NANO HYBRID OIL PALM ASH/SHELL FILLED KENAF FIBER REINFORCED VINYL ESTER COMPOSITES

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NANO HIBRID ABU/TEMPURUNG KELAPA SAWIT TERISI GENTIAN KENAF DIPERKUAT KOMPOSIT VINIL ESTER

ABSTRAK

Dalam penyelidikan ini, penggunaan nano hibrid abu (OPA) tidak organik /tempurung (OPS) organik kelapa sawit telah dikaji ke atas komposit vinil ester bersama/tidak bersama diperkuatkan dengan gentian kenaf yang tidak diekstrak/ekstrak. Penukaran OPA dan OPS mentah kepada partikal nano melalui pengisaran bebola bertenaga tinggi. Pengisian nano hibrid OPA dan OPS telah dinilai menggunakan Penghantar Mikroskopi Elektron (TEM), Pengimbas Mikroskopi Elektron dilengkapi Tenaga Sebaran Sinar-X (SEM-EDX), 'Malvern ZetaSizer', Belauan Sinar-X (XRD) dan Spektroskopi Inframerah Transformasi Fourier (FT-IR). Kedua-dua pengisian partikal nano hibrid yang dihasilkan berstruktur bentuk hancur dan tidak teratur, dan mempunyai silika dan karbon sebagai komposisi utama masing-masing di dalam OPA dan OPS. Saiz zarah bagi nano partikal OPA dan OPS masing-masing adalah diantara 68-97 nm dan 51-95 nm. OPA mempunyai darjah indeks hablur yang tinggi iaitu pada 66 %, manakala didapati rendah pada OPS iaitu pada 35 %. Perincian gentian kenaf dilakukan menggunakan Pengimbas Mikroskopi Elektron (SEM) dan sudut pendarjahan telah menunjukkan penyingkiran bahan penyimenan pada permukaan gentian dan peningkatan sudut pendarjahan dari 65 ° ke 95 ° selepas ektraksi. Gentiakan kenaf yang diekstrak menunjukkan peningkatan terhadap sifat-sifat komposit berbanding gentian kenaf tidak diekstrak. Kesan penambahan pengisi nano hibrid OPA/OPS terhadap sifat fizikal, mekanikal, morfologi dan terma telah dikaji pada kadar yang berbeza iaitu 0, 1, 3, dan 5 % terhadap komposit. Peningkatan terhadap muatan pengisi nano hibrid telah meningkatkan sifat-sifat fizikal seperti ketumpatan dan kandungan ruang kosong, manakala penyerapan air menurun di dalam komposit. Kesemua sifat-sifat mekanik kecuali pemanjangan pada takat putus, meningkat sehingga pengisi muatan pada 3 % dan menurun pada 5 %. Manakala pemanjangan pada takat putus mempamerkan penurunan pada penambahan pengisi nano hibrid. Sifat-sifat kestablian terma pada komposit menunjukkan aliran yang sama seperti sifat-sifat mekanikal yang telah dinyatakan. Analisa TEM menunjukkan penyegerakan dan pengagihan yang bagus berlaku pada muatan pengisi nano hibrid sebanyak 3 %. Oleh tu, penambahan muatan pengisi nano hibrid OPA dan OPS sebanyak 3 % diperkuat bersama gentian kenaf diekstrak dipercayai adalah kondisi komposit yang optimum.

NANO HYBRID OF OIL PALM ASH AND OIL PALM SHELL FILLED IN KENAF FIBRE REINFORCED VINYL ESTER COMPOSITES

ABSTRACT

In this present research, the utilization of nano hybrid of inorganic oil palm ash (OPA)/organic shell (OPS) in vinyl ester composites with/without unextracted/extracted kenaf fibre reinforcement was studied. The raw OPA and OPS were subjected to high-energy ball milling and converted into nanoparticles. The characterization of nano hybrid OPA and OPS filler were evaluated by using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy equipped with Energy Dispersive X-ray (SEM-EDX), Malvern ZetaSizer, X-ray Diffraction (XRD), and Fourier Transform Infrared (FT-IR) Spectroscopy. Both nano hybrid OPA and OPS filler particle produced were crushed and irregular shape structures, and consists of silica and carbon as the major element composition, respectively. The OPA and OPS particle size ranged between 68-97 nm and 51-95 nm indicates their nanometric nature. The OPA shows high in the degree of crystallinity index at 66 %, while OPS were found to be low at 35 %. The characterization of kenaf fibre was identified using Scanning Electron Microscopy (SEM) and contact angle revealed the removal of cementing materials on the surface of fibre and increases in contact angle from 65 ° to 95 ° after extraction. The extracted kenaf fibre helps in further enhanced the properties of composites compared to unextracted kenaf fibre. The effect of different filler loading in 0, 1, 3, and 5 % of nano hybrid OPA/OPS on physical, mechanical, morphological and thermal properties of composites were studied. As the incorporation of nano hybrid filler loading increases, the physical properties were increased such as the density and void content, while water absorption of composites were reduced. All mechanical properties of the composites except for elongation at break were increased up to 3 % and decreased upon 5 % filler loading. Meanwhile, the elongation at break was reduced with the addition of nano hybrid filler. Thermal stability exhibits the same trends with aforementioned mechanical properties. TEM analysis revealed the good dispersion and distribution was achieved on 3 % nano hybrid filler loading. Therefore, the addition of 3 % of hybrid OPA and OPS filler loading with reinforcement of extracted kenaf fibre was believed to be as an optimum condition of composites.

CHAPTER 1

INTRODUCTION

1.1 Overview/ General Introduction

As the world move towards environmental concern in achieving sustainable, economical and highly developed high performance material with fascinating properties has led to the utilization of local lignocellulosic materials. These fibers have become an alternative to traditional materials due to its desirable properties. They are renewable, biodegradable, high in specific properties, low cost, low density, less equipment abrasion, and energy efficiency while promoting the sustainability concept (Abdul Khalil et al., 2012, Abdul Khalil et al., 2011, Dittenber and GangaRao, 2012). The agricultural solid waste from oil palm in Malaysia attracts a steady growing interest in various fields due to its increment in number per year (Foo and Hameed, 2009, Hashim and Chu K. H., 2002). Currently, oil palm biomass are mostly used as mulching mats, fertilizer, plywood, automotive parts, pulp, paper, food packaging, activated carbon, compostable plastic and boiler fuel. Thus, the innovation of the existing technologies in manipulating and creating the structure of oil palm biomass down to nano-scale in the nanotechnology research area has provides potentials and benefits in the exploration of this bio-agricultural wastes (Salamon et al., 2010).

Nanotechnology market is rapidly growing as the industries being competitively improved and creates remarkable dimension of materials with extended properties in the emergence of various new areas from high performance material to daily used products (Chujo, 2007, Dastjerdi and Montazer, 2010, Karimi et al., 2013, Malshe and Deshpande, 2004). Currently, over 85 % of the market are filled with nanomaterial, such as sport equipment and consumer electronics (Wegner and Jones, 2009, Harper et al., 2015). Nanomaterial is defined as 1 to 100 nanometers (nm) sized of at least one dimension of the material. With the specific area of more than 60 m^2/cm^3, it can be found in the state of an unbound, particles, tube, rods, fibers, aggregate, or agglomerate (Liden, 2011, Salamon et al., 2010). To produce more functional materials, broad range of fillers can be applied together to embrace diverse favorable properties and quality from nanocomposites (Abdul Khalil et al., 2011, Ryszard M et al., 2012).

The word hybrid was derived from Greek-Latin word which can be found in numerous scientific fields. In the case of polymer composites, hybrid composites consists of two or more reinforcing materials are present in a single matrix (Abdul Khalil H. P. S. et al., 2011, Abu Bakar et al., 2005, Abdul Khalil et al., 2007). The incorporation of two or more natural fibers into a single matrix has led to the development of hybrid composite. The behavior of hybrid composites is a weighted sum of the individual components in which there is a more favorable balance between the inherent advantages and disadvantages. While using a hybrid composite that contain two or more types of fiber, the advantages of one type of fiber could complement the lacking in the other. Thus, a balance between cost and performance could be achieved through proper material design.

Nano hybrid composites consisting of polymeric matrix material with reinforcement of lignocellulosic fibre and nano hybrid fillers has attracts scientist's interest for academic research as well as development in innovative industrial application due to their unusual features. Hybrid of fillers will open a land of promising application such as thermal interface materials (Goyal and Balandin, 2012), photonic devices (Yaacoub et al., 2014), flooring (Bauer et al., 2006), and food packaging (Uysal Unalan et al., 2014). Thus, by reinforcing both inorganic and organic nano-particles as fillers into the nano hybrid biocomposites, magnificence properties could be achieved.

1.2 Problem Statement

Natural fibre become as promising raw material for reinforcement in polymer composites due to its recyclability, low density and biodegradability. In spite its numerous advantages, there are certain drawbacks were reported toward reinforcement of natural fibre such as lack of interfacial adhesion, aging towards humidity, low in melting point, and low modulus elasticity, which make the use of natural fibre reinforced composites less attractive.

To be realized with this scenario, nano particles have been identified as material that enhanced the natural fibre reinforced polymer composite properties. Although other concept of reinforcement has been studied, using single nano particle of oil palm ash (OPA) or oil palm shell (OPS) as nano filler in biocomposites, but the study regarding hybrid of both OPA and OPS as nano fillers is still limited.

Thus, the current study intends to fill up this gap and combine the knowledge on hybridization of nano-structured materials using OPA and OPS particles as hybrid nano filler, with knowledge on kenaf fibre reinforced vinyl ester composites. The utilization of these abundance and low in cost of biomass from oil palm industry as nano fillers could play a positive impact towards the environment and eliminate the disposal problem, environmental pollution, and health hazard. The addition of nano materials leads to enhancements in properties of materials in producing highly value added product which meets industry requirements. Thus, a balance in cost and performance of the product could be achieved through proper material design.

1.3 Objective of Study

The objectives of this present research work are:

- To characterize fundamental properties of nano-structured oil palm ash, oil palm shell and kenaf fibre.
- To fabricate kenaf fibre reinforced vinyl ester composites enhanced with hybrid nano OPA/OPS fillers.
- To study effect of filler loading of hybrid nano OPA/OPS on physical, mechanical, morphology and thermal properties towards kenaf fibre reinforced vinyl ester composites.

1.4 Outline of Dissertation Structure

This dissertation has been structured into 5 respective chapters, which are:

Chapter 1: Focus on the general introduction and background, problem statement, and objectives of this present research.

Chapter 2: Devote on the literature review of composites, oil palm biomass, nanomaterial, biocomposites, and hybrid nano- biocomposites.

Chapter 3: Explain regarding materials and methodology of production of nano-structured OPA and OPS, characterization, and fabrication of hybrid nanocomposites.

Chapter 4: Provide the results and discussion of characterization of nano-structured OPA and OPS, and properties of hybrid fillers vinyl ester composites with reinforcement of unextracted or extracted or without kenaf fibre.

Chapter 5 : Encapsulate the overall conclusion and recommendation for future research of this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

Composites are defined as engineered materials which made up of two or more constituent materials with significantly different properties; chemically and physically which mechanically separated by a distinct interface. The incorporation of divergent systems creates a new system with bulk structural and functional properties significantly different from individual of the constituents. The composites contain characters of the primary phase which more ductile, less hard, holds the secondary phase, and share load, which is known as matrix. While the secondary phase is discontinues phase that embedded in the matrix and higher in strength, known as reinforcement (Malhotra et al., 2012).

2.1.1 Classification of Composites

The classification of composites is based on the matrix and reinforcement phases of materials. The classification according to type of matrix phase can be classified as three different composites; ceramic matrix composites (CMCs), metal matrix composites (MMCs), and polymer matrix composites (PMCs). The matrix can be classified as either degradable or non-degradable matrices. While, particulate, fibrous, and laminate are included in the reinforcement phase classification of composites. These reinforced composites are distinguished based on the size, shape, orientation and interlocking mechanisms of their constituent. The fibrous composites can be further subdivided into based on natural fibre or synthetic fibre. The classification scheme of composites is shown in Figure 2.1.

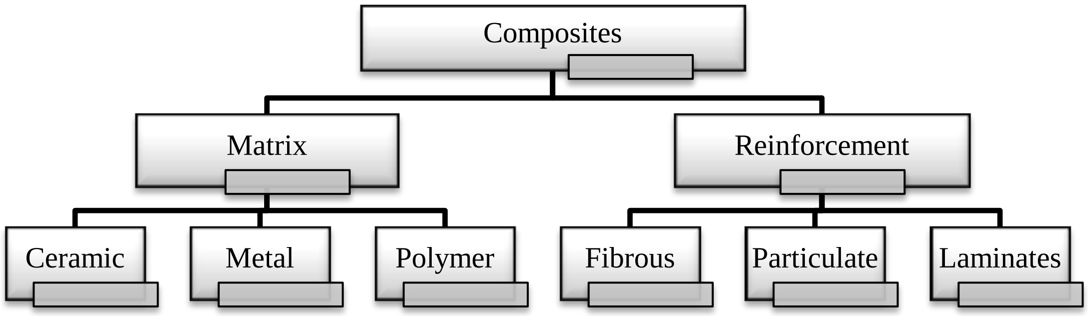

Figure 2.1 The classification composite materials (Ilie and Hickel, 2009, Malhotra et al., 2012)

2.2 Polymer Composite

The polymer composites consist of polymer matrix or known as resin and reinforcement that provide strength and stiffness as the raw materials. The composites are designed structurally for the mechanical loads are supported by the reinforcement. The type and properties of composites depend on the type of raw material being used. The reasons behind the high usage of desirable polymer composite material are low cost and simple in fabrication processes (Malhotra et al., 2012).

With the great strength of reinforced raw material, the polymer composites capable to obtain high specific strength, high specific stiffness, high fracture resistance, good resistance towards impact, abrasion, fatigue and corrosion. However, the drawback of this composite is low in thermal resistance and high coefficient of thermal expansion. The properties of polymer composites are affected by interfacial adhesion of matrix and reinforced materials, physical properties of reinforcement phase, and the properties of matrix constituents (Bednarcyk, 2003, Tabiei and Aminjikarai, 2009, Huang and Talreja, 2006).

2.2.1 Matrix

Matrix is a material consists of one or more components in its composition. Matrix serves as supportive system that protect the composites from the incursion of external agents as it binds the reinforcement together, as it helps in stress and load transfer within the composite structure (Thakur and Singha, 2010). In addition, the matrix also helps in protecting the surface of reinforcement from mechanical abrasion. Matrix can be divided into thermosets and thermoplastics. There are various types of matrices with distinct in characteristic features that create composites with a wide range of properties. The selection of the matrix depends on the application of the end products.

2.2.1.1 Thermoset based matrix

Thermoset polymer consists of amorphous structure which molecules are linked by network structure of strong covalent bonds. Once the polymerization reaction (curing) occurs, the network cannot undergo reshaped upon heating, but instead permanently degrade (Daniel et al., 1994, Jones, 1975). Among the frequent thermoset matrix that's used in composites areas are unsaturated polyester, vinyl ester and epoxy resins.

2.2.1.1a Vinyl Ester Resin

Vinyl ester resin is one of the thermoset polymers which were first introduced commercially in the early 1960s. Vinyl ester resins exhibit various fascinate attributes, such as the capability to cure in room temperature, low in viscosity, cheap and equivalent characteristics with other common thermoset matrix (Stone et al., 2000). This polymer exhibit fascinate attributes which merger the thermal and mechanical properties of epoxy and the easy and fast curing process as unsaturated polyester resins. It's also known to be great in wetting as a result of low molecular weight (Abadie et al., 2002). However, there are certain drawback regarding this resin such as requires postcure process to produce high properties of material, use high styrene content as its monomer, and high cure shrinkage.

Vinyl ester resin has become widespread of industrially engaging as a result of its fascinating chemical and mechanical properties. These resins are high in tensile strength and Young’s modulus as well as remarkable in acids, alkalis, solvents, degradation, and moisture resistance as a result of the structure of its cross-linking network (Athijayamani et al., 2015, Cook et al., 1997, Guo et al., 2009). Amongst its application due to commercial interests are sewer pipes, swimming pools, reinforcements for bridges, electrical applications, solvent storage tanks, adhesives, automotive parts, and aerospace applications (Alhuthali et al., 2012).

There are many current research works using reinforcement of natural fibre towards vinyl ester polymer composites has been studies, such as bamboo, kenaf, flax, sisal, banana, jute, coir, oil palm EFB, pineapple leaf, and bagasse (Athijayamani et al., 2015, Chen et al., 2009, Fairuz et al., 2015, Mahato and Goswami, 2014, Mohamed et al., 2014, Ghosh et al., 2014, Praharaj et al., 2015, Amiri et al., 2015, Khalil et al., 2009). The reinforcement of lignocellulosic fibre helps in increasing the properties of the vinyl ester polymer composites such as mechanical performance. Meanwhile, the addition of nano filler in vinyl ester composites such as nanoclay leads to favorable thermal stability and flammability (Alhuthali et al., 2012). The mechanical and physical effect of different layer arrangement of oil palm EFB/glass fibre reinforced vinyl ester composites also was studied by previous researcher, which affects the dimensional stability of the composites (Khalil et al., 2012).

The vinyl monomer contains terminal reactive sites on double bonds that derived from acrylic acids as shown in Figure 2.2. The high viscosity property of this resin leads to necessary to add styrene as reactive monomer during the crosslinking reaction after formation of random distribution of ester group and carbon-carbon double bonds at the end of the polymer chains due to co-polymerization (Sankar et al., 2015) . Among the other monomers that can be used are -methyl styrene, triethylene glycol dimethacrylate, methyl methacrylate, and epoxyacrylic compounds (Rosu et al., 2006) . However, styrene monomer is the one that usually being used in industrial field with about 40 to 50 wt. %. Styrene monomer is reactive diluents that helps to control the viscosity, improve the wetting behavior of resin, and reduce the cost of the resin system (Fink et al., 2002).

The network of vinyl ester oligomer and styrene are cured by free-radical initiation of polymerization (Li, 1998). The curing process can be done either in elevated temperature or room temperature and followed by a post cure process, but the rate depends on amount of accelerator, catalyst, temperature, etc (Abadie et al., 2002). The storage of the material was vital as the exposure to high humidity could affect the interfacial strength of the final product (Chen et al., 2009).

The degree of curing relates to the viscosity of the matrix. Complete wetting can be achieved when the time consumed for infiltrate during the process is less than gelation time of matrix (Stone et al., 2000). The origin of the termination structure, the amount and type of coreactant, and type as well as molecular weight of the backbone of the resin affect the properties of this matrix. Increases in molecular weight of matrix lead to higher in toughness and resiliency while reducing the heat and solvent resistances (Launikitis, 1982). Among the application of vinyl ester resin are for construction part of automobiles in military ground vehicles, bridges, marine application, and other materials which needs resistant towards chemical and enviromental (Sankar et al., 2015).

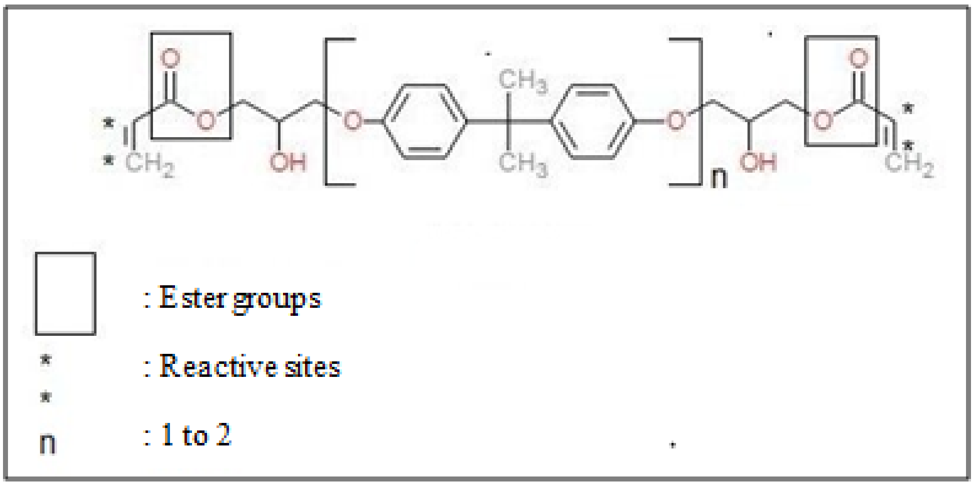

Figure 2.2: The chemical structure of the vinyl ester monomer

2.2.2 Reinforcement

Reinforcements are responsible for the high strength, rigidity and stiffness of composites. They also correspond for resistance towards heat and corrosion to the composites. In order to have strong composites, the reinforcement must have higher strength and stiffer than the matrix, as it increases the brittleness and reduce the ductility of the composites (Pandey, 2004). Reinforcement of composites can be variations in types such as fibres, filler, particles, flakes, or whiskers. They can be either from organic or inorganic resources. The resources are subdivided into natural or synthetic materials. The natural based can be subdivided into lignocelulosic based and non-cellulose (animal and mineral) based (Dicker et al., 2014). However, natural fibres from lignocellulosic are the commonly used for composites material. The classification of reinforcement is shown in Figure 2.3.

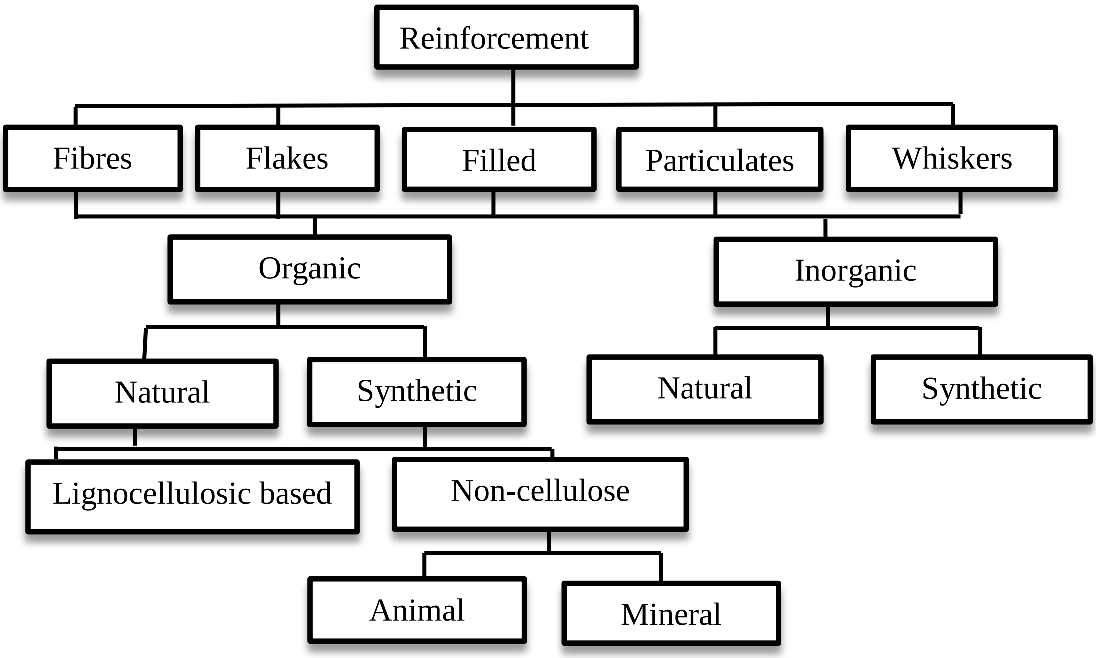

Figure 2.3: The classification of reinforcement (Dicker et al., 2014)

2.2.2.1 Lignocellulosic fiber

Lignocellulosic fibre can be classified into bast, fruit, grass, leaf, seed, stalk, and wood. The strength of these natural fibres are affected by aspect ratio (length/width) (Han and Rowell, 1997). The level of strength, stiffness and coarseness are differs from one plant to another. High variety of natural fibers are known to be cheaper, lighter and more flexible alternative towards uses of synthetic fiber such as glass fiber (Sabu Thomas et al., 2012 , Dittenber and GangaRao, 2012). These renewable resources are low in carbon dioxide (CO_2) emission, required little energy and biodegradable.

Generally, the chemical composition of lignocellulosic fibre consists of cellulose, hemicellulose, lignin, extractive and minor of inorganic matter. The amount of chemical compositions is strongly dependent on various factors such as species, growth condition, position, and the age of lignocellulosic material (Sjostrom, 1993, Mossello et al., 2010). Thus, it was different from each lignocellulosic fibre.

2.2.2.2a Kenaf fibre

Kenaf (*Hibiscus cannabinus*) also known as Bimbli Ambary, Ambary Hemp, Deccan Hemp and Bimlipatum Jute. Figure 2.4(a) shows kenaf which was primarily cultivated for its fibre. As shown in Figure 2.4(b-c), this lignocellulosic fibre consists of two types of fibre which are bast and core with constitutes about 30-40 % and 60 % of the total dry weight, respectively. The bast fibres are comparable with softwood fibres while core fibres are comparable with hardwood fibre in term of length with the average of 2.6 mm and 0.6 mm for bast and core respectively. The appearance of kenaf core is light and porous with a bulk density about 0.10 to 0.20 g/cm^3 (Saad and Kamal, 2013).

The chemical composition of kenaf fibre consists of about 45-57 % of cellulose content, 21.5 % of hemicellulose, 8-13 % of lignin and 3-5 % of pectin (Smole et al., 2013). Kenaf bast fibre shows high in α-cellulose, extractive, and ash content. Meanwhile, kenaf core fibre results in higher in holocellulose and lignin (Ibrahim et al., 2009). Kenaf bast fibre is among the most attractive that being continued applies in many of the industries and by researches. This is due to their quality and fascinating properties.

With fast duration of maturity with nearly 5 meter in height in 5 to 6 months depends on several conditions, it become an advantage towards this agricultural fibre as it shows high availability for market potential. Furthermore, the properties of kenaf bast which are low cost, low density, recyclable, good toughness, acceptable strength properties and biodegradable makes it more favorable as an alternative resource towards synthetic fibre (Xue et al., 2007).

Kenaf has a long history of cultivation for its fibre, especially in India, Thailand, United States, Africa, Bangladesh, Southeast Europe and as well as Brazil

(Shi et al., 2011). Meanwhile, in Malaysia, their plantation and cultivation becomes a subject of interest due to their diverse capability in further advancement in various applications, as well as tobacco plant replacement. There is plenty of research are conducted in order to explore the uniqueness of kenaf towards commercialization. Among the products are insulation boards (Saad and Kamal, 2013), polymer composites (Nishino et al., 2003), particleboard (Juliana and Paridah, 2009), water treatment (Gharehchahi et al., 2013), lamination (Ramaswamy et al., 2003), medical application (Reed et al., 2000), building materials (Mohanty et al., 2005), and automotive (Salleh et al., 2014).

In the composites field, many previous studies show an enhancement in the properties of composites are achieved with the reinforcement of kenaf fibre and this fibre become an alternative material for glass fibre reinforcement (Anuar and Zuraida, 2011). Higher tensile strength is obtained as compared to wood based. According to previous study, kenaf fiber shows comparable in tensile strength and modulus with glass fiber (Wambua et al., 2003). It also shows an evidence of increasing in fiber weight fraction of kenaf fibre leads to increasing in tensile modulus, impact strength, and tensile stress.

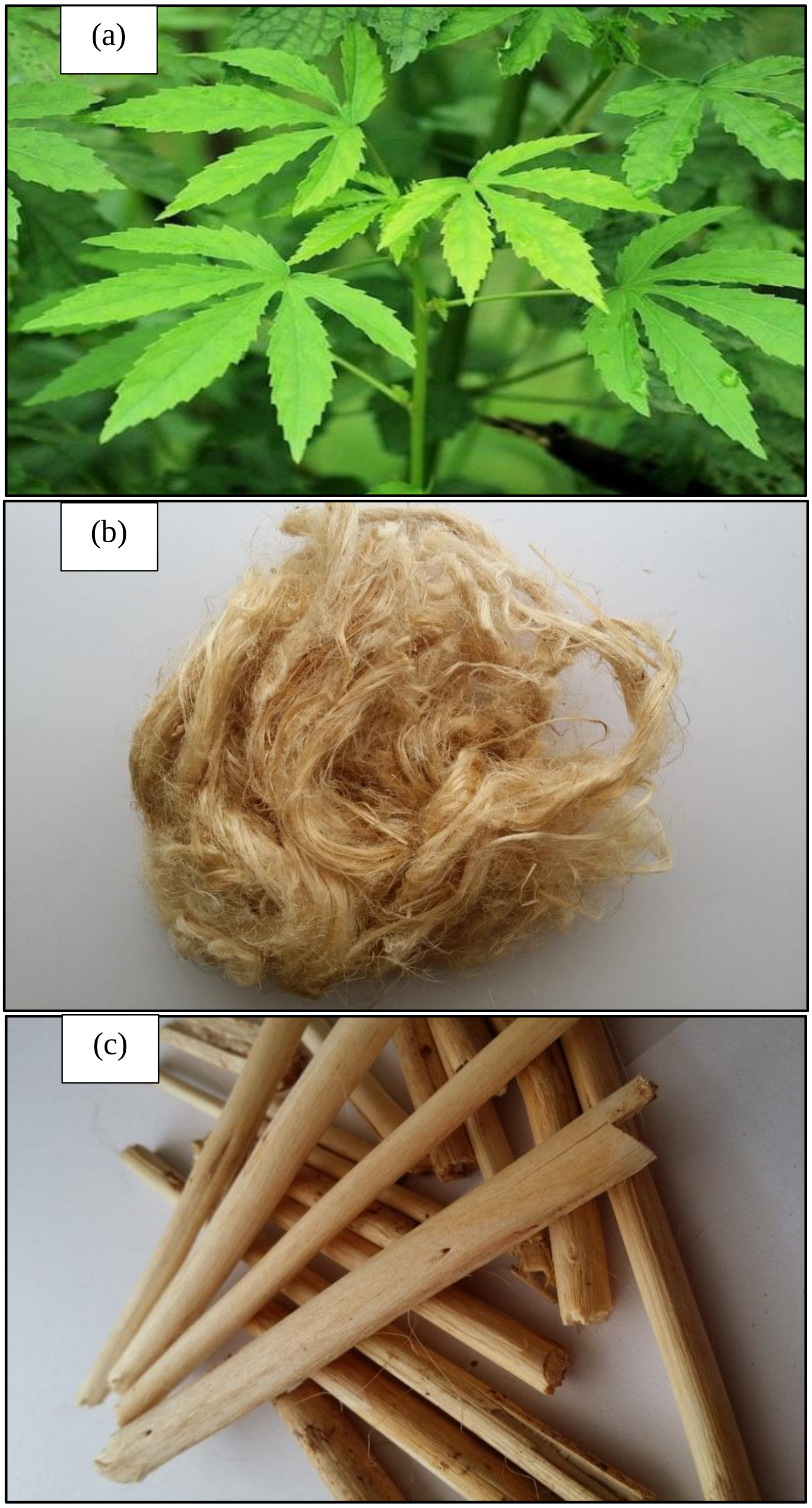

Figure 2.4 : (a) Kenaf plant (Blog, 2014) , (b) Kenaf bast, and (c) Kenaf core

2.3 Nanomaterial

Nanomaterial is defined as 1 to 100 nanometers (nm) sized for one or more external dimensions and about 1 to 10 nm of one or more internal/structure surface dimensions made up of material (Jung et al., 2006). At this range of dimensions, unusual properties are often encountered as it triggers large specific surface areas (Jajam and Tippur, 2012). Nanomaterial is known to be a fundamental product in nanotechnology, which creates a remarkable dimension of materials with extended properties that lead to an emergence of fascinating new areas. (Chujo, 2007, Salamon et al., 2010, Commission, 2012). Enhancement in properties are discussed by many researchers such as increased thermal resistance, increase in mechanical, lower resistivity, improvement in resistance towards chemical and moisture, and reduced the shrinkage of the composites.

Numerous of progressive studies in a variety of discipline results in discovery of enormous application, from biomedical and scaffolds for tissue engineering (Jayakumar et al., 2010, Karimi et al., 2013, Madhumathi et al., 2009), to optical materials (Malshe and Deshpande, 2004), electronic (Jung et al., 2006), ceramic (Hao et al., 2012), and composite materials (Njuguna et al., 2008). Currently, over 85 % of the markets are filled with nanomaterials, predominantly for nanocomposites and nanoparticles (Wegner and Jones, 2009).

2.3.1 Structure and Morphology of Nanomaterials

The classification of nanomaterials depends on the dimension of the particles, where it can be found in the state of nanoparticles, nanotubes and nanolayers (Alexandre and Dubois, 2000, Manocha et al., 2006). With the specific area of more than $60m^2/cm^3$, nanomaterial can be formed in the state of an unbound, particles, tube, rods, fibers, granulates, crystal, (Liden, 2011, Salamon et al., 2010, Wegner and Jones, 2009). Nanoparticles are particulates with nanometer sized in all three dimensions. They can also be found in nanogranules and nanocrystals. While, when the only two dimensions of materials at the nanometer scale, it is known as nanotubes, or also known as nanofibre, whiskers, nanorod and nanoplates. Whereas, the particulates with only one dimension with less than 100 nm, is known as nanolayers, nanosheets or nanoplates (Marquis et al., 2011).

2.3.2 Nanofiller

The enhancement of composites in some of their features in term of physical, mechanical, and thermal properties as well as cost reduction can achieve with the presence of particulate material called fillers (Suresha et al., 2013). However, not all the features could obtain with a reinforcement of filler due to the properties of filler itself, such as size, shape, morphology, distribution, and the interfacial interaction with the matrix. Particle size of fillers directly affects the physical performance of composites. The reduction of filler size to nanometers leads to the unique characteristics from an increase the surface area to significant aspect ratio, surface functionalities flexibility and complicated anisotropic structure while giving a dramatic change towards material properties such as in barrier and mechanical (Njuguna et al., 2008, Majeed et al., 2013). These fascinating features lead in many researches have been carried out which produce encouraging results (Majeed et al., 2013).

The incorporation of nanofiller in the matrix resin at low level of amount, which about 1% to 10% (in mass) (Marquis et al., 2011). According to Jajam and Tippur, (2012) , nano-structure filler particles give advantages toward the composite compared to micro-structured filler particles as it provides higher terminal velocities, and higher in surface ruggedness under quasi-static conditions as well as enhanced the toughness and lower in dynamic crack-initiation toughness. The incorporation of nano-structured filler in the composites does not influence the crystalline phase of the system as reported in many studies (Reynaud et al., 2001, Jordan et al., 2005).

The inorganic particulate fillers are often added to the process of polymer composites to overcome the limitations of clear polymers such as low in power and stiffness, as well as typically combines the advantages of their constituent phase (Fu et al., 2008). Among the inorganic fillers that being used are amorphous silica, ceramic, glass, quartz, and carbon black. The increment of researchers' interest in the replacement of the conventional inorganic fillers that are mostly made up of synthetic materials to inorganic fillers based on lignocellulosic resources are due to their properties which are cheap, abundant, low density, free disposal problem, good in thermal insulation and high in mechanical properties (Ayrilmis et al., 2013). Various types of lignocellulosic resources can be used as both inorganic or organic filler and even reinforcement.

2.3.3 Nano hybrid fillers

Hybrid of organic and inorganic nanoparticles offers various possibilities in terms of tailoring the chemical and physical properties, which are determined by the phase of each nanoparticles and their interface (Pinna, 2007). The high interfacial adhesion between both organic and inorganic particles through the formation of hydrogen or covalent bonds could leads to homogenous dispersion in the polymer matrix (Mammeri et al., 2005). Pinna (2007) also emphasis on the high specific surface area and structure of hybrid particles affects the intrinsic physical properties.

The properties of composites are significantly affected by the ratio between nanofillers and matrix resin (Marquis et al., 2011). Thermal stability, tensile strength, Young’s modulus, modulus of elasticity, fracture toughness, hardness and resistance towards abrasion and wear of the composites tends to increases with the incorporation of hybrid organic and inorganic phases (Macan et al., 2006, Zeng et al., 2015). While, it also results in reduction of thermal expansion, amount of matrix material, water absorption by minimized the swelling, shrinkage of polymerization of matrix material and cost simultaneously (Yang and Gu, 2010).

2.4 Potential fillers of Byproduct of Oil Palm

2.4.1 Byproduct of Oil Palm

Oil palm tree as shown in Figure 2.5 belongs to the Palmae family and known as Elaeis guineensis (Teoh, 2002). Originated from West Africa and being introduced to Malaya in 1875. However, it is first commercial plantation in Malaysia was on 1917 that located at the Tennamaran Estate in Kuala Selangor (Basiron, 2007, Jagoe, 1952). At present, it is planted in all tropical regions in the world, especially in some South East Asia countries such as Malaysia, Indonesia and Thailand. The plantation of oil palm in Malaysia is raised throughout the year due to the growth in demand of edible oil of palm oil (Shuit et al., 2009). As Malaysia becomes the largest producer and export more than 90% of its palm oil to the international market, resulting in a tremendous wealth of biomass besides the crude palm oil (Hameed et al., 2007, Ooi et al., 2013).

It is known that about 50 to 70 tons of biomass residues were produced in one hectare of oil palm plantation (Salathong, 2007). An average of 53 million tons of biomass of oil palm was generated per year in Malaysia, and by the year 2020, the total amount of solid oil palm biomass is estimated to increase up to 100 million dry tons and it leads to serious issues regarding waste disposal problem (Ooi et al., 2014, Umar et al., 2014). High in transportation cost and limitation in landfill availability, leads to the open burning of biomass to reduce the solid waste. Only 10% of the oil palm biomass consists of palm oil and palm kernel oil, whilst remaining 90% is in solid form of biomass (Bhat and Khalil, 2011). Among the solid biomass from this agricultural industry are oil palm ash (OPA), empty fruit bunch (EFB), oil palm frond (OPF), mesocarp fibre (MF), palm kernel shell (PKS), palm kernel expeller (PKE) and oil palm trunk (OPT) (Sumathi et al., 2008). Unfortunately, only about 10% of the waste are being used and numbers of solid waste are still currently under-utilized (Tanaka et al., 2004). Thus there are many researchers keep on exploring and discover the benefits of these waste that produced from about 200 palm oil mill in Malaysia towards other industries (Foo and Hameed, 2009, Hashim and Chu K. H., 2002, Awal and Hussin, 1997).

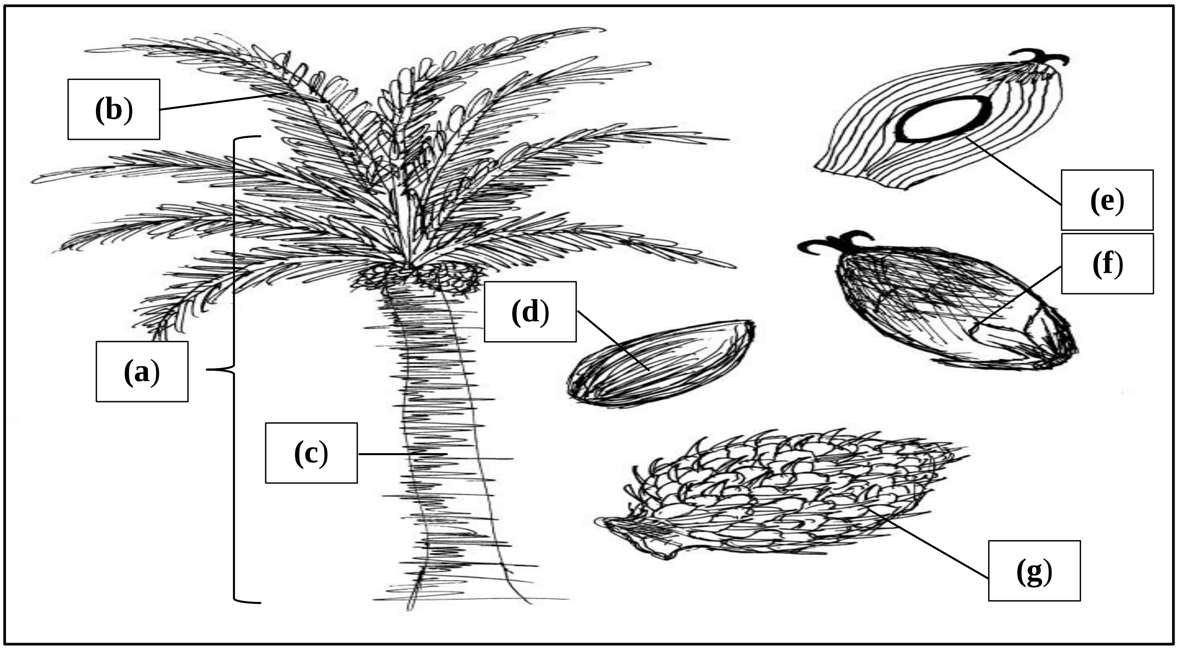

Figure 2.5: The (a) oil palm tree, (b) oil palm front,(c) oil palm trunk, (d) oil palm seed, (e) flesh cut of oil palm fruit, (f) oil palm fruit, and (g) fresh oil palm fruit bunch

2.4.1.1 Oil Palm Ash (OPA)

The OPA is known to be the inorganic constituent of lignocellulosic material that obtained as the byproduct of combustion of organic matter at high temperature (about 800 to 1000 °C) which generate steam during the production of oil palm (Rowell et al., 2000, Hameed et al., 2007). Among the solid waste that are used as organic matter for boiler fuel are MF, EFB, and PKS (Ismail and Shaari, 2010). About 4 million tons of OPA are produced annually (Foo and Hameed, 2009). The numbers are estimated to increase per year significantly with the globally high demand of palm oil.

OPA is a low-molecular weight substance which is classified as non-toxic waste (Fengel and Wegener, 1983, Yin et al., 2008). According to previous research, large amount of OPA end up in landfill for disposal without any beneficial economic return value, leading to severe environmental pollution and requires more large areas (Ismail and Shaari, 2010, Sombatsompop et al., 2007). Thus, the utilization of OPA at zero cost leads to the reduction in compounding cost.

2.4.1.1a Structure and Composition of Oil Palm Ash

The morphological characteristic of OPA particles shows spongy and porous in structure (Abdul Khalil et al., 2011, Jaturapitakkul et al., 2007). The irregular shapes of OPA might trigger formation of voids within the fillers and matrix resins. The various particle size of OPA upon collecting might leads to obstacles during processing of polymer as the large particles create stress concentration points, thus decrease in the strength of the composites (Ooi et al., 2014). Thus, the OPA particles are subjected to size separation to overcome this problem. The OPA obtained from mill varies in colour, it can be whitish grey to darker shades depends on their carbon content (Olutoge et al., 2012).

Among the main constituent of OPA content are various metal salts such as silicates, carbonates, oxalates, and phosphates of potassium, silicon (Si), aluminum (Al) calcium (Ca), magnesium (Mg), iron, and manganese (Mossello et al., 2010) The minimum and maximum amount of chemical constituent composition of OPA that were obtained in several studies are listed in Table 2.1. According to Yin et al. ,(2008) , high percentage of potassium and silica content were detected in OPA. Silica is most commontly fund in nature as sand or quartz, with the density of 2.65 g/cm^3 (Fairus et al., 2009). The amount of mineralogical composition varies and affected by many factors such as nutrient uptake by oil palm trees, ferterlizers, soil chemistry, climatic variation, and time collection (Ooi et al., 2014).

Table 2.1: The chemical composition of OPA

	Weight (%)	References
Silicon dioxide	43.6-65.3	a, b
Aluminum oxide	1.6-11.4	c, a
Calcium oxide	4.8-7.6	a, c
Magnesium oxide	0.4-4.2	a, d
Potassium oxide	3.5-8.3	a, e
Iron oxide	1.4-8.4	c, a
Sulfur trioxide	0.2-2.8	c, a
Sodium oxide	0.1-4.7	c, a
Loss of ignition	9.6-10.5	c, e
SiO_2+Al_2O_3+Fe_2O_3	63.4-69.9	a, b

*(Awal and Hussin, 1997)[a], (Jaturapitakkul et al., 2007)[b], (Chindaprasirt et al., 2008b)[c], (Tangchirapat et al., 2009)[d], (Tangchirapat et al., 2007)[e]

2.4.1.1b Application of Oil Palm Ash

The composition of OPA are highly corresponds to the properties of potential application. As the OPA is high in silica and low in calcium, it leads to the suitability as filler for cement and concrete replacement material (Yin et al., 2008, Jaturapitakkul et al., 2007). The incorporation of OPA results in a remarkable reduction in water permeability and enhancement in strength with lighter concrete. The improvement in properties also shows when OPA was used as filler in composites application (Bhat and Khalil, 2011). The high number in potassium in OPA is expected to be correlated to the high amount in EFB and indicates the capability of transferring OPA into crude fertilizer (Yin et al., 2008). In addition, the active compound (alumina, silica, calcium, potassium, and hydrated water) that exists in OPA that produced as absorbent, responsible towards the high absorption capacity of sulfur dioxide in toxic gas removal (Zainudin et al., 2005). Activated oil palm ash shows the capability in removing the direct dye from aqueous solution has been reported in previous studies (Ahmad et al., 2007, Alemdar and Sain, 2008).

2.4.1.2 Oil Palm Shell

OPS or known as endocarp is one of the organic based biomass of oil palm production. OPS comprises about 64% of the fresh fruit bunch mass (Okoroigwe et al., 2014). About 2.6 million tons of OPS are produced annually was reported (Amiruddin, 1998). By referring to Figure 2.5, the OPS tends to cover hard kernel (seed) and surrounded by a fleshy mesocarp (Sumathi et al., 2008). Commonly, OPS is highly end up, burned as fuel to generate power in the palm oil mill (Hameed et al., 2007). While, the remaining excess OPS are used to fill up and cover the road surface in the plantation area.

2.4.1.2a Structure and Composition of Oil Palm Shell (OPS)

OPS are light, hard, and high in porosity in nature. As compared to other biomass, OPS are relatively dense and give positive effect on transportation for processing. OPS contain high in volatile matter, calorific value and fixed carbon, but low in ash content. The amount of structural carbohydrates and chemical composition of OPS is shown in Table 2.2. Hemicellulose and lignin are the main structure in OPS particles. The hemicellulose content in OPS makes it suitable as a pentose source accompany with reduction in lignin via pretreatment (Okoroigwe et al., 2014). Carbon and oxygen are the main elements found in OPS particles, with other minor elements which are hydrogen and nitrogen.

Table 2.2: The structural carbohydrates and chemical composition of OPS

	Parameter	**Weight (%)***
Structural Carbohydrates	Lignin	53.85
	Hemicellulose	26.16
	Cellulose	6.92
Chemical composition	Carbon (C)	46.75
	Oxygen (O)	37.97
	Hydrogen (H)	5.92
	Nitrogen(N)	0.68
	Silica(Si)	<0.08

* (Ndoke, 2006)

2.4.1.2b Application of Oil Palm Shell (OPS)

OPS show the ability to be utilized as a resource of sustainable and renewable energy (Sumathi et al., 2008). As a small amount of oil exists in the OPS, they are used as boiled fuel together with MF or wood to generate steam in palm oil mills. However, the combustion process leads to the production of volatiles and particulates that offer pre-ignition and pollution concern (Okoroigwe et al., 2014). Thus, other alternative products have been considered to use OPS on the market instead for energy. The reinforcement of OPS shows its ability as aggregate in producing lightweight concrete structure (Mannan and Ganapathy, 2002, Teo et al., 2007). This is due to their light weight in nature, where the density of OPS is 20-25 lower than normal weight of concrete (Shafigh et al., 2010).

Carbonization of OPS are potential to be used as absorber for water, sound and gaseous phase filtration (Yusof et al., 2012, Okoroigwe et al., 2014). In addition, previous study also emphasis on the utilization of OPS for quality grade charcoal due to high in grade solid, low in ash and sulfur content, and high in calorific value. As OPS are high in amorphous and low in crystalline region, which correspond towards high in lignin and hemicellulose contents, makes it suitable as filler material and can be incorporated in composites (Faieza, 2012, Okoroigwe et al., 2014).

2.5 Biocomposite

Biocomposite is a composite material derived from the polymer matrix resin reinforced by biological origin of the fibers and act as green material. The mixture of natural fibers with matrix yields a composite material competitive with synthetic composites which demands on certain attention. Biocomposite devote in increasing in energy efficiency and foster the idea of sustainability (Mohanty et al., 2000). Besides, it received high attention among academic and industrial areas, and emerging as it offers various advantages in term of recyclability, renewability, biodegradable, low in specific gravity, high in specific strength, and economical (Jamaludin et al., 2011).

2.5.1 Nano-biocomposite

Nano-biocomposite is an enhancement of biocomposite that bring the existing technologies down to a nanoscale by manipulating the structure of at least one material at the nano dimension (Salamon et al., 2010, (Liden, 2011). This dimension of material contributes in fascinate the properties by maximizing the interfacial adhesion between nano particles and matrix resin (Agag and Takeichi, 2000). A wide