Construction and Building Materials 135 (2017) 21–29

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Characterization of palm oil clinker powder for utilization in cement-based applications

Mohammad Razaul Karim, Huzaifa Hashim, Hashim Abdul Razak *, Sumiani Yusoff

Department of Civil Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

HIGHLIGHTS

- POCP consist of inorganic oxides with small fraction of organic carbon.
- Microstructure analysis confirms that the particle of POCP is irregular in shape and porous in nature.
- Amorphisity hump occurs at the angular 2θ range of 10°–35° in XRD pattern.
- The crystallinity index of quartz in POCP is 0.97 which means that the quartz is partially disordered.

ARTICLE INFO

Article history:
Received 13 August 2016
Received in revised form 1 November 2016
Accepted 28 December 2016

Keywords:
Palm oil clinker powder
Microstructure
Chemical composition
Mineralogical composition
Organic carbon and thermogravimetric analysis

ABSTRACT

Palm oil clinker (POC) is a waste material produced as result of using palm oil shell and mesocarp fibers as fuel to run stream turbines in palm oil mills. The current practice is to dump this waste in open land or landfill sites, which leads to environmental problems. The characterization of such waste to identify its suitability as a cement replacement materials, can ultimately lead to lower carbon footprint concrete. This paper presents the results of a study on the physical properties (particle size, specific surface, specific gravity, loss of ignition, morphology), chemical composition, organic carbon, thermal stability and mineralogical composition of palm oil clinker powder (POCP). The characterization was carried out using particle size analyzer, scanning electron microcopy (SEM), X-ray fluorescence (XRF), field emission scanning electron microcopy and energy-dispersive X-ray analysis (FESEM-EDX), thermogravimetric analysis (TGA), total organic carbon (TOC) analysis, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. From the laboratory works conducted results are defined and compared to existing literatures in tabulated form. The results of this extensive study on POCP characterization will provide guidance on future research work on utilization of POCP as a supplementary cementitious material in concrete.

1. Introduction

In recent years, very few studies have been conducted in utilization of palm oil clinker powder (POCP) as a filler and palm oil clinker (POC) as aggregate in concrete [1–3]. The chemical composition of POCP has been mentioned in previous studies, which is a mixture of inorganic oxides. The mineralogical composition analysis presents the principal phases in POCP consisting of quartz and cristobalite [4]. However, limited information on amorphisity of POCP for assessing the pozzolanic activity of a newly recognized cementitious waste material [5,6]. Moreover, the extensive information on organic carbon content, the microstructure and mineralogical composition identification are important aspects for utilization of new waste byproducts as cement supplementary materials in concrete [7,8].

Palm oil mills produce large amount (equivalent to around 70% of raw material) of solid waste byproducts in the form of fibers, nutshells, and empty fruit bunches. The nutshells and fibers are used extensively as biomass fuel, replacing fossil fuels such as petroleum in generating electricity. Combustion in a steam boiler produces approximately 5% of POC. This waste is left in open land that can lead to serious pollution in the environment. Nowadays, the increasing awareness on environmental issues requires the implementation of strict laws for industrial activities. On the other hand, the challenge faced by modern ordinary Portland cement (OPC) producer is to minimize carbon footprint from Portland cement clinker production as well as to meet up to the increasing demand of cement for present development. According to [9], the cement production will increase from 2540 million tonnes (Mt) in 2006

* Corresponding author.
E-mail address: hashim@um.edu.my (H. Abdul Razak).

http://dx.doi.org/10.1016/j.conbuildmat.2016.12.158
0950-0618/

to between 3680 Mt and 4380 Mt in 2050. In addition, the cement industry is responsible for 5–8% of the total global CO_2 emission which threaten the environment [10,11].

POC is a blackish colored solid waste material. It is considered stable and non biodegradable under normal environmental condition. The chemical composition of such waste material can be determined by widely used XRF spectrophotometer [4,12]. The XRF observation revealed that low calcium content in POCP, which contains a mixture of SiO_2, Al_2O_3, and Fe_2O_3. In addition, low concentrations of several transition metal and alkali oxides are also present [13]. In replacing cement directly, some wastes require thermal treatment and small particle size to improve their pozzolanic reactivity [14,15]. The pozzolanic activity increases due to the disorder of the molecules. Many researchers have investigated on the mineralogy of synthetic materials as well as waste materials such as fly ash (FA), municipal solid waste (MSD), bottom ash (BA) and thermally activated waste by XRD spectrophotometer [16]. Thermal activation causes disorder of molecules in the crystalline lattice of the waste leading to increase pozzolanic activity [17]. Moreover, this process also removes the unburned carbon from waste containing carbon. The unburned carbon is a significant factor to be considered [18], since its presence results in an increase in water requirement and also dosage of superplasticizer (SP) due to absorption by the carbon particles [19].

The crystallinity can be defined as the fraction of crystalline materials in a mixture of crystalline and non-crystalline materials. However, amorphisity is inversely proportional to crystallinity of materials. The degree of crystallinity has a significant effect on pozzolanic activity because only amorphous materials take part in pozzolanic reaction [20]. Crystallinity cannot be evaluated directly, but is determined from the crystallinity index. The crystallinity index for ash can be calculated from FTIR, XRD and ^{13}C NMR data. However, FTIR spectra can provide a useful assessment of the crystalline state of quartz. The crystallinity index of quartz calculated by comparing the intensity of the characterization peak at 695 cm^{-1} and 778 cm^{-1} of tetrahedron of SiO_4 [21]. The performance of waste materials in concrete or blended cement mortar is largely related with the pozzolanic activity [22]. Moreover, the mechanical properties such as flexural strength, elastic modulus and fracture toughness of concrete is dependent on the development of the crystallization phase of the hydration compounds [23].

The mineralogical phases present in ordinary Portland cement (OPC), such as tricalcium silicate (C_3S) and dicalcium silicate (C_2S), is known to react with water and form calcium silicate hydrates (C-S-H) gel and calcium hydroxide ($Ca(OH)_2$) [24]. Similar phases such as C_2S and C_3S are also present in industrial byproduct such as granulated blast furnace slag, but the percentage is low compared to OPC clinker [25]. The waste materials such as FA, rice hush ash (RHA), BA, and sugarcane baggage ash (SBA) are siliceous where SiO_2 is the main ingredient with small percentage of Al_2O_3, Fe_2O_3, MgO and other inorganic oxides. The constituent of POCP resembles that of the siliceous waste material. Moreover, the amorphous silica reacts with $Ca(OH)_2$ to form C-S-H gel which develop strength at later age [26]. The C-S-H increases the density of the concrete or mortar matrix. As a result the compressive strength increases. Another form of waste of palm oil mill is POFA which shows pozzolanic activity [27,28] and also liberate low heat of hydration reaction in blended cement [29]. Usage of POCP in concrete-based application as pozzolanic materials has not been widely investigated.

The primary objective of this study is to determine the chemical composition, microstructure, specific gravity, thermal stability and organic carbon, mineralogical composition as well as amorphisity of POCP. This information is important for utilization of POCP in cement-based applications and for understanding their effects on the properties of concrete or mortar.

2. Material and methods

2.1. Material

The POC and POFA are collected from a palm oil mill, located in Dengkil in Kuala Lumpur, Malaysia. It contains 1%–3% of moisture, and oven dried prior to crushing at a temperature of 100 ± 5 °C. Initially the large size chunks of POC were crushed using a jaw crusher. The smaller pieces after crushing were then ground in a ball mil to produce palm oil clinker powder (POCP).

2.2. Methods for characterization of POCP

2.2.1. Physical properties

Blaine specific surface area (SSA) and loss on ignition (LOI) was measured according to EN 196-6 and EN196-2, respectively [30,31]. Specific gravity was observed as hydrostatic weighing of powder in non-reactive liquid (kerosene). The Malvern particle size analyzer was used for the particle size determination. The Phenom tabletop SEM along with Pro Suite software was used for morphological analysis of POCP. Acceleration voltage used was 10 kV.

2.2.2. Chemical characterization

A fully integrated XRF spectrometer (Epsilon-5) comprising advanced elemental excitation capability with sophisticated instrument control and analytical software was used for chemical composition assessment in this study. The elemental composition was investigated using FESEM – EDX analysis (model-SU8220, Hitachi).

2.2.3. Thermal stability and organic carbon analysis

TGA was used to determine the thermal stability of POCP by monitoring the weight loss with respect to time when the specimen was heated using TGA/SDTA851. This measurement was carried out using 27.5 mg samples in inert atmosphere using N_2 gas. The heating rate was 10 °C/min from 47 °C to 970 °C. This technique was used by many researchers for investigation of thermal behavior of waste materials, synthetic products, nano composite and alloys [32–34]. The TOC-L series was used for the determination of the organic and inorganic carbon present in POCP. This apparatus adopts the 680 °C combustion catalytic oxidation method, which was developed by Shimadzu Corporation. This is the highest level of detection sensitivity available with the combustion catalytic oxidation method. The blank check function evaluates system blanks by measuring ultrapure water processed automatically within the instrument.

2.2.4. Mineralogical characterization

The XRD (model name "Empyrean" of Penalytical Company) was used for the mineralogical composition investigation. This XRD has a platform for the characterization of materials. The XRD analysis was conducted at room temperature and operated with a Cu Kα X-ray source set to cover a 2θ range of 10–80 and to record data at 0.04 steps at a speed of 0.004 min^{-1}. The ground samples were dried in an oven at 110 °C to remove moisture content. Using the KBr pellet technique, the sample was mixed with KBr at ratios of 1:30. The mixture was then pressed into a transparent disc in the die at sufficiently high pressure. Using the Perkin Elmer Frontier FTIR spectrometer, the infrared spectra of POCP sample was recorded in the region 400–4000 cm^{-1}. The resolution of the instrument is 0.001 cm^{-1} and the accuracy is 74 cm^{-1}.