Comparison of Physical and Chemical Properties of Micro-Silica and Locally Produced Metakaolin and Effect on the Properties of Concrete

S. U. Khan, T. Ayub, N. Shafiq

Abstract**—**The properties of locally produced metakaolin (MK) as cement replacing material and the comparison of reactivity with commercially available micro-silica have been investigated. Compressive strength, splitting tensile strength, and load-deflection behaviour under bending are the properties that have been studied. The amorphous phase of MK with micro-silica was compared through X-ray diffraction (XRD) pattern. Further, interfacial transition zone of concrete with micro-silica and MK was observed through Field Emission Scanning Electron Microscopy (FESEM). Three mixes of concrete were prepared. One of the mix is without cement replacement as control mix, and the remaining two mixes are 10% cement replacement with micro-silica and MK. It has been found that MK, due to its irregular structure and amorphous phase, has high reactivity with portlandite in concrete. The compressive strength at early age is higher with MK as compared to micro-silica. MK concrete showed higher splitting tensile strength and higher load carrying capacity as compared to control and micro-silica concrete at all ages respectively.

Keywords**—**Metakaolin, compressive strength, splitting tensile strength, load deflection, interfacial transition zone.

I. Introduction

METAKAOLIN (MK) is a processed amorphous siliceous material and it is obtained from calcination of pure or refined kaolinite or kaolin [1], [2]. In 1990, MK was recognised as mineral admixture [1]; however, at that time due to variation of its quality, it was not assured that MK has positive effect on the strength of concrete. In 1995, Martin [3] reported that the inclusion of MK in concrete increases the compressive strength up to 110 N/mm^2 (16 ksi) [1]. In 2002, Ding and Li [4] compared the MK and silica fume concrete in terms of compressive strength, chloride diffusivity and shrinkage and reported that MK and silica fume are comparable. In 2005, Poon et al. [5] reconfirmed the results of Ding and Li [4] and added that both MK and silica fume give low porosity and smaller pore size and results in improvement of the microstructure of concrete [5]. Recently in 2013, Duan et al. [6] examined the pore structure and interfacial transition zone (ITZ) of concrete using slag, silica fume and MK and reported that effect of MK on microstructure is better as compared to silica fume and slag. These results showed the performance of MK as mineral admixture; however, performance of MK primarily depends upon the chemical and mineralogical compositions of the parent rock [7] from which it is formed and it may vary from one place to another.

In Malaysia, huge reserves (around 1.12 x 10^8 tonnes) of kaolin have been discovered in the states of Perak, Johor, Kelantan, Selangor, Pahang, and Sarawak [8]. However, few studies have been performed to check the possibility of calcination of kaolin to form MK. Though it has been reported that Malaysian kaolin thermally treated at 750 ˚C (1382 ˚F), and then, replacing cement up to 10% has comparative compressive strength [9], the properties of concrete like splitting tensile strength, flexural strength (load deflection response under bending), and microstructure have not been studied. In addition, the XRD pattern has not been reported to identify whether the fully amorphous phase of siliceous material has been achieved or not. Moreover, the reactivity of thermally treated Malaysian kaolin has not been compared with the available high reactive pozzolan such as micro-silica. The current investigation is focusing on the properties of locally produced MK from Malaysian kaolin as cement replacing material and the comparison of reactivity with commercially available micro-silica. Compressive strength, splitting tensile strength, and load-deflection under bending are the properties of concrete that have been studied. XRD pattern has been analysed to study and compare the amorphous phase of MK with micro-silica. In addition, FESEM of raw kaolin, micro-silica, and MK has been performed to observe Pore size distribution and ITZ.

II. Experimental Program

Three mixes of concrete have been prepared. One of the mixes is without cement replacement (C-0) as control mix, and the remaining two mixes are 10% cement replacement with micro-silica (S-10) and Metakaolin (MK-10). Mix proportions detail of the concrete has been mentioned in Table I. Three specimens for all concrete mixes have been prepared to determine the average compressive strength, splitting tensile strength, and load carrying capacity under bending. The effect of cement replacement by micro-silica and MK on the compressive strength, splitting tensile strength and load carrying capacity of concrete at 7 days, 28 days, 56 days, and 90 days has been investigated.

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Ordinary Portland cement (OPC) has been used. Sand passing through 3.125-mm (1/8") opening sieve and retained on sieve # 200 has been used as fine aggregates in all concrete mixes. 20-mm (3/4") opening sieve passing and 10-mm (3/8") opening sieve passing have been used as coarse aggregates. The Malaysian kaolin has been obtained from Kaolin (Malaysia) Sdn. Bhd. named as KM40. It is kaolin clay chemically known as hydrated aluminium silicate and structurally unmodified. This kaolin clay has been calcined at temperature 800 ˚C for 3 hours using electric melting furnace. The temperature has been decided after several trials of thermal treatment of kaolin on different temperature and duration. Based on XRD pattern at different temperature and duration, 800 ˚C and 3 hours thermal treatment has been found suitable and has been used for the comparison with micro-silica in this study. Elkem Micro-Silica Grade 955 has been used for the comparison of reactivity of locally produced MK-10. Superplasticizer of Type F or G of ASTM C 494 with a dosage 0.25 to 1% by weight of cement with a variation of 0.25% has been added in concrete mixes to achieve the slump of 100±10 mm in all concrete mixes, and water cement ratio has been taken as 0.4 in all concrete mixes.

TABLE I
MIX DESIGN FOR EXPERIMENTAL PROGRAM AND MIX PROPORTIONS

Constituent	Mix ID			Remarks
	C-0	S-10	MK-10	
Cement, kg/m^3(lb/ft^3)	450 (28.64)	405 (25.78)	405 (25.78)	Superplasticizer has been set up to attain minimum slump of 100 ± 10 mm (2 in. ± 0.4)
Micro silica % , kg/m^3(lb/ft^3)	-	10, 45 (2.86)	-	
Metakaolin %, kg/m^3(lb/ft^3)	-	-	10, 45 (2.86)	
Sand kg/m^3(lb/ft^3)	670 (42.61)	670 (42.61)	670 (42.61)	
CA (<20mm, >10mm) kg/m^3(lb/ft^3)	500 (31.8)	500 (31.8)	500 (31.8)	
CA (<10mm) kg/m^3(lb/ft^3)	600 (38.16)	600 (38.16)	600 (38.16)	
Water/ binder ratio	0.4	0.4	0.4	
Superplasticizer %	0.25	1	0.75	

III. DETAIL OF EXPERIMENTS

Mechanical properties (compressive strength, splitting tensile strength and load carrying capacity) of concrete have been tested based on BS standards. Prior to testing, all concrete mixes have been tested for slump test to set a slump of 100±10 mm. Specimens were prepared as per BS standard for determining the mechanical properties. Slump test was performed as per BS 1881 for setting up the minimum content of superplasticizer for the required workability. Casting procedures and standards were compliance as per BS 1881: Part 102 standards.

A. Compressive Strength

Specimens for determining compressive strength of concrete have been cast according to BS 1881: Part 108. Cube specimens of 100×100×100 mm have been used for testing of compressive strength.

B. Splitting Tensile Strength

Specimens for determining the splitting tensile strength of concrete have been cast as per BS 1881: Part 110. Cylinders of 150 mm diameter and 150 mm height (ratio 1:1) have been used for testing of splitting tensile strength.

C. Load Carrying Capacity Under Bending

Specimens for determining the load carrying capacity under bending have been adapted similar to the specimen for flexural strength as per BS 1881: Part 109. Beam specimens of 100×100×500 mm have been used for testing for load carrying capacity and load-deflection response under bending.

D. XRD Pattern

XRD pattern of raw kaolin, micro-silica, and MK have been determined to check the amorphous phase of MK in comparison with raw kaolin and Micro-silica. Though compressive strength is a good way of confirming reactivity of any pozzolan, compressive strength is dependent on several factors including water content, aggregate selection, aggregate gradation, quality of cement and mixing. Therefore, another method is required to confirm the results of compressive strength. XRD pattern is that method to confirm the amorphous phase of MK. The XRD pattern provides information about the crystal and amorphous material presents in a substance. Amorphous materials like amorphous SiO_2 do not create scattered peaks in diffraction pattern due to absence of long-range atomic order [10].

E. Field Emission Electron Microscopy

To observe the atomic order and particle size, FESEM of raw kaolin, micro-silica and MK has been performed. Pore size distribution and ITZ has been observed through FESEM of all concrete mixes.

IV. RESULTS AND DISCUSSION

Table II presents the physical and chemical properties of raw kaolin, OPC, MK and micro-silica. BET surface area of MK is quite close to the micro-silica infer the packing ability of MK and possible refinement of microstructure of concrete. By comparing percent content of SiO_2 and Al_2O_3, it is clear that micro-silica has the maximum SiO_2 content; however, Al_2O_3 content is significantly higher in MK. This may result in higher early age strength of concrete due to high reactivity of Al_2O_3 to form calcium aluminate hydrate (CAH). Though Al_2O_3 content is high, it requires amorphous phase to be reactive with portlandite.

Fig. 1 represents the XRD pattern of Raw Kaolin, MK and micro-silica. XRD pattern of raw kaolin shows the presence of kaolinite and crystal form of SiO_2 (quartz) showing the possibility of primary material to be used for calcination to form metakaolin. Kaolinite and quartz are crystals, and on right temperature and duration, these crystals release their crystalline water and convert into amorphous form of alumina Al_2O_3 and silica SiO_2. XRD pattern of MK is quite different from raw kaolin as broad peaks at angle of 9˚, 12˚, and 25˚ have been vanished showing the conversion of kaolinite into di-alumino silicate and amorphous SiO_2. MK has scattered diffraction pattern, and only one broad peak of quartz about 27˚ is visible. Throughout the XRD pattern, di-alumino silicate and amorphous phase of SiO_2 have been detected. This shows that the calcination of kaolin has been performed properly, and MK, due to presence of Di-alumino silicate and amorphous phase of SiO_2, should give high early strength in concrete. On the other hand, micro-silica has the most scattered diffraction pattern and even there is no broad peaks on the XRD pattern showing fully amorphous phase of SiO_2, but there is glimpse of crystal form of SiO_2 (Quartz) showing that even micro-silica contains little amount of non-reactive SiO_2.

TABLE II
PHYSICAL AND CHEMICAL PROPERTIES [11]

	Raw Kaolin	OPC	Metakaolin	Micro-Silica
Specific Gravity	2.5	3.05	2.5	2.6-3.8
BET Surface Area, m^2/g (ft^2/lb)	12.667 (61891)	1.066 (5208)	12.174 (59482)	16.455 (80399)
Loss of ignition, %	111.0 – 14.0 at 1025° C	-	11.06	Max. 2.0 at 950° C
Moisture %	Below 2.0	-	Max. 1.0	
Average Particle Size, µm (in.)	2.5 - 4.5 (0.00009-0.00018)	-	-	-
pH	3.0 - 5.0	-	-	6.5 – 8.0
SiO_2, %	48.45	20.44	53.87	91.40
TiO_2, %	0.85	0.17	0.95	0.00
Al_2O_3, %	34.75	2.84	38.57	0.09
Fe_2O_3 (t) , %	1.28	4.64	1.40	0.04
MnO, %	0.01	0.16	0.01	0.05
MgO, %	0.85	1.43	0.96	0.78
CaO, %	0.03	67.73	0.04	0.93
Na_2O, %	0.02	0.02	0.04	0.39
K_20, %	2.40	0.26	2.68	2.41
P_2O_5, %	0.09	0.10	0.10	0.38

Figs. 2-4 represent the microstructure of raw kaolin, MK, and micro-silica through FESEM. By comparing Figs. 2 and 3, it is evident that though MK has fully amorphous phase based on XRD pattern, but there is not very distinct difference in the microstructure of raw kaolin and MK. This means that calcination of kaolin does not cause any change chemically, and most of the physical characteristics of kaolin remain the same. The only change is that most of the water from crystal has been evaporated due to thermal process without disturbing the chemical composition.

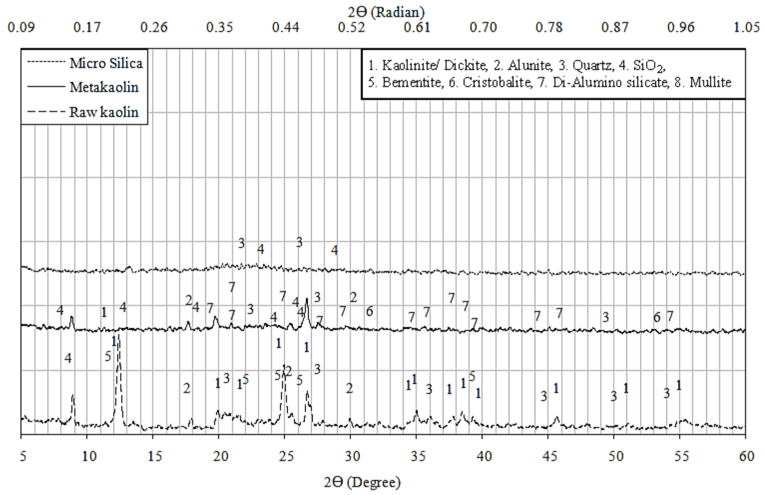

Fig. 1 XRD pattern of raw kaolin, MK, and micro-silica

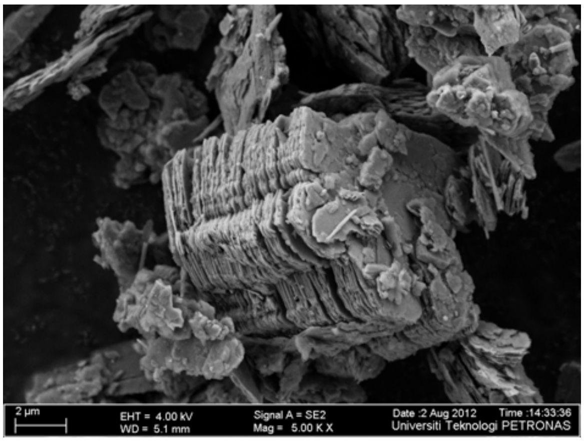

Fig. 2 Microstructure of raw kaolin through FESEM

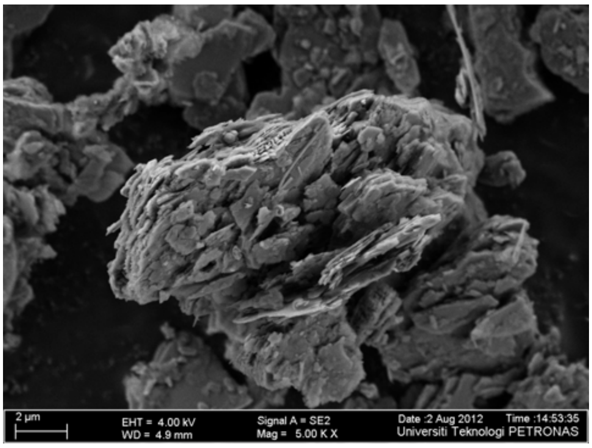

Fig. 3 Microstructure of MK through FESEM

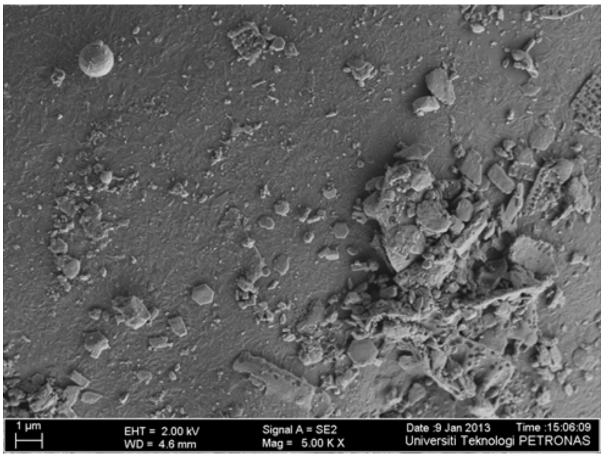

Fig. 4 Microstructure of micro-silica through FESEM

In Figs. 3 and 4, there is discrete difference in microstructure of MK and micro-silica. MK has layered, flat, and flaky structure, whereas micro-silica has granular and angular structure showing impurity of micro-silica which is also reported by Newman [1]. Although micro-silica has higher surface area due to granular structure, MK should also have high reactivity due to irregular structure with portlandite in concrete which is also reported by Shvarzman et al. [12] and Kakali et al. [13].

Based on XRD pattern and microstructure, it may infer that locally produced MK has potential of being reactive with portlandite in concrete and probably will give the high strength; however, the effect of locally produced MK on the microstructure of concrete and on ITZ is still not clear. To do this, FESEM of concrete C-0, MK-10, and S-10 has also been performed as shown in Figs. 5-7. Fig. 5 is the microstructure of control C-0 without cement replacement. There are white dots visible showing portlandite $Ca(OH)_2$ left without reaction with silica or alumina. The pore size is bigger and width of ITZ is about 4.697 µm. On the other hand, the pore size in MK concrete (MK-10) is very small, the width of ITZ is about 1.801 µm, and there is no visible portlandite showing complete utilization of $Ca(OH)_2$, which in return prevents alkali silica reaction as reported by Siddique and Klaus [14]. Smaller pore size and improvement in ITZ will result in impermeable MK concrete which is helpful in preventing the chloride ion penetration and ingress of other hazardous substance, which is also reported by Poon et al. [5] and Justice et al. [15]. The microstructure of concrete with micro-silica (S-10) is shown in Fig. 7. There are few glances of portlandite $Ca(OH)_2$ left without reaction in micro-silica concrete as well. The pore size is smaller with micro-silica, and the width of ITZ is about 2.578 µm, which is smaller than the control but greater than MK concrete. This infers that though micro-silica has improved microstructure to provide highly impermeable concrete and will result in prevention of alkali silica reaction, chloride ion penetration, and ingress of other hazardous substance, locally produced MK will better reduce the alkali silica reaction and chloride ion penetration than micro-silica, which is also reported by Justice et al. [15].

Cube compressive strength of concrete has been plotted against the age of specimen as shown in Fig. 8. The most obvious trend is the increase in compressive strength with the age and higher compressive strength of MK concrete at all ages. This confirms the predictive behaviour of MK based on physical, chemical properties, XRD pattern and microstructure characteristics as discussed in the preceding section. It is also interesting to note that, with the age, the difference in compressive strength of MK concrete and micro-silica concrete is getting smaller; however, the compressive strength at age of 7 and 28 days is much higher with MK as shown in Fig. 8. This shows that locally produced MK has higher reactivity than commercially available micro-silica.

Splitting tensile strength has also been plotted against the age of specimen as shown in Fig. 9. Similar response has been observed in splitting tensile strength as MK concrete gives higher splitting tensile strength at all ages as compared to control (C-0) and micro-silica concrete (S-10). This is due to highly dense concrete and improved ITZ with MK.

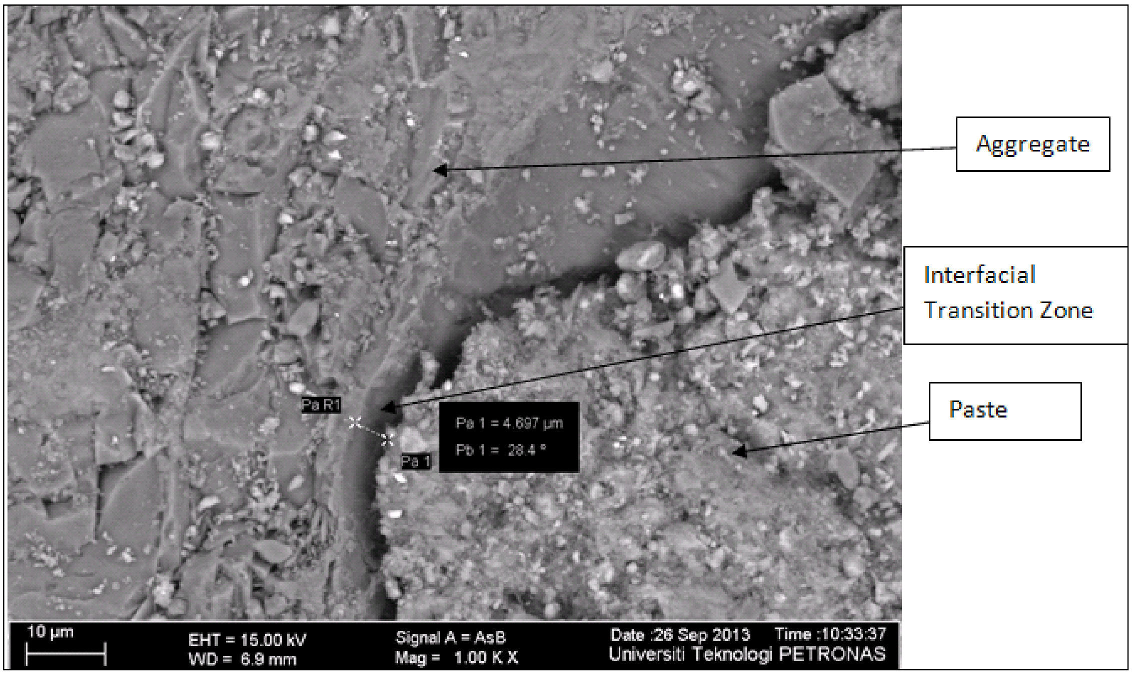

Fig. 5 Microstructure of concrete C-0 through FESEM

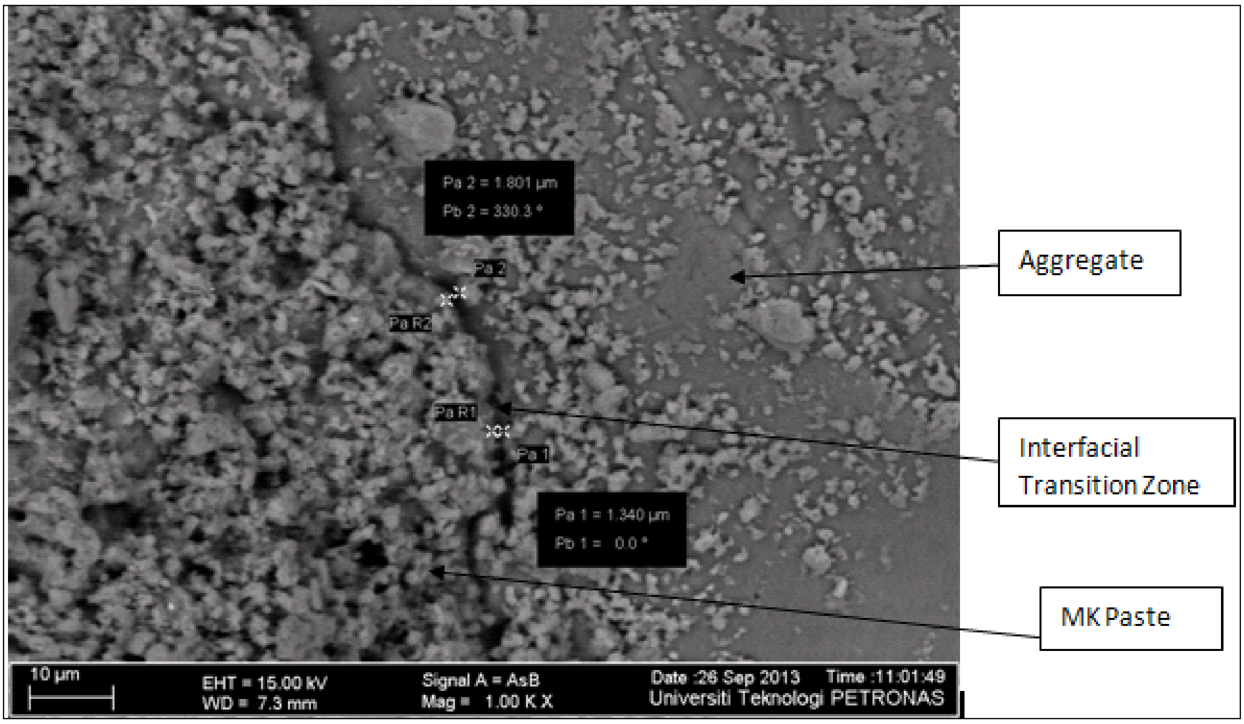

Fig. 6 Microstructure of concrete MK-10 through FESEM

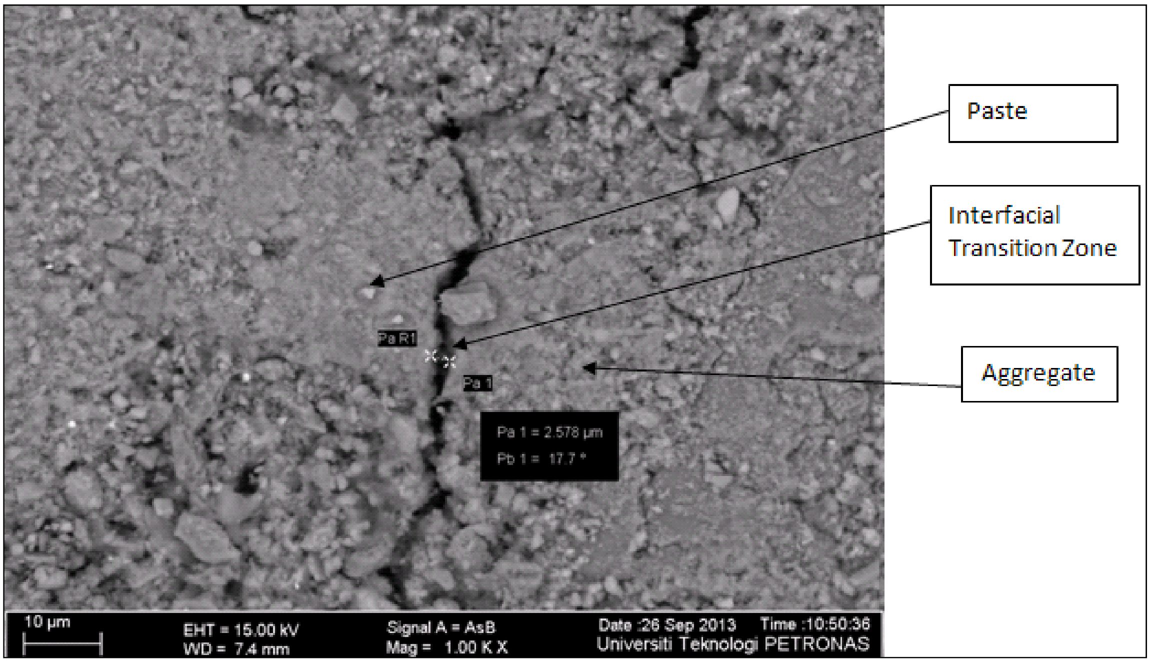

Fig. 7 Microstructure of concrete S-10 through FESEM

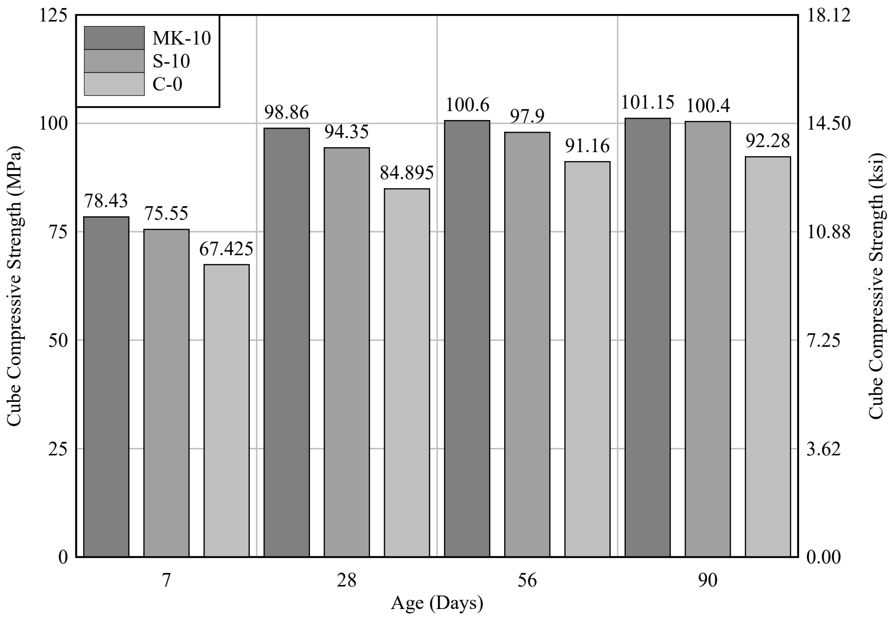

Fig. 8 Cube compressive strength

From Figs. 10-12, load deflection diagrams under bending have been plotted. In comparison with control (C-0), load carrying capacity at all ages of MK concrete (MK-10) is comparable. And in comparison with micro-silica concrete (S-10), the load carrying capacity is higher in MK concrete (MK-10). Conversely, the slope of initial ascending branch is lesser than micro-silica concrete (S-10). This means that the stiffness of the beam made of micro-silica concrete (S-10) is higher and it is offering more rigid behaviour against the bending as compared to control (C-0) and MK concrete (MK-10). In general, locally produced MK is playing a significant role providing strength to cement matrix and enhancing the microstructure. Locally produced MK has great potential and it is confirming the similar characteristics reported in the other parts of the world.

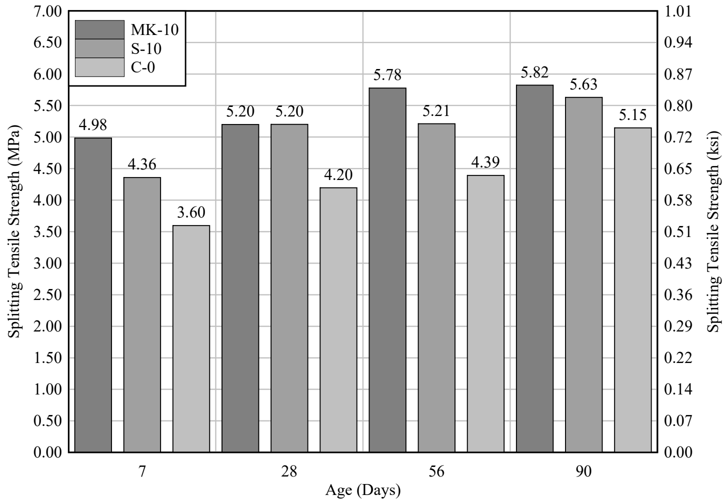

Fig. 9 Splitting tensile strength

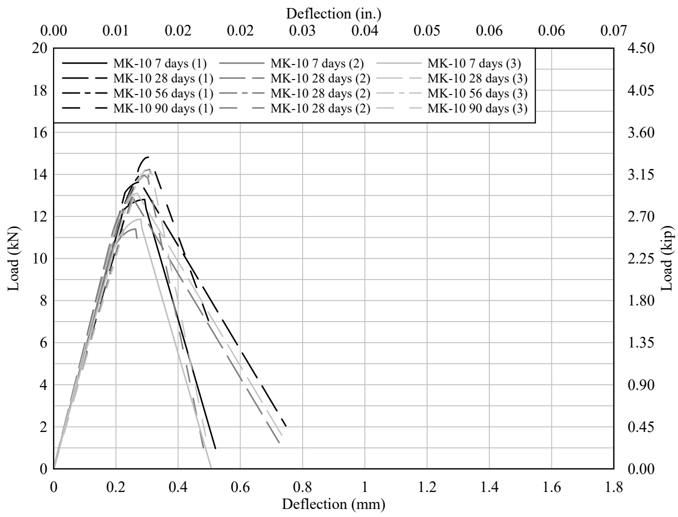

Fig. 10 Load deflection curve of MK concrete (MK-10) under bending

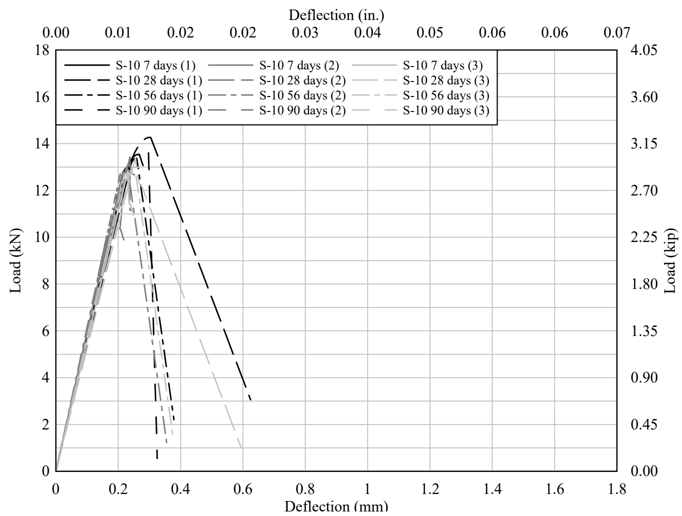

Fig. 11 Load deflection curve of micro-silica concrete (S-10) under bending

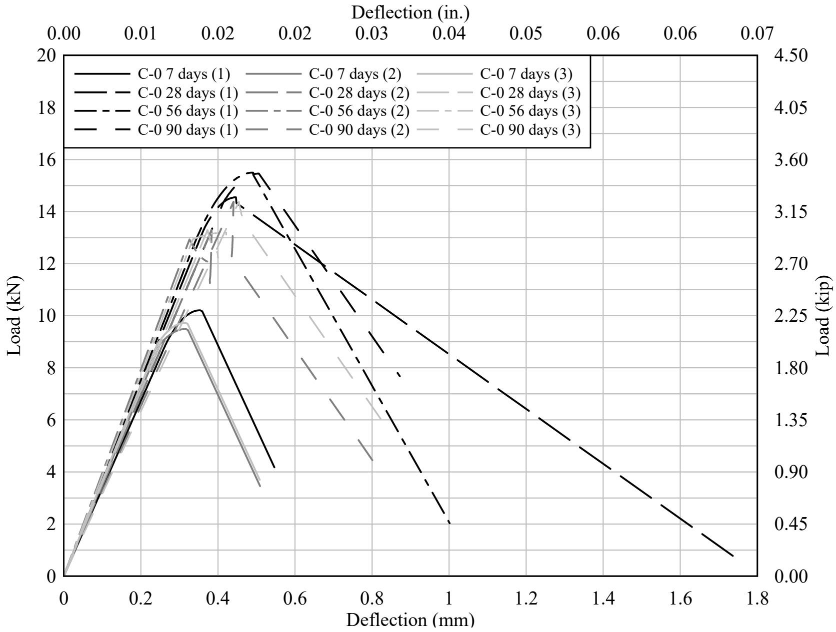

Fig. 12 Load deflection curve of Control C-0) under bending

V. Conclusions and Recommendations

1. Locally produced MK confirms the similar properties reported in the literature. It has high specific area and amorphous siliceous materials which give high early strength in concrete.
2. Calcination of kaolin does not cause chemical and physical changes. The only change is the dehydroxylation of kaolinite due to thermal process without disturbing the chemical composition.
3. MK has layered flat and flaky structure. Due to this irregular structure, MK has high reactivity with portlandite in concrete.
4. MK concrete has lesser width of ITZ as compared to control and micro-silica concrete.
5. With the age, the difference in compressive strength of MK concrete and micro-silica concrete is getting smaller; however, the compressive strength at age of 7 and 28 days is much higher with MK. This shows that locally produced MK has higher reactivity than commercially available micro-silica.
6. MK concrete gives higher splitting tensile strength at all ages as compared to control (C-0) and micro-silica concrete (S-10). This is due to highly dense concrete and improved ITZ with MK.
7. In comparison with micro-silica concrete (S-10), load carrying capacity at all ages of MK concrete (MK-10) is higher.

References

[1] J. B. Newman, Advanced Concrete Technology: Constituent Materials. Butterworth-Heinemann, 2003.
[2] ACI Committee 363, "State of the art report on high-strength concrete," in ACI J. Proc., 1984.
[3] S. J. Martin, "The use of metakaolin in high strength concrete." RMC Readymix Limited., Tech. Rep. Laboratory Report 78, 1995.
[4] J. Ding and Z. Li, "Effects of metakaolin and silica fume on properties of concrete," ACI Mater. J., vol. 99, pp. 393-398, 2002.
[5] C. Poon, S. Kou and L. Lam, "Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete," Constr. Build. Mater., vol. 20, pp. 858-865, 2006.
[6] P. Duan, Z. Shui, W. Chen and C. Shen, "Effects of metakaolin, silica fume and slag on pore structure, interfacial transition zone and compressive strength of concrete," Constr. Build. Mater., vol. 44, pp. 1-6, 2013.
[7] H. Baioumy and A. R. Ibrahim, "Mineralogical Variations among the Kaolin Deposits in Malaysia,".
[8] http://malaysianminerals.com/kaolin.html. Accessed on 02/02/2014.
[9] O. C. HUAT, "Performance of Concrete containing Metakaolin as Cement Replacement Material," 2006.
[10] S. A. Speakman, "Basics of X-ray powder diffraction," the Center for Materials Science and Engineering at MIT, Tech. Rep. Massachusetts-USA, 2011.
[11] S. U. Khan, M. F. Nuruddin, T. Ayub and N. Shafiq, "Effect of Different Mineral Admixtures on the properties of Fresh Concrete." The Scientific World J., vol. 2014, pp. 11, 2014.
[12] A. Shvarzman, K. Kovler, G. Grader and G. Shter, "The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite," Cem. Concr. Res., vol. 33, pp. 405-416, 2003.
[13] G. Kakali, T. Perraki, S. Tsivilis and E. Badogiannis, "Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity," Appl. Clay. Sci., vol. 20, pp. 73-80, 2001.
[14] R. Siddique and J. Klaus, "Influence of metakaolin on the properties of mortar and concrete: A review," Appl. Clay. Sci., vol. 43, pp. 392-400, 2009.
[15] J. Justice, L. Kennison, B. Mohr, S. Beckwith, L. McCormick, B. Wiggins, Z. Zhang and K. Kurtis, "Comparison of two metakaolins and a silica fume used as supplementary cementitious materials," in Proc. Seventh International Symposium on Utilization of High-Strength/High Performance Concrete, 2005.