ENHANCEMENT OF BAMBOO NANOFILLER IN PINEAPPLE LEAF FIBER REINFORCED POLYESTER COMPOSITES

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
EDX	Energy Dispersion of X-Ray
FT-IR	Fourier Transform Infrared Spectroscopy
GPa	Giga Pascal
MEKP	Methyl Ethyl Ketone Peroxide
MPa	Mega Pascal
PALF	Pineapple Leaf Fiber
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
PSA	Particle Saiz Analyzer

LIST OF SYMBOLS

%	Percentage
^{o}C	Degree Celsius
cm	Centimeter
d	Thickness
g	Gram
J	Joule
kg	Kilogram
M	Mega
m	Meter
w	Mass
mg	Miligram
mm	Milimeter
nm	Nanometer
Tg	Glass Transition Temperature
V	Volume
Vf	Volume Fraction
ρ	Density
ρ_c	Composite Density
ρ_f	Filler Density

PENAMBAHBAIKAN DARIPADA PENGISI NANO BULUH DI DALAM KOMPOSIT POLIESTER YANG DIPERKUAT GENTIAN DAUN NANAS

ABSTRAK

Dalam kajian ini, komposit polyester yang diperkuat gentian daun nanas (PALF) telah dibangunkan dan dipertingkatkan dengan pengisi nano buluh. Pencirian pengisi nano buluh seperti morfologi permukaan, unsur-unsur komposisi dan kumpulan berfungsi telah dinilai dengan menggunakan Pengimbas Mikroskopi Elektron dilengkapi dengan Tenaga Sebaran Sinar-X (SEM-EDX) dan Spektroskopi Inframerah Transformasi Fourier (FT-IR). Imej-imej SEM-EDX menunjukkan bahawa pengisi nano buluh yang dihasilkan terdiri daripada struktur bentuk hancur dan tidak teratur dengan kehadiran karbon dan oksigen sebagai komposisi utama. Selain itu, Penghantar Mikroskopi Elektron (TEM), Analisis Belauan Sinar-X (XRD) dan Analisis Termogravimetri (TGA) telah digunakan untuk mencirikan saiz pengisi, indeks penghabluran dan sifat haba pengisi nano buluh. Mikrograf TEM menunjukkan bahawa saiz pengisi nano buluh adalah diantara 10 hingga 30 nm yang menunjukkan sifat nano mereka. Analisis yang dijalankan dengan menggunakan XRD menunjukkan pengisi nano buluh mempunyai darjah indeks penghabluran yang rendah iaitu sebanyak 42.90%. Kesan penambahan pengisi nano buluh yang berbeza (0, 1, 3, dan 5 berat peratusan) ke dalam komposit polyester yang diperkuat serat daun nanas (PALF) telah dikaji. Ciri-ciri fizikal, mekanikal, morfologi dan sifat haba bagi komposit ini telah dikaji. Dapat diperhatikan bahawa kemasukan pengisi nano buluh ke dalam komposit telah meningkatkan sifat-sifat fizikal seperti ketumpatan, kandungan ruang kosong dan penyerapan air seiring dengan peningkatan muatan pengisi. Untuk sifat-sifat mekanik, kekuatan tegangan, lenturan dan hentaman serta

modulus tegangan dan lenturan komposit meningkat apabila muatan pengisi bertambah sehingga 3%, namun menjadi sebaliknya apabila muatan pengisi ditambah sehingga 5% muatan. Sementara itu, bagi pemanjangan pada takat putus bagi komposit, aliran bertentangan diperhatikan di mana kenaikan pengisi muatan mengurangkan pemanjangan pada takat putus. Sifat-sifat kestabilan haba bagi komposit mempamerkan aliran yang sama dengan sifat-sifat mekanikal. Dari segi kekuatan mereka mengikut arah gentian, untuk ujian tegangan, ia boleh diperhatikan bahawa serat selari sebelah arah diuji mencatatkan kekuatan tegangan yang lebih tinggi berbanding dengan serenjang sampingan arah serat. Walau bagaimanapun, dalam kes ujian lenturan dan hentaman, apabila serat adalah mendatar (tegak lurus) ke arah daya pintu masuk, hasilnya adalah lebih cekap. Pada morfologi struktur hentaman, 3% muatan pengisi komposit menunjukkan ruang kosong minimum yang lebih kecil dan kehadiran gentian patah dan bukannya gentian tarik keluar. Oleh itu, penambahan sebanyak 3% muatan pengisi nano buluh dipercayai adalah muatan optimum untuk komposit polyester yang diperkuat oleh PALF dan menunjukkan sifat-sifat luar biasa berbanding dengan peratusan muatan pengisi nano yang lain.

ENHANCEMENT OF BAMBOO NANOFILLER IN PINEAPPLE LEAF FIBER REINFORCED POLYESTER COMPOSITES

ABSTRACT

In this research, pineapple leaf fiber (PALF) reinforced polyester composites were developed and enhanced with nanofiller bamboo particles. Characterization of bamboo nanofiller such as surface morphologies, elemental composition and functional groups were evaluated by using Scanning Electron Microscopy equipped with Energy Dispersive X-ray Analysis (SEM with EDX) and Fourier Transform Infrared Spectroscopy (FT-IR) respectively. The SEM-EDX images revealed that bamboo nanofiller produced consisted of crushed and irregular shape structures with presence of carbon and oxygen as a major elements composition. Besides, Transmission Electron Microscope (TEM), X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA) were used to characterize particle size, crystallinity index and thermal properties of bamboo nanofiller respectively. The TEM micrograph revealed that bamboo particles size ranged between 10 to 30 nm indicates their nanometric nature. Percentage crystallinity of bamboo nanofiller by XRD analysis comes out to be 42.90%, show its lower degree of crystallinity index. Effect of different filler loading (0, 1, 3, and 5 wt %) of bamboo nanofiller into pineapple leaf fiber (PALF) reinforced polyester composites were studied. The physical, mechanical, morphological and thermal properties of the composites were studied. It was observed that with incorporation of bamboo nanofiller into the composites increased its physical properties such as the density, void content and water absorption as filler loading increases. As for mechanical properties, the strength of tensile, flexural and impact as well as modulus of tensile and flexural increased as the filler increases up to 3 % filler loading, however became vice versa when filler loading added up to 5 % loading. Meanwhile for the elongation at break of the composites, opposite trend observed where increments of filler loading reduce the elongation at break. The thermal stability properties of the composites exhibit similar trends with mechanical properties. In terms of their strength according to the fiber direction, for tensile test, it can be observed that parallel fiber direction side tested recorded higher tensile strength compared to perpendicular fiber direction side. However, in the case of flexural and impact test, when the fibers are horizontal (perpendicular) to the direction of force entrance, the outcome is much more efficient. On morphological of impart structures, 3 % filler loading of composites showed smaller minimum voids and presence of fiber fracture instead of fiber pull out. Therefore, addition of 3 % bamboo nanofiller loading was believed to be the optimum for the PALF reinforced polyester composites and shows remarkable properties compared to other filler loading.

CHAPTER ONE

INTRODUCTION

1.1 Overview

The demand for a new high performance material with at affordable costs in making products for various applications has becoming buzzword. The materials needed particularly focused on eco-friendly matter that will able to drive into a biodegradable, recyclable, renewable and sustainable products. This matter was being focused nowadays because of growing environmental awareness in community, greatly developed technology and abundant amount of natural resources.

Due to the shortages of woody materials recently plus high rising cost of raw materials supplied products in the market, there was need an alternative sources of lignocellulosic biomass. For some structural applications, cellulose fibers were more likely being utilized and have increased steadily compared to synthesis fibers as reinforcement in polymer matrix because of its better properties and also influenced by the environmental aspects (Jawaid et al., 2014).

In this case, the application of cellulose fibers reinforced composite materials have been developed to ensure future generations getting green and sustainable materials. In composite application, the most commonly used type of cellulose fibers are the bast: flax, hemp, jute, ramie; and the leaf: abaca, curaua, date palm, pineapple, sisal, banana. The term `green biocomposite' could soon be widely used whenever any of these biofibers being embedded with renewable resourcebased biopolymers such as polylactides (cellulosic plastics) or polyhydroxyalkanoates (starch plastics) (Kalia et al., 2011).

The **pineapple** (*Ananas comosuss* L.), is a tropical plant that developed one of the most popular and delicious triploid fruit with consisting of coalesced berries, and the most economically significant plant in the Bromeliaceae family. Native to southern Brazil and Paraguay area, the pineapple was domesticated by the Indians and carried by them up through South and Central America to Mexico before the arrival of Europeans. It obtained an output of 18.4 million tonnes in 2009 and gradually increased to 23.3 million tonnes total world production quantity in 2012. (de Souza et al., 2012)(FAO 2015). The fibers extracted from the leaves, gives an excellent potential as reinforcement in polymer composites other than various natural fibers because it exhibits excellent mechanical properties (Arib et al., 2006).

The bamboos (Bambusoideae) are a sub-family of flowering perennial evergreen plants in the family Poaceae. The origin of bamboo is believed to be grows in ancient China. This plant also well-known as low-cost material that is used especially in the regions of Southeast Asia, South America and Africa and the species known today evolved from prehistoric grasses between thirty and forty million years ago. It then became the major food source for herbivorous animals, eventually becoming a food source for the modern human being as well. Bamboo is recognised as a material that can contribute as a competitive and environmentally friendly alternative to conventional construction materials (Sharma et al., 2015b), based on their character of rapidly renewable, sustainable resource and has mechanical properties similar to timber (Sharma et al., 2015a).

Nanotechnology, or nanoscience, refers to the research and development of an applied science at the level of atomic, molecular, or macromolecular. The prefix "nano" is defined as a unit of measurement in which the characteristic dimension is one-billionth of meter. Although the nano scale is small in size, its potential is wide.

Nano-particles are presently considered as high-potential filler materials for the improvement of mechanical and physical properties of polymer composites (J. Njuguna, 2007).

The application of nanotechnology in the automotive industry is diverse or manifold. They show diversity from energy conversion, light-weight construction, interior cooling, power train, surveillance control up to recycle potential, pollution sensing and reduction, driving dynamics and wear reduction etc. Besides automotive industry, the application of nanotechnology also covered the food processing and food safety industries that able to provide high-barrier packaging materials and revealing food-relevant analytes by creating more effective antimicrobial agents (Duncan, 2011).

Nano fillers could be organic and inorganic in nature. The filler, such as cellulosic nanofiller, coir nanofiller, carbon black and many others are derived organically and naturally represent organic nanfillers. Meanwhile, the examples of particles that forming inorganic filler are silica (SiO_2), titanium dioxide (TiO_2), calcium carbonate ($CaCO_3$), or polyhedral oligomeric silsesquioxane (POSS) and etc. (Naheed Saba, 2014). The diverse nanofillers that are used in nano composites are nanoclays, nano-oxides, carbon nanotubes, and organic nanofillers. However, according to the nanofillers the nanocomposites can be distributed, as classified in ISO/TS 27687.

1.2 Problem statement and justification

Most fibres that are considered are bast fibres. Bast fibre is plant fibre collected from the phloem (the "inner bark") surrounding the stem. These derive from tall plants that require high stiffness fibres in their stalk to maintain stability.

This includes hemp, flax, kenaf and jute. Fibres from the leaf of a plant (e.g. pineapple, sisal) do have industrial use but are less often considered due to their generally lower stiffness properties. Research on natural fibre processing generally includes a stage to modify the surface, commonly with sodium hydroxide, to provide a consistent bonding surface (Thakur and Thakur, 2014).

After the harvesting activity of the pineapple fruit, its residues is disposed off and this will increase the quantity of waste, thus waste disposal space becomes limited. The non-renewable based materials are replaced by renewable bio-based materials in several applications due to their renewability and sustainability. Environmental legislation (landfill directive) aims to reduce the negative effects on the environment by reducing the land filling and using sustainable, renewable and biodegradable materials (González-Olmedo et al., 2005).

Without any effort to utilize the pineapple waste, especially its leaf that give material of high cellulosic content, the waste will just ended as waste, unable to transform into other product, thus no income can be generate. Besides that, the waste also being burnt in an open field, creating uncomfortable condition and polluting the air. Efforts should be made to reduce the environmental impact. One of the solutions is by introducing these materials in automotives and aircraft industry, thus its lightweight properties able to reduce the fuel consumption of the aircraft. It is estimated that a 1% weight reduction in aircraft corresponds to 0.75% reduction in fuel consumption (Thakur and Thakur, 2014)

1.3 Objectives of study

The aim of this thesis was to develop an environmentally friendly biodegradable thermoset (polyester) biocomposite from pineapple leaf fibre (PALF), together with enhancement using bamboo particle nanofiller. The study was divided into four parts: -

1. To study the characteristics and properties of bamboo nanoparticle as enhancement in PALF-polyester composite.
2. To develop pineapple leaf fiber with bamboo nanoparticle reinforced polyester composites.
3. To evaluate the physical, mechanical, thermal and morphological properties of the PALF-polyester composites.
4. To determine the optimum percentage of bamboo nanofiller that gives maximum performance to the PALF-polyester composites.

1.4 Organization of Thesis

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

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

Chapter 2: Devoted on the literature review of agro-waste, pineapple plant, pineapple leaves fibre and composites.

Chapter 3: Explanation regarding materials used and methodology of the extraction of pineapple leaf fiber (PALF), production of PALF mat and nano-structured bamboo fiber powder, their characterization, and fabrication of nano-fiber enhanced biocomposites.

Chapter 4: Provide all the results and discussion of characterization of nano-structured bamboo nano-fiber powder together with the properties of pineapple leaf fiber (PALF)/ Bamboo nano-fiber powder enhanced polyester composites.

Chapter 5: Encapsulate summarization of overall conclusion of this study and recommendation for future research work that are related for better improvement.

CHAPTER TWO

LITERATURE REVIEW

2.1 Management of agro-residue

Agro-residue is a type of residue which is produced usually through farming or collected residue from various agriculture activities. Examples of agro-residue are manures, bedding, leaves, plant stalks and vegetable matter. The accumulation of these agro-residues will create many negative effects and being introduced into our life. The reason for this is due to agro-residue is often not being use and just waited to be discarded. The problems that may occur by improper agro-residue management could be in terms of health, safety, environmental, and aesthetic matter. Thus, safe and effective agro-residue disposal is really required to avoid such kind of problems (Sud et al., 2008). Agro-residues contain insoluble chemical constituents such as cellulose and lignin plus with other soluble constituents which are amino acids, organic acids and sugar. Other constituents such as fats, oil waxes, protein, and mineral are also present (Subba Rao, 1993).

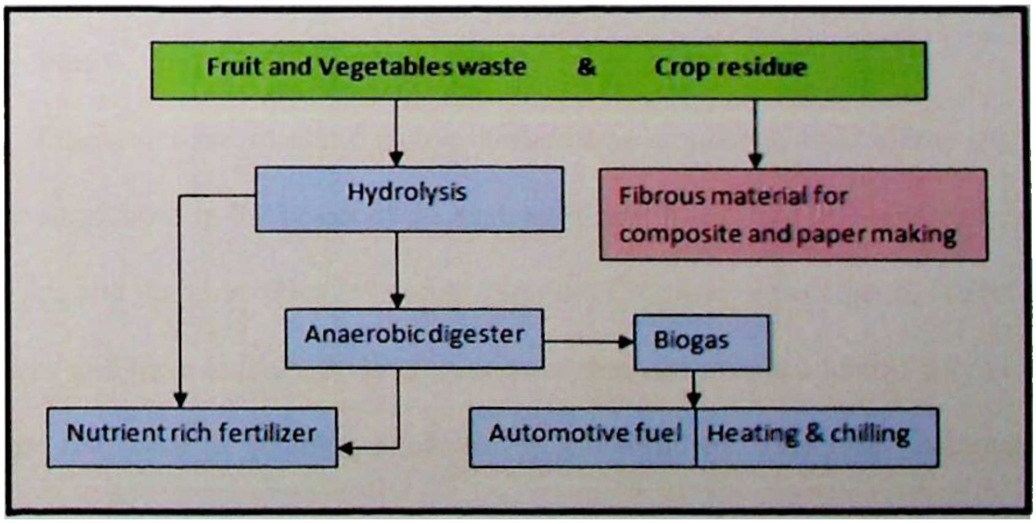

Figure 2.1: Recycling of agricultural residues (Subba Rao, 1993)

2.2 Botanical description of pineapple plant

The pineapple, *Ananas comosus*, is a member of the Bromeliaceae, a large, diverse family of about 2000 species. Figure 2.2 shows different parts of pineapple plant. Pineapple plant is one of the few important fruiting monocots, which is one of the most popular and delicious tropical fruit and propagated vegetatively through suckers. It is esteemed for its flavour and nutritive contents (Mengesha et al., 2013).

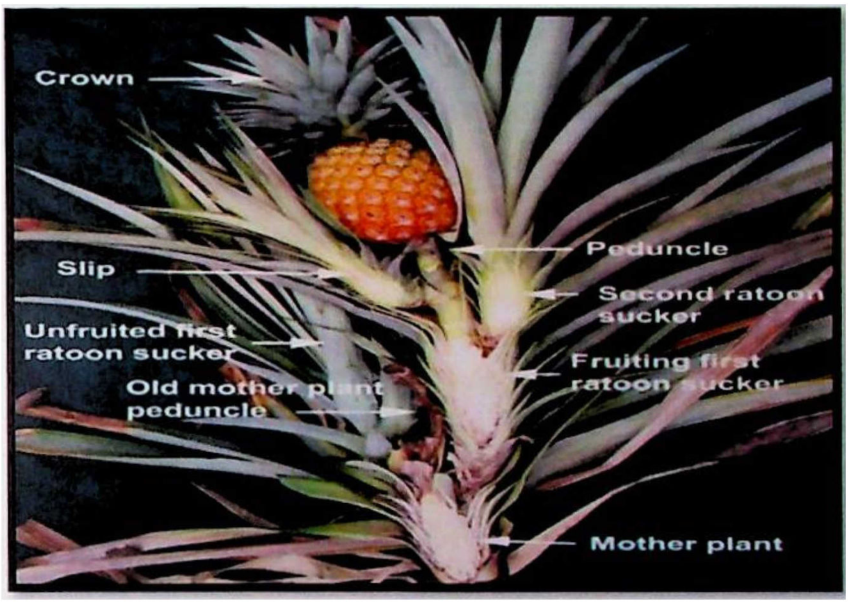

Figure 2.2: Parts of pineapple plant (Mengesha et al., 2013)

2.2.1 Plant

Pineapples are rosette-forming, herbaceous monocots, their stems are short, and inconspicuous in the center of the rosette of long linear leaves. Spines are present at the tips and margins of leaves except 'Smooth Cayenne' type. Leaves are arranged on stems and have axillary buds at their base that can produce lateral shoots called suckers; that used as planting stock for propagating the next crop. Alternatively, plants are trimmed back after harvest, leaving only one sucker to grow in place of the original plant yielding a second crop or called as ratoon crop of the same field (Morton, 1987).

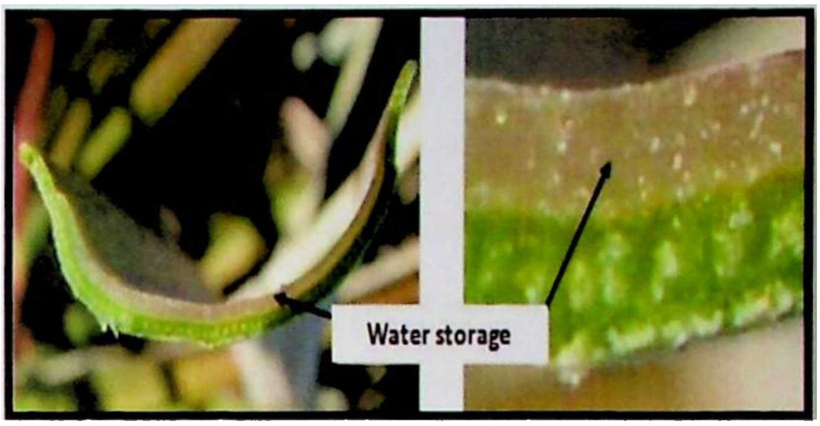

Figure 2.3: Pineapple leaf cross-section (Morton, 1987)

Figure 2.3 shows cross-sections of pineapple leaf which is a primary photosynthesis organ for a plant. It consists of an epidermis, palisade parenchyma, spongy mesophyll and fiber bundle. This plant vascular bundle consists only thick-walled fibers, without other vascular tissues. This was one of the adaptations for annual plants, to provide strength and stiffness to the leaf (Alwani et al., 2014).

2.2.2 Flowers

Pineapple flowers are small, purple-red, subtended by a single yellow, green or red bract and borne laterally on the rachis of a spike of 100-150 individuals. The apex of inflorescence is vegetative. Bromeliads are unusual plants in that flowering can be induced by chemicals auch as the gaseous hormone ethylene that able to initiates flowering. Chemicals are applied when plants achieve a certain size, about 6-12 months after planting or cutting back to suckers in ratoon crops (approx the 30-leaf stage). Ethephon, naphthalene acetic acid (NAA), calcium carbide, and BOH (ßhydroxyethyl hydrazine) are used commercially, with ethephon being the most widely used chemical (González-Olmedo et al., 2005).

2.2.3 Pollination

Pineapple is highly self-incompatible, exhibiting gametophytic incompatibility where the pollen germinates on the stigma, but fails to grow through the style and effect fertilization (Ayenew et al., 2013). Seedless fruit are set parthenocarpically. If flowers are cross-pollinated, a few small, brown seeds may be found just beneath the peel of the fruit. Hummingbirds are the natural pollinators.

2.2.4 Fruit

The fruit type is a multiple of berries, formed from the fusion of adjacent flower ovaries on the spike as they mature. Another name for this type of fruit is syncarp. The core is the fleshy rachis of the spike, often fibrous and unpalatable. The fruit is covered with a waxy, leathery rind, made up of hexagonal "eyes", arranged spirally, which denote the position of individual flowers. One fruit per plant is produced, and the shoot it was borne on dies back or is cut off. Fruit require about 6 months from forcing to harvest. Total production time is 15-18 months from transplanting, or about 12 months for a ratoon crop (Nweze et al.).

2.3 Bamboo plant

Bamboo, or *Bambusa vulgaris* (Figure 2.4) forms moderately loose clumps and has no thorns. It has lemon-yellow culms (stems) with green stripes and dark green leaves. Stems are not straight, not easy to split, inflexible, thick-walled, and initially strong (Tchoundjeu and Atangana, 2011). The densely tufted culms grow

10–20 m (30–70 ft) high and 4–10 cm (2–4 in) thick. Culms are basally straight or flexuose (bent alternately in different directions), drooping at the tips. Culm walls are slightly thick. Nodes are slightly inflated. Internodes are 20–45 cm (7.9–17.7 in). Several branches develop from mid-culm nodes and above. Culm leaves are deciduous with dense pubescence. Leaf blades are narrowly lanceolate (Wu"Zheng-yi et al., 1994).

Flowering is not common, and there are no seeds. Fruits are rare due to low pollen viability caused by irregular meiosis. At the interval of several decades, the whole population of an area blooms at once, and individual stems bear a large number of flowers (Louppe et al., 2008). Vegetation propagates through clump division, by rhizome, stem and branch cutting, layering, and marcotting. A clump can grow out of stem used for poles, fences, props, stakes, or posts. Its rhizomes extend up to 80 cm before turning upward to create open, fast-spreading clumps (Meredith, 2009).

Figure 2.4: Bamboo plant
(Amie Taylor, Demand Media. Bamboo plant. Web. 26 April 2016.)

2.4 Composites

2.4.1 Definition and Classification

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

The classification of composites is based on the matrix and reinforcement phases of materials. Based from the Figure 2.5, the classification of composites were 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. Meanwhile, particulate, fibrous, and laminate are included in the reinforcement phase classification of composites (Tabiei and Aminjikarai, 2009).

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 (Huang and Talreja, 2006).

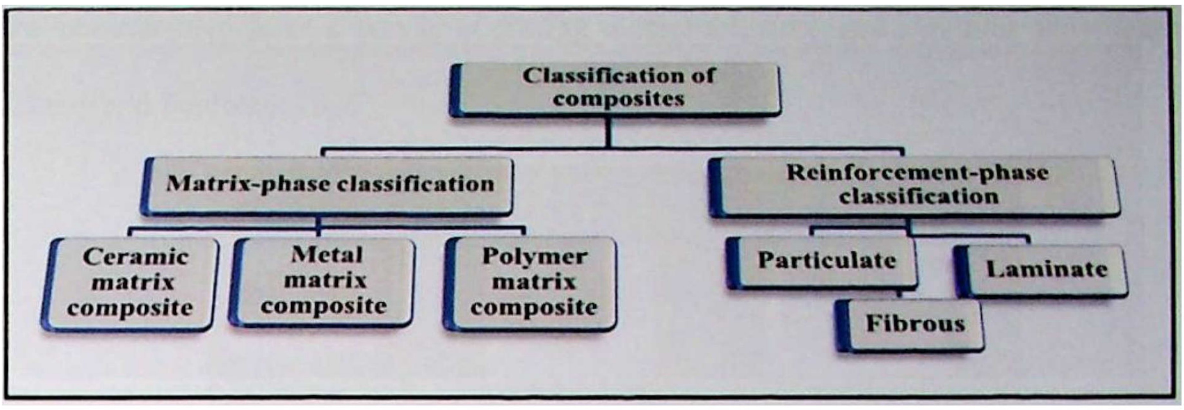

Figure 2.5: The classification of composites (Tabiei and Aminjikarai, 2009)

Lately, there has been a growing interest in the use of natural cellulosic fibres as the reinforcement for polymeric matrix. While these fibres may not be as strong as others from synthetic type fibers, their main advantages are low cost and biodegradability. This may due to the high price of composites, the user industries demand a lower price for production of fibre components, at the same time with an improvement in quality (George et al., 1995). It was found that these could be achieved by the use of natural fibres. plant fibers are the most popular of the natural fibers, used as reinforcement in fiber reinforced composites. Plant fibers include bast (or stem, soft, or sclerenchyma) fibers, leaf or hard fibers, seed, fruit, wood, cereal straw, and other grass fibers (Akil et al., 2011).

Synthetic fibers are from the types that have been incorporated into cement matrices include polyethylene (PE), polypropylene (PP), acrylics (PAN), poly (vinyl alcohol) (PVA), polyamides (PA), aramid, polyester (PES) and carbon. The properties of synthetic fibres vary widely, in particular with respect to the modulus of elasticity, an important characteristic when fibres are used for producing composites. A synthetic fibre can be described as a flexible, macroscopically homogeneous body, with a high length to thickness ratio (aspect ratio) and a small cross-section. Fibres are manufactured from naturally occurring macromolecules and synthetic polymers (Zheng and Feldman, 1995).

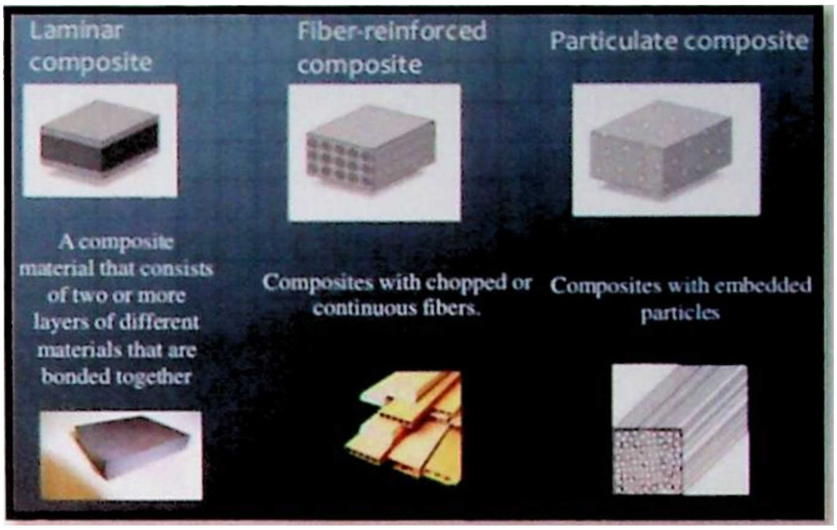

Figure 2.6: Different types of composite (Tabiei and Aminjikarai, 2009)

2.4.2 Biocomposites

Biocomposites or in a specific terms was a new class of fully biodegradable 'green' composites by combining natural or bio fibres with biodegradable resins. The major attractions about biocomposites are due to its environmentally friendly, fully degradable and sustainable, thus they are truly 'green' in every way. At the end of their life they can be easily disposed of or composted without harming the environment (Netravali and Chabba, 2003).

Biocomposites comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibres such as cotton, flax, hemp and the like, or fibres from recycled wood or waste paper, or even by-products from food crops. Regenerated cellulose fibres (viscose/rayon) are also included in this definition, since ultimately they too come from a renewable resource, as are natural 'nano fibrils' of cellulose and chitin (Oksman et al., 2003).

Resin that holds the fibers may be polymers, ideally derived from renewable resources such as vegetable oils or starches. Alternatively, and more commonly at the present time, synthetic, fossil-derived polymers preponderate and may be either 'virgin' or recycled thermoplastics such as polyethylene, polypropylene, polystyrene and polyvinyl chloride, or virgin thermosets such as unsaturated polyesters, phenol formaldehyde, isocyanates and epoxies (Jawaid and Khalil, 2011).

Rising environmental awareness related to raw materials, its costs for the supplied products in the market, shortages of woody materials, and concerns regarding the sustainable resource management make the wood-based industries need alternative sources of lignocellulosic biomass. According to them, large amount of wood used as feedstock could be reduced together with preservation of environment can be achieved by the usage of agricultural and agro-industrial residues and non-wood plants as the replacement (Khalil et al., 2012).

Figure 2.7: Variety of bio-composites manufactured (Jawaid and Khalil, 2011)

2.4.2(a) Nano-biocomposites

The concept of nanostructured materials design is gaining widespread importance among the scientific community (Mohanty et al., 2005). The strong reinforcement effects at low volume fraction resulted in a tremendous interest from the industry and research circles. With this as an inspiration, the potential of nanoscale cellulose structures as reinforcement in novel composite materials was extremely interesting. The concept of cellulose nanocomposites for load bearing applications is fairly new.

Property enhancements are expected due to higher Young's modulus of pure cellulose reinforcement and finely distributed reinforcing microfibrils. A major problem in the commercial use of cellulose microfibrils in structural materials is the disintegration of cellulose from plant cell wall at reasonable cost and without severe degradation (Van de Velde and Kiekens, 2001). Another major problem is dispersion of cellulose microfibrils in a polymer matrix (Njuguna et al., 2011).

Nowadays, engineering materials at the atomic and molecular levels are creating a revolution in the field of materials and processing. The discovery of new nanoscaled materials such as nanoclays, carbon nanotubes, and others offer the promise of a variety of new composites, adhesives, coatings, and sealant materials with specific properties (Joseph et al., 2000).

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

A wide array of ingredient has been used in nano-engineered material for composite application. Generally, it is the combination of fibers with polymer matrix,which provides benefits, especially in term of the production quality, sustainability and economy. Nanocomposite is known to have superior properties compared to classical composite. It improved in term of mechanical, electrical properties in combination with economic benefit. The properties of composites were affected by the rate of distribution and dispersion of nano particles into matrix resin (Kalia et al., 2011).

Enhancement in mechanical properties of nanocomposites was expected to be achieved with a well distributed and dispersed nano particles. High potential of agglomeration tends to occur in the inhomogeneous distribution and dispersion of nano particles. The agglomerates of filler lead to negative effects towards the nanocomposites due to reduction in surface area of filler-matrix interaction and results in inhibit the stress transfer mechanism. Figure 2.8 depicts a schematic representation of the degree of dispersion and distribution of nanoparticle s in matrix resin (Hedayati et al., 2011).

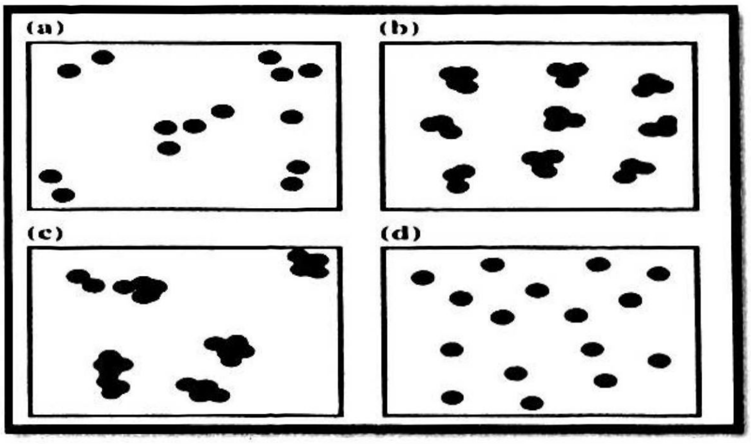

Figure 2.8: Schematic representation of the degree of dispersion and distribution of particles in matrix resin (a) good dispersion, poor distribution, (b) poor dispersion, good distribution, (c) poor dispersion, poor distribution, (d) good dispersion, good distribution (Hedayati et al., 2011)

2.5 Polymer Composite

Most commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, polyether ether ketone (PEEK), and others. The reinforcement materials are often fibers but can also be common ground minerals (Mkaddem et al., 2008).

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 (Tabiei and Aminjikarai, 2009).

Various methods have been developed to reduce the resin content of the final product. As a rule of thumb, hand lay up results in a product containing 60% resin and 40% fiber, whereas vacuum infusion gives a final product with 40% resin and 60% fiber content. The strength of the product is greatly dependent on this ratio. PMCs are very popular due to their low cost and simple fabrication methods. Use of nonreinforced polymers as structure materials is limited by low level of their mechanical properties, namely strength, modulus, and impact resistance (Bakar et al., 2003).

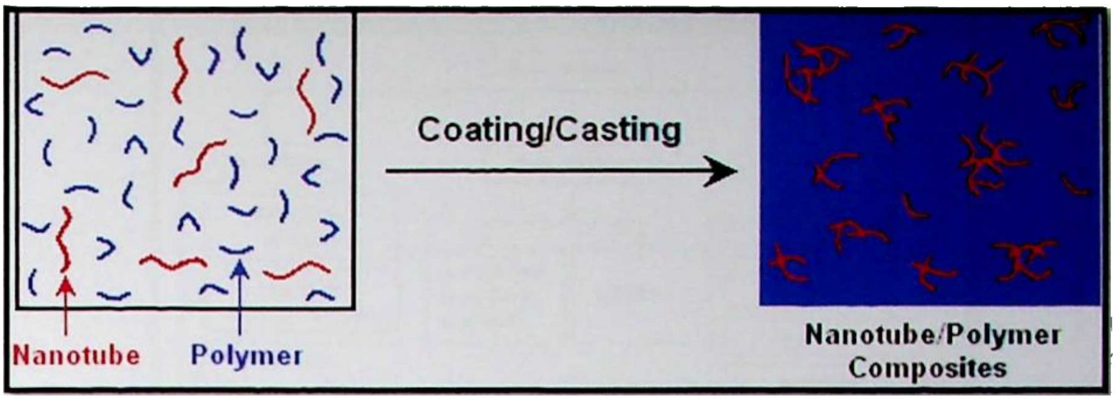

Figure 2.9: Schematic illustration for the random aggregation of nanotubes in nanotube/polymer composites synthesized by traditional approaches. (Peng et al., 2008)

2.5.1 Reinforcement

2.5.1(a) Natural Fibers

The idea of using natural fibers as reinforcement in polymer composite materials is not a new or recent one. Man had used this idea for a long time, since the beginning of our civilization when grass and straw were used to reinforce mud bricks. In the past, composites, such as coconut fiber or natural rubber latex, was extensively used by the automotive industry (Mohanty et al., 2005). There is a wide variety of natural fibers that can be used to reinforce thermoplastics. These include wood fibers, such as steam-exploded fibers, and a variety of agro-based fibers such as stems, stalks, bast, leaves and seed hairs. Other large sources are recycling agro fiber-based products such as paper, waste wood, and point source agricultural residues such as rice hulls from a rice processing plant. Figure 2.10 list out the classification of available natural fibers (Mohanty et al., 2005).

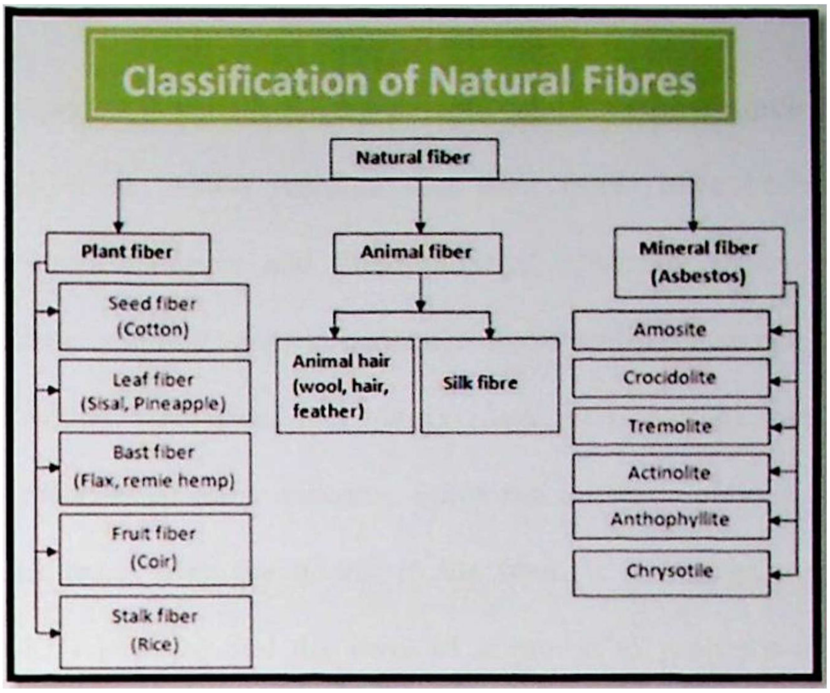

Figure 2.10: Classification of natural fibers (Mohanty et al., 2005)

The performance and properties of composite materials depend on the properties of the individual components and their interfacial compatibility. To ensure appropriate interfacial interactions their surface properties must be modified accordingly. Also, the use of thermoplastic polymers with particulate fillers or short-fiber reinforcements has grown rapidly because of their good processability and ability to be recycled. Fillers are added to the polymeric matrix with the aim of improving its thermal and mechanical properties. There are, however, some adverse effects, i.e. toughness, and ultimate elongation that polymers often suffer because of the addition of fillers. A properly selected interface has a significant effect on the dispersion quality and adhesion between the polymer and the filler (Herrera-Franco and Drzal, 1992).

Natural fibers are gaining attention as a reinforcing agent in thermoplastic matrices. Low density and a highly reduced wear of the processing machinery may be mentioned as attractive properties, together with their abundance and low cost (Cazaurang-Martinez et al., 1991) pointed out that these hard fibers posses mechanical properties that make them a suitable candidate to reinforce thermoplastic resins. (Joseph et al., 1993) reported that hard fibers have been successfully incorporated into elastomers and thermoplastics. (Herrera-Franco et al., 1997) deposited a silane coupling agent to henequén fibers and have shown that adhesion between the natural hard fibers and matrix plays an important role on the final mechanical properties of the composite. Since the interface plays a major role in transferring the stress from the matrix to the fiber, it is important to be able to characterize the interphase and the level of adhesion to properly understand the performance of the composite.

2.5.1(b) Pineapple Leaf Fiber (PALF) as Reinforcement in Composites

Pineapple leaf fiber (PALF) which is rich in cellulose, relatively inexpensive, and abundantly available has the potential for polymer reinforcement (Devi et al., 1997). Inclusion of natural fiber such as pineapple leaf (PALF) in some thermosetting polymer has not only changed their brittle character and some other thermal properties but also brought reduction in cost and made the composite more environmentally friendly (Mangal et al., 2003). The present study investigated the tensile, flexural, and impact behavior of PALF-reinforced polyester composites as a function of fiber loading, fiber length, and fiber surface modification (Devi et al., 1997).

It has been found that PALF consists of following chemical entities; holocellulose (87.56%), alpha-cellulose (78.11%), hemicellulose (9.45%), lignin (4.78%). This composition gives the thermoplastic composite for construction application. Apart from this dietary fibre is also of great importance for commercial purposes. The superior mechanical properties of pineapple leaf fiber are associated with its high cellulose content and comparatively low microfibrillar angle (the angle that the cellulose microfibril make to the axis of the cell wall) (Cherian et al., 2011).

Pineapple fibres (PALF) come as viable and abundant substitutes for the expensive and non-renewable synthetic fibres. These with high specific strength improved the mechanical properties of the polymer matrix. In tropical countries, fibrous plants are available in abundance and at least some of them are agricultural crops. Pineapple is among them. PALF at present is a waste product of pineapple cultivation. Hence, without any additional cost input, pineapple fibres can be obtained for industrial purposes. Among various natural fibres, pineapple leaf fibres exhibit excellent mechanical properties. These fibres are multicellular and lignocellulosic (Devi et al., 1997).

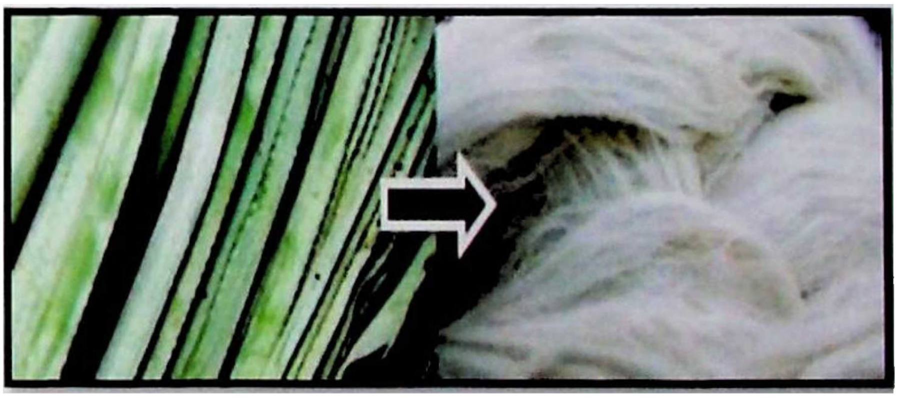

Figure 2.11: Extracting PALF from pineapple leaves (Devi et al., 1997)

2.5.2 Matrix

2.5.2(a) Thermoset-based Matrix

Thermoset polymer matrices are synthetic polymer reinforcements that have been developed and used in many applications. Thermoset polymers are the most widely used matrix material in composite materials. Thermoset polymer consists of amorphous structure which molecules are linked by network structure of strong covalent bonds. Once the crosslinking reaction occurs, the network cannot undergo reshaped upon heating, but instead decomposed (Daniel et al., 1994). The different types of thermoset polymer matrices used in composites are bis-maleimids (BMI), epoxy (epoxide), phenolic (PF), polyester (UP), polyimide, polyurethane (PUR) and silicone (Thakur and Thakur, 2014).

2.5.2(b) Unsaturated Polyester Resin

This is an extremely versatile, fairly inexpensive, polymer. Unsaturated polyester combines an unsaturated dibasic acid and a glycol dissolved in a monomer, generally styrene, including an inhibitor to stabilize the resin. Organic peroxides, such as methyl ethyl ketone peroxide (MEKP) and a promoter are combined with the resin to initiate a room temperature (R.T.) cure. In this liquid state, polyester may be processed by numerous methods, including Hand Layup (HLU), vacuum bag molding, and spray-up and compression molded Sheet Molding Compound (SMC) (El-Tayeb, 2008).

2.6 Nano-materials

Nanomaterials are coming into use in healthcare, composites, electronics, cosmetics and other areas. Their physical and chemical properties often differ from those of bulk materials. 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).

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).

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. Currently, over 85% of the markets are filled with nanomaterials, predominantly for nanocomposites and nanoparticles (Wegner and Jones, 2009).

2.6.1 Structure and Morphology of Nano-materials

Nanotechnology is the general term for designing and making anything whose use depends on specific structure at the nanoscale- generally taken as being 100 nanometres (100 millionths of a millimetre or 100 billionths of a metre) or less. It includes devices or systems made by manipulating individual atoms or molecules, as well as materials which contain very small structures (Zimmermann et al., 2010).

Nanomaterials are may be in the form of particles, tubes, rods or fibres usually considered to be materials with at least one external dimension that measures 100 nanometres or less or with internal structures measuring 100 nm or less. The nanomaterials that have the same composition as known materials in bulk form may have different physico-chemical properties than the same materials in bulk form (Kashiwagi et al., 2002).

Nanoparticles are particulates with nanometer sized in all three dimensions. They can also befound 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 100nm, is known as nanolayers, nanosheets or nanoplates (Madhumathi et al., 2009).

2.6.2 Nanofillers as Potential Enhancement

Polymeric composites that show great prospective applications in constructions and buildings, automotive, aerospace and packaging industries are developed from the polymeric matrix with suitable and proper filler together with better filler and matrix interaction (Suresha et al., 2013). Other than that, new and advanced methods or approaches also are the one to contribute to this effort.

2.6.2(a) Bamboo Particles

Bamboo has many advantages as a construction material: it is a rapidly renewable sustainable resource and has mechanical properties similar to timber. Worldwide, there is a growing interest in the development of bamboo products as a sustainable, costeffective and ecologically responsible alternative construction material (De Flander, 2005). Partially due to the faster growth rate, and therefore