PREPARATION AND CHARACTERIZATION OF NANO-STRUCTURED MATERIALS FROM OIL PALM ASH: A BIO-AGRICULTURAL WASTE FROM OIL PALM MILL

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Oil palm ash (OPA), a bio-agricultural waste from oil palm mills, was subjected to high-energy ball milling for 30 h and was converted into a nano-structured material. The nano-structured OPA was characterized for its particle size and crystallinity index by using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) analysis. The crystallite size obtained from TEM and XRD was found to be 50 nm and 54.32 nm respectively, and the crystallinity index of OPA was 66.54%. The shape and texture of raw and nano-structured OPA were studied using scanning electron microscopy. The raw OPA had an irregular shape with spongy and porous structure, while the nano-structured powder had a mostly irregular and crushed shape. The elemental studies of OPA used Energy Dispersive X-ray (EDX) analysis, XRD, and Fourier Transform Infrared Spectroscopy (FT-IR). The elemental compositions found in OPA were silica, potassium oxide, calcium oxide, magnesium oxide, aluminium oxide, and iron oxide.

Keywords: Oil palm ash; Nano structured materials; X-ray diffraction; Silica

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INTRODUCTION

Worldwide efforts are going on to achieve sustainable economic growth and development of high performance products with good properties. Thus, the utilization of local waste materials that are abundant and cheap, especially from clean resources, has become more pressing than ever. The needs for efficient utilization of waste products are especially critical in the case of oil palm biomass. It is estimated that there were 4.69 million hectares of oil palm biomass in Malaysia during 2009, giving rise to 77.24 million tonnes per year of residuals, comprising 13.97 million tonnes of oil palm trunks, 44.84 million tonnes of oil palm fronds, 6.93 million tonnes of empty fruit bunch (EFB), 4.21 million tonnes of oil palm shell, and 7.29 million tonnes of mesocarp (all dry weight) (Foo *et al.* 2011). Currently, oil palm biomass is mostly used for the purpose of compost and fertiliser, mulching mats, plywood and veneer from oil palm trunks, oil palm fibre-filled automotive upholstery parts, dampening sheets for automotive industry using oil palm fibres, moulded particleboard, pulp and paper from empty fruit bunch (EFB), moulded pulp products for food packaging, containers from EFB, medium density boards, furniture, oil palm lumber, activated carbon, and compostable plastic film. But these oil palm biomass are still often used as fuel for boilers in oil palm mill to produce

steam for electricity generation (Hashim and Chu 2002), and after combustion in the steam boiler, there is approx. 5% of ash being produced (Tay and Show 1995), i.e., another class of solid waste.

Oil palm ash (OPA) is an abundant agricultural solid waste in Malaysia. This bio-agricultural waste, which is rich in siliceous material, is produced after the combustion of oil palm fiber, shell, EFB, and mesocarp as boiler fuel to produce steam for palm oil mill. Although there are some studies on the utilization of OPA such as a cement replacement material (Tay and Show 1996), as an adsorbent for the removal of zinc from aqueous solution (Chu and Hashim 2002), and flue gas desulphurization (Zainudin *et al.* 2005), most of the ash is still disposed of in landfills that require a lot of land area and have the potential to cause environmental problems. Thus, creating, manipulating, and exploring OPA in nanotechnological research as nano-structured material has the potential to lead to beneficial uses of this bio-agricultural waste material.

Nanotechnology has become a rapidly growing field with potential applications ranging from advanced applications to daily-used products. It includes the production and application of biological, chemical, and physical systems at scales ranging from individual atoms or molecules to submicron level, as well as integration of the resulting nano-structure to larger systems (Bhushan 2004). Nanomaterial is defined as the material having dimensions roughly 1 to 100 nanometers (Koo 2006) or at least one dimension in the nanometer range. A variety of ways have been reported to synthesize nanomaterials, such as high intensity ball milling, sol-gel synthesis, electro-deposition, chemical vapour deposition, plasma arching, etc. (Cao 2004). Among these, high intensity ball milling has the advantage of being simple, reasonably low-cost to conduct, applicable to various class of materials, and easily scaled up to large quantities (Baraton 2003). By this mechanical action, particles are subjected to severe deformation due to repetitive compressive loads arising from impacts between the balls and the particles. This produces crystalline and amorphous material with crystallite sizes at the nanometer scale (Koch 2006).

The objective of this study was to explore and to modify the OPA by transforming the micro-size particles into nano-structured material using high-energy ball milling. The nano-structured material obtained from OPA was characterised by using sophisticated analytical techniques. The nano structured material is to be used as reinforcement for fabrication of polymer composites.

EXPERIMENTAL

Materials

Oil palm ash (OPA) was provided from an incinerator at palm oil mill at Ulu Keratong, Segamat, Johor, Malaysia.

Preparation of Oil Palm Ash as a Nano-Filler Material

The OPA taken from oil palm mill was sieved by 60 mesh size sieve to separate micro-sized particles such as sands, stones, and marco-particles from the incinerator. Fine OPA powder was further ground using a grinder/refiner, followed by high-energy ball milling for 30 hours at 170 rev min^{-1}. The ball mill was loaded with a ball-to-powder

weight ratio of 10:1 in a stainless steel chamber using stainless steel balls of diameter 19 mm, 12.7 mm, and 9.5 mm. The OPA was kept at high temperature condition at 250°C in drying oven for 24 hours to prevent agglomeration and kept in a dry place to avoid contact with moisture.

Characterization of Nano-structured Materials

X-ray diffraction (XRD) analysis was carried out with a Philips PW1050 X-pert diffractometer using Cu-Ka1 radiation and operation at 40kV and 25Ma and $\lambda = 1.54$ Å. The diffractrograms were scanned from 2° to 90° (2θ) and in steps of 0.05° using a scanning rate of 0.5° min^{-1} at room temperature. The XRD analysis was used to determine the particle size, crystallinity, and chemical composition of OPA.

Transmission electron microscopy (TEM) was carried out with a Philips CM12 instrument; the sample was oven dried before using the TEM to characterise the size and morphology of the particles. The samples were prepared in acetone and dispersed with an ultrasonicator for ten minutes. The samples for TEM analysis were obtained by placing a drop of colloidal dispersion containing OPA nanoparticles onto a carbon-coated copper grid and allowing it to dry at room temperature before being examined under the TEM.

Scanning electron microscopy (SEM) was employed to characterize the morphology of the OPA. Small portions of samples were taken and coated with gold with an ion sputter coater (Polaron SC515, Fisons Instruments, UK). A LEO Supra 50 Vp, Field Emission SEM, Carl-Zeiss SMT, Oberkochen, Germany was used for microscopic study. The SEM analysis was extended to obtain the elemental composition of the OPA by means of energy dispersive X-ray analysis (SEM-EDX)

Fourier Transform Infrared Spectroscopy (FT-IR), Nicolet Avatar 360, (USA), was used to examine the functional groups presents in the OPA. Perkin Elmer spectrum 1000 was used to obtain the spectra of each sample. 0.5 grams of samples were mixed with KBr (sample/KBr ratio 1/100). They were then pressed into transparent thin pellets. A FT-IR spectrum of OPA was obtained in the range of 4000 to 400 cm^{-1}. Spectral output was recorded in the transmittance mode as a function of wave number.

RESULTS AND DISCUSSION

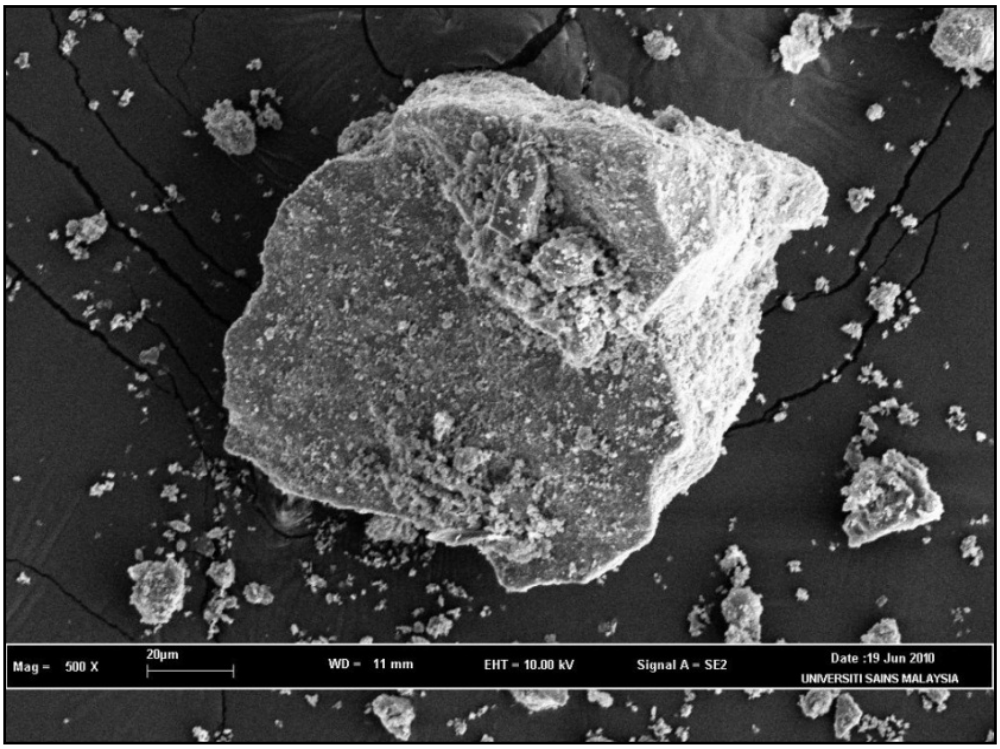
Characterization of OPA

Surface morphologies, elemental composition, and structure of OPA

A morphological study of the fresh OPA is presented in Fig. 1. Typically, raw OPA (Fig. 1a) consists of irregular-shaped particles with spongy and porous structure, with a sizable fraction showing cellular textures (Chindaprasirt *et al.* 2008). After the OPA had been subjected to ball milling (Fig. 1b), the particles became smaller with irregular and crushed shape.

The elemental compositions of the OPA were studied by scanning electron microscopy equipped with energy dispersive X-ray analysis (SEM-EDX) and X-ray diffraction (XRD) analysis. Figure 2 shows the energy dispersive X-ray analysis (EDX) spectra with the elemental composition of OPA. An essential observation is that the OPA contained a high weight percentage of silicon (Si), which was 25.43 wt. %.

(a)



(b)

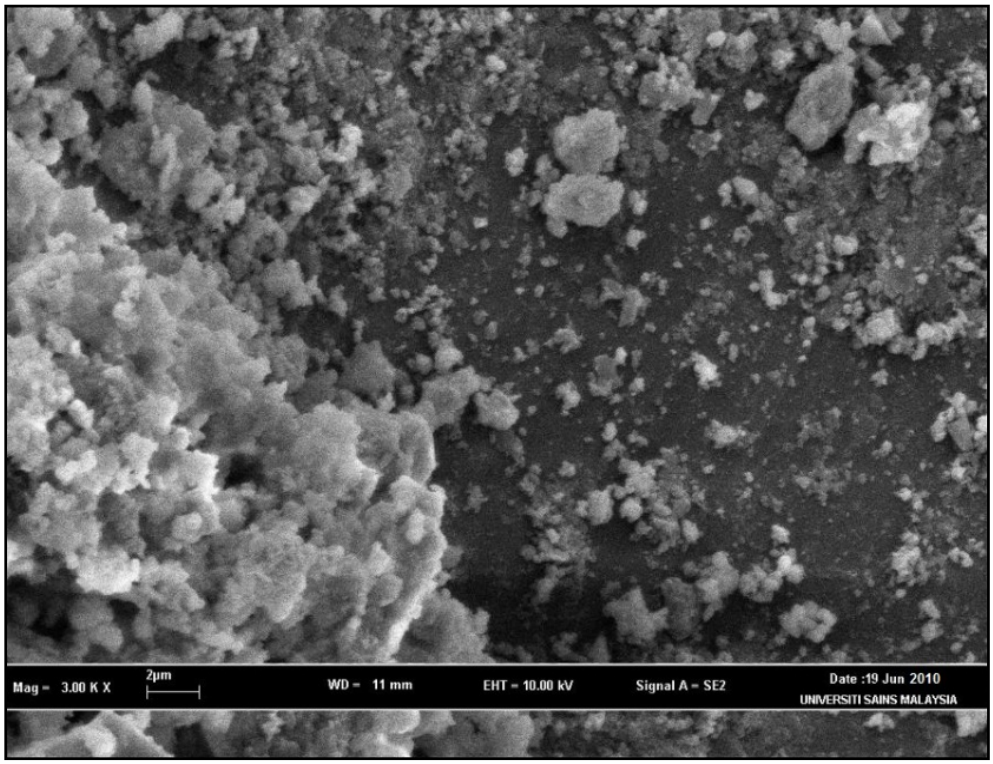
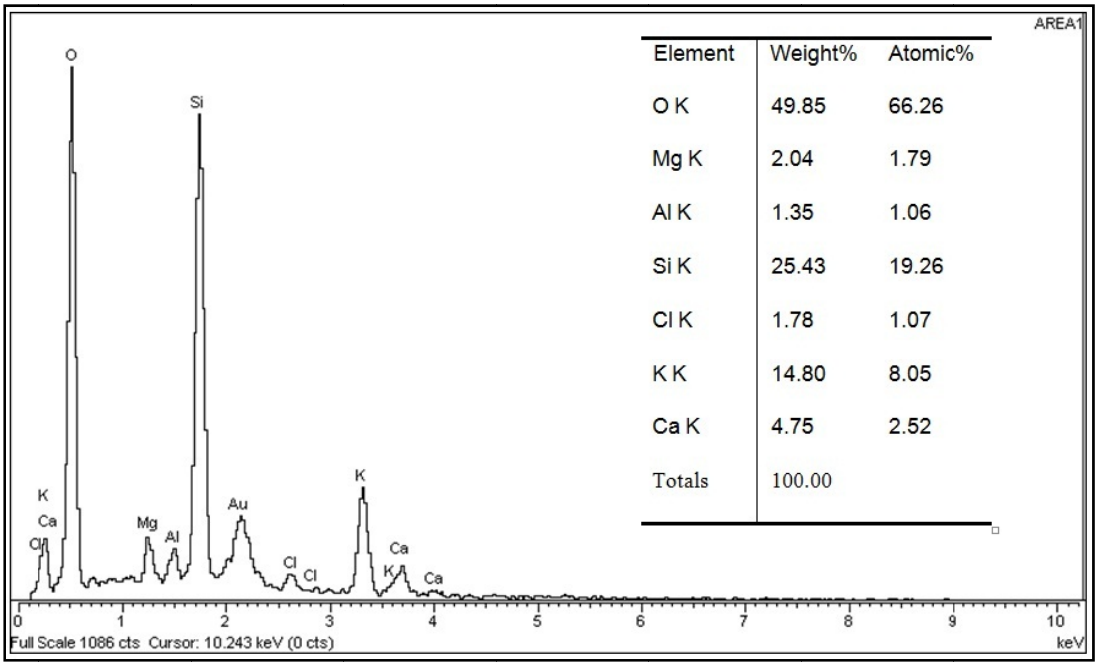


Fig. 1(a). SEM Micrographs of raw OPA, (b) OPA after ball milling



Element	Weight%	Atomic%
O K	49.85	66.26
Mg K	2.04	1.79
Al K	1.35	1.06
Si K	25.43	19.26
Cl K	1.78	1.07
K K	14.80	8.05
Ca K	4.75	2.52
Totals	100.00	

Fig. 2. EDX analysis of OPA

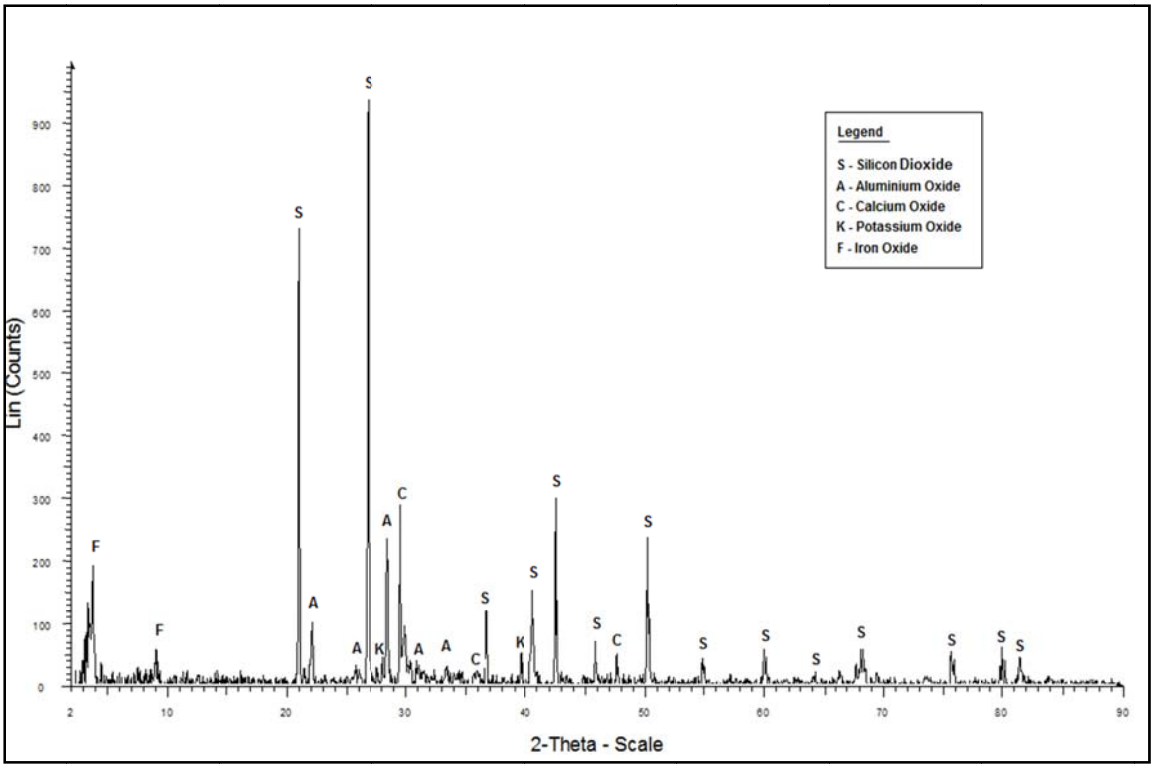


Fig. 3. XRD spectroscopy of the OPA

Other elemental components included potassium, magnesium, calcium, chlorine, and aluminium. Due to high weight percentages of oxygen (49.85%), it can be assumed that silicon, magnesium, aluminium, calcium, and potassium may exist in oxide form. Silica or silicon dioxide (SiO_2) is perhaps the most essential substance found in the OPA. This interpretation was demonstrated to be true by the XRD spectroscopy results shown in Fig. 3, where silica was found at almost all major peaks. Researchers report that OPA contains up to 40% silica (Zainudin *et al.* 2005). Beside silica, other chemical components detected by XRD analysis in OPA were potassium oxide, calcium oxide, magnesium oxide, aluminium oxide, and iron oxide. The mineralogical compositions of ashes tend to be very complex in nature due to the complex formation process (vaporization, melting, crystallization, vitrification, condensation, and precipitation) during combustion of waste (Saikia *et al.* 2006). The composition can be expected to fluctuate due to variation in the proportion of irrigated area, geographical conditions, fertilizer used, climatic variation, soil chemistry, timeliness of production, and agronomic practices in the oil palm growth process (Foo and Hameed 2009).

Fourier transform infrared (FT-IR) Analysis

Fourier transform infrared (FT-IR) spectroscopy was used to detect the presence of the functional groups that exist in the OPA. It is an excellent tool for studying the physico-chemical and conformational properties of silica as a source of siliceous material found in OPA. Figure 4, the FT-IR transmission spectrum of the OPA, shows

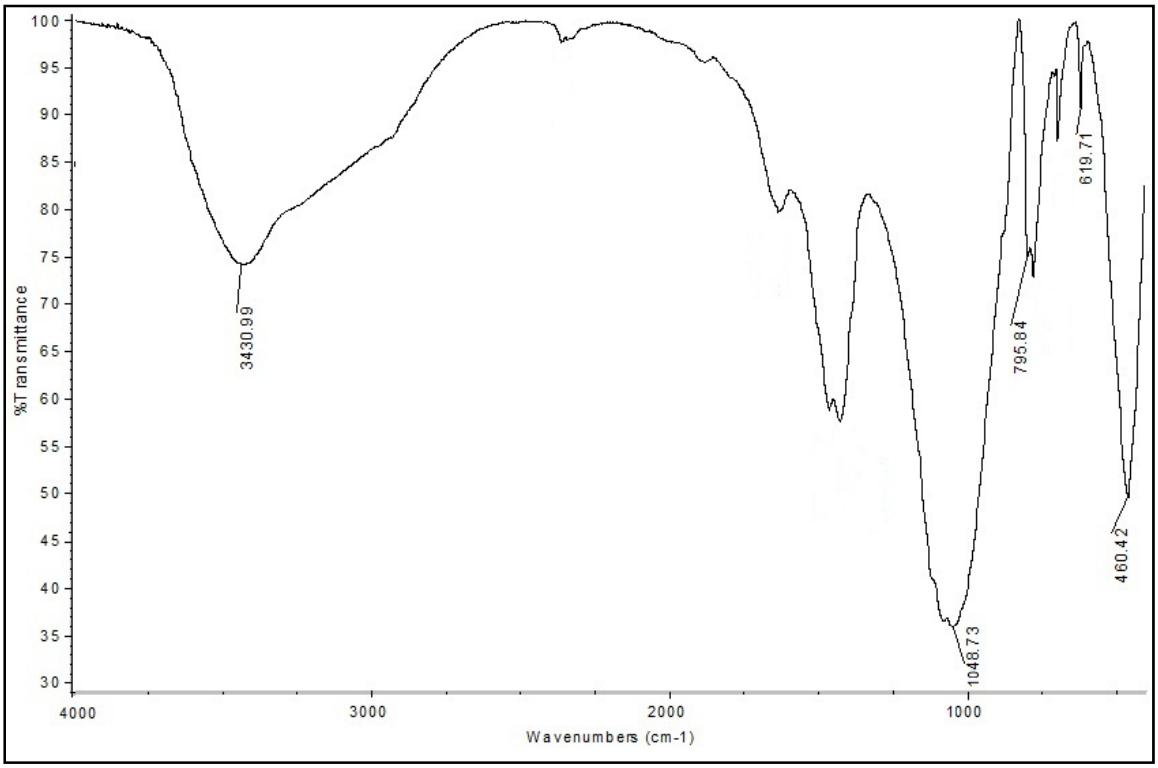


Fig. 4. FT-IR transmission spectrum of OPA

characteristic vibrational bands at 1048, 795, and 460 cm^{-1}, corresponding to the stretching, bending, and out of plane deformation of Si-O bonds, respectively. The position and shape of the main Si-O vibrational band at 1048 cm^{-1} imply a stoichiometric silicon dioxide structure (Hamelmann *et al.* 2005). A weakly discernable band at 619 cm^{-1} is characteristic of the crystalline cristobalite (Prasetyoko *et al.* 2006). The broad band at 3430 cm^{-1}, which was insignificant in the OPA, became noticeable in the case of ball milled OPA (Fig. 4). This was attributed to the presence of the silanol (Si-OH) functional group in the OPA. Paul *et al.* (2007) reported that the presence of silanol, is evidence for the breaking down of the silica structure and formation of Si-OH groups due to the ball milling effect.

Particle Size

The average particle size was determined from the X-ray diffraction peaks using Scherrer's equation (Patterson 1939),

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

where D is the particle diameter, λ is the X-Ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak, θ is the diffraction angle, and K is the Scherrer's constant of the order of unity for usual crystals. The reflecting peaks at 2θ = 20.9°, 26.7°, 28.4°, 29.45°, 40.55°, 42.5°, and 50.15° were used to estimate the average size of OPA, which was calculated to be 54.323 nm.

Transmission Electron Microscopy (TEM)

The TEM technique provides information about the particle size and nano-dispersion of filler within the matrix. The TEM micrograph obtained in this research also shows that the average particle size was close to 50 nm (Fig. 5).

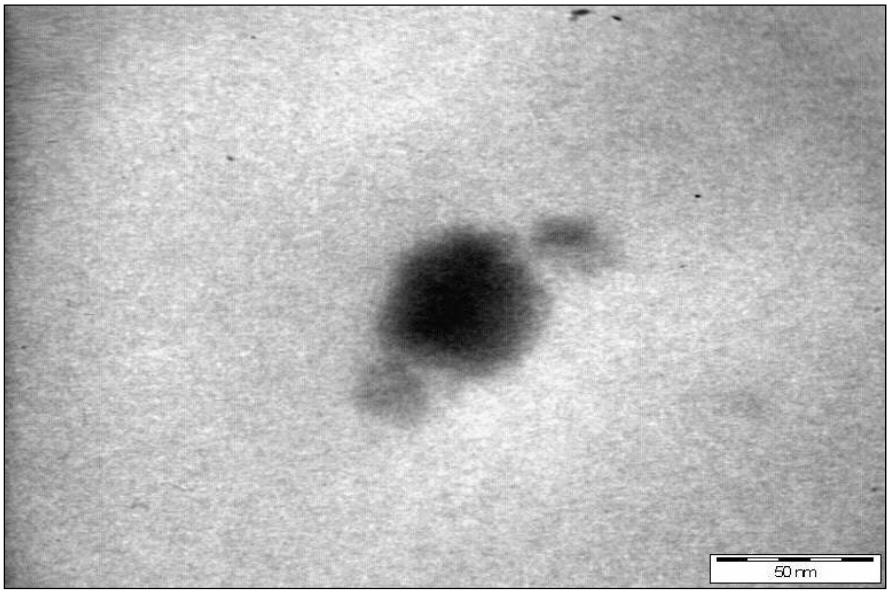


Fig. 5. TEM image of OPA

Crystallinity index

The crystallinity index (*CI*) of OPA was calculated from XRD intensity data using the peak deconvolution method; individual crystalline peaks were extracted by a curve-fitting process from the diffraction intensity profiles by a peak fitting program, assuming Gaussian functions for each peak. *CI* is calculated from the ratio of the area of all crystalline peaks (A_{Cr}) to the total area (A_{total}) (Park *et al.* 2010).

$$CI = \frac{A_{Cr}}{A_{total}} \text{x } 100\% \quad (2)$$

The XRD spectroscopic results in Fig. 6 were deconvulated to obtain the crystallinity index. From Eq. (2), the crystallinity index of OPA was found to be 66.54%. OPA exhibited a higher degree of crystallinity, as evidenced by a number of crystalline peaks in the difractogram.

Silicon dioxide (26.7°), aluminium oxide (28.4°), and calcium oxide (29.45°) peaks were significant and showed crystal form. An amorphous hump was observed between 30° and 35°; this may be due to the presence of amorphous glassy material (Williams *et al.* 2005).

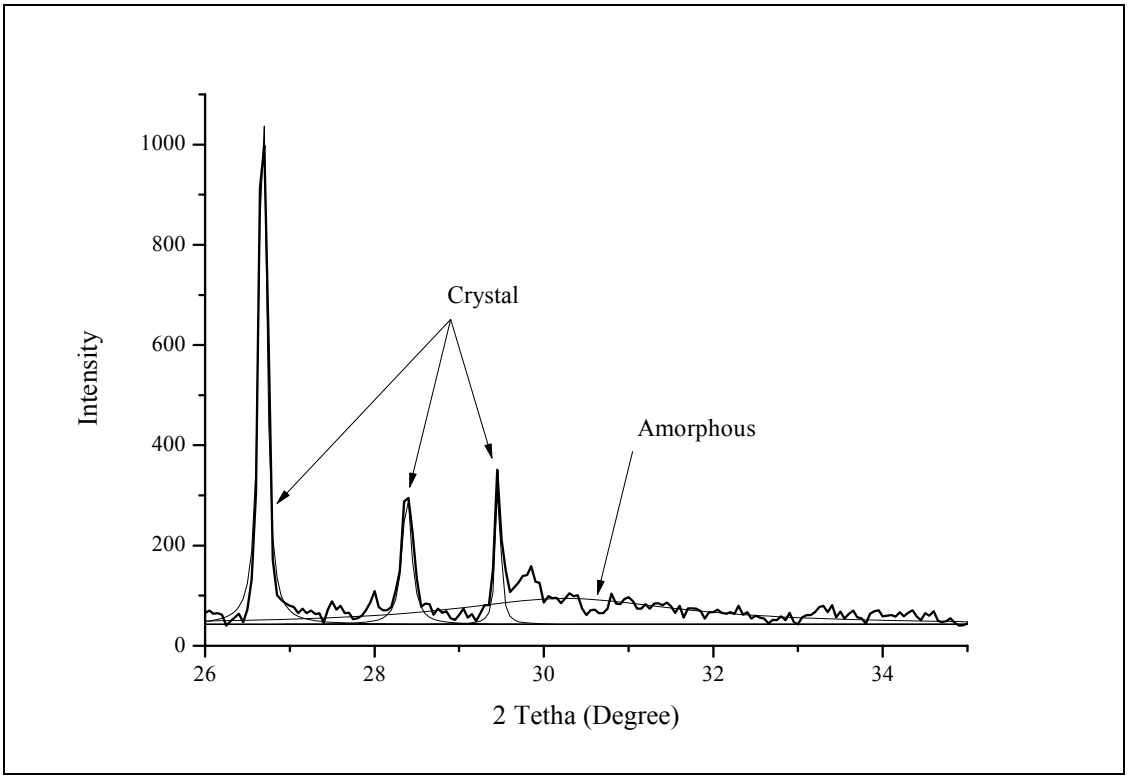


Fig. 6. XRD spectroscopy of OPA ranging from 2θ (26° - 35°)

CONCLUSIONS

1. The nanostructure materials from oil palm ash were obtained in this research. It was concluded that the size of the OPA had been successfully reduced from macromolecular to the nano-size range by high energy ball milling; it was confirmed by TEM that nano-sized particles had been achieved, with up to 50 nm diameter.
2. The OPA apparently contained a high amount of silica, which was confirmed by SEM-EDX, XRD, and FT-IR analyses. This indicates the presence of silicon-based material. Other chemical components found in OPA were potassium oxide, calcium oxide, magnesium oxide, aluminium oxide, and iron oxide.
3. The crystallinity index of nano-particle OPA was found to be 66.54%, which indicates an increase in the degree of crystallinity of the OPA in comparison to the starting material.
4. The nature of nano-structured OPA appears to be suitable for consideration as reinforcement for fabrication of nano-composites.

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