Carbon Nanofiller-enhanced Ceramic Composites: Thermal and Electrical Studies

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The present research is focused on the manufacturing and analysis of the thermal and electrical properties of advanced ceramics from alumina (Al_2O_3) with carbon nanofiller (CNF) from oil palm ash (OPA). The oil palm ash was used to produce carbon black nanofillers with a size of 50 to 100 nm *via* a ball milling process after undergoing pyrolysis in a furnace at 1000 °C. CNFs were added to the alumina at varying weight fractions and sintered at 1400 °C for the production of CNF ceramic composites. The coefficient of thermal expansion (CTE), electrical conductivity (EC), and electrostatic discharge (ESD) of the ceramic composites were measured. The CTE did not increase with increasing CNF weight and behaved like an alumina matrix. The EC (I-V) showed positive results with increasing CNF weight. The ESD measurement gave predictable results on the dissipative characteristics of ceramic composites due to the insulating nature of alumina with the addition of CNF. Thus, the addition of OPA to alumina may present a suitable route for improving the electrical properties of advanced ceramics.

Keywords: Alumina; Oil palm ash (OPA); Thermal coefficient (CTE); Electrostatic discharge (ESD); Voltage –current (IV)

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INTRODUCTION

The use of high-performance, advanced composites for engineering applications geared toward demanding working conditions has seen increased growth in recent years. To ensure safety and economic efficiency, these composites should provide superior properties as well as low weight and high resistance to degradation. Due to their superior mechanical performances and low density, these composites are also considered for applications where a certain degree of electrical conductivity and expansion are required.

Oil palm ash (OPA), the waste produced by the industrial use of oil palm, has been studied by several researchers for its potential as a filler in composites with positive reviews (Ismail and Haw 2008; Ismail and Shaari 2010; Bhat and Abdul Khalil 2011; Abdul Khalil *et al.* 2013). Because OPA is a natural fiber with high carbon content, there is an increasing interest in utilizing oil palm waste as a renewable source of OPA. The mechanical, thermal, physical, and morphological properties of composites have been shown to improve upon the incorporation of OPA into the composites, with some variation due to filler loading (Ismail and Haw 2008; Ismail and Shaari 2010; Abdul Khalil *et al.* 2013), the compatibility of raw materials with OPA (Bhat and Abdul Khalil

2011), and the size of filler particles (Bhat and Abdul Khalil 2011). Fillers often favorably stiffen the material and increase the strength under certain load conditions. However, they have a detrimental effect on the material's toughness and resistance to impact. Nano-sized fillers have increasingly been used in recent years as reinforcement elements in polymers to improve the mechanical, thermal, and/or electrical properties of composites. The particle size, morphology, surface treatment, amount, and dispersion homogeneity within the matrix all strongly influence the performance of the nanocomposite.

Advanced nanocomposites have gained popularity for their wide range of engineering applications. Many researchers have also demonstrated the use of nanostructured materials such as nanoapatite, nanoclay, and nanofibers (polymer-based or carbon nanotubes) as reinforcements to enhance the mechanical and electrical properties as well as thermal stability (Lau *et al.* 2009). The use of carbon nanoparticles improves thermal shock resistance due to their low thermal expansion, high thermal conductivity, and low modulus of elasticity, although they do increase oxidation (Amin *et al.* 2009). The addition of a small amount of carbon nanotubes (CNTs) and carbon nanofillers (CNFs) will considerably improve the mechanical, thermal, and/or electrical properties of composites (Riggs *et al.* 2000). OPA, as a precursor of carbon black, is a form of amorphous carbon that can be transformed into nano-sized materials with an extremely high surface-area-to-volume ratio, electrical conductivity, low cost, porosity, malleability, and good chemical and electrochemical resistivity (Mudimela *et al.* 2009). The addition of CNF into the ceramic matrix enhances the electrical properties of insulating ceramics, allowing electrical discharge while other properties of the ceramic are either preserved or improved.

This study has been carried out to determine the effects of varying load percentages of OPA CNF in an alumina matrix on the thermal and electrical properties of the composite. Characterization of OPA CNF has also been performed to understand the particle geometry and the interaction between the CNF and alumina matrix.

EXPERIMENTAL

Materials

OPA was collected from a palm-oil processing mill in Penang, Malaysia, and was dried in an oven at 105 °C for 24 h. The dried OPA was sieved through a 60-mesh sieve to remove oversized particles. The OPA particles were pyrolyzed at a temperature of 1000 ºC in a laboratory furnace to increase the purity of the carbon. The resulting OPA powder was further ground using a grinder/refiner, followed by high-energy ball milling for 30 h at 170 rpm to produce nanofillers (Swami *et al.* 2009). CNFs that were 50 to 100 nm in size were chosen for the study. Alumina (Al_2O_3) having an average monolithic particle size of 0.5 μm and 99% purity (Martinswerck, Germany) was chosen as a base material for the ceramic matrix.

The ceramic composites for the study were prepared from alumina and various CNF loadings, *i.e.*, 0.00%, 0.05%, 0.1%, 0.5%, and 1.0%. Both the alumina and the CNF powders were mixed together evenly and pressed at 295 MPa using a hydraulic press. The CNF ceramic composites were then sintered in a Lenton electric hearth vacuum furnace at 1400 °C for 4 h with a 5 °C/min sintering rate. At least 10 samples were prepared for each type of CNF ceramic composite. These samples were tested for their thermal and electrical properties.

Methods

Characterization of OPA CNFs

The OPA CNFs were analyzed with a field emission scanning electron microscope (FESEM) (A LEO Supra 50 Vp, Carl-Zeiss SMT, Oberkochen, Germany) equipped with an energy dispersive X-ray spectrometer (EDX) (Leica Cambridge S-360 SEM.), a transmission electron microscope (TEM) (Philips CM12 Instrument, Germany), and an X-ray diffractometer (XRD) (Philips PW1050 X-pert) to determine their morphology, structure, and crystallinity index, respectively. The crystallinity index of OPA CNFs was calculated from XRD spectroscopy data using the peak deconvolution method. Each of the crystalline peaks was extracted using a curve-fitting process by a peak fitting program that assumed Gaussian functions for each peak. The crystallinity index is calculated from the ratio of the area of all total crystalline peaks (A_{Cr}) to the total area (A_{total}), as mentioned in Eq. 1 (Abdul Khalil *et al*. 2011).

$$\text{Crystallinity index} = \frac{A_{\mathrm{Cr}}}{A_{total}} x\ 100 \tag{1}$$

Coefficient of thermal expansion (CTE)

Linseis thermal expansion equipment was used to measure the coefficient of thermal expansion of CNF ceramic composites in the form of a bar having the dimensions of 12 ± 0.01 mm (length) x 5 ± 0.01 mm (width) and 4 ± 0.01 mm (thickness). Equation 2 was used to measure the CTE,

$$l_f - l_0 / l_0 = \alpha\ (T_f - T_0) \tag{2}$$

where l_0 and l_f respectively represent the original and final lengths with a temperature change from T_0 to T_f. The parameter α (CTE) is called the linear coefficient of thermal expansion and has units of reciprocal temperature (K^{-1}).

Electrical conductivity (EC) I-V

The CNF ceramic composite was transformed into a tabular dimension having a diameter of 11.50 ± 0.01 mm and a thickness of 3.14 ± 0.01 mm. The EC was measured according to the ASTM D4496 standard using a Keithley 4200-SCS parameter analyzer (USA) with a ± 5 V supply to measure the current in mA of the CNF ceramic composite.

Electrostatic discharge (ESD)

A CNF ceramic composite having a size similar to the EC was used to measure the surface resistivity at ground level with a universal resistance checker (A-400, USA).

RESULTS AND DISCUSSION

Characterization of Nano-structured OPA

Figure 1 demonstrates that the OPA CNFs have rough surfaces and irregular, crushed shapes (Ooi *et al*. 2013). OPA was reported as having a similar structure, though the particles were not nano-sized. Similar results were also reported in earlier experiments (Paul *et al.* 2007), which revealed similar shapes in nano-sized fly ash, where the size reduction and the irregularities in size and shape were developed during high-energy ball milling. A TEM micrograph showed that the average particle size was close to 50 nm, with particle sizes ranging from 50 to 100 nm (Fig. 2). This size reduction in OPA particles was due to the processing of particles for extended periods of time in the ball milling process, causing the surface area of the materials to become bigger.

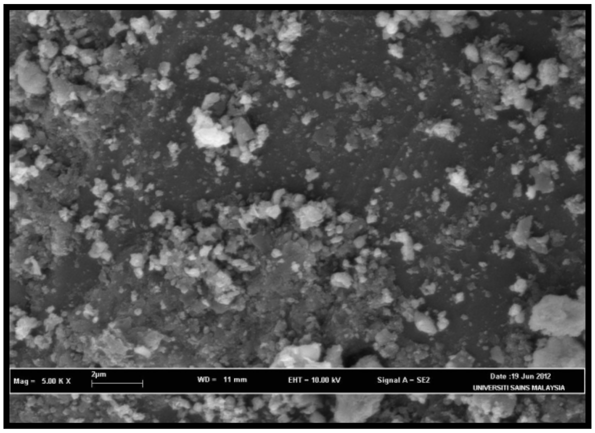

Fig. 1. SEM micrograph of OPA CNFs (3000x)

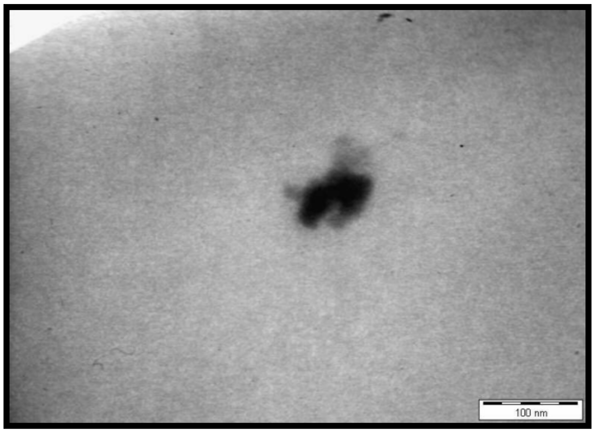

Fig. 2. TEM micrograph of OPA CNF

The EDX spectrum (Fig. 3) showed that the OPA contained a high weight percentage of carbon (C), which was 49.85 wt. %. Other elemental components included silicon (31.45 wt. %) and calcium. Due to high weight percentages of oxygen (30.25 wt. %), it can be assumed that silicon and calcium might exist in oxide form. In some studies, it was reported that OPA contained significant amounts of silicon (Ooi *et al.* 2013), which could reach up to 40% (Zainudin *et al*. 2005). The mineral composition of ash is very complex because it is formed after vaporization, melting, crystallization, vitrification, condensation, and precipitation (Saikia *et al*. 2006) which might be the cause of this elemental variations in ash.

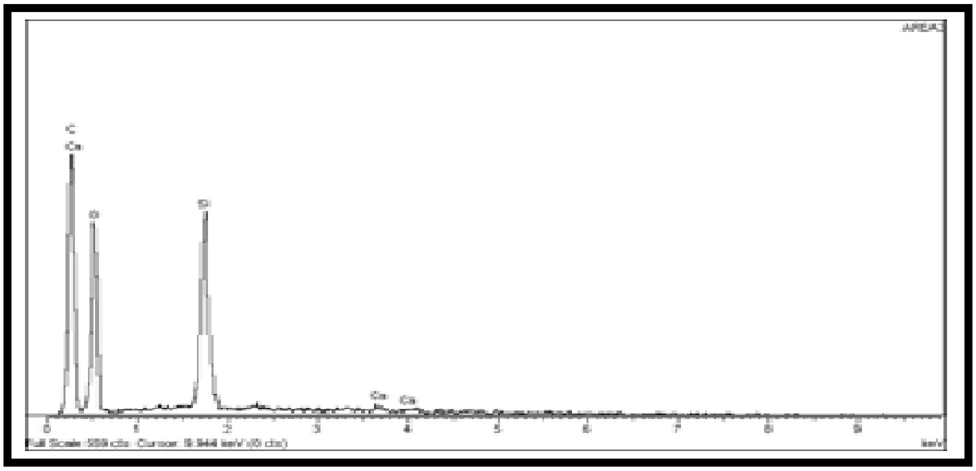

Fig. 3. EDX analysis of OPA CNFs

The crystallinity index of OPA CNFs was calculated from XRD spectroscopy data using the peak deconvolution method and was found to be 61.9% (Fig. 4). OPA exhibited a high degree of crystallinity because it contained various minerals in oxide form, such as silicon, magnesium, and calcium, which generally form crystals.

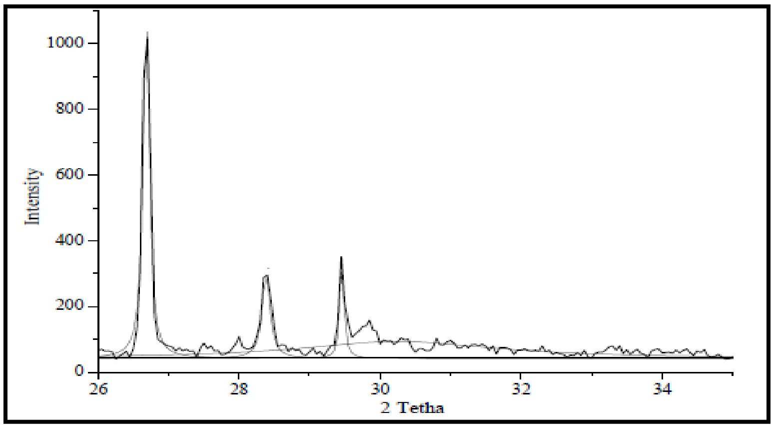

Fig. 4. XRD spectrum of OPA CNFs

CTE of CNF Ceramic Composites

Over small temperature ranges, the thermal expansion of uniform linear objects is proportional to the change in temperature. Table 1 shows the CTE of a CNF ceramic composite, which did not show significant changes in relation to the CNF increase. Alumina, being resistant to thermal expansion, has a CTE of 8.4 x 10^{-6}/°C and can expand at temperatures up to 1600 °C (Amin *et al.* 2009). An increase in OPA CNF did not yield positive results for thermal expansion; rather, they were almost the same as the alumina's CTE. The ceramic composites showed strong interatomic bonding forces, which is reflected in the comparatively low coefficients of thermal expansion; values typically range between about 0.5 x 10^{-6} and 15 x 10^{-6}(°C)$^{-1}$ (Callister and Rethwisch 2007).

Table 1. CTE *versus* CNF wt.% for CNF Ceramic Composite

OPA CNF Loading (%)	**CTE $10^{-6}(^0C)^{-1}$** Average	Std Dev
0.00	8.415	0.224
0.05	8.426	0.277
0.10	8.427	0.242
0.50	8.430	0.241
1.00	8.451	0.186

Amin *et al.* (2009) showed that the relative heat resistance of composites increases with an increase in carbon black. This can be correlated to the filling of pores and voids in the alumina matrix by CNFs, which leads to a higher relative heat resistance. Therefore, there is no significant change of CTE with an increase of CNF in the alumina matrix. Moreover, carbon fibers themselves have a negative CTE, meaning that they shrink when they are heated. This result is attributed to the ability of compressible carbon black to absorb the expansion of alumina grains (Khalil 2004). Thermal expansion is due to the asymmetric curvature of the potential energy trough, rather than the increased atomic vibrational amplitudes with rising temperature (Ruoff and Lorents 1995). The loading of extra CNFs into alumina matrix did not give a change of alumina matrix and maintained the original characteristics of alumina in terms of thermal expansion.

EC of CNF Ceramic Composites

It is well known that ceramics such as alumina are among the leading candidates for insulators, radiofrequency windows, and feed-through applications in magnetic fusion reactors (Carter 1985). Current-voltage (I-V) behavior is one of the most important basic electrical properties and can provide insight into the phenomena responsible for the ohmic or nonohmic behavior of semiconductors and insulators (Shiiyama *et al.* 1998). Figure 5 shows that an increase of CNF in the alumina matrix subsequently yields a higher current. At 0.5 and 1% CNF, ceramic composite conducted close to 3.0E-10 mA of current compared to 0.05% and 0.1% CNF loading. This additional CNF gave the availability of free charge, which was carried in the alumina matrix. It has been shown that carbon black particles effectively form an additional conductive network in composites (Du and Jana 2007) by increasing the number of conductive channels when the carbon black percentage is increased (Ji *et al.* 2010). Similar studies using clay and carbon black with a ratio of 2:1 have also been performed, and it was found that electrical conductivity increased with increasing carbon black in the composite (Etika *et al.* 2009). However, the conductive performance of carbon black depends on the type of carbon black, the quality of its dispersion, and the steps by which it is processed (Aman *et al.* 2011).

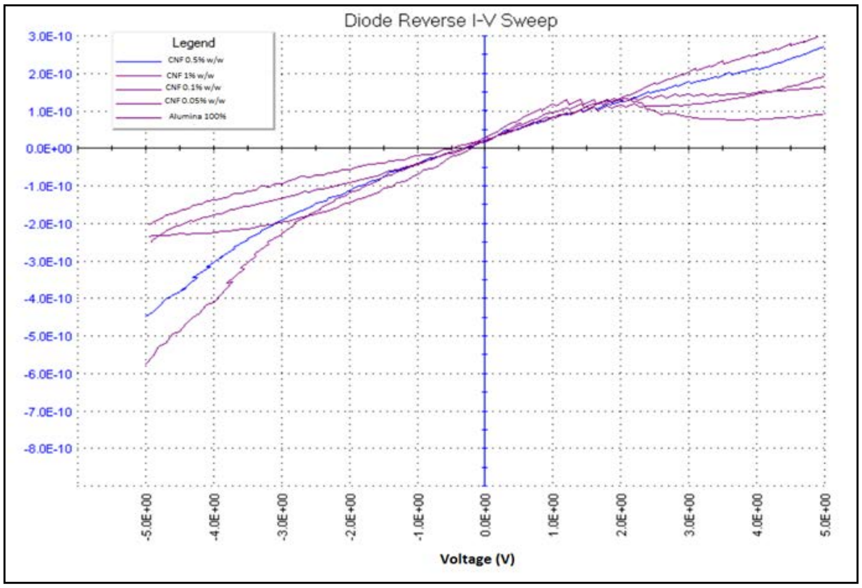

Fig. 5. Voltage-current relationship for CNF wt. % filled ceramic composites

ESD of CNF Ceramic Composites

Table 2 shows that an increased CNF percentage in ceramic composites caused them to become static-dissipative in nature. The addition of carbon nanotubes greatly enhanced the electrical properties of insulating ceramics, allowing electrical discharge machining to be used in the manufacture of complex parts (Malek *et al.* 2011). This property is very important for packaging because it can allow the charge to be drained safely away from a sensitive electronic device (Tenbohlen *et al.* 2010). Adding electrically conductive fillers such as carbon black into a polymer matrix increases its conductivity by several orders of magnitude, making the resulting composites suitable for applications of antistatic dissipation and ESD protection (Konter *et al*. 2009).

Table 2. CNF Wt. % Loading in Alumina Matrix and ESD Measurement Range

CNF load (%)	ESD ohm.mm
0.0	$\geq 1 \times 10^{11}$
0.05	$\geq 1 \times 10^{10}$ to $< 1 \times 10^{11}$
0.1	$\geq 1 \times 10^{9}$ to $< 1 \times 10^{11}$
0.5	$\geq 1 \times 10^{9}$ to $< 1 \times 10^{11}$
1	$\geq 1 \times 10^{6}$ to $< 1 \times 10^{11}$

CONCLUSIONS

1. CNF from OPA was successfully produced with particle sizes ranging from 50 to 100 nm by a high-energy ball milling process; the CNF had a crystallinity index of 61.9%.
2. Minimal thermal expansion was observed after loading CNF into a ceramic matrix, while other properties remained the same. This makes the composite resistant to thermal shock, which is important for high-temperature applications.
3. Electrical conductivity increased with the addition of CNF in the ceramic composite, which means that the new composites may be suitable for applications in electrical and semiconductor arenas. They may also be suitable for electronic packaging.
4. The addition of CNF in the ceramic matrix resulted in a composite with a static-dissipative nature, which is ideal for use in the semiconductor, data storage, and aerospace industries.

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