Available online at www.sciencedirect.com

ScienceDirect

Procedia Manufacturing 2 (2015) 512 – 518

Procedia MANUFACTURING

2nd International Materials, Industrial, and Manufacturing Engineering Conference, MIMEC2015, 4-6 February 2015, Bali Indonesia

Morphological characteristics of hardened cement pastes incorporating nano-palm oil fuel ash

Mohd Azrul Abdul Rajak[a, b, *], Zaiton Abdul Majid[a,*] and Mohammad Ismail[c]

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia.*
[b]*Preparatory Centre of Science and Technology, Universiti Malaysia Sabah, Jalan UMS, 88400, Kota Kinabalu, Sabah, Malaysia.*
[c]*UTM Construction Research Centre, Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia.*

Abstract

Recently, nano-sized additives and supplementary cementing materials (SCM) have shown to improve the mechanical and durability of mortars and concretes. This study investigates the incorporation of nano-POFA (nPOFA) into cement paste so as to observe its effect towards the microstructure development of cement. Additionally, the effect of micro-sized POFA (mPOFA) was also carried out for comparison. The mPOFA were subjected to milling for the generation of nPOFA. The prepared nPOFA exhibited a BET specific surface area of 145.35 m^2/g with an average particle size ranging between 20 nm to 90 nm. Cement pastes were prepared with 10% - 50% replacement of nPOFA and 10% - 30% replacement of mPOFA. The morphological analysis of hardened cement paste (hcp) containing nPOFA (nPOFA-hcp), mPOFA (mPOFA-hcp) at the curing ages of 7, 28 and 90 days were conducted and compared with Ordinary Portland cement paste. At 7 days curing, the nPOFA particles acted as fillers and nucleation sites to accelerate cement hydration. The nPOFA particles reduced the appearance of lime crystals in the nPOFA-hcp at later curing ages due to the occurrence of pozzolanic reactions which formed secondary calcium-silicate-hydrates gel, resulting in a compact microstructure. The study concluded that the nPOFA particles created a dense and closely-packed microstructure of the hardened cement pastes due to the filling effect and pozzolanic reactions in the pastes.

Selection and Peer-review under responsibility of the Scientific Committee of MIMEC2015

Keywords: Nano-palm oil fuel ash; supplementary cementing material; cement hydration; pozzolanic reaction

* Corresponding authors. Tel.: +6075534129; fax: +6075566162.
*E-mail address:*zaiton@kimia.fs.utm.my

Selection and Peer-review under responsibility of the Scientific Committee of MIMEC2015
doi:10.1016/j.promfg.2015.07.088

1. Introduction

Nano-particles are known as particles having sizes ranging from 1 to 100 nm [1]. The application of nanotechnology has attracted global attention in multidisciplinary scientific research area due to their promising revolutionary changes in the physical and chemical properties of various downstream products. Research on the implementation of nano-materials as additives and supplementary cementing materials (SCM) in cement matrix has grown rapidly in recent years. A high specific surface area of nanoparticles has the potential to fill the pore system of cement pastes. These particles are also able to act as nucleation sites, which intensify the kinetics of cement hydration [1-4]. At later curing age, calcium hydroxide (CH) crystals resulting from cement hydration reaction, which are normally embedded in the nano-pozzolan initiated the production of secondary calcium-silicate-hydrate (C-S-H) gels via pozzolanic reaction resulting in the densification of the microstructure of hardened cement paste (hcp)[1]. Instead of acting as fillers, the deposited nano-pozzolan in the pores system reacted rapidly with free lime to produce additional C-S-H gels at later ages [3, 4]. Thus, the incorporation of nano-additives and nano-cement replacements such as silica fume, nano-SiO_2, nano-clay, carbon nanotubes and nano-fly ash in cement matrix has significantly refined the pastes microstructure. Furthermore, it has directly improved strength to the cement pastes and enhanced the durability of mortar and concrete [5-9].

In the production of crude palm oil, significant amounts of palm oil biomass are generated, which are utilized at the palm oil mills as the main energy resources. In the generation of energy, the biomass are burned at high temperature (800-1000ºC) and results in the production of yet another waste, palm oil fuel ash (POFA) . The ability of POFA to act as filler and production of secondary C-S-H gels via pozzolanic reactions has contributed in the enhancement of mechanical properties and durability of mortars and concrete [10-13]. Previous studies have shown that the fine particles of POFA could amplify the pozzolanic behaviors in cement paste to improve the fresh properties of cement paste, reduction in the amount of calcium hydroxide and enhancement of mechanical properties and durability of concrete [14,15].

Currently, no study has been reported on the utilization of the nano-particles of POFA as pozzolan. Hence, a comprehension in employing nPOFA as SCM would be beneficial towards understanding the effects of nano-sized particles POFA in cement hydration particularly in the microstructural development of hardened cement paste. The present study examined the morphological characteristics of cement pastes in the presence of nano-palm oil fuel ash (nPOFA) with the purpose of exploring the significant of incorporating nPOFA in cement-based system.

2. Experimental

2.1. Material

Palm oil fuel ash (POFA) from palm oil mill at Bukit Benut, Malaysia was used as a source of SCM in this study. Large and foreign particles of the unburned biomass were isolated from the POFA particles by sieving the ash through a 150 µm sieve and further oven-dried for 24 hours at a temperature of 110 ± 5ºC. The POFA was placed in the Los Angeles abrasion machine and ground to obtain micro-sized POFA (mPOFA) with specific surface area of 16.63 m^2/g. The production of nano-POFA (nPOFA) with a specific surface area of 145.35 m^2/g was achieved by grinding the mPOFA with a high energy ball milling machine for 30 hours [16]. The prepared nPOFA was immediately oven-dried at a temperature of 110 ± 5ºC to reduce agglomerations between nPOFA particles. The chemical composition of Ordinary Portland cement (OPC) Type I and mPOFA were analyzed using XRF and the results are shown in Table 1. Particle size of nPOFA was measured using Transmission electron microscopy (TEM). The nPOFA was subjected to acetone before dispersing using ultrasonicator for 10 minutes. A drop of colloidal nPOFA was placed in the carbon-coated copper grid and was further dried at 25 ºC before analysis.

Table 1. Chemical composition of Ordinary Portland Cement (OPC) and POFA.

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	LOI
OPC	21.45	3.62	60.98	1.22	4.89	2.30	-
POFA	54.80	7.40	14.00	4.14	4.47	0.71	9.3

2.2. Mixing and curing of cement paste.

The replacement of mPOFA and nPOFA in the cement paste were carried out in the range of 10 to 30% and 10 to 50% respectively. The nPOFA was mixed with cement using ball milling for 30 minutes to achieve an optimal dispersion of nano-particles in the blended cement. All of the pastes were prepared with a constant cement-to-water ratio of 0.35 by weight. After 24 hours, the cement pastes were removed from the moulds and further cured in saturated lime solution at a temperature of 23 ± 2 ºC

2.3. Morphological analysis

The morphology of hardened cement pastes specimens at 7, 28 and 90 days curing age were analysed using Scanning Electron Microscopy (Phenom ProX). The hydration of the pastes was arrested by immersing the hardened cement paste in acetone for 3 days to remove the water content in the specimens. This was followed with oven drying at a temperature of 50 ± 5 ºC for 24 hours to allow for the evaporation of the remaining acetone.

3. Results and discussions

3.1. Particls size of nano-palm oil fuel ash (nPOFA)

Fig. 1 shows the dispersion of nPOFA particles in the matrix via TEM analysis. The average particle size of nPOFA was found to be in the range of 20 to 90 nm.

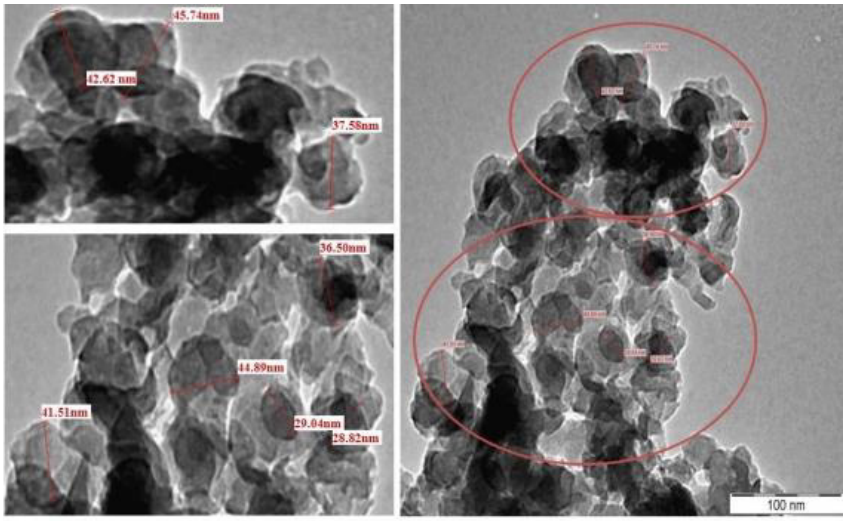

Fig 1. Particles size of nPOFA using TEM analysis

3.2. Morphological characteristics of cement pastes

The morphology of hardened cement pastes (hcp) at 7 days curing age are shown in Fig. 2. At this stage, the hydration products consisting of flaky and fibrous calcium silicate hydrate (C-S-H) gels and hexagonal calcium hydroxide (CH) crystals were observed surrounding anhydrous cement grains and coating the POFA particles. Needle-like ettringite crystals were observed to occupy the unfilled areas. However, the formation of ettringite was observable in the nPOFA hardened cement paste (nPOFA-hcp) in a lesser amount compared to the other pastes since

the appearance of the nPOFA particles hindered the growth of ettringites in the nPOFA-hcp. This observation has also been reported by Morsy *et al*.[17].

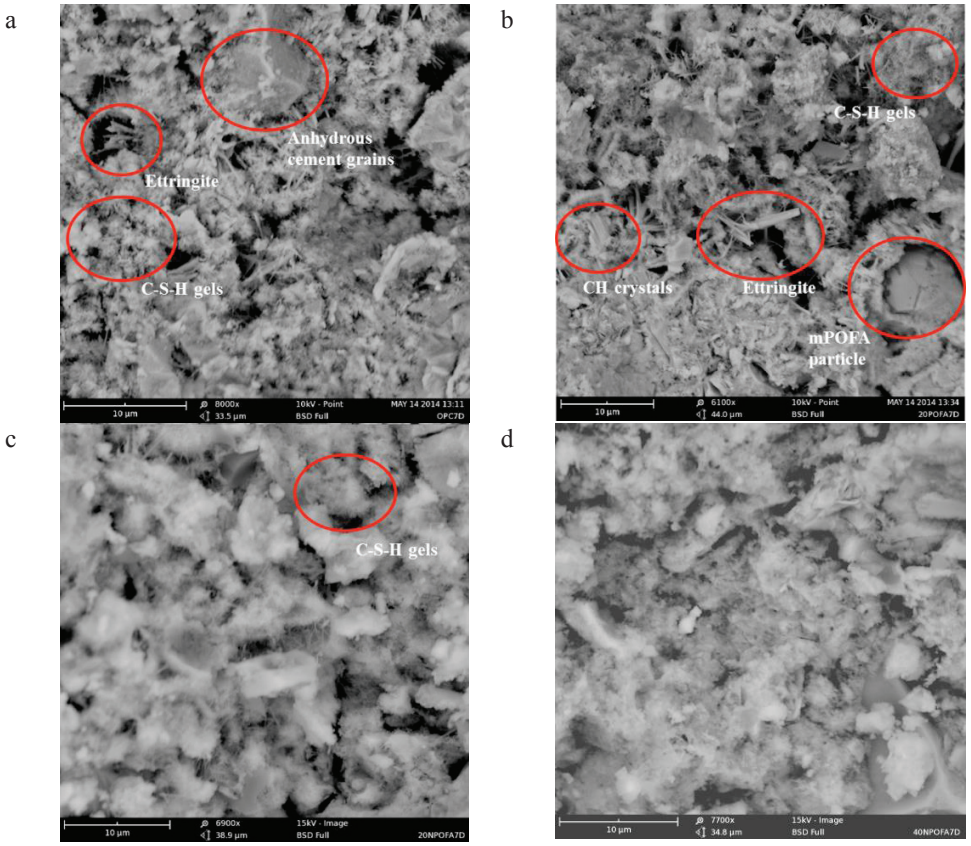

Fig 2. Morphology of (a) OPC-hcp (b) 20POFA-hcp (c) 20NPOFA-hcp (d) 40NPOFA-hcp of cement pastes at 7 days of curing age.

The presence of mPOFA and nPOFA particles as fillers in Fig. 2b, Fig. 2c and Fig. 2d enhanced the densification of hcp and improved the microstructure of hcp at the early age. Evidently, the nPOFA-hcp in Fig. 2c and Fig. 2d showed a densified microstructure compared to the hcp of Ordinary Portland cement and mPOFA. The nPOFA particles incorporated cement disseminated evenly and filled the pore system in the pastes which then reduced the average diameter size of pores and voids. Additionally, the mPOFA and nPOFA particles acted as nucleation sites and accelerated the precipitation of hydration products especially the C-S-H gels in the cementitious matrix. The nPOFA particles have significantly stimulated the precipitation of hydration products due to the high specific surface area of the particles [1]. The nPOFA particles promoted higher absorption rates of calcium (Ca^{2+}) ions and reduces the saturation of Ca^{2+} in the pore systems which expedites the dissolution rate of tricalcium silicate (C_3S) grains to generate more hydration products [1]. Consequently, it increased the development of fibrous C-S-H gels and created a highly compact and dense cementitious matrix.

At this curing age, the strength of hardened cement paste mainly depended on the formation of C-S-H gels via the hydration of tricalcium silicate (C_3S) since the pozzolanic behaviors of POFA particles during the early age were not active. The mPOFA and nPOFA particles performed as fillers in the early age to compress the microstructure of pastes [11, 15].

The micrographs of hcp at 28 days of curing age are shown in Fig. 3. The hydration products, the secondary C-S-H gels and anhydrous cement grains existed in a compact layer of pastes at this stage. The needle-like ettringite are less noticeable in the specimen since it has dissolved to form other cement hydration products which can increase the densification of the paste. The growth of C-S-H gels and crystalline hydrates occupied the pore system and reduced porosity and voids. During this stage, the nPOFA particles had started to generate secondary C-S-H gels from the reaction with CH crystals [15]. As a result, the fibrous secondary C-S-H gels were observed in the surface area of CH crystals. The high specific surface area of nPOFA particles has intensified the occurrence of pozzolanic reactions to generate supplementary C-S-H gels which helped in the formation of highly dense structure of hardened cement paste [1].

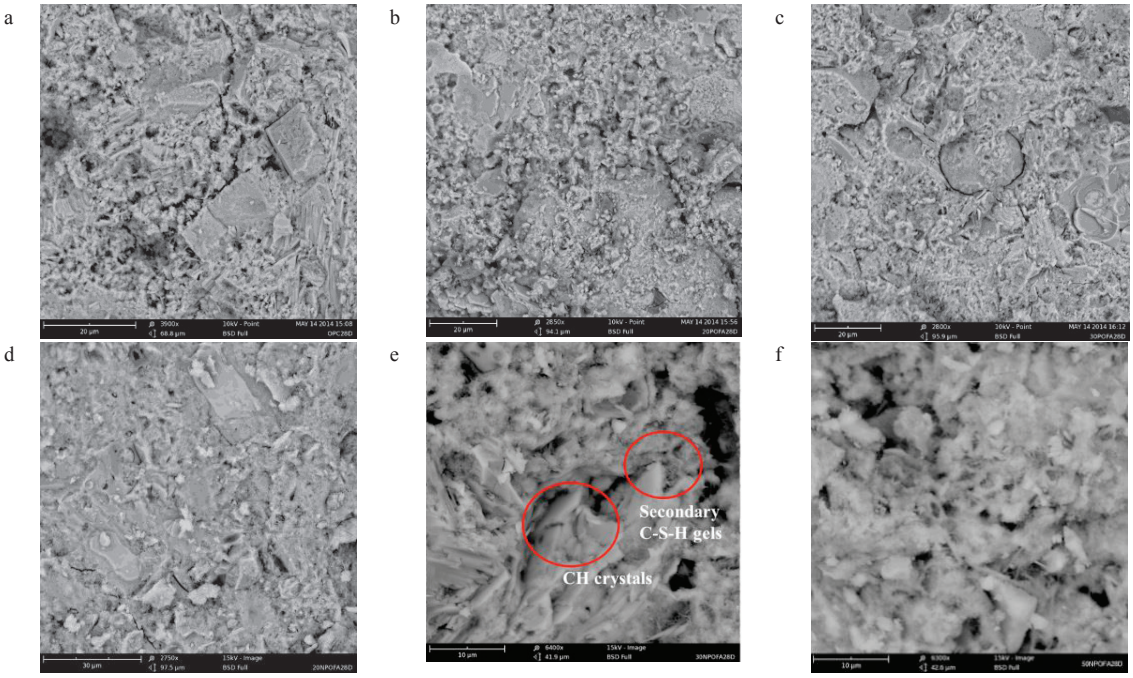

Fig. 3. Morphology of (a)OPC-hcp (b)20POFA-hcp (c)30POFA-hcp (d)20nPOFA-hcp (e)30nPOFA-hcp (f)50nPOFA-hcp of cement pastes at 28 days of curing age.

The morphology of the mPOFA-hcp specimens in Fig. 3b and Fig. 3c depicted inert mPOFA particles which acted as fillers and remained in the pore system. Cracks are observed in the mPOFA particles with high silica content, which will eventually dissolve and react with the crystalline hydrates which surround the mPOFA particles to form additional C-S-H gels [15].

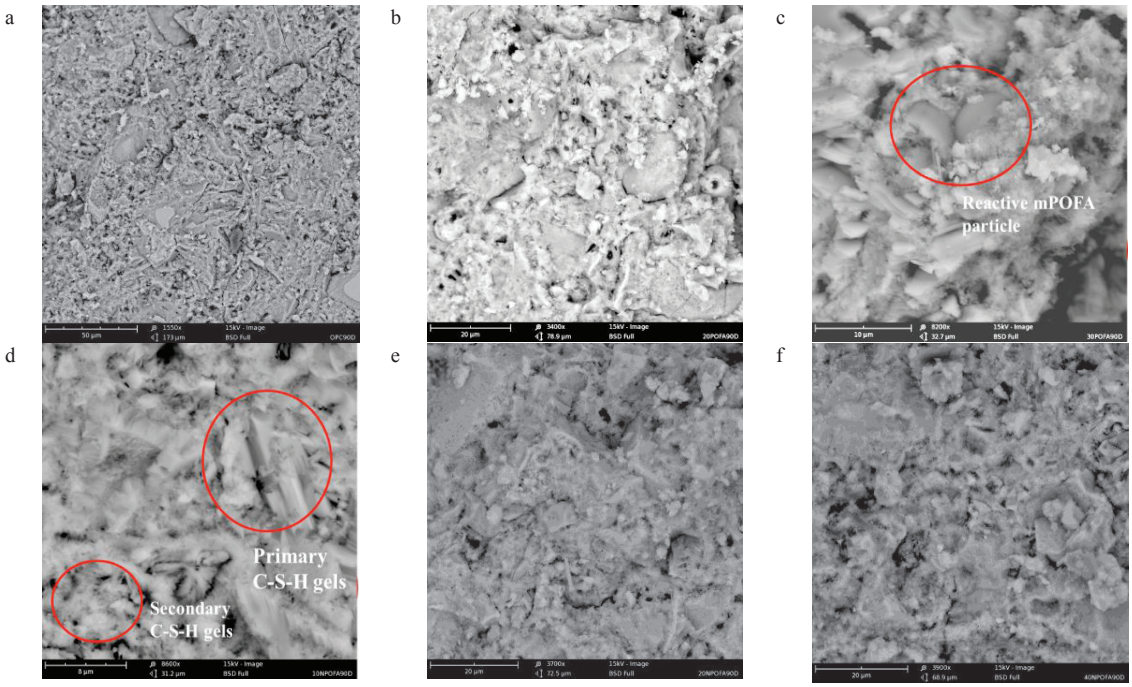

Fig. 4. Morphology of (a)OPC-hpc (b)20mPOFA-hpc (c)30mPOFA-hpc (d)10nPOFA-hpc (e)20nPOFA-hpc (f)40nPOFA-hpc of cement pastes at 90 days of curing age.

Fig. 4 highlighted the micrographs of nPOFA-hcp and mPOFA-hcp at 90 days curing age. At this stage, the hardened cement microstructures primarily composed of mature C-S-H gels that accommodated the rigid and closely-packed pastes. The nPOFA-hcp in Fig. 4d, Fig. 4e and Fig. 4f indicated highly dense and compact microstructures compared to the OPC-hcp and mPOFA-hcp in Fig. 4a, Fig. 4b and Fig. 4c due to the early formation of dense cementitious matrix following the growth of primary and secondary C-S-H gels. However, the appearance of fibrous C-S-H gels were still observable especially at the surface of CH crystals due to the continuous pozzolanic reaction of nPOFA particles towards crystalline hydrates to produce secondary C-S-H gels. The mPOFA particles in Fig. 4b and Fig. 4c had cracked continuously, eroded and dissolved in the cement matrix to react with CH crystals. This explains the presence of fibrous C-S-H gels on the surface of mPOFA particles. In comparison to the OPC paste in Fig. 4a, the CH crystals remained unreacted in the hcp, which can be susceptible to carbonation reaction.

4. Conclusions.

The nPOFA particles exhibited convincing pozzolanic behaviors and filler actions compared to mPOFA particles due to their high specific surface area. At the early age of the hcp, nPOFA particles triggered the hydration of cement and acted as fillers to refine the microstructure of pastes. The pozzolanic behaviors of nPOFA particles had led to the production of secondary C-S-H gels via pozzolanic reactions with free lime. As a result, the presence of CH crystals was much less during the later ages in the nPOFA-hcp and this created a desirable dense and compact microstructure of the paste which eventually led to the enhancement of mechanical and durability properties of hardened cement.

Acknowledgements

The authors acknowledge the staff of Department of Chemistry, Faculty of Science and Department of Structure and Materials, Faculty of Civil Engineering, Universiti Teknologi Malaysia. The authors also thank Universiti Malaysia Sabah and Ministry of High Education Malaysia for the financial support. The authors greatly appreciate the financial support received form the Ministry of Science, Technology and Innovation (MOSTI) under the Nanotechnology Research Grant Scheme (NanoFund) (Vote no.: 4H008).

References

[1] L.P Singh, S.R. Karade, S.K. Bhattacharyya, M.M. Yousuf, S. Ahalawat. Beneficial role of nanosilica in cement based materials – A review. Constr. Build. Mater. 2014; 47: 1069-1077.
[2] M. Stefanidou and I. Papayianni. Influence of nano-SiO2 on the Portland cement pastes. Compos. Part B: Eng. 2012; 43: 2706-2710.
[3] L. Senff, J. Labrincha, V.M. Ferreira, D. Hotza, W.L. Repette. Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. Constr. Build. Mater. 2009; 3: 2487-2491.
[4] a.E. Al-Salami, M.S. Morsy, S. Taha, H. Shoukry. Physico-mechanical characteristics of blended white cement pastes containing thermally activated ultrafine nano clays. Constr. Build. Mater. 2013; 47: 138-145.
[5] K. Al-jabri and H. Shoukry. Use of nano-structured waste materials for improving mechanical, physical and structural properties of cement mortar. Constr. Build. Mater. 2014; 73: 636-644.
[6] S. Abd. El Aleem, M. Abd, Heikal, W.M. Morsi. Hydration characteristic, thermal expansion and microstructure of cement containing nano-silica. Constr. Build. Mater. 2014; 59: 151-160.
[7] Arulraj, G. P, M, Jemimah Carmichael, M.,J. Effect of nano- fly ash on strength of concrete. Inter. J. Civil Struc. Eng. 2012; 2: 475.-482
[8] B. Suhendro. Toward green concrete for better sustainable environment. Procedia Eng. 2014; 95: 305-320.
[9] G. Yakovlev, G. Pervushin, I. Maeva, J. Keriene, I. Pudov, A. Shaybadullina, A. Buryanov, A. Korzhenko, S. Senkov. Modification of construction materials with multi-walled carbon nanotubes. Procedia Eng. 2013; 57: 407-413.
[10] Md. Safiuddin, A. Salam, A., M.Z. Md. Jumaat. Utilization of palm oil fuel ash in concrete: a review. J. Civ. Eng. Manag. 2011; 17; 234-247.
[11] a.S.M. A. Awal and W.M. Hussin. Effect of palm oil fuel ash in controlling heat of hydration of concrete. Procedia Eng. 2011; 14: 2650-2657.
[12] S.O. Bamaga, M.A. Ismail, Z.A. Majid, M. Ismail, Mohammad, M.W. Hussin. Evaluation of sulfate resistance of mortar containing palm oil fuel ash from different sources. Arab. J. Sci. Eng. 2013; 38: 2293-2301.
[13] M. Ismail, M.E. Ismail, B. Muhammad. Influence of elevated temperatures on physical and compressive strength properties of concrete containing palm oil fuel ash. Constr. Build. Mater. 2011; 25: 2358-2364.
[14] M.a.a. Aldahdooh, N.M. Bunnori, M.A.M. Johari. Development of green ultra-high performance fiber reinforced concrete containing ultrafine palm oil fuel ash. Constr. Build. Mater. 2013; 48: 379-389.
[15] W. Kroehong, T. Sinsiri, C. Jaturapitakkul. Effect of palm oil fuel ash fineness on packing effect and pozzolanic reaction of blended cement paste. Procedia Eng. 2011; 14: 361-369.
[16] H.P.S.A. Khalid, H.M. Fizree, M. Jawaid, O.S. Alattas. Preparation and characterization of nano- structured materials from oil palm ash: A bio- agricultural waste from oil palm mill. BioResources. 2011; 6: 4537-4546.
[17] M.S. Morsy, S.H. Alsayed, M. Aqel. Effect of nano-clay on mechanical properties and microstructure of ordinary portland cement mortar. Inter. J. Civ. Env. Eng.2010; 10: 21-25.