CHARACTERIZATION AND PRODUCTION OF CONDUCTIVE FILLER FROM OIL PALM ASH AND ITS PERFORMANCE IN EPOXY MATRIX

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ABSTRACT

Oil Palm Ash (OPA) was investigated and the FESEM studies showed medium sized particle with a crushed structure. An XRD diffractogram of OPA showed that the obtained OPA contain aluminum, silicon and they exist in their oxide form as indicated by the high percentage of oxygen (36%) with little traces of potassium oxide, calcium oxide, magnesium oxide. while FTIR analysis indicated the occurrence of functional groups such as OH groups, silanol hydroxyl groups of silica or the N-H stretching vibration free imines, aromatic C-H and C-Br alkyl functional group and the presence of methyl CH₃. OPA was carbonized in a furnace with the control flow of nitrogen and ball milled at 100 rpm for 3 hours to obtain a carbonized particle with a diameter of 77.9-140.9 nm. The synthesized carbon black (CB) Particle was dispersed in epoxy resin (DGEBA) at different loading to produce an electrically conductive polymer with a well-dispersed network of electrical conducting particles.

Key words: Electrical conductive Particle, Epoxy Resin, Oil palm Ash, Carbon Black, Dispersion, Composite

INTRODUCTION

Oil palm ash (OPA) is a bio agricultural waste from oil palm mills (Zarina et al., 2013), (Abdul Khalil et al., 2011), Palm fibers, kernel shells, kernel and empty fruit bunch from oil palm mills are incinerated in boilers at about 800-1000°C and use as fuel for the production of energy (Hashim and Chu, 2012), 5% ash which is the bye product obtained from this process (Tay and Show, 1995) is known as OPA. There are about 42 countries involved in the production of *Elaeisguineensis* (palm oil tree) which is a non-temperate plant that is cultivated in hot and humid condition at altitudes not higher than 500 meters above sea level (Udoetok, 2012) with about 27 million acre of land area (Abdul Khalil et al., 2012). Malaysia is among the largest manufacturer and exporter of palm oil in the world, and there is approximately 4 million tons of oil palm ash generated annually (Ooi et al., 2014), (Ooi et al., 2015). OPA is available in great quantity, renewable, can be obtained at no cost and show a good performance at high thermal condition (Ibrahim et al., 2012).

OPA has attracted the interest of researchers, for instance OPA has long been used and recognized by planters as the best and the most economical source of Potassium (K) which is vital in plants growth (Palm NRJ, 2011) and it have been used for the creation of activated carbon by the route of pyrolysis (Gua and Lua, 1998). More recently Abdul Khalil et al., 2011 prepared nanofibre from OPA with 93.39-192 nm diameter and a width of 18.17-43.45 nm and in another research Abdul Khalil et al., 2012 (Characterisation of Various Organic Waste Nanofiller Obtained from OPA) obtained a nanoparticle from OPA having 66.54% crystallinity index and diameter of 50-54.32 nm. OPA as fillers in composite materials have been reviewed with positive result as shown by Sasthiryar et al., 2014 when they used carbon nano fibre (CNF) obtained from OPA for the reinforcement of ceramic alumina to improve their electrical and thermal properties, also Sasthiryar et al., 2014 (Nanobioceramic Composites: A Study of Mechanical Morphological, and Thermal Properties) studied the morphology, thermal and mechanical properties of ceramic alumina toughened with CNF derived from OPA. OPA have been used to partially replace metakoalin in the production of geopolymers (Hawa et al., 2012). Ibrahim et al. 2012 research the usage of OPA as a filler to form composites through the investigation of the outcome of different filler addition on the properties of OPA-loaded unsaturated polyester (UP/OPA) composites.

Nanotechnology is the art of manipulating, organizing and measurement of matter at the atomic scale or the nanometer scale (≤ 100 nm) (Sheetz et al., 2005). It has been proving that material properties can be dramatically improved through the use of nanoscale building unit. When polymers are reinforced using this nanoscale unit or filler particles in a homogeneously dispersed state a nanocomposite is formed (Kochetov, 2012). Nanoparticle fillers possess a large surface area to volume ratio and usually form a polymer nanocomposite (PNC) with an outstanding property. Nanofillers can be organic or inorganic and can be classified according to their geometry as 3D fillers or particulate, nanofibres or nanowires, nanotubes and nanoplatelets (Supova, 2011).

In recent times, nanotechnology is progressively being used in polymers to enhance a variety of properties and to expand their application, for instance, carbon nanofibres (CNF) thermoplastic laminates are known to have excellent heat stability, mechanical property and low flammability making them good candidate material for use in aerospace industry (Hong, 2010). Kochetov, 2012 investigated the use of inorganic nanoparticulate fillers (Al₂O₃, MgO, SiO₂, boron and aluminum nitrides) to improve the dielectric and thermal property epoxy resin. Aldrahem et. al., 2009 fabricated a functional paint for vibration monitoring by dispersing carbon black (CB) nanoparticulate in epoxy resin. Cochrane et al., 2007 developed a flexible strain censor for textile structures by the homogenous dispersion of CB nanoparticulate in evoprene. Despite these advances research have shown that most polymers are incompatible with nano-size fillers causing lack of adhesion between polymer and nanofillers (agglomeration of the nanoparticle) and, therefore, difficulty in achieving uniform dispersion (Pham et al., 2007), (Supova et al., 2011), (Kochetov, 2012).

Polymers are substances made up of a persistent structural unit which can be regarded as resulting from a definite compound called a monomer. Polymers in whatever form they exist (natural or synthetic) usually have the desirable property of being light weight, flexible, ease of production, good mechanical properties and resistant to corrosion attack. Synthetic polymers can be classified into Thermoplastic (e.g. Polyethylene), thermoset (e.g. epoxy resin or polyesters) and Elastomers. Polymers can be considered as engineering materials and have therefore been the subject of research to improve its property and expand its usage in the engineering profession. Polymers have low stiffness, low strength and some polymers (e.g. resin) have low resistance to crack initiation (Dong et al., 2004). Reinforcing of polymer have being in existent for sometimes, polymers reinforcement using both synthetic and natural fibrous material such as glass fibre, wood, kenaf, rice husk, carbon fibre etc. have being carried out, with significant improvement in the mechanical properties of polymer being achieved and much more so when the fibre reinforcing efficiency is further enhanced by chemical modification (Hornsby, 1997).

Electrical conductive polymer composites can be made by dispersing electrically conductive particles such as silver (Ag), copper powder, carbon nanotubes (CNTs) etc. in a polymer base. Polymers are usually dielectric in nature and are often use as insulators of electricity however when conducting nanoparticles are dispersed uniformly within the polymers matrix they became semiconductors and the electric conducting part is largely dependent on the forces or phenomena acting on the nanocomposite hence they act as sensors. The main factor inducing the nanocomposite conductivity is the concentration of the nanofiller particles, at low filler content the conducting medium between the adjacent nanoparticles, the transport charge is not efficient and conductivity is very low. As the nanoparticle concentration is increased conductivity gradually rises because resistance to charge transport get relaxed until at the percolation threshold when conductivity precipitously increases (Blythe and Bloor, 2005).

Polymers such as epoxy resin, has a low percolation threshold due to active percolation routes, which happen during the curing process, preceding gelation (Sandler et al., 2003). Current findings show that the networks of electrical conducting particles in epoxy resin react to mechanical loading and is being utilized for sensing stress-/strain and damage detection in polymer composite material (Boger et al., 2008). Therefore, this paper is reporting the characterization of OPA and CB obtained from the pyrolysis of OPA. The work also investigated the electrical conductivity performance of CB at different filler loading in epoxy resin.

DETAILS EXPERIMENTAL METHOD

Materials and Procedures

OPA was obtained from an oil palm mill in Bota, Perak, Malaysia. The distilled water was used to wash the ash and stored for 48 hours in an oven at a temperature of 100 °C. The ash was sieved using 60 μ m sieve and subjected to the process of pyrolysis in the furnace equipped with nitrogen flow at 1000 °C for 3 h. The obtained carbon black (CB) is ground using Fritsch pulverisette and then ball Milled for 6 h.. 4.8g representing 15%wt CB was dissolved in methanol and stirred at 500 rpm until they are well dispersed, this was followed by ultrasonication for 30 minutes, 20g of epoxy resin (DGEBA) was then poured into the mixture and the mixture is further stirred with a high speed mixer at 1000rpm for 30 minutes and then ultrasonicated to obtain good dispersion and the mixture was heated to 76°C to evaporate the methanol, 12g of hardener was added and stirred

using a mechanical stirrer at a high speed to obtain a homogenous suspension. The suspension was poured into a mold with dimension 50 x 50 x 5mm and cured at ambient temperature for 24 hours. This procedure was repeated for 20, 22, 24, 26, 28, 30, 32 and 33%wt of CB. To obtain the conductivity of the sample of compacted conductive filler was placed in between two aluminum plate to obtain their resistance R to electricity using a DT9205A digital multimeter and the conductivity is obtained using the formula in equation (1) and (2) below

$$R = \rho \frac{L}{A} \tag{1}$$

Where L is the length, A being cross-sectional area of sample and ρ is the resistivity, the conductivity is given by

$$C = \frac{1}{\rho} \tag{2}$$

The characterization of the OPA was done using FESEM, TEM, FTIR and SAP analyses.

Field Emission Scanning Electron Microscope

The elemental constituent, particle size and surface morphology of raw and derived conductive Filler were investigated using a variable Pressure Field Scanning Electron Microscope model Zeiss Supra55 VP equipped with energy dispersive x-ray (EDX) microanalysis system which senses the x-rays emitted from the sample because of the high-energy electron beam piercing into the test piece. The x-ray spectra were obtained and analyzed, resulting in a quantitative information of the elemental constituent of the test piece. A routine was utilized, which results to in accuracy of 1-2% and sensitivities for some elements down to 0.1 weight percent.

Fourier Transform Infrared Spectroscopy

Elemental studies including the functional group of the OPA was examined using FTIR spectrometer model Pelkin Elmer, Spectrum One. 0.5g of OPA sample is placed on the ATR which consists of a diamond crystal in the center of the mounting plate, the sample is placed over the crystal and the infrared (IR) beam is directed from the bottom to a depth of about 1-2 μ m and information about the infrared radiation at all frequency is collected for the sample.

Transmission Electron Microscope

A Zeiss Libra 200 model TEM was used for the morphological studies of OPA samples, the sample was dispersed in methanol solvent using sonication for 30 minutes, The OPA sample was observed to have dispersed in the solution the during sonication process, yielding a homogeneous suspension of the sample. Drops of the suspension were placed on lacey carbon grids for electron microscopy analysis. Zeiss Libra 200/FEG transmission electron microscope, working at 200 kV with Koehler illumination. initially, the area having OPA sample was found in TEM mode and using a condenser aperture of 15 μ m and a convergent beam size of 5 nm, the large angle dark-field STEM imaging utility of the Libra was used to acquire a scanning image of the located area as shown in fig. 1. to acquire a clear diffraction pattern, the STEM stationary beam utility of the Libra was then use to create a small, nearly parallel beam with a diameter of 300 nm.

Surface Area Analyzer and Porosimetry

The OPA sample was also characterized for its surface area properties by using a Micromeritics ASAP 2020 and porosity analyzer. The pore textural properties including Langmuir and BET specific surface area, pore volume, and pore size were obtained by analyzing the nitrogen adsorption and desorption isotherms with the aid of Micromeritics ASAP 2020 built-in software. Firstly the sample was degassed in situ at 300^oC for 4 h to remove any foreign molecule from the pores of the OPA sample.

RESULTS AND DISCUSSION

TEM Image

Fig 1 shows the TEM image of the raw OPA sample showing traces of carbon Black with cellular cell structure.



Fig 1: TEM image of Obtained OPA

3.2. FESEM Image

The FESEM image (Fig.2A) revealed medium sized particle with crushed shapes structure, the shape differ from spongy and porous structure reported by Jaturapitakkul et al., 2007 but with cellular texture with somewhat regular spaces. Fig. 2B shows the FESEM image of the obtained electrically conductive filler with evidence of spherical nanoparticle of diameter 77.9-140.9nm.



Fig 2: FESEM image of (A) obtained OPA and (B) the produced CB

FTIR spectrum of obtained OPA

The FTIR spectrum of raw OPA obtained at mid-infrared region is shown in Fig. 3. The broad absorption band at 3392.86 cm⁻¹ which is between 3400-3500cm⁻¹ showing the stretching vibration of OH groups and

silanol hydroxyl groups of silica which stick it self to the OPA (Ismail and Shaari, 2009), (Najib, 2007) or the N-H stretching vibration fee Imines, the strong and weak band at 883.65cm⁻¹ and 705.28cm⁻¹ represent isolated aromatic C-H and C-Br alkyl functional group and the medium intensity 1384.92cm⁻¹ indicate the presence of methyl CH₃.



Fig.3: FTIR spectrum of obtained OPA

Surface Area Analyzer and Porosimetry system

Adsorptive properties of a molecular cross-sectional area of 0.162 nm² and inside diameter of sample tube: 9.53 mm and The Surface area analysis is as shown in Table 1.

Table 1: Surface Energy

Energy (e/k)	Cumulative Area (m ² /g)	Incremental Area (m ² /g)	
98.00	4.401	0.000	
100.00	4.440	0.039	

EDX Spectrum of obtained OPA

Fig.4A shows the area of interest for the EDX analysis of raw OPA which is obtained as in Fig. 4B.



Fig 4: (A) area of interest for the EDX analysis, (B) EDX image of obtained OPA

The EDX spectrum of raw OPA shows that it contained a high weight of potassium about 34.71%, other elemental components include silicon 4.71%, calcium 3.79% and chlorine 7.06%, present in small %weight include phosphorus, aluminum and sulphur, the high %weight of oxygen is an indication that element like Si, Al and Mg exist in their oxide form (see Table 2)

Element	Ο	Si	Cl	K	Ca
Weight %	46.81	4.71	7.06	34.71	3.79

Table 2: Elemental Analysis of Obtained OPA

XRD Image of OPA

The XRD which is a mechanical means of expressing x ray strength as a function of the angle between the incident and the diffracted beam was used to obtain a diffractogram of OPA with peak indicating the traces of K, Ca, Mg (0.98%) and CO (0.88%), with significant presence of Al (5.1%), Si (12.9%), O (36%). Fig. 5 below shows The existence of significant crystalline peaks at 5°, 28° and 41.5° is indicative of the existence of crystal structure. Amorphous structure exists between $10^{\circ}-26^{\circ}$ and $30^{\circ}-39^{\circ}$, the area covered by the crystalline peak is indicative of high crystallinity index or degree of crystallinity. The Crystallinity index is calculated as 52.2% using the equation

$$CI = \frac{A_{cr}}{A_{Total}} \times 100\%$$

Where A_{cr} is the area covered by the crystalline structure and A_{Total} is the total area under the graph.



Fig. 5:XRD diffractogram for Opa (2°-41.5°)

Electrical Conductivity Performance of CB

The result shows that electrical conductivity of the nanocomposite depends on the CB nanofiller loading, Fig 5 clearly shows the relation between weight fraction of CB and the electrical conductivity. At low filler loading, the CB nanoparticles are insulated from each other within the matrix resulting in low or no conductivity.



Fig 6: Relationship between CB Filler loading and Conductivity of Nanocomposite

(2)

There is a transition from the insulating property of epoxy to a conductive nanocomposite at 14% wt of CB with a conductivity of about 32.25 S/m, further loading increases the conductivity until a percolation threshold is observed at 19-24% wt of CB with maximum conductivity observed at 33% wt of CB. Any further loading does not change the conductivity of the nanocomposite.

CONCLUSIONS

OPA which contains a high content of silicon and oxygen was carbonized to obtain an improved conductive filler with particle size distribution of OPA was reduced from 60μ m to about 77.9-140.9nm. The study showed that OPA has good potential to be used as nanofiller for the improvement of material such as a polymer. The conductivity of the composite indicated well dispersed conductive filler with a suitable network of the conductive particle within the epoxy matrix. Though the result showed that a smart material can result from this findings, there is research opportunity to improve the conductivity of the obtained CB from OPA and subsequently the nanocomposite.

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