

PAPER • OPEN ACCESS

## Characterization of palm oil fuel ash and eggshell powder as partial cement replacement in concrete

To cite this article: N H A Khalid *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **431** 032002

View the [article online](#) for updates and enhancements.

# Characterization of palm oil fuel ash and eggshell powder as partial cement replacement in concrete

N H A Khalid<sup>1,\*</sup>, N N A Rasid<sup>1</sup>, A R Mohd.Sam<sup>2</sup>, N H A S Lim<sup>1</sup>, M Ismail<sup>1</sup>,  
L Zardasti<sup>1</sup>, A Mohamed<sup>1</sup>, Z A Majid<sup>3</sup> and N F Ariffin<sup>4</sup>

<sup>1</sup>Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 Johor, Malaysia

<sup>2</sup>UTM Construction Research Centre (UTM CRC), Institute for Smart Infrastructure and Innovative Construction (ISIIC), Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 Johor, Malaysia

<sup>3</sup>Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor, Malaysia

<sup>4</sup>Faculty of Civil Engineering & Earth Resources, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia

\*Email: nur\_hafizah@utm.my

**Abstract.** The utilization of palm oil fuel ash (POFA) and eggshell powder (ESP) in concrete as a cement replacement is possible as green concrete materials. However, the POFA has original cellulose and physical modification is needed. This paper presents the characterization of POFA; unground POFA (UPOFA) and ground POFA(GPOFA) and ESP under microstructure examination includes x-ray fluorescence (XRF), scanning electron microscopy (SEM), and particle size analyzer (PSA). Then, the POFA-ESP as a cement replacement in concrete was investigated. Optimum mix proportion of POFA-ESP concrete was determined from compression test and GPOFA-ESP and UPOFA-ESP were through further investigation on pozzolanic reaction under x-ray diffraction (XRD) test at 14 days-concrete age. It was found that the combination of GPOFA-ESP as a cement replacement produced a concrete enhanced the compressive strength than normal concrete. ESP in this study seems like a catalyst which acting as mild accelerator or booster to improve the early age of strength development without disturb the later strength development of concrete. In addition, combination of GPOFA-ESP could increase the C-S-H gel at early age of concrete. It can be concluded that the combination of GPOFA-ESP had dual function; ESP and GPOFA took at early and later strength development, respectively.

## 1. Introduction

Reusing the abundant waste materials such as palm oil fuel ash (POFA) and chicken eggshell (ES) has become possible for supplementary of cement in concrete. POFA is an agricultural waste that is uncontrollably dumped in landfills in Malaysia. The usage POFA is very minimal and unmanageable, while its quantity increases and most of the POFA are disposed of as waste in landfills causing environmental problems. As the second largest global palm oil producer, Malaysia has the second highest wastage of POFA after Indonesia. While, ES is an abundant waste material with chemical composition nearly same as limestone. The use of chicken eggshell instead of lime in concrete can have benefits such as lowering the cement usage, preserving natural lime and utilizing waste material eggshell that is rich in calcium carbonate ( $\text{CaCO}_3$ ). Eggshell is aviculture byproduct waste that is abundantly generate in Malaysia. The Ministry of Agriculture and Agro-based Industry Malaysia [1] stated that



approximately about 14 million of eggshell wastes were produced and this statistic was stated in year 2016. To date, the lime-derived eggshell is widely utilized in various industries such as painting [2], cosmetic [3], health [4], agriculture [5], livestock [6], and medical [4]. This material is chosen because eggshell lime has unique properties and the utilization trend is towards materials sustainability and this become motivation to the researchers to utilize the materials in concrete as well.

Palm oil fuel ash (POFA) can be a cement replacement to enhance strength than normal concrete [7]. The fineness size of POFA gives a better effect as a binder and filler in a concrete. The silica content of POFA is higher than OPC [8]. However, previous authors stated that POFA has different characteristics depending on its source due to the different ways of production including the combustion temperature used [9]. The high amount of silica can increase the strength and durability of the concrete. Therefore, POFA has to be processed before being used and sieved to get homogeneous size of POFA. Additionally, the POFA attributes to later concrete strength development and it happen after 28 days. As known fact, combination between ordinary Portland cement with any pozzolanic materials have long duration of concrete curing time due to low thermal conductivity of concrete. Therefore, accelerator is considered in a concrete mix design to boost-up the early-age strength development of the concrete [10,11,12]. In contrast, eggshell powder (ESP) is non-pozzolan materials but rich content with calcium oxide (CaO). The presence of calcium carbonate ( $\text{CaCO}_3$ ) could be a good cement replacement since previous study has been proved that the ESP has special character as environment-friendly catalyst [13]. Previous study from Chen [14] reported by current study on the new trend on  $\text{CaO-SiO}_2$  activate the catalyst activity. This give strong hypothesis that, the combination between POFA and ESP is possible as partial cement replacement to activate the dual function in concrete which that attribute to the early strength and later strength of the concrete without change the properties of concrete. Additionally, in the most condition, concrete mix with POFA as cement replacement was added up to 40% to observe strength development and the strength gradually decreased if the replacement of POFA increased, however, in this case, the strength was reduced at 20% of POFA replacement [15].

The main objective of the research is to investigate the characteristic of POFA and ESP under microstructure test; x-ray fluorescence (XRF), scanning electron microscope (SEM) and particle size analyzer (PSA). Second objective is to determine the optimum mix proportion of concrete containing combination materials between POFA and ESP under compression test. Ground POFA (GPOFA) and unground POFA (UPOFA) were utilized with ESP to investigated further their concrete strength development at curing age 1, 14, 28 and 56 days. The last stage, the reactivity of POFA-ESP binder was investigated as early as 14 days of curing age under x-ray diffractive (XRD) test.

## 2. Experimental Program

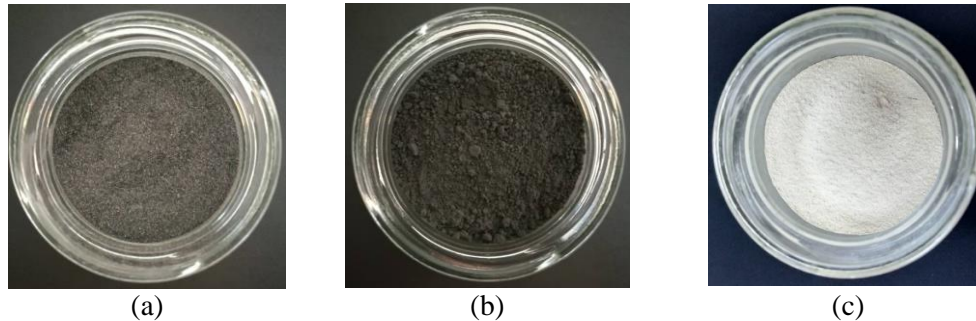
### 2.1. Materials

Two main materials were partially replaced as cementitious material; palm oil fuel ash (POFA) and eggshell powder (ESP). However, in order to investigate the pozzolan reactivity, the POFA was divided into two categories; Ground POFA (GPOFA) and Unground POFA (UPOFA). Both main materials (POFA and ESP) were collected at the southern part of Peninsular Malaysia and the physical features of the materials as shown in Figure 1. The grinding process was involved and the details of grinding medium as given in Table 1.

The POFA was oven-dried at  $100^\circ\text{C} \pm 5^\circ\text{C}$  before being further divided into two portions which are UPOFA and GPOFA. The UPOFA was obtained directly by passing the POFA through the sieve purposely to separate their natural substances and make homogenize the particles size. Meanwhile, the GPOFA was obtained after passing through  $45\ \mu\text{m}$  sieve by using laboratory grinding mill with rod bar to obtain finer particles. The grinding process took approximately about 4 hours every 500 grams to obtain the GPOFA.

The eggshell (ES) waste was through some normal treatment processes. First, the ES was trough the drying process and it very important to make sure the eggshells are clean from any egg yolk residues. The eggshells were then crushed using bare hands while in the water into small particles. The cleaned eggshells were then laid into trays. Eggshells was dried into the oven at a temperature of  $100^\circ\text{C} \pm 5^\circ\text{C}$  for 24 hours. The eggshells were taken out and left for normal ambient cooling process. The crushed

and dried eggshells are finally ground using grinder to obtain a fine powder of eggshells and named as eggshell powder (ESP).



**Figure 1.** Main cementitious replacement materials (a) UPOFA (b) GPOFA (c) ESP

**Table 1.** Grinding mill information

Grinding medium for GPOFA	
Dimension of grinding drum (inside)	: 711 mm (diameter) x 508 mm (length)
Weight and number of rod bar	: 1.13 kg/ bar and 7 numbers
Dimension of rod bar	: 20 mm (diameter) x 480 mm (length)
rotational speed	: 30 to 33 rpm
Total milling rotational	: 4000 rotational per session
Weight per cycle	: 5kg/session
Duration per cycle	: 4 hours
Grinding medium for ESP	
Type	: Swing type high speed universal mill
Voltage	: 220 V/50 Hz
Rotational speed	: 25000 rpm
Power	: 1500 W
Maximum weight per cycle	: 600 gram/cycle
Exact weight per cycle	: 500 gram/cycle
Duration per cycle	: 1 minute

## 2.2. Microstructure examination

**2.2.1. X-Ray Fluorescence (XRF).** XRF is fast and accurate analytical equipment to determine the elemental composition of materials. The POFA (UPOFA and GPOFA) and ESP were through the oven dried process about  $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 24 hours to eliminate the excessive moisture. Then, the sample was mixed with the wax based CH<sub>2</sub> with the ratio 4:1 in order to produce in pallet form and the pallet sample was pressed by using press machine at the pressure reached approximately  $15 \times 10^4$  N. The samples were stored in desiccator with silica gel until it will be tested under XRF equipment.

**2.2.2. Scanning Electron Microscope (SEM).** SEM represents a high-performance method used to investigate the morphology image of the materials. GPOFA, UPOFA, and ESP was sowed onto the thin double cellophane that attached on the miniature disk. All specimens were coated beforehand using the gold sputter coater machine. Significant morphology images were captured immediately after the selections' image has been made with 2500 magnifications.

**2.2.3. Particles Size Analyzer (PSA).** PSA is the test conducted purposely to investigate the particle size distribution of the materials. This is very important method to identify the consistency of particle size before and after grinding process and this significant for unground POFA (GPOFA) and ground POFA (GPOFA). The particle size distribution of all materials including ESP was compared to the ordinary

Portland cement (OPC) to obtain the significant comparison. All these materials were done using the PSA machine by wetting method with laser scattering technique. The sample was weighted about 1 mg by using high accuracy balance. The sample was diluted with 2 mg of distilled water. The measurement of water is by using micro tube which the water was taken by using pipette. The dilution sample was sonicated into ultrasonic bath for 10 minutes at 40°C. The dilution sample was place in cell about 2 to 5 microliters. Then the cell was inserting into the machine to run.

### 2.3. Mix proportion

The mix proportion of GPOFA-ESP and UPOFA-ESP were tabulated. Normal concrete was designated as control specimen. The combination of GPOFA-ESP and UPOFA-ESP replacement were limited to 0%, 5%, 10%, 15%, and 20% of total 455 kg/m<sup>3</sup> of OPC. The fine and coarse aggregates were fixed 932 kg/m<sup>3</sup> and 763 kg/m<sup>3</sup>, respectively with the water cement ratio 0.55. Quality of concrete was monitored through trial mix and the workability of fresh concrete was tested under targeted 60-180 mm slump. At this stage, about 11 design mixes were designed for concrete grade of 30 MPa at 28 days. Tables 2 and 3 state the replacement and the design notation of specimen for GPOFA-ESP and UPOFA-ESP, respectively.

**Table 2.** Notation and percent replacement of GPOFA-ESP

Concrete Type	Mix Design		Notation
	GPOFA %, (kg/m <sup>3</sup> )	ESP %, (kg/m <sup>3</sup> )	
GPOFA-ESP	0, (0)	20, (91)	G1
GPOFA-ESP	5, (22.75)	15, (68.25)	G2
GPOFA-ESP	10, (45.5)	10, (45.5)	G3
GPOFA-ESP	15, (68.25)	5, (22.75)	G4
GPOFA-ESP	20, (91)	0, (0)	G5
Normal Concrete	-	-	NC

**Table 3.** Notation and percent replacement of UPOFA-ESP

Concrete Type	Mix Design		Notation
	UPOFA %, (kg/m <sup>3</sup> )	ESP %, (kg/m <sup>3</sup> )	
UPOFA-ESP	0, (0)	20, (91)	U1
UPOFA-ESP	5, (22.75)	15, (68.25)	U2
UPOFA-ESP	10, (45.5)	10, (45.5)	U3
UPOFA-ESP	15, (68.25)	5, (22.75)	U4
UPOFA-ESP	20, (91)	0, (0)	U5
Normal Concrete	-	-	NC

### 2.4. Compression Test

A total of 132 concrete including normal concrete cube with dimensions of 100 mm x 100 mm x 100 mm were tested under compression test in order to determine the compressive strength for each of the mix proportion strictly according to the BS 1881-108 [16]. The fresh concretes were left in the mould for 24 hours before being demoulded and then subjected to water curing until the time to be tested. The test is conducted on concrete cube specimens at curing age of 1, 14, 28 and 56 days. The specimens were tested by using universal testing machine with machine capacity of 2000 kN and with a loading rate of 6 kN/s.

### 2.5. X-ray diffractive (XRD) Test

XRD is an analytical technique principally used for phase identification of a crystalline material and provide information at intensity peaks of specific 2-theta unit. The materials were finely ground and before it was inserted into the special chamber of XRD machine. In this study, the reactivity of between POFA and ESP in binder system can be examined under XRD, however, only desired mix proportions

were involved throughout the test. From similar mix proportion, the miniature hardened specimens were prepared for the test by eliminating the presence of fine and coarse aggregates. In this case, the reactivity of miniature hardened binder paste only was investigated; it covered for GPOFA-ESP and UPOFA-ESP paste, and compared to the normal cement paste as early as 14 days of curing age. The binder hydration was break down by immerse the specimens at curing age of 14 days into acetone liquid for 24 hours.

### 3. Results and Discussion

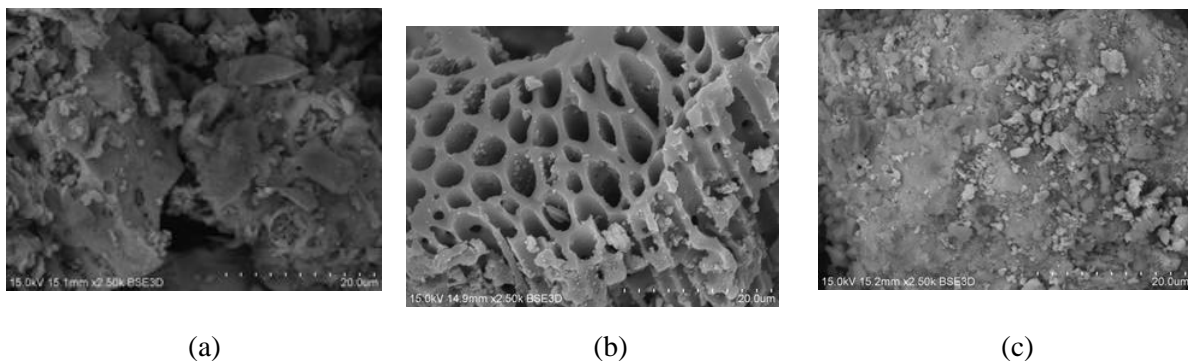
#### 3.1. Microstructure examination

**3.1.1. Chemical Composition of POFA and ESP.** The chemical composition of POFA and ESP are shown in Table 4. In this study, GPOFA and UPOFA were categorized as POFA categories due to both materials are from similar source. From the results, POFA was moderately rich in pozzolan of  $\text{SiO}_2$  with 53.30%. However, ESP has superior CaO content about 98.00%. The combination of these materials could be categorized as high calcium-palm oil fuel ash and this combination could provide high potentiality to produce moderate strength concrete.

**Table 4.** Chemical composition of POFA and ESP

Chemical Composition (%)	POFA	ESP
$\text{SiO}_2$	53.30	0.05
MgO	4.10	1.12
CaO	9.20	98.00
$\text{K}_2\text{O}$	6.10	0.11
$\text{Fe}_2\text{O}_3$	1.90	0.02
$\text{Al}_2\text{O}_3$	1.90	0.05
$\text{P}_2\text{O}_5$	2.40	0.10
$\text{SO}_3$	-	0.49

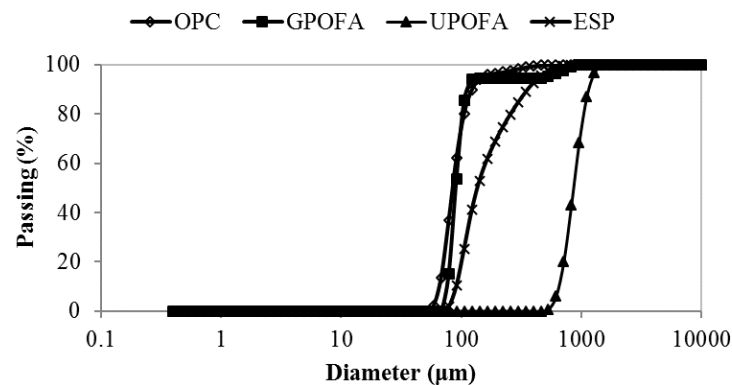
**3.1.2. Morphology Image.** The morphology images of GPOFA, UPOFA, and ESP under SEM were captured as shown in Figure 2. It was found that, there is no presence of pores were spotted on GPOFA (Figure 2a) and contradic to UPOFA, which it has a porous cellular structure (Figure 2b). This is the reason the POFA must through the grinding process before it can be used as cementitious material. Since the POFA is an agriculture-based waste material and it has naturally porous cellular structure, therefore the purpose of grinding process is to break the open cellulose structure. This demonstrated a higher potential for GPOFA being as cement replacement than UPOFA. For the morphology image of ESP, it have irregular shaped structure (Figure 2c).



**Figure 2.** Morphology image at 2500 magnifications of (a) GPOFA (b) UPOFA (c) ESP



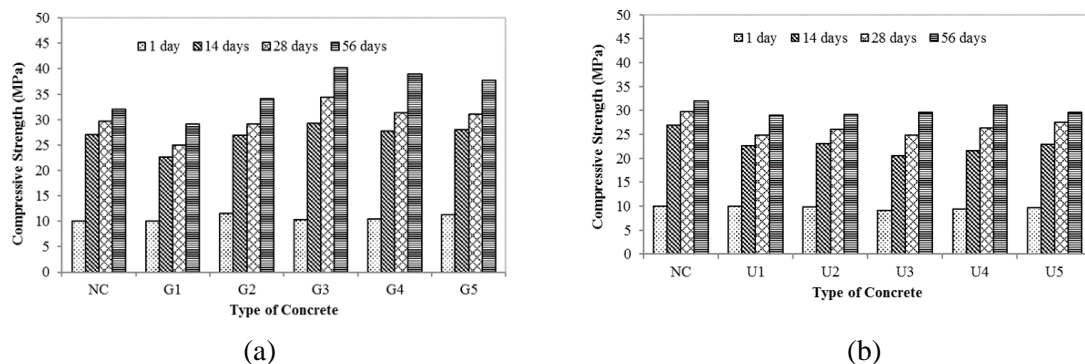
**3.1.3. Particle Size Distribution.** Figure 3 shows the particle distribution of cementitious materials involved this study. This test is important to investigate the fineness of OPC, GPOFA, UPOFA, and ESP. All materials were compared in terms of the fineness and particle size distribution curves as shown in Figure 3. From the figure, the GPOFA improved the fineness as compared to UPOFA after being through the grinding process. The fineness of GPOFA and ESP had comparable fineness to the OPC, except UPOFA. In this case, it can be concluded that, the GPOFA and ESP can be used as a part of cementitious materials due their comparable fineness.



**Figure 3.** Particles size distribution of OPC, GPOFA, UPOFA and ESP

### 3.2. Compressive strength

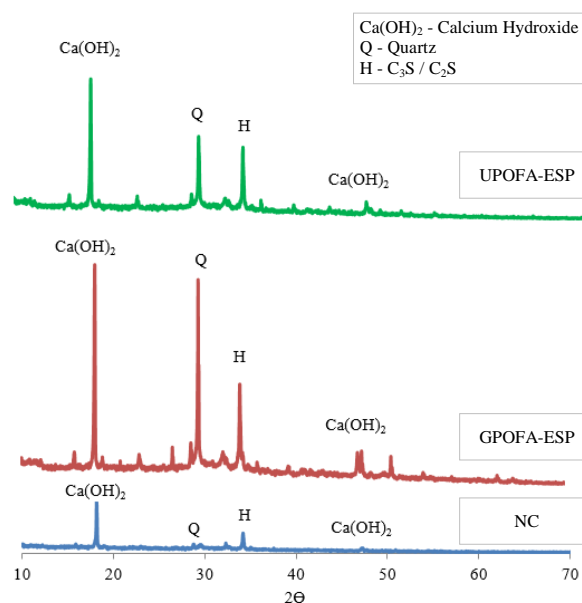
Figure 4 graphically represents the compressive strength of concrete with partial replacement of cement by GPOFA-ESP and UPOFA-ESP at 1, 14, 28, and 56 days. The overall pattern of the compressive strength showed the increment of strength development with the increment of curing age. However, GPOFA-ESP concrete had higher compressive strength as compared to UPOFA-ESP and NC at age 28 and 28 days. Maximum compressive strength for GPOFA-ESP concrete with notation of G3 (10 % GPOFA with 10 % ESP) was reached approximately about 40 MPa. While, compressive strength for UPOFA-ESP concrete with notation of U4 (15% UPOFA with 5% ESP). For UPOFA-ESP concrete category, there was insignificant strength development. The porous cellular structure (see Figure 2b) of UPOFA is expected to have poor workability of concrete since it would mean a higher tendency to absorb more water during production of concrete. This fact was supported by Khalid [17]; the structure significantly affected to the workability as well. Additionally, the coarser fine particle of UPOFA also bring no reactivity in concrete and act as filler in concrete (see Figure 3). If the G3 was compared to NC at curing age of 14 days, the compressive strength significantly increased. The situation gives insight that the combination of GPOFA-ESP gives ‘energy’ to increase the concrete strength. As known, the effect of solely GPOFA bring to the later strength in concrete and commonly the strength development obviously after 28 days. In this case, the ESP took part to give mild acceleration to the concrete strength and this only happened with the combination with GPOFA as partially as cementitious materials; activate the dual function-ESP and GPOFA took part early and later strength development, respectively.



**Figure 4.** Compressive strength of concrete at different curing age (a) GPOFA-ESP (b) UPOFA-ESP

### 3.3. X-ray diffraction (XRD) Analysis

Figure 5 exhibits the XRD patterns for the normal cement paste, cement paste containing GPOFA-ESP, and UPOFA-ESP at 14 days of curing (obtain from optimum concrete's mix proportion). From the figure, both GPOFA-ESP and UPOFA-ESP had overall higher peaks as compared to NC. However, GPOFA-ESP had the highest intensity peaks as compared to UPOFA-ESP and NC. When the cement is mixed with water, C-S-H gel and  $\text{Ca(OH)}_2$  is produced. Reactions with pozzolanic materials with hydration product will produce more C-S-H gel is produced. In this case, when GPOFA and ESP was utilized, more C-S-H gel was produced. This evidence was proved by referring to the figure, the element of Q ( $\text{SiO}_2$ ) at 29  $\theta$  scale increased the intensity peaks as compared to UPOFA-ESP and NC. The similar phenomenon was happened at 18  $\theta$  and 48  $\theta$  scale, and at range 31 to 33 for  $\text{Ca(OH)}_2$  and  $\text{C}_3\text{S}/\text{C}_2\text{S}$ . Additionally, the utilization of GPOFA-ESP activated the hydration reaction as well. This reaction becomes more effective with the higher amount of  $\text{Ca(OH)}_2$  which come from the hydration process of cement. In contrast, the utilization of UPOFA-ESP had lower intensity peaks at similar  $\theta$  scale locations and this was happened due to the UPOFA-ESP seems act as 'passive' particles or filler in concrete. This situation indicates the fineness attribute to hydration; the more fineness of pozzolan materials more reactivity and effective hydration to the concrete. It can be concluded that GPOFA with combination ESP leads to increase the C-S-H gel and hydration reaction.



**Figure 5.** XRD analysis of GPOFA, UPOFA and NC concrete at 14 days curing age



#### 4. Conclusion

The conclusions drawn from this study to fulfill the research objectives are as follows:

- i. Palm oil fuel ash (POFA) was moderately rich in pozzolan of silica dioxide ( $\text{SiO}_2$ ) content whereas ESP has superior calcium oxide (CaO) content. Eggshell powder (ESP) have irregular shaped structure while unground palm oil fuel ash (UPOFA) has a porous cellular structure. No pores were spotted on ground palm oil fuel ash (GPOFA) on morphology image. GPOFA and ESP has high potential to be replaced as cementitious as compared to UPOFA due to the original features.
- ii. The optimum mix proportion was selected based on the strength properties and workability of concrete. Cement replacement of 10% GPOFA and 10% ESP achieved optimum desired compressive strength. There was insignificant strength development on UPOFA-ESP cement replacement. Concrete with GPOFA-ESP gives higher compressive strength than concrete with UPOFA-ESP and interestingly, ESP act as mild accelerator or catalyst if it combined with GPOFA in concrete. Both combination took part early and later strength development.
- iii. The presence of higher silica content in GPOFA influences the pozzolanic reaction to produce extra C-S-H gels. While, the utilization of UPOFA and ESP act as a filler in concrete. The fineness of pozzolan materials attributes to the strength of concrete if the pozzolan materials combine with ESP. In overall, combination of GPOFA-ESP helps in increasing the C-S-H gel and hydration reaction.

#### References

- [1] Ministry of Agriculture and Agro-based Industry Malaysia 2016 *Output of Livestock Product*
- [2] Yuanyuan L 2016 Research on Form of Natural Beauty and Artistic Beauty in Modern Lacquer Painting *Journal of Residuals Science & Technology* **13**(8) 1–7
- [3] Mohammadi R, Mohammadifar M A, Mortazavian A M, Rouhi M, Ghasemi J B and Delshadian Z 2016 Extraction Optimization of Pepsin-Soluble Collagen from Eggshell Membrane by response Surface Methodology (RSM) *Food Chemistry* **190**186–193
- [4] Hosseini B, Mirhadi S M, Mehrazin M, Yazdani M and Motamedi M R K 2017 Synthesis of Nanocrystalline Hydroxyapatite using Eggshell and Trimethyl Phosphate *Trauma Monthly* **22**(5) 1-6
- [5] Bro E, Millot F, Decors A and Devillers J 2015 Quantification of Potential Exposure of Gray Partridge (*Perdix perdix*) to Pesticide Active Substances in Farmlands *Science of the Total Environment* **521–522** 315–325
- [6] Wiaćkiewicz S, Arczewska-Włosek A, Krawczyk J, Puchała M and Józefiak D 2015 Dietary Factors Improving Eggshell Quality: An Updated Review with Special Emphasis on Microelements and Feed Additives *World's Poultry Science Journal* **71**(1) 83–93
- [10] Yerramala A 2014 Properties of Concrete with Eggshell Powder as Cement Replacement *Indian Concrete Journal* **88**(10) 94 -102
- [11] Liew K M, Sojobi A O and Zhang L W 2017 Green Concrete: Prospects and Challenges *Construction and Building Materials* **156** 1063–1095
- [12] Cree D and Rutter A 2015 Sustainable bio-Inspired limestone eggshell powder for potential industrialized applications *ACS Sustainable Chemical Engineering* **3**(5) 941–949
- [13] Amanda L, Adriana L and Mario D Eggshell waste as catalyst: A review *Journal of Environmental Management* **197** (2017) 351-359
- [14] Chen G, Shan R, Shi J and Yan B 2015 A biomimetic silicification approach to synthesize CaO- $\text{SiO}_2$  catalyst for the transesterification of palm oil into biodiesel *Fuel* **153** 48-55
- [15] Sooraj V M 2013 Effect of Palm Oil Fuel Ash (POFA) on Strength Properties of Concrete *International Journal of Scientific and Research Publications* **3**(6) 2250-3153
- [16] BS 1881-108 1983 *Testing concrete. Method for making test cubes from fresh concrete*
- [17] Khalid N H A, Hussin M W, Mirza J, Ariffin N F, Ismail M A, Lee H, Mohamed A and Jaya R P 2016 Palm Oil Fuel Ash as Potential Green Micro-Filler in Polymer Concrete *Construction and*

*Building Materials* **102** 950–960

### **Acknowledgments**

This study was developed thanks to financial support from the Ministry of High Education (MOHE) through project Q.J130000.2722.02K54 and R.J130000.7822.4F722.