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Tanggal: Selasa, 16 Juni 2015 11.43 WITA

Dear Enih,
Salam, Please refer to the attachment.

Thank You
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From: **Advanced Composite Materials** <em@editorialmanager.com>
Date: Mon, Jun 15, 2015 at 9:39 AM
Subject: Your Submission
To: "H.P.S Abdul Khalil" <akhalilhps@gmail.com>

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Properties enhancement using oil palm shell nanoparticles of fibers reinforced polyester hybrid composites
Advanced Composite Materials

Dear Prof Abdul Khalil,

Reviewers have now commented on your paper. You will see that they are advising that you revise your manuscript. If you are prepared to undertake the work required, I would be pleased to reconsider my decision.

For your guidance, reviewers' comments are appended below.

If you decide to revise the work, please submit a list of changes or a rebuttal against each point which is being raised when you submit the revised manuscript.

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Yours sincerely

JOUNG-MAN PARK, Ph.D.
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Reviewers' comments:

Reviewer #1: This paper studied property enhancement by integrating oil palm shell into fiber reinforced composites. The paper shows originality and is well organized. However, the following minor corrections are necessary.

1. In abstract, it is better to specify the content of OPS was by weight fraction. So that readers easily recognize it.

2. The following sentence In Section 4.2.1 should be corrected.
"Table 1 presents the theoretical density, measured density and void content of OPS nanoparticles in kenaf-coconut-kenaf fiber reinforced composite."
The sentence means that the authors measured density and void content of OPS nanoparticles in the composites. How the authors obtained void content of OPS in the composites?
It sounds like the density and void content were composites's properties rather than OPS's properties. I think the sentence should be corrected.

3. In Section 4.2.2, the tensile property (tensile strength, tensile modulus, and tensile toughness) degradation of 5 wt% from 3 wt% composites was not explained. It should be explained.

4. The section numbers should be corrected, 4.2, 4.2.1, and 4.2.2 to 3.2, 3.2.1, and 3.2.2.

5. For Figures 3 and 4, each figure's indication '(a), (b) and (a), (b), (c), (d)' should be specified. So that readers will not be confused.

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Advanced Composite Materials

Properties enhancement using oil palm shell nanoparticles of fibers reinforced polyester hybrid composites

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Abstract:	Oil palm shell (OPS) nanoparticles were utilized as filler in fibers reinforced polyester hybrid biocomposites. The OPS nanoparticles were successfully produced from the raw oil palm shell by using high energy ball milling process. Fundamental properties including morphology, crystalline size and particle size of the OPS nanoparticles were determined. Tri-layer natural fiber reinforcement (kenaf-coconut-kenaf fiber mat) polyester hybrid biocomposites were prepared by hand lay-up techniques. The influences of the OPS nanoparticles loading in the natural fibers reinforced polyester hybrid biocomposites were determined by analyzing physical, mechanical, morphological and thermal properties of the composites. Results showed that the incorporation of the OPS nanoparticles into the hybrid biocomposites enhanced the composite properties. Further, the natural fibers reinforced polyester hybrid composite had the highest physical, mechanical, morphological and thermal characteristics at 3 wt% OPS nanoparticles loading.
Response to Reviewers:	Dear Editor, Thanks to reviewer for his useful comments and suggestions to improve the manuscript quality. However, the manuscript has revised with amending the reviewer comments and suggestions. The changes made in the manuscript have marked in

	yellow color. Please find the response has take on the reviewer comments, below Sincerely, Prof. Abdul Khalil HPS Reviewer Comments 1: In abstract, it is better to specify the content of OPS was by weight fraction. So that readers easily recognize it. Action taken: Specified to 3 wt.%. Revewer Comments 2: The following sentence In Section 4.2.1 should be corrected. "Table 1 presents the theoretical density, measured density and void content of OPS nanoparticles in kenaf-coconut-kenaf fiber reinforced composite." The sentence means that the authors measured density and void content of OPS nanoparticles in the composites. How the authors obtained void content of OPS in the composites? It sounds like the density and void content were composites's properties rather than OPS's properties. I think the sentence should be corrected. Action taken: Corrected to: Table 1 presents influence of OPS nanoparticles on density (theoretical and experimental) and voids content of natural fiber reinforcement hybrid composites Reviewer comments 3: In Section 4.2.2, the tensile property (tensile strength, tensile modulus, and tensile toughness) degradation of 5 wt% from 3 wt% composites was not explained. It should be explained. Action taken: Amended the degradation of 5 wt% from 3 wt% OPS loading in composite: The deceased of tensile properties (tensile strength, tensile modulus, and tensile toughness) with an increase of OPS nanofiller from 3% to 5% was due to the agglomeration of the nanofiller with the higher loading, which influences the stress transfer mechanism and poor wetting the polymer systems [25]. Reviewer Comments 4: The section numbers should be corrected, 4.2, 4.2.1, and 4.2.2 to 3.2, 3.2.1, and 3.2.2. Action taken: Corrected. Reviewer Comments 5: For Figures 3 and 4, each figure's indication '(a), (b) and (a), (b), (c), (d)' should be specified. So that readers will not be confused. Action taken: Added.

Properties enhancement using oil palm shell nanoparticles of fibers reinforced polyester hybrid composites

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Abstract

Oil palm shell (OPS) nanoparticles were utilized as filler in fibers reinforced polyester hybrid biocomposites. The OPS nanoparticles were successfully produced from the raw oil palm shell by using high energy ball milling process. Fundamental properties including morphology, crystalline size and particle size of the OPS nanoparticles were determined. Tri-layer natural fiber reinforcement (kenaf-coconut-kenaf fiber mat) polyester hybrid biocomposites were prepared by hand lay-up techniques. The influences of the OPS nanoparticles loading in the natural fibers reinforced polyester hybrid biocomposites were determined by analyzing physical, mechanical, morphological and thermal properties of the composites. Results showed that the incorporation of the OPS nanoparticles into the hybrid biocomposites enhanced the composite properties. Further, the natural fibers reinforced polyester hybrid composite had the highest physical, mechanical, morphological and thermal characteristics at 3 wt% OPS nanoparticles loading.

Keywords: Hybrid composite; Natural fiber; Polymer-matrix composites; Mechanical properties; Physical properties.

1. Introduction

With increasing ecological safety concern, the natural fibers are increasingly in demand across a wide range of polymer composite application [1]. Natural fiber offers potential advantages over synthetic fibers such as abundant availability, lost cost, low density, degradable and renewability; which turns the natural fiber as a potential replacement of synthetic fibers to be used as a filler/ reinforcement in polymer composites [1-3]. Studies reported that the utilization of natural fiber as reinforcement materials in polymer composites

would minimize materials cost and make the composite partially biodegradable [3, 7, 8]. [2, 4-8]. Taking into consideration of raising environmental awareness, natural fibers can be considered as the most promising material in advanced composites engineering applications [9].

In a hybrid composite, two or more reinforcements are utilized into a single matrix to gain the composite properties diversity [10]. Therefore, designing the hybrid composite with apposite combination of reinforcements and filler is urged to gain superior strength performance in numerous innovative applications [11]. The performances of hybrid composites primarily rely upon the fiber content, length of individual fibers, orientation, extent of intermingling of fibers, fiber to matrix bonding and homogenous distribution fibers reinforcement and filler matrix into the composite [7, 11]. Studies have been conducted on the preparation and characterization of hybrid composites using thermoplastic matrix as reinforcement and conventional fillers [12-14]. Wherein, nanoparticles are being utilized as an alternative tool for enhancing mechanical and thermal properties of natural fiber reinforced polymer composites [15-17]. There is a few studies have been conducted using nano structured particles as filler.

Nanoparticles, due to nano size, would offer the matrix high surface area. However, the utilization of inorganic nanoparticles in polymer composite is challenging, since the homogenous dispersion of inorganic nanoparticles into the polymer matrix is difficult to ensure [15, 18]. Inorganic nanoparticles have the tendency towards agglomeration. Therefore, the use of inorganic nanoparticles as a filler might lead the materials deterioration, decrease the mechanical and thermal properties of polymer composite [7,19]. Besides, synthetic fibers arises ecological concern and health hazard to the personnel involved in the manufacturing composites [20, 21]. In recent years, lignocellulosic materials have been utilized an

alternative of conventional fiber in the development of polymer composite due to environmental friendly nature. However, the use of lignocellulosic materials in fiber reinforced polymer composite have certain limitation, including poor fiber/matrix interactions, water resistance and relatively lower durability [22, 23]. The weak interfacial bonds between highly hydrophilic natural fibers and hydrophobic non-polar organophilic polymer matrix might lead into a considerable decrease in physical, thermal and mechanical properties of composite. There are several approaches could be applied to overcome the deficiency of the natural fiber matrix compatibility including the introduction of nanoparticles into the fiber matrix [24, 15].

The oil palm shell is a lignocellulosic material, which is considered as agricultural waste [26]. Usually, OPS is burned or used as cover the surface of the roads in the plantation area. Although, the incorporation of nanoparticles in fiber reinforced polymer matrix have the possibility to gain optimal composite performance [27], combination of filler-resin with three-phase fiber reinforced composites is still in infancy. Therefore, the present study was conducted to produce three phased hybrid polyester composite. Wherein, the OPS nanoparticles was utilized as a filler in order to enhance the mechanical, physical, thermal and morphological properties of the prepared natural fiber reinforced hybrid composite.

2. Materials and Method

2.1 Materials

Woven kenaf fiber mat (250 x 200 mm^2) used in this research was procured from Nibong Tebal Paper Mills, Seberang Prai, Penang, Malaysia. Coconut fiber mat (250 x 200 mm^2) used in this research was provided by Ecofiber Technology Sdn. Bhd, Malaysia. The oil palm shell (OPS) chips were collected from Ulu Keratong palm oil mill, Segamat, Johor, Malaysia.

Unsaturated polyester resin P9509 and methyl ethyl ketone peroxide (MEKP) were obtained from Euro Chemo-Pharma Sdn. Bhd, Malaysia.

2.2 Preparation of Oil Palm Shell Nanofiller

The collected OPS chips converted into granular particles by grinding in the Wiley mill. Subsequently, OPS granular was sieved (60 mesh size) to separate micro-sized particles such as sand, stones and micro particle from the mill. Sieved OPS granular was then oven dried in the oven at 110°C for 24 h to reduce its moisture content. The dried OPS granular was ground and further sieved to a particle size fraction range of 2-2.8 mm. Fine OPS powder (total evaporable moisture content of 1.50%) was further grounded using high energy ball milling process at 170 rev min^{-1} for 30 h. Wherein, the ball mill was filled with a ball-to-powder weight ratio of 10:1 in a stainless steel chamber using stainless steel balls (diameter: 19 mm X 12.7 mm X 9.5 mm). The samples were then oven dried at 110°C for 24 h to prevent agglomeration and avoid contact with moisture.

2.3 Characterization of Oil Palm Shell nanoparticles

The morphology of OPS nanoparticles was determined by using Scanning Electron Microscope (Model: EVO MA10, Carl ZEISS). The samples were placed onto SEM holder using double sided electrically conducting carbon adhesives tapes to avoid surface charge on the specimens, when exposed to the electron beam. The specimen was then coated with a thin gold palladium layer using sputter coater Polaron SC515. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 5kV. The Energy Dispersion of SEM analysis of the OPS nanoparticles was conducted by Leica Cambridge S-360 SEM.

A Fourier Transform Infrared Spectroscopy (FT-IR) test was carried out to examine functional groups present in OPS nanoparticles. About 1 mg of OPS nano particles was mixed with 100 mg of KBr powder. Then, the powder mixtures were pressed into transparent thin pellets. Spectral outputs were recorded in the transmittance as a function of wave number and represented in a graph.

X-ray diffraction (XRD) (D8 Advanced, Bruker, Germany) analysis was performed by using Cu-Kal radiation at 40kV and 25 Ma and $\lambda = 1.54$ Å. About 2 g of OPS nano filler was run at a scan ratio of 0.05 degree/Sec. The X-Ray pattern was recorded in 2θ values range of 10º-90º. The crystallinity index (CI) was calculated using the following equation:

$$CI(\%) = \frac{I_{200} - I_{AM}}{I_{200}} \times 100 \quad (1)$$

where, I_{200}-I_{AM} is the height ratio between the intensity of the crystalline peak, and I_{200} is total intensity

The particle size OPS nanoparticles were measured using transmission electron microscope (TEM) image and particle size distribution analyses. The dried OPS nano filler was dissolved in acetone and dispersed with an ultra sonicator for ten minutes. Next, the sample was placed on copper grids and cloud with 2% uranyl acetate and Reynold's lead citrate. Finally, copper grids contained 0.1 µm samples were viewed under TEM (energy filter – Zeiss Libra® 120) at certain magnifications. Particle size distribution of OPS nanoparticles was assessed on a MALVERN Zetasizer Ver. 6.11, serial number: MAL 1029406 Nano Series by dynamic light scattering measurements by mean of a 532 NM laser. The analysis was repeated for three times according to the equipment internal setting.

The thermal properties of OPS nanoparticles were assessed by means of simultaneous thermogravimetric and differential thermogravimetric analyses by using A Perkin Elmer thermal gravimetric analyzer Pyris 1 TGA. About 4-5 mg of OPS nano filler was distributed evenly in an open platinum crucible used and heated from 30°C to 800°C under nitrogen at a heating rate 10°C/min.

2.4 Preparation of Polyester hybrid biocomposites

OPS nanofiller/polyester matrix was prepared with adding OPS nanoparticles (1% to 5%) into the polyester resin and then mixed using a mechanical stirrer for 15 min at 200 rpm prior to adding 1% MEKP as a curing agent. Tri-layer hybrid biocomposites (kenaf-coconut-kenaf) were prepared by keeping total fiber loading of both fibers at 40% by following hand lay-up techniques. Subsequently, the prepared hybrid biocomposites were immerged into OPS nanofiller/polyester matrix until the fibers melted. A stainless steel mold with dimensions 250 mm x 200 mm x 7 mm was used for soaking the fiber mats. Then, the molds were closed for cold press at 200 psi, and subsequently cure at room temperature for 24 h. Pure hybrid composite without filler was also prepared as a control.

2.5 Analysis of enhancement Properties of Fibers Reinforced Polyester hybrid biocomposites

2.5.1 Physical Properties

Composite density was measured according to the ASTM standard [28]. Composite samples were cut into the dimensions of 30 x20 x7 mm^3 according to standard prior to calculate the density. The density of the samples was calculated following the equation 2. The results were expressed as average value of 5 excremental runs.

$$Density(gcm^{-3}) = \frac{m}{v} \qquad (2)$$

where, m is the mass of the composites (g), v is the volume of the composites (m^3).

The void content in the prepared hybrid biocomposites was determined according to ASTM standard 1999 [29] as follows:

$$Void\ content(\%) = \frac{\rho_{theoretical} - \rho_{experimental}}{\rho_{theoretical}} \quad (3)$$

Wherein the *theoretical* was calculated as:

$$\rho_{theoretical} = \frac{1}{\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}} \quad (4)$$

where W_f is the reinforcement weight fraction, W_m is the matrix weight fraction, P_f is the reinforcement density and P_m is the matrix density.

2.5.2 Mechanical Properties

Tensile test was performed by using INSTRON 5582 universal testing machine. A rectangular composite sample with dimensions 120 x 20 x $7mm^3$ was used as per ASTM 2000 standard [30]. The gauge length was set at 60 mm with a crosshead speed 5 mm/min. Tensile properties including tensile strength, modulus, toughness and elongation at break were acquired from data recorded. In each case, five specimens were tested and the average value was tabulated.

Flexural properties including strength, modulus and toughness were determined by following three-point flexural testing method in accordance with ASTM 2003 standard [31]. The test was carried out using INSTRON (Model 5582) universal testing machine. The crosshead speed was 2 mm/min. Izod notched impact testing was performed by using GEOTECH testing machine (Model GT-7045 MD). The Impact strength was determined according to ASTM 2006 standard method [32].

2.5.3 Morphology Properties

Scanning Electron Microscopy (SEM) was used to determine the tensile fracture surface of the hybrid biocomposite. The test sample was coated with a thin gold palladium layer using sputter coater polaron SC515 to prevent electrical charge accumulation during examination. The fiber-matrix adhesion was then studied using SEM. The SEM micrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 5kV.

2.5.4 Thermal Properties

A Perkin Elmer thermal gravimetric analyzer Pyris 1 was used to study the thermal stability of the composites. The powder of composites (about 5mg) was distributed evenly in an open platinum crucible used and heated from 30°C to 800°C under a nitrogen atmosphere with a heating rate of 10°C/min.

3. Results and Discussion

3.1 Characterization of Oil palm shell nanoparticles

The Scanning Electron Microscopy (SEM) image revealed that OPS nano particle were crushed with irregular structural shape (Figure 1a). This happened probably due to the preparation of OPS nanoparticles using high energy ball milling process. Guo and Lua [33] observed that the OPS nanoparticles have the similar porosity with sufficiently solid density in both angular and irregular structural shaped. Similarly, Dungani et al. [34] reported the crushed and irregular structural shape of the OPS nanoparticles due to ball milling process. The elemental composition of the OPS nanoparticles was determined by Scanning Electron Microscopy equipped with Energy Dispersive X-ray Analysis (SEM-EDX), as presented in Figure 1 (b). Result shows that the presence of carbon (67.47 wt.%) and oxygen (43.04 wt.%)

in the OPS nanoparticle as major elements. Other elemental composition was detected in the OPS nanopartice are sodium, chlorine and indium. Similarly, Dagwa et al. [34] reported the presence of carbon (63.02%) and oxygen (36.04%) as major elements in the OPS nanoparticle.

Figure 2 (a) presents the TEM image of the OPS nanoparticles. The micrograph reveals nanomatriac irregular shape formation of the OPS nanoparticles with a size between 10 to 30 nm, without having any agglomeration. Moreover, the particle size analysis revealed the wide range of particle size distribution of OPS nanoparticles (Figure 2b). The average diameter of OPS nano particles was within the range of 50.75 to 91.28 mm. It was found that the size distribution intensity of the OPS nanoparticles was 75.30%. X-ray diffraction (XRD) analysis of oil palm shell (OPS) was conducted to investigate the crystalline index (CI) of the fillers. The-Ray Diffraction (XRD) pattern of OPS nano particles is shown in Figure 3(a). However, the crystalline index of OPS nanoparticles was found to be 34.56 %. This result proved that the OPS nanoparticles had the crystalline nature with the lower degree of crystalline index.

The thermal decomposition curves of OPS nanoparticles, analyzed by Thermogravimetric analysis **(**TGA), are shown in Figure 3 (b). It was observed that first stage of degradation occurred at temperature below 100°C, probably due to the evaporation of moisture present in the sample. Meanwhile, the second stage degradation occurred in 200 to 500°C temperature. The weight loss at this temperature region corresponds to the formation of volatile product arose from random scission and intermolecular transfer involving tertiary hydrogen abstractions from hemicelluloses, cellulose and lignin [35]. In this study, $T_{10\%}$ and $T_{50\%}$ were determined in the thermal degradation process OPS nanoparticles at 10% and 50 % weight losses, respectively. Wherein, $T_{10\%}$ is selected as T_{onset}. It was observed that $T_{10\%}$ and $T_{50\%}$

weight loss occurred at temperature of 187ºC and 280°C respectively. The constant weight was found at a temperature of 600 to 800°C. However, the total residual content was determined to be 0.84 % at 800 °C.

3.2 Oil palm shell nanaofiller in fiber reinforced polyester hybrid biocomposites

3.2.1 Physical Properties

The physical properties of the hybrid biocomposites including density, void content and water absorption were analyzed with varying the filler loading. Table 1 presents influence of OPS nanoparticles on density (theoretical and experimental) and voids content of natural fiber reinforcement hybrid composites. It was observed that the density was increased with filler loading. The density for hybrid composites without filler was 1.125 g/cm^3. Meanwhile, density of hybrid biocomposites with adding OPS nanoparticles from 1% to 5% increased the density from 1.133 gcm^{-3} to 1.141 gcm-^{3}. The finding indicated the hybridization of OPS nanoparticles into the fibers reinforced hybrid biocomposites would increase the density. However, the measured density values of hybrid biocomposites were slightly varied with the theoretical density values might be due to the presence of voids in composites [3].

The void content of the biocomposites decreased with increasing filler up to 3% from 5.143% to 4.933% (Table 1). This because of the OPS nanoparticles might replace into the void in matrix, which may reduce the void content of composites [27]. Homogenous dispersion of filler in polyester resin also is a possible reason for this low void content of hybrid prepared biocomposites. In contrary, the hybrid biocomposites with the incorporation of 5% filler loading had the highest void content (5.624%). This was probably due to the particle-to-particle interaction rather than particle-to-polymer interaction with higher amount of OPS nanoparticles at 5% loading. The particles tend to agglomerate and create lumps which

affected the interaction between polymer chains and reduced the cross linking, and thereby increased the void content in polymer itself [8].

3.2.2 Mechanical Properties

The influence of OPS nanoparticles on the mechanical properties including tensile properties, flexural properties and impact properties of hybrid biocomposites were evaluated, as presented in Table 2 and Table 3. It was observed that the tensile properties such as tensile strength, tensile modulus and tensile toughness increased with increasing nanoparticles loading up to 3% and decreased thereafter (Table 2). Hybrid composites without the addition of nanoparticles contributed the lowest tensile strength (30.10 MPa), tensile modulus (0.77 GPa) and tensile toughness (38.76J/m3). However, The addition of OPS nano filler into the composite increased the tensile strength, tensile modulus and tensile toughness of hybrid composite. Wherein, the highest tensile strength (37.56 MPa), tensile modulus (1.15 GPa) and tensile toughness (46.21 J/m3) were gained at 3% OPS nanoparticles loading into the hybrid composite. This result indicated the addition of nanoparticles in biocomposites played role in the increasing surface area, energy absorbing capability and minimizing free space within the hybrid composite, thereby enhanced tensile properties. This indicates that 3% filler loading of the OPS nanoparticles successfully increased the optimum polyester ability to transmit and distributed stress. Moreover, this scenario was also probably due to uniformity dispersion of the OPS nanoparticles in matrix, which creates better filler-matrix interaction and interface region with fibers. Thus, the loading transfer became easier and the sample was able to sustain more load resulting higher tensile strength of hybrid biocomposites. Homogenous dispersion of particles gave better filler-matrix interaction and better interface adhesion with fibers as well resulting increases in energy absorption. The deceased of tensile properties (tensile strength, tensile modulus, and tensile toughness) with an increase of OPS

nanofiller from 3% to 5% was due to the agglomeration of the nanofiller with the higher loading, which influences the stress transfer mechanism and poor wetting the polymer systems [25]. The Poor wetting between fibers and filler/matrix influenced tendency of voids formation in composites, which can be a stress point to reduce the tensile properties of composites. According to Neitzel et al. [36], nano particles have a strong tendency to gather each other and formed some aggregation thus minimized their surface area. The agglomerated filler particles would decrease filler-matrix interaction as a result reduced fiber-matrix adhesion interface.

The percentage elongation at break decreased with an increase of the OPS nanoparticles loading (Table 2). The high elongation at break (6.06%) was obtained without filler loading in hybrid biocomposites. Meanwhile, 5% filler loading had gained the lowest elongation at break (4.25%). This phenomenon occurred might be due to the high rigidity of OPS nano structure rather than the matrix. As high rigidity of OPS filler loading increased, it would restrict the chain mobility of matrix that was available for elongation [25]. Thus, lead to a higher breaking tendency (lower deformation) of the composites which in turn decreased the percentage elongation at break of composite. The increases of filler loading resulted in reduction of elongation at break might be due to the decrease of deformability of interface between filler and the matrix [36]

Table 3 represents the flexural properties including strength, modulus and toughness hybrid biocomposites with the incorporation of OPS nanoparticles. The flexural properties exhibit similar behavior with tensile properties. It was observed that the flexural properties increased with increasing the OPS nanoparticles loading up to 3%. However, an increase of OPS nanoparticles loading from 3% to 5%, decreased the flexural properties of the hybrid composite. The rate of the inter-particle interactions of the nanoparticles in biocomposites is

crucial, which may attribute to this trend of results [23]. It is understandable that homogeneous dispersion of filler improves interfacial interaction between filler-matrix hence reduce flexibility of chain polymer. Furthermore, the increasing filler loading means a higher surface area of the filler which increases effective bonding between fillers/matrix and results in higher flexural modulus of the biocomposites [25]. Factor level of dispersion of nano particles in matrix influenced increment by flexural toughness properties. Therefore, the deceased of flexural properties with an increase of OPS nanofiller from 3% to 5% might be due to the agglomeration of the nanofiller, which influences the stress transfer mechanism and high viscosity of polymer systems [25, 27].

The impact strength of hybrid biocomposites was found to increase with the increase of filler loading (Table 3). The high impact strength (13.5 kJ/m^2) of the hybrid composites was observed at 3% filler loading. Higher impact strength of nanocomposites is related with the rate dispersion of the nanofiller. Excellent homogeneous dispersion of nanofiller increased filler-matrix interaction and creates good interfacial adhesion with fibers. Hence, energy would be absorbed easily and crack propagation would be prevented, thus improve impact strength. In contrast, poor nano filler dispersion increases the tendency of particles to agglomerate and thus minimize its surface area. The agglomerated particles disturb the formation of better adhesion region between fiber-matrix therefore reduces the efficiency of energy absorption during crack propagation. This phenomenon explained the decrease of impact strength at 5% OPS nanoparticles loading into hybrid composite.

3.2.3 Morphology Properties

Figure 4 shows SEM images of the tensile fracture surface of natural fiber reinforced polyester composite with the incorporation OPS nanoparticles. It was observed that the

nanoparticles were not exhibited in the SEM micrographs of composites. This was might be due to the effective amalgamation of OPS nanoparticles with the matrix. It was apparent the fiber detachment and voids formation without loading filler in hybrid biocomposites, which implied weak adhesion between the fiber and the matrix (Figure 4a). The addition of OPS nanoparticles into the composite influenced the composite properties Figure 4b, 4c and 4d). At 1% OPS nanofiller loading (Figure 4b), it was observed that the surface of the hybrid biocomposites become smooth with minimizing the fiber detachment. Although, skin matrix formation of the composite was observed, the adhesion between fiber and matrix was poor. The presence of clean fiber pulling out from the composite was detected and there is a small gap between fibers and matrix (Figure 4b). Better skin matrix formation of the composite was observed with the increasing the OPS nanofiller loading from 1% to 3% (Figure 4c). Further, absence of fiber pulling out from the composite and the gap between fibers and matrix indicates that the effective adhesion between fiber and matrix in the hybrid biocomposites. However, there were some voids and fiber fracture was observed at 3% nanoparticles loading into the composite. The further increased of OPS nanoparticles loading from 3% to 5%, the occurrence of the fiber detachment and higher number voids were detected in the hybrid biocomposites (Figure 4d). The increase of the fiber pull out voids and the fiber detachment on the surface of natural fiber reinforced polyester composite were probably due to the poor wetting the fiber do the higher OPS nanoparticles content in polymer matrix [37].

3.2.4 Thermal Properties

Figure 5 shows the influence of OPS nanoparticles into natural fiber reinforced polyester hybrid biocomposites. It was observed that the biocomposites had the 2 stage degradations. Wherein, first stage degradation occurred below the temperature of 100°C and second stage degradation was observed at a temperature range of 200 to 550°C. The thermal degradation

temperatures ($T_{10\%}$ and $T_{50\%}$) and percentage of the char residue of hybrid biocomposites are tabulated in Table 4. It was observed that the thermal stability of hybrid biocomposites increased with increasing OPS nanoparticles loading into the thermal stability up to 3% and decreased with further increased of the nanoparticles loading (Figure 5 and Table 4). Results indicated that the incorporation of OPS nanoparticles enhanced the thermal stability of the natural fiber reinforced polyester hybrid composites. This was because of the inter-particle interaction of nano OPS nanoparticles consumed heat from the matrix, hence improved the thermal stability of hybrid biocomposites [38]. However, the reduction of the thermal degradation temperature at 5% OPS nanofiller loading into the natural fiber reinforced polyester hybrid biocomposites might be due to the agglomeration of OPS nanoparticles, which leads to decrease the molecular mobility restriction [39]. The decomposition of cellulosic materials at higher generates carbonaceous residues, which is known as char, which forms as a barrier heat source and polymeric materials. It was found that the percentage char residue increased with an increasing of OPS nanoparticles into hybrid composite (Table 4). However, the highest percentage of char residue was detected at 3% OPS nanoparticles loading into the hybrid composite. The char residue may correspond to the lignin and cellulose content in the hybrid composite.

4. Conclusions

The OPS nanoparticles were successfully prepared from the oil palm shell by ball milling process. The analysis of the fundamental properties of the prepared OPS nanoparticles revealed the OPS nanoparticles contains a high amount of carbon and oxygen. The crystalline index of the OPS nanoparticles was found to be 34.56%. In the present study, the OPS nanoparticles was utilized as a natural filler in order to enhance the physical, mechanical and thermal properties of the natural fibers reinforced polyester hybrid biocomposites. Results

showed that the OPS nanoparticles had the potential to be used as natural filler in place of synthetic fillers. Further, 3 wt.% OPS nanoparticles loading into the natural fibers reinforced polyester hybrid biocomposites had the optimal physical, mechanical, and thermal characteristics of the hybrid composite. The analysis of fracture surface using SEM revealed the presence of fiber pulling out voids and fiber fracture at 3 wt.% OPS nanoparticles loading into the composite. However, this minimal incompatibility between nanoparticles and matrix at 3 wt.% OPS nanoparticles loading into the hybrid biocomposites could be overcome by treating the fiber with coupling agent.

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Figure

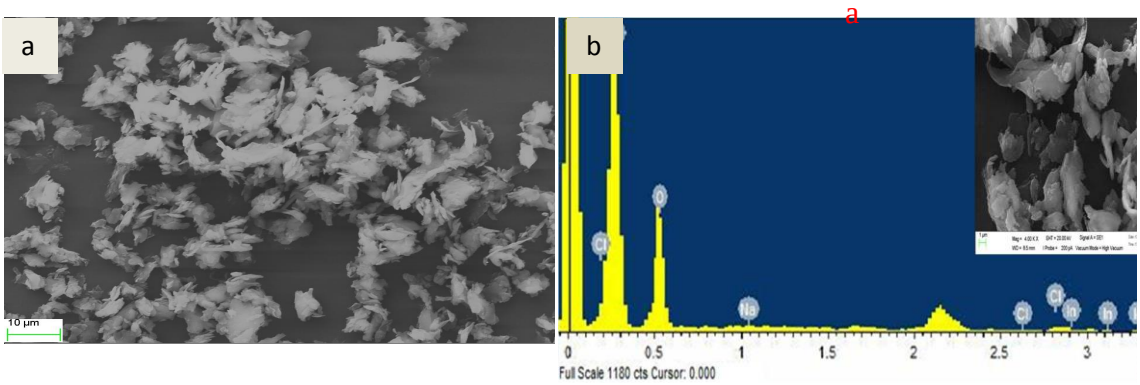

Figure 1. (a) Scanning Electron Microscopy and (b) Energy-dispersive X-ray spectroscopy analysis of Oil palm shell nanoparticles.

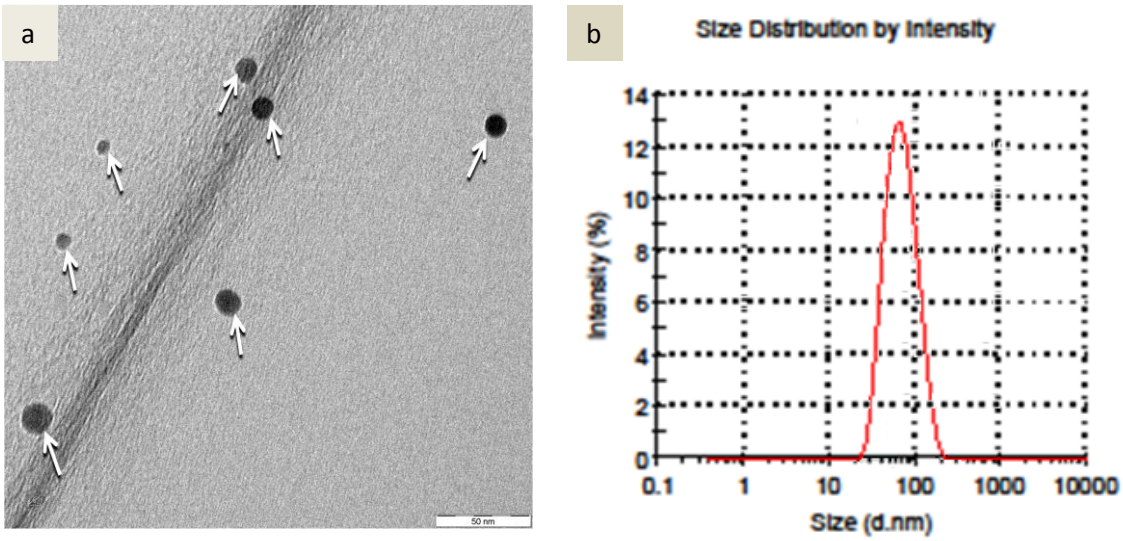

Figure 2. Particle size analaysis of OPS nanoparticles (a)TEM images of OPS nano particle; (b) Particle size distributions of OPS nanoparticles.

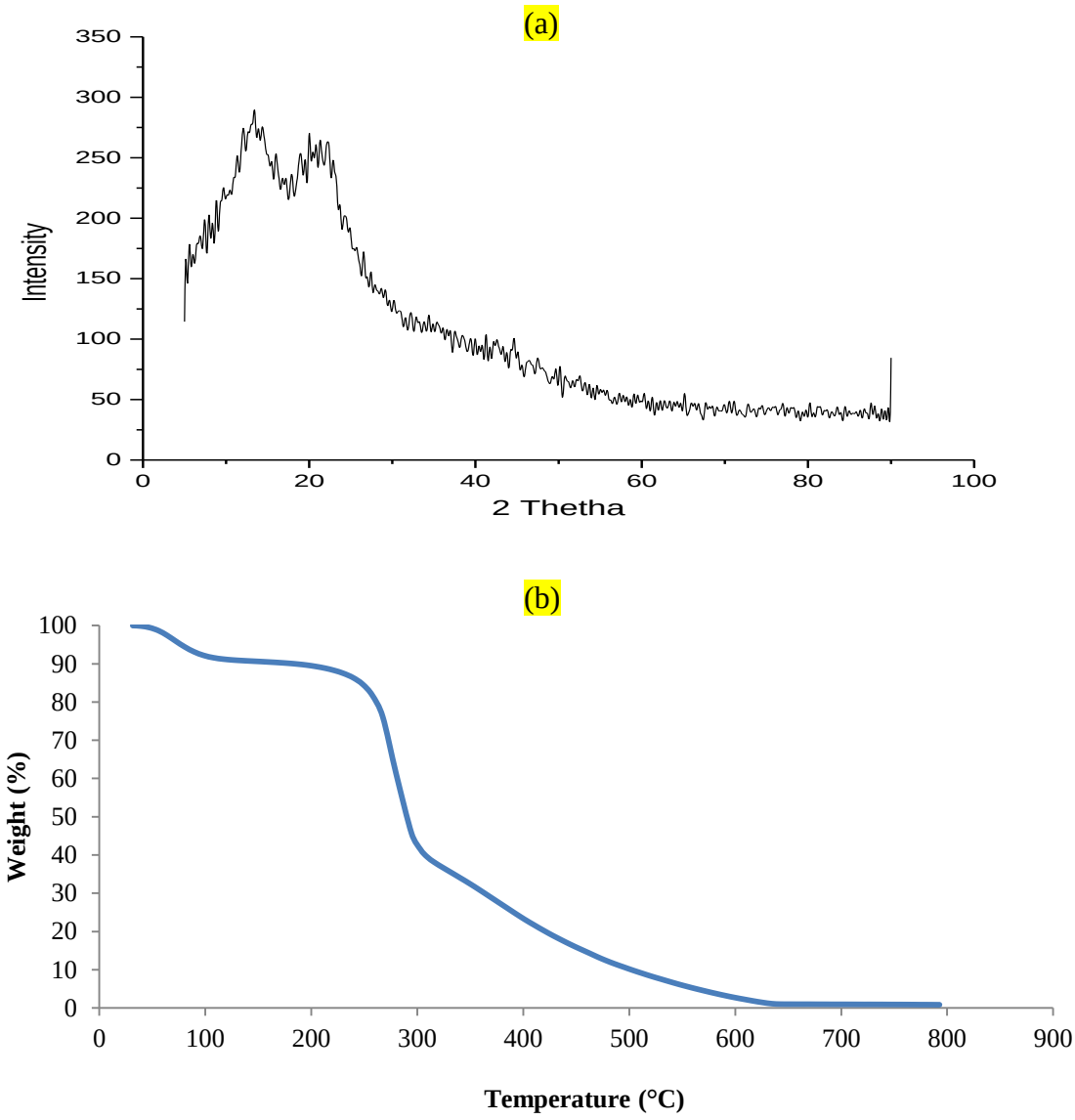

Figure 3. X-Ray Diffraction pattern (a) and thermogravimetric curve (b) of oil palm shell nanoparticles

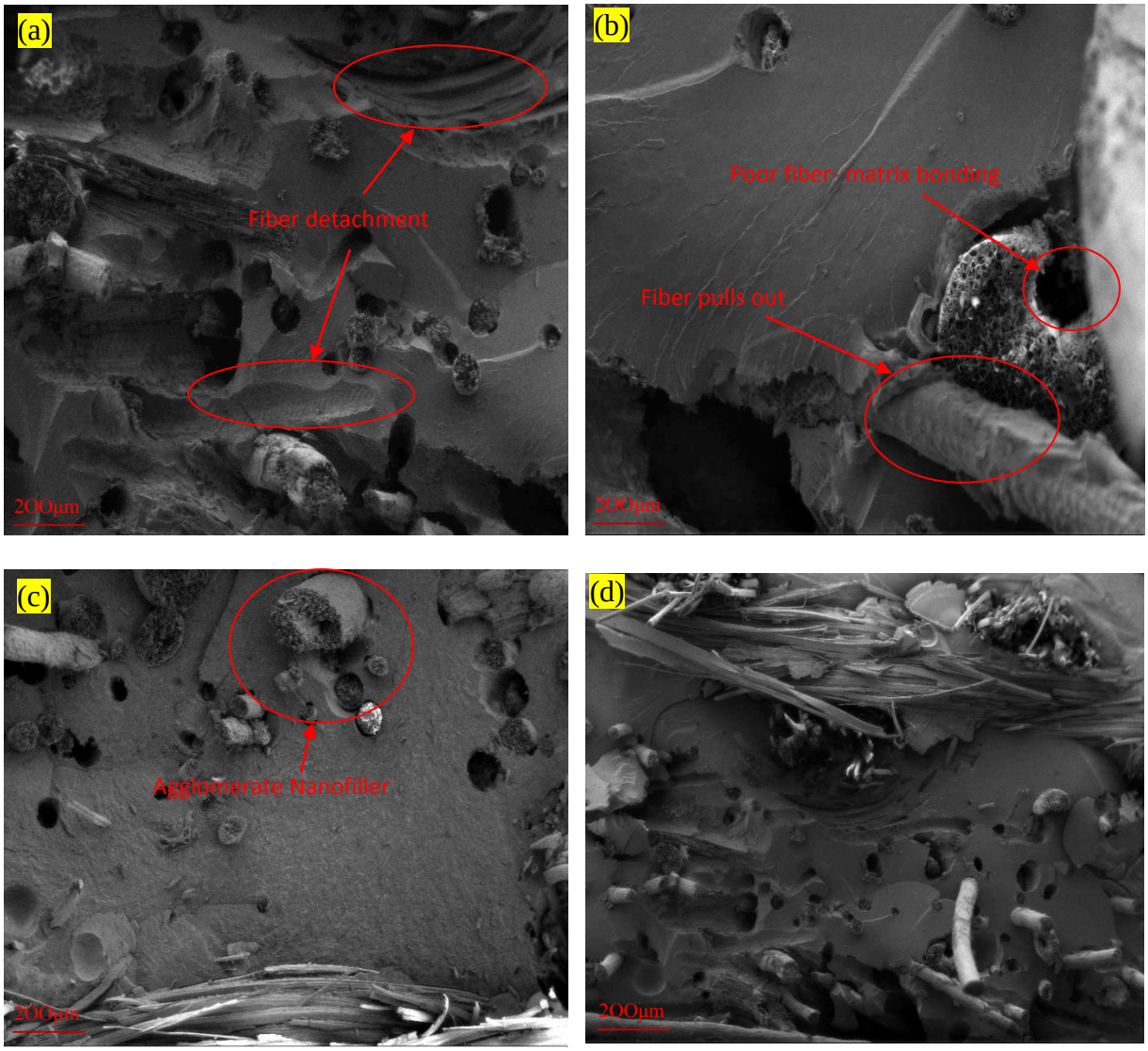

Figure 4. Scanning electron microscopy images of natural fiber reinforced hybrid composite with the incorporation of OPS nanoparticles. (a) Control; (b) 1wt.% OPS nanoparticles (c) 3 wt.% OPS nanoparticles; (d) 5 wt.% OPS nanoparticles.

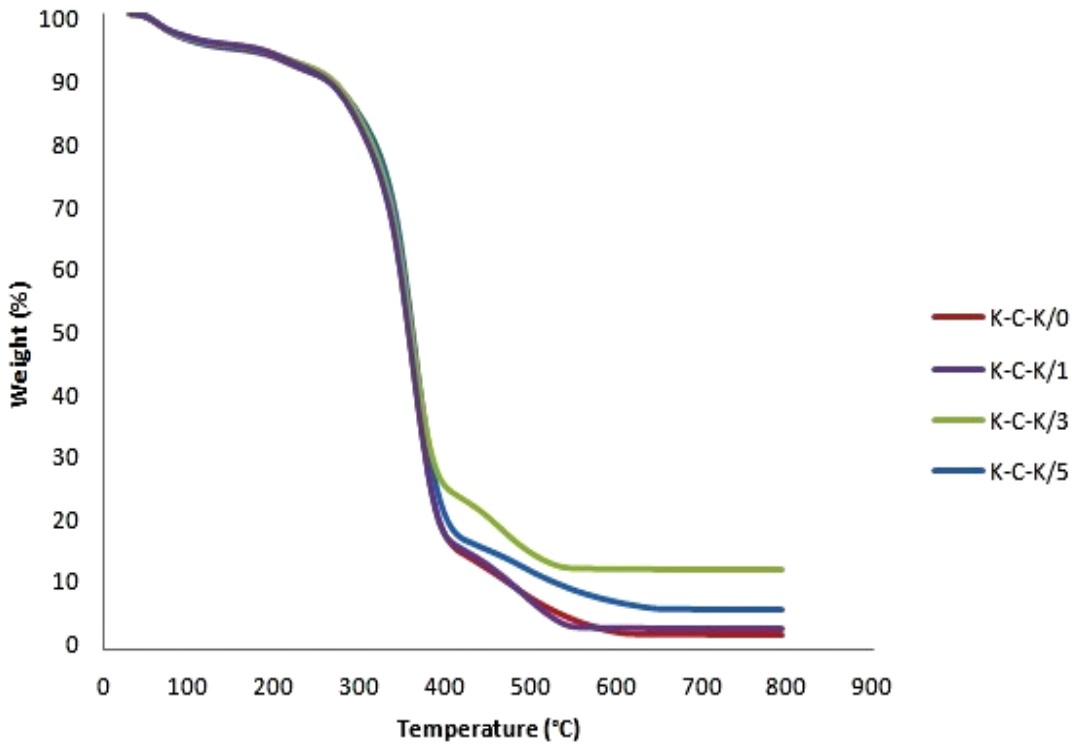

Figure 5. TGA curve on the effect of oil palm shell nanofiller loading in natural fibre reinforced hybrid polyester composites

Table

Table 1. Influence of OPS nanoparticles on density and voids content of natural fiber reinforcement hybrid composites

Filler Loading (Wt. %)	Theoretical Density (g/cm^3)	Measured Density (g/cm^3)	Void Content (%)
Control	1.186±0.053*	1.125±0.046	5.143±0.035
1	1.189±0.021	1.133±0.024	4.710±0.048
3	1.196±0.043	1.137±0.016	4.933±0.052
5	1.209±0.035	1.141±0.024	5.624±0.062

± Standard deviation

Table 2. Influence of tensile properties with OPS nanofiller loading in natural fiber reinforced hybrid composite

	Control	OPS nanoparticles		
		1 wt.%	3 wt.%	5 wt.%
Tensile strength (MPa)	30.10±1.03	33.07±1.26	37.56±1.12	34.02±1.08
Tensile modulus (GPa)	0.76±0.04	0.91±0.06	1.15±0.05	1.03±0.06
Tensile toughness (J/m3)	38.76±1.24	41.82±1.54	46.21±1.25	39.15±1.16
Elongation at break (%)	6.06±0.36	5.58±0.28	5.18±0.42	4.25±0.46

± Standard deviation

Table 3. Influence of flexural properties with OPS nanofiller loading in natural fiber reinforced hybrid composite

Flexural properties and Impact test	Control	OPS nanoparticles		
		1 wt.%	3 wt.%	5 wt.%
Flexural strength (MPa)	60.42±2.19	65.3±2.14	75.27±2.43	69.45±2.12
Flexural modulus (GPa)	4.41±0.24	4.88±0.46	6.17±0.38	5.39±0.18
Flexural toughness (J/m3)	45.76±1.58	49.82±1.62	56.21±1.06	46.15±1.38
Izod Notched Impact Test (kJ/M2)	10.84±0.56	12.01±0.68	13.42±0.49	12.72±0.64

± Standard deviation

Table 4. Influence of the OPS nanofiller on thermal degradation temperature of natural fiber reinforced polyester hybrid biocomposites.

Nanofiller loading (wt.%)	Degradation Temperature (°C)		Char Residue (%)
	$T_{10\%}$	$T_{50\%}$	
Control	240	346	0.8
1	247	353	1.0
3	265	355	11.0
5	256	354	6.5