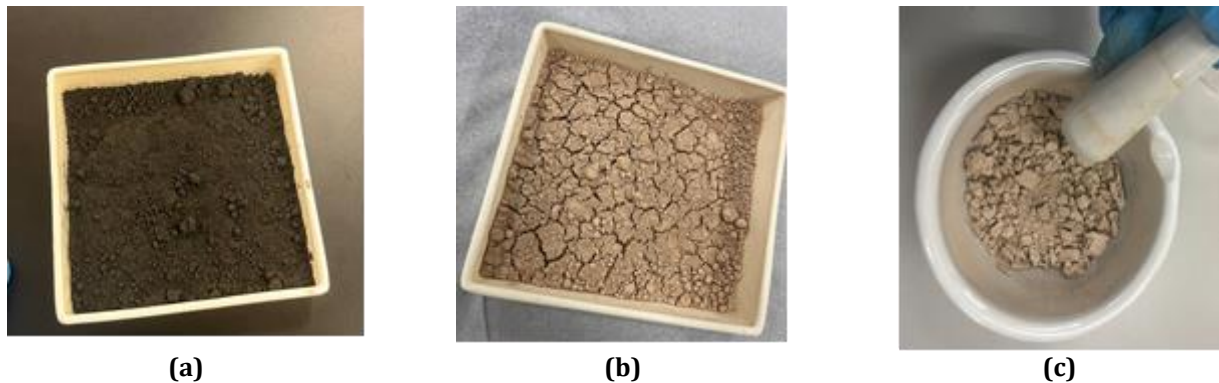
The POFA powder were divided into three different mixtures. Firstly, untreated POFA (UPOFA) mix with cement and water next is treated POFA (TPOFA) mixed with cement and water then treated POFA mixed with cement, sand and water ((TPOFA + sand)). As for UPOFA it does not went through heat treatment while the TPOFA went through heat treatment at 800  $^\circ\text{C}$  for 1.5 hours and also acid treatment using citric acid. After the UPOFA undergoes heat treatment and acid treatment it will become TPOFA and mixed in cement and water with different composition of POFA which are 10%, 20%, 30%, 40% and 50% by using Kakuhunter Planetary Centrifugal Mixer SK-350TII. After that, the mixture poured into the three-inch PVC pipe acting as a mould. Then the mixture will be cured at 7 days and 14 days. After 7 days and 14 days a few testings conducted which were density testing, water absorption testing and compressive strength. The Metler Toledo density kit XS64 were used to test density and water absorption. Universal Testing Machine (Testometric) used to test compressive strength. The ratio for UPOFA and TPOFA for POFA: cement: water is 2: 1 :1 and the ratio for TPOFA mixed with sand, POFA: cement: water: sand is 0.38: 1: 1: 0.75. Figure 1 shows (a) Heat treatment for POFA and (b) Acid treatment for POFA.

## 3. Results and Discussion

### 3.1 Heat and Acid Treatment

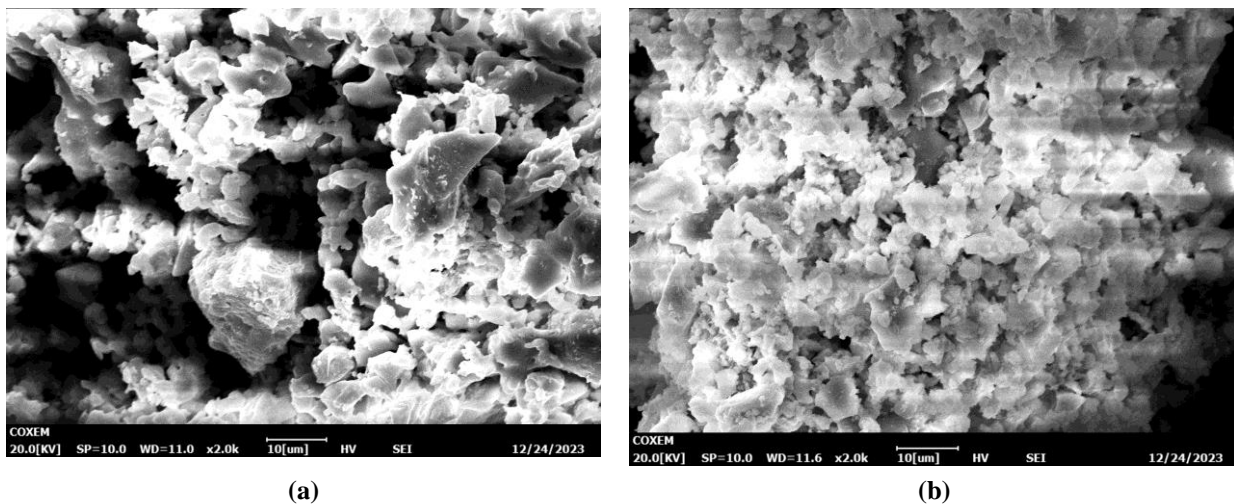
After subjecting the heat treatment and acid treatment to POFA, discernible alterations in its color were evident, albeit with a subtle nuance. Notably, following the heat treatment, there was an approximate reduction of 3% in total weight of POFA, a figure that increased to 30% after the subsequent acid treatment. These findings underscore the efficacy of the treatment process in successfully eliminating impurities, particularly metals intricately bound with silicates, owing to the inherently toxic and corrosive properties of citric acid. Furthermore, the ultra-fined POFA exhibited a notable decrease in the percentage of unburned carbon content, thereby augmenting its pozzolanic characteristics. This shift in composition, marked by an increased in silicate-based elements, directly contributed to an observable enhancement in the compressive strength of the sample. Despite these positive outcomes, the residual presence of some black ashes was noted, implying the persistence of a few remaining carbon residues. The observed color changes in POFA during heating can be attributed to the combustion of carbon containing compounds, leading to the formation of various oxides including those of carbon and other elements present in the material, thereby influencing the overall coloration of the ash residue. The color change observed during citric acid treatment is attributed to mineral dissolution, chemical reactions forming new compounds, surface modifications and the removal of impurities, collectively influencing the

material's color changes. This nuanced observation adds complexity to the characterization of the treated POFA, suggesting the need for further investigation into the residual carbon content and its potential implications for the material's overall properties. Fig. 1 shows the photos of the UPOFA, TPOFA after heat treatment, and TPOFA after acid treatment.



**Fig. 1** (a) UPOFA before heat treatment, (b) TPOFA after heat treatment and (c) TPOFA after acid treatment

The microstructure analysis of the sample was conducted by using Scanning Electron Microscopy (SEM). The research focused on samples heat at 800 °C with 100% POFA. Fig. 2 illustrates SEM microstructure of two samples of (a) Heat treatment of 100% POFA and (b) Acid treatment of 100% POFA at 800 °C.

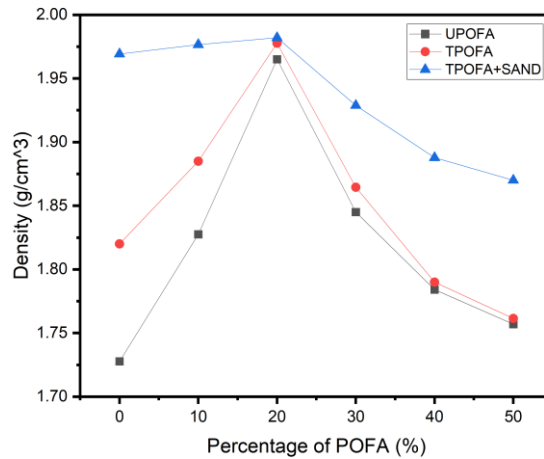


**Fig. 2** SEM microstructure of two samples: (a) Heat treatment of 100% POFA and (b) Acid treatment of 100% POFA at 800 °C.

### 3.2 Density and Water Absorption

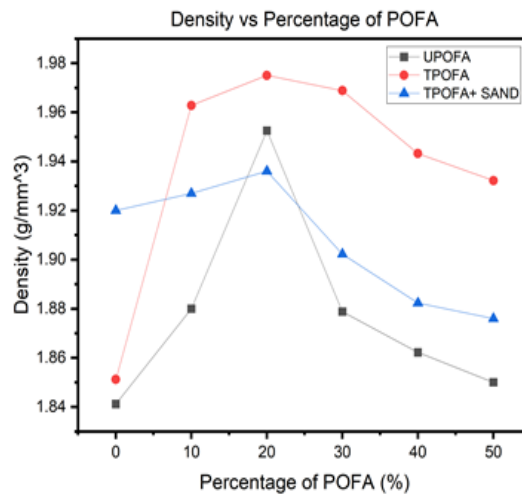
This study encompassed the measurement of three distinct physical properties which are density and water absorption. Fig. 3 shows the graph of relationship between density and the percentage of POFA for Untreated POFA (UPOFA), Treated POFA (TPOFA) and Treated POFA mixed with sand (TPOFA + sand). Three distinct lines shows the density behavior of UPOFA, TPOFA and TPOFA mixed with sand. As the graph reveals, the density of all three POFA types consistently increases with a rising POFA percentage. This trend stems from the inherent density difference between POFA and sand. POFA boasts a higher density than sand hence, its increasing presence in the mixture elevates the overall density. Moreover, TPOFA consistently exhibits a higher density that UPOFA across all POFA percentages. This phenomenon can be attributed to the heat treatment process, which compacts the POFA particles, leading to greater density throughout the range due to the presence of less dense sand particles diluting the overall density. As the graph indicated an increasing pattern in density as the percentage of POFA increases. However, the graph shown a decreasing pattern at 30% to 50% of POFA percentage. Despite the pozzolanic reaction inherent in the ashes, the samples may still exhibit lower density due to the presence of voids spaces. This also could be a result of POFA containing a higher concentration of unburnt carbon compared to amorphous silica, making it less reactive. The maximum density for 7 days is

recorded at 20% of POFA percentage which for UPOFA is 1.9650 g/cm<sup>3</sup>, TPOFA is 1.9777 g/cm<sup>3</sup> and TPOFA mixed with sand is 1.9820g/cm<sup>3</sup>.



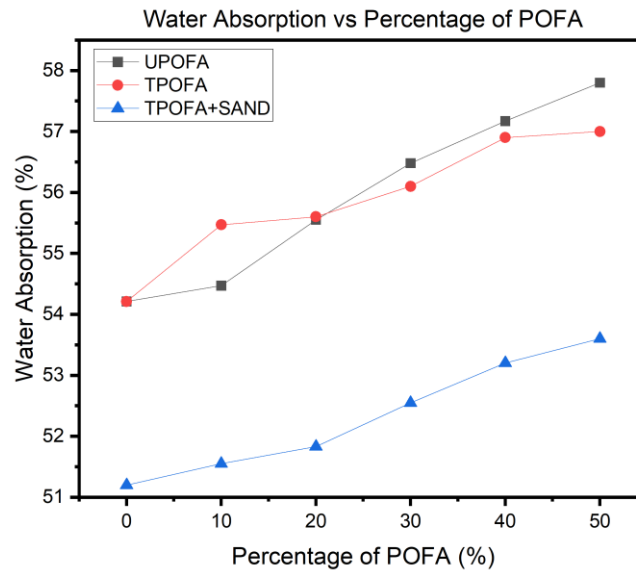
**Fig. 3** Density vs Percentage of POFA for untreated POFA (UPOFA), treated POFA (TPOFA) and treated POFA + sand (TPOFA+SAND) for 7 days

Fig. 4 shows the graph of density vs percentage of POFA for UPOFA, TPOFA and TPOFA + sand for 14 days. From the Fig. 4, as for the 14 days of curing time the density of TPOFA shows decreasing pattern. This may happen due to the density can be decreased due to the lower gravity of POFA than cement and the possibility that POFA will deceive discuss bubbles [7]. The result of this graph shows that the density was influenced by the curing time and the percentage of POFA used. These formed phases may fill the void spaces and blinds the materials in the stabilized cement leading to decrease in water absorption and increase in density. However, the use of the untreated POFA (UPOFA) for the study shows the denser of the samples because of the Ca (OH)<sub>2</sub> content of hydrated cement and reduces the voids between the hydration products [8]. The density of concrete tends to increase with increasing substitution level of POFA up to a certain level. In one study, the density of POFA concrete increased up to 15% POFA replacement and then decreased with further increase in POFA content [16]. Overall, the research suggests that the density of POFA concrete tends to increase up to a certain level due to pozzolanic reaction and the resulting denser microstructure.



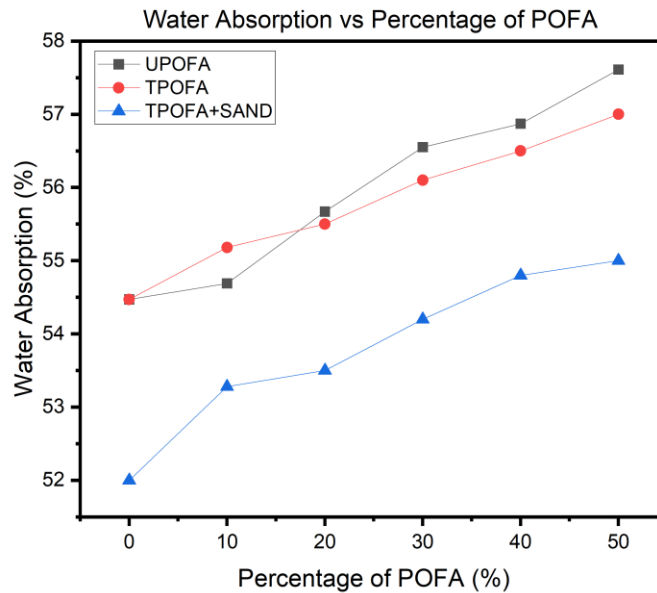
**Fig. 4** Density vs Percentage of POFA for untreated POFA (UPOFA), treated POFA (TPOFA) and treated POFA + sand (TPOFA+SAND) for 14 days

One of the physical properties of cement paste is the ability to absorb water. Fig. 5 shows water absorption against the different percentage of POFA. Water absorption is one of the methods to estimate pore volume in the sample. It is the easiest test method to evaluate the total amount of water absorbed in certain period. It is observed that the water absorption decreases with the different percentage of POFA at different curing times which are 7 days and 14 days. According to the Figure 6 the samples for TPOFA mixed with sand has the lowest water absorption compared to UPOFA and TPOFA.



**Fig. 5** Water absorption against different percentage of POFA for 7 days

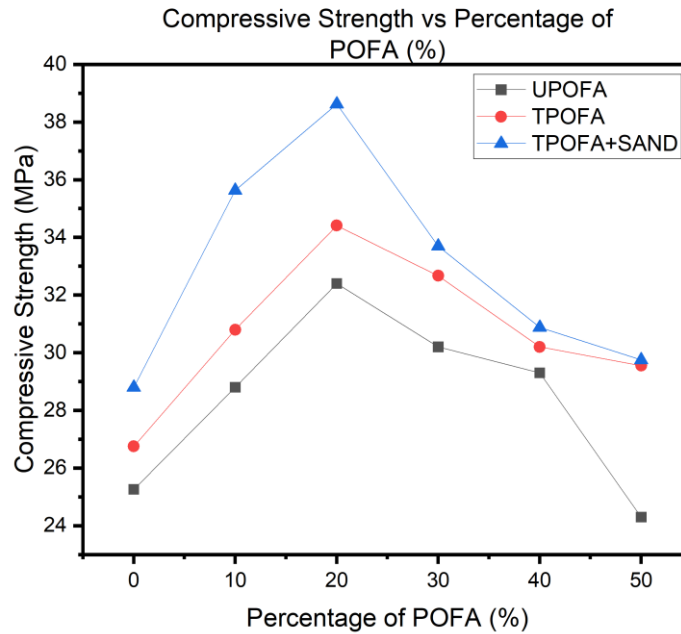
Fig. 5 and 6 show the samples containing 0% of POFA for UPOFA are 54.47% and 54.21% for 7 days and 14 days curing time respectively. This is because the curing time for 14 days causes the cement to shrink which leads to tensile stresses within the cement. As the results, surface cracking of the samples may occur at 14 days curing time than 7 days of curing time, especially if the stresses develop before the concrete attain adequate tensile strength. Continuous moist curing had been done for the entire 14 days curing period to kept it damp. If this is not possible, the cement surfaces should be protected from drying out. These findings demonstrate that the samples of water absorption were very high. The water absorption of high-quality cement is ordinarily less than 5% [9], [10]. The low water absorption was fulfilled generally owing to the cement was low penetrable porosity. This may well be attributed to POFA's increased water absorption because the POFA utilized in this study features a bigger surface area than cement. Besides, the POFA cement is more permeable and contains more unground POFA. In any case, the cement might not get sufficient curing period for hydration prepare which influenced the densification since of less generation of by- product and it increments the pores interior the concrete. The water absorption is caused by the capillary impact of pores [11],[12].



**Fig. 6** Water absorption against different percentage of POFA for 14 days

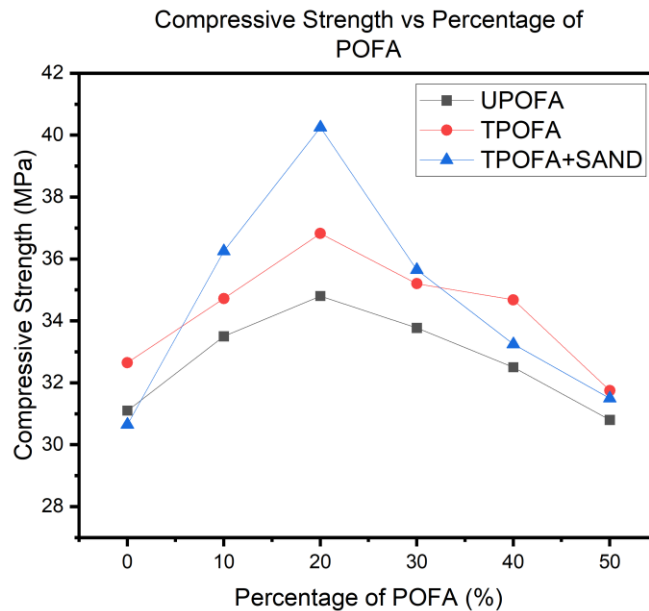
### 3.3 Compressive Strength

Mechanical properties of cement are closely related to its compressive strength, and it is utilized to classify and identify the material of the sample. Fig. 7 shows the graph of compressive strength vs different percentage of POFA (0%, 10%, 20%, 30%, 40% and 50%). The graph shows increasing pattern from 0% to 20% of POFA for 7 days. As for UPOFA the increasing pattern is from 25.26 MPa to 32.40 MPa while for TPOFA it increases from 26.75 MPa to 34.41 MPa and for TPOFA mixed with sand it increases from 28.80 MPa to 38.62 MPa. However, starting from 30% to 50% of POFA it shows decreasing pattern for UPOFA, TPOFA and TPOFA mixed with sand. The increase in compressive strength can be attributed to several factors. This improvement is linked to the pozzolanic material reactivity of POFA, which contributes to the formation of additional cementitious material, leading to denser microstructure and enhanced the compressive strength [14]. The influence of curing techniques, curing temperature, wet-mixing time, and the addition of typical additives on the compressive strength of POFA concrete has also been documented [15]. Normal compressive strength for concrete usually is 17 MPa to 39 MPa [15], so this shows that with adding the treated POFA into concrete it can improve the compressive strength of the concrete.



**Fig. 7** Compressive Strength vs Percentage of POFA for UPOFA, TPOFA and TPOFA + SAND for 7 days

The curing is continued to 14 days. Cement cured utilizing membrane-forming compound has the highest compressive strength after curing for 14 days [8]. Fig. 8 shows a rise from 31.10 MPa to 34.80 MPa for 0% to 20% of UPOFA. For 0% to 20% of TPOFA it increases from 32.65 MPa to 36.82 MPa and for 0% to 20% of TPOFA mixed with sand it rises from 30.65 MPa to 40.25 MPa. As it reached 30% of POFA it decreases as the percentage of POFA increases. This applied for UPOFA, TPOFA and TPOFA mixed with sand. The compressive strength of POFA concrete typically improves with longer curing periods. In general, a concrete mix that undergoes a more extended curing period tends to exhibit higher compressive strength values. In conclusion, a concrete that was cured for 14 days has a higher compressive strength than the concrete that were cured for 7 days. Studies have shown that the mechanical performance of POFA concrete improve up to 25% replacement levels, with the highest enhancements observed in compressive strength [13]. The compressive strength of cement paste containing POFA of particle size 2 micrometer and 10 micrometers to 30% replacement levels by total cement weight presented higher compressive strength [14].



**Fig. 8** Compressive Strength vs Percentage of POFA for UPOFA, TPOFA and TPOFA + SAND for 14 days

#### 4. Conclusion

Based on the experimental results and discussion the following conclusion can be drawn as the increment of POFA content and curing period affects the physical and mechanical properties of the samples. The 20% percentage of POFA is the best composition of POFA for UPOFA, TPOFA and TPOFA mixed with sand both for 7 days and 14 days. The density for 20% of POFA for UPOFA (1.9650 g/cm<sup>3</sup>), TPOFA (1.9777 g/cm<sup>3</sup>) and TPOFA mixed with sand (1.9820 g/cm<sup>3</sup>) for 7 days while for 14 days UPOFA (1.9525 g/cm<sup>3</sup>), TPOFA (1.9750 g/cm<sup>3</sup>) and TPOFA mixed with sand (1.93600 g/cm<sup>3</sup>). As for compressive strength the highest composition is 20% of percentage of POFA for UPOFA (32.40 MPa), TPOFA (34.41 MPa) and TPOFA mixed with sand (38.68 MPa) for 7 days of curing period while for 14 days of curing period of UPOFA (34.80MPa), TPOFA (36.82MPa) and TPOFA mixed with sand (40.25MPa). Therefore, the best sample to be used is TPOFA mixed with sand as it has the highest compressive strength and lower water absorption compared to UPOFA and TPOFA mixed with cement.

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#### Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

#### Author Contribution

The authors confirm contribution to the paper as follows: **study conception and design, data collection, methodology, analysis and interpretation of results:** Nur Syazwani Ilyana Shukri and Mohamad Zaky Noh. All authors reviewed the results and approved the final version of the manuscript.

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