CHARACTERIZATION, PROPERTIES AND DEGRADATION OF CARBONIZED *JATROPHA* SEED SHELL FILLED VINYL ESTER COMPOSITES

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CHARACTERIZATION, PROPERTIES AND DEGRADATION OF CARBONIZED *JATROPHA* SEED SHELL FILLED VINYL ESTER COMPOSITES

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance two factor-factorial design
ASTM	American Society for Testing and Materials
DF	Degree of freedom
DSC	Differential Scanning Calorimetry
DTG	Differential thermogravimetry
FT-IR	Fourier Transform Infrared
HCl	Hydro Chloride Acid
HDPE	High density polyethylene
IUPAC	International Union of Pure and Applied Chemistry
LDPE	Low density polyethylene
PMCs	Polymer matrix composites
PP	Polypropylene
PS	Polystyrene
MMC	Metal matrix composite
MEKP	Methyl Ethyl Keton Peroxide
NaOH	Sodium Hydroxide
PVC	Poly (vinyl chloride)
SEM	Scanning Electron Microscope
TEM	Transmission electron microscopy
TGA	Thermogravimetric Analysis
UV	Ultraviolet
WPCs	Wood-plastic composites
XRD	X-ray diffraction

LIST OF PUBLICATIONS

		pages
APPENDIX A	Abdul Khalil, H.P.S., **N.A. Sri Aprilia**, A.H. Bhat, M. Jawaid, M.T. Paridah, D. Rudi, 2013. A *Jatropha* biomass as renewable materials for biocomposites and its applications, *Renewable and Sustainable Energy Reviews*, 22, 667–685	195
APPENDIX B	**N.A. Sri Aprilia**, H.P.S. Abdul Khalil, A.H., Bhat, Rudi Dungani, Md. Shorab Hossain, 2014. Exploring material properties of vinyl ester biocomposites filled carbonized *jatropha* seed shell, Bioresouces, 9 (3), 4888-4898.	196

CIRI, SIFAT-SIFAT DAN DEGRADASI VINYL ESTER KOMPOSIT TERISI KULIT BIJI JARAK TERKARBON

ABSTRAK

Pada masa kini, penggunaan sisa biomas telah digunakan secara meluas sebagai pengisi dalam biokomposit. Dalam kajian ini, kulit biji jarak (*jatropha)* melalui proses karbonisasi dengan menggunakan kaedah relau iaitu pada suhu 600˚c serta mengambil masa selama 1 jam. Analisis termal dan sifat-sifat fizikal kulit biji jarak telah dilakukan terlebih dahulu sebelum proses pengkarbonan dijalankan. Analisis taburan purata partikel telah dilakukan dalam empat saiz iaitu 45, 129, 227 dan 880 mikron (melalui saringan: > 300, 150-300, 100-150 dan 74-100 mesh) dengan penggunaan Sinar-X (EDX), TEM, FT-IR, XRD dan SEM. Kajian penambahan partikel dan saiz partikel kulit biji jarak terkarbon dalam vinil ester komposit telah dicirikan oleh sifat-sifat fizikal, mekanikal, morfologi dan termal serta ketahanan terhadap persekitaran. Sifat-sifat fizikal komposit vinil ester terisi kulit jarak terkarbon terdiri daripada ketumpatan, penyerapan air dan rongga-rongga kosong. Sifat-sifat mekanikal komposit ini telah dilakukan untuk mengkaji pengaruh penambahan partikel serta saiz partikel. Analisis menunjukkan, peningkatan dalam kekuatan tensil pada penambahan partikel hanya mencatatkan 10 wt % berbanding komposit tulen vinil ester serta pemuatan yang mencatatkan peratusan yang lebih tinggi. Kekuatan fleksural komposit menurun dengan peningkatan partikel terkarbon sementara itu modulus tegangan dan modulus lenturan menunjukkan arah yang bertentangan. Analisis degradasi termal menunjukkan peningkatan dalam kandungan sisa bahan-bahan komposit dan kestabilan termal menjadi lebih baik. Seterusnya, transisi gelas dalam analisis DSC pada suhu lebur yang semakin meningkat apabila

ditambah partikel pengisi sebanyak 10 wt% tetapi menurun pada penambahan partikel pengisi yang lebih banyak. Analisis morfologi menunjukkan permukaan komposit menjadi licin dengan berselang seli ketulan penumpuan pada penambahan peratusan partikel yang lebih banyak. Selain itu, kerosakan komposit vinil ester yang mengandungi kulit biji jarak terkarbon turut diteliti untuk mendapatkan ketahanan rencam terhadap kesan pendedahan kepada UV serta kesan pemeluwapan yang dijalankan selama 96, 240 dan 360 jam. Kajian menunjukkan, semakin lama masa pendedahan semakin berkurangan sifat-sifat mekanikal komposit vinil ester kulit biji jarak terkarbon ini. Salah satu masalah yang timbul berkenaan biokomposit sebagai tangki penyimpanan cecair ialah tindak balas hakisan terutama pada persekitaran yang agresif. Oleh yang demikian, untuk kajian ini, komposit vinil ester kulit biji jarak terkarbon ini telah direndam terlebih dahulu dengan NaOH 5%, HCI 5% serta air suling pada suhu bilik. Ketahanan medium pengakis untuk komposit vinil ester dapat dilihat dalam penambahan berat serta perubahan dalam sifat-sifat mekanikal dan morfologi.

CHARACTERIZATION, PROPERTIES AND DEGRADATION OF CARBONIZED JATROPHA SEED SHELL FILLED VINYL ESTER COMPOSITES

ABSTRACT

Nowadays, the use of biomass waste has been widely used as fillers in biocomposites. In this study, carbonized *jatropha* seed shell has been produced in furnace method at 600^{o}C temperature for 1 hour. Thermal and physical analysis of *jatropha* seed shell has been done before carbonization. The average distributions of particle analysis in four-size are 45, 129, 227 and 880μm (pass through sieving: >300, 150-300, 100-150 and 74-100 mesh). Morphology properties of carbonized particle was analyzed by X-ray (EDX), TEM, FT-IR, XRD, SEM, and TEM. The study of particle loading effect and particle size for carbonized *jatropha* seed shell filled vinyl ester composites have been characterized by physical, mechanical, morphological, and thermal properties and durability of environment. Physical properties of the vinyl ester composites consist of density, water absorption, and void content. The mechanical properties of carbonized *jatropha* seed shell filled vinyl ester composites have been investigated to determine the effects of carbonized *jatropha* seed shell loading and particle size. The mechanical properties showed an enhancement in tensile strength at 10 wt.% carbonized particle loading of filler material as compared to the neat polymer and higher loading percentage. Flexural strength decreased with an increase in the carbonized particle loading percentage, while the tensile modulus and flexural modulus showed an opposite trend. Thermal degradation analysis showed enhancement in the residual content of the composite materials, thereby ameliorates thermal stability. Glass transition and melting temperatures by DSC analysis were observed to have increased up to 10 wt.% loading of filler but decreases

subsequently at higher loading percentage. The morphological analysis showed smooth morphology with intermittent lumps of agglomeration at higher loading percentage. Accelerated weathering for carbonized *jatropha* seed shell filled vinyl ester composites has been investigated to get the durability of composites with the effect of UV exposure and condensation at exposure time of 96, 240, and 360 hours. Mechanical properties decrease when increasing the exposure time. One of the problems for using bio-composite as storage tank/water tank is corrosion, especially in aggressive environments. For this study, the carbonized *jatropha* seed shell filled vinyl ester composite has been done by soaking in environment solution i.e.: NaOH 5%, HCl 5%, and distilled water at room temperature. The durability analysis of environment solution for vinyl ester composites includes weight gain, change in mechanical properties, and morphology.

CHAPTER 1

INTRODUCTION

1.1 Introduction and Background

Composite consists of two or more different constituents or phases, strong load carrying material (known as amplifier) and embedded weak material (known as matrix), this material has got properties completely different from those of each component. Reinforcement gives it strength and stiffness and helps to support structural load. The matrix, or the binder can be of organic or inorganic, maintaining the position and orientation of the reinforcement. Significantly, composites of the individual retain their physical and chemical properties, but together they produce a combination of qualities that a constituent will individually be able to produce its own. The most common composites are polymer matrix composites. There are polymer thermoplastic and thermosetting that are reinforced by fiber (natural carbon or boron) into composites. This material can be made into various shapes and sizes. They provide great strength and stiffness along with resistance to corrosion. The most common reason for this is the low cost, high strength, and simple principles of manufacturing them (Taj et al., 2007).

In accordance with the developments of the times, many researchers do develop bio-composites. In terms of reinforcement, this can include plant fiber such as flax, hemp, cotton, kenaf, jute, bamboo, and others, or fiber of the recycling of wood or waste paper, or even with the products of plant food (Fowler et al., 2006). In recent years, because of their low cost and abundance, agricultural products have received increasing attention as alternative fillers. Farm gift shop can be used in both thermoset and thermoplastic polymer matrix and polymer composites to make the

choice really dependent on the intended application of the material. The use of agricultural filler reinforcements in a thermoplastic or thermoset has been gaining acceptance in many applications in the last few years. Filler is the material widely used for polymer materials added on to enhance the nature and processing capabilities or to reduce production cost (Ibrahim et al., 2012). The filler in composite materials is to achieve desired service and improve product quality. An approach that is more economical is to combine agricultural filler to composite in the form of particulate filler, in a form similar to flour, to replace the use of traditional filler of minerals like calcium carbonate, mica, and talc.

In the polymer industry, particle fillers are often used to improve the properties of the material and reduce costs. The interest in developing the composite is to expand the range of applications of polymers. Because of their light weight, low cost, and permanent conductivity, carbon black conductive fillers are the most widely used (Iqbal at al., 2007; Costa and Henry, 2011) to improve the ability of processing, electrical properties, mechanical properties, fire retardancy (Wu at al., 2008; Yin et al., 2011; Jasem and Hussain, 2012), and thermal properties (Rosas, 2011). Carbon black is an intense black powder or beads that serve as indispensable and pigmenting property-modifying agent in a variety of composite products (Mark and John, 2001). Kozlowski (2005) has developed materials, which could be applied as chemical sensors on polymer/carbon black composites. Kakati and Deka (2007) studied the effects of resin matrix precursor of carbon black composite bipolar plate for polymer electrolyte membrane. Abdul Khalil et al. (2010), used biomass from several resources based on carbon black as filler in epoxy composites, and Abdul Khalil et al. (2007), also developed bamboo as carbon black and activated carbon for its high potential of good mechanical properties, high rigidity, high carbon content, and the

degree of porosity which gives better carbon properties in polyester composite. The main use of carbon black is as a strengthening agent in rubber compounds (mainly tyres) and as a black pigment printing ink, coating, paper, and plastic surfaces.

However, the matrix also plays an important role because matrix composite can be designed for a particular application if a polymer is chosen properly. Vinyl ester is a thermoset popymers, widely used for advanced composites where good stiffness, dimensional stability, chemical resistance, being more powerful than polyester resins, and being cheaper than epoxy resins are of significance (Suresha and Kumar, 2009). They can be easily handled at room temperature and has mechanical properties similar to those of epoxy resins, especially the hydrolytic stability, and at the same time offering greater control over the curing condition levels and reaction of epoxy resins. Vinyl ester resins are brittle and one approaches to improve performance and minimize the cost of resin by reinforcing it with filler (Ku et al., 2012). As the structural products are cast to shape, the best option for strengthening the ester vinyl resin is to mix it with a filler particulate.

Commercially available particulate fillers carbonization is obtained from the thermal cracking of natural gas and furnace black produced by the combustion of oils not perfectly filled stocks. Carbonized product is called carbon black, which is relatively expensive because of its dependence on dwindling supply of crude oil (Abdul Khalil et al., 2010). Therefore, it is important to develop an alternative source of fillers from renewable resources such as biomass of fiber which are carbonaceous in nature and rich in organic matter. Biomass that is rich in ligno-cellulosic fibers can produce bio-carbon (carbon black) after pyrolysis or carbonization because they have high fixed carbon content. Today, experts have done improvements to the science of knowledge and applications product materials by using bio-resource as carbon black.

Many studies have been carried out on carbon black from biomass as filler in composites such as bamboo (Onyeagoro, 2012; Abdul Khalil et al., 2010; Acharya and Samantarai, 2012), coconut shell, oil palm empty bunch (Abdul Khalil et al., 2010), and rice husk (Acharya and Samantarai, 2012). This filler is commonly used in composite materials to reduce cost and to improve processing capabilities, mechanical properties, electrical properties, and fire retardancy. The effect of fillers on the properties of the composite depends on their concentration, their interactions with the matrix, the size, and the shape of the filler and filler dispersion.

Some researchers have investigated to use carbonized biomass as filler to encourage and recommend the possibility of the application of structural and thermal composite. To fulfill those criteria, percentage of filler loading, filler shape, particle size distribution, and rate of filler dispersion in the matrix, as these affected the properties of filled composites, were important considerations (Ibrahim et al., 2012).

The kinetic parameters and the thermal degradation of polymer composites, such as activation energy of thermal degradation process, were also investigated through dynamic thermogravimetric analysis at different heating rates (Ahmat et al., 2012). Mangeloglu and Karakus (2008) evaluated the thermal degradation of neat and wheat straw flour filled recycled thermoplastic composites. Liang et al. (2013) studied accelerated weathering test of kenaf fiber unsaturated polyester sheet molding compounds to evaluate the performance of natural and modified kenaf fiber sheet molding compound when exposed to cyclic wet/dry cycles in an accelerated weathering cabinet. Stark et al. (2007) studied the characterization of weathered wood plastic composite surface using FT-IR spectroscopy.

Burnner et al. (2005) accelerated weathering device for life service predictions for organic lining. Fisgoscy et al. (2010) have investigated the chemical

resistance for new polymer concrete with poly-butadiene binder. Reis (2009) also studied mechanical characterization of polymer mortars by exposing them into degradation solutions.

1.2 Problem Statement

As biomass, *jatropha curcas L* is a great attention from all over the world as renewable energy sources as well as fossil fuel alternatives. *Jatropha* seed shell is one part of the waste after taking out the oil and has high carbon content so that can be used as carbonized filler (Abdul Khalil et al., 2013). *Jatropha* is a potential to be used as an alternative as filler on parts of plant such as, seed, seed cake, shell, and seed shell because they have high carbon content. Processed from the seeds of *jatropha,* bio-diesel will definitely help conserving the renewable energy resources. During the extraction of bio-diesel from *jatropha* seed, seed shell disposal will be a concern for environmentalists.

The increasing areas of plantations of *jatropha curcas L* in India, China, and Indonesia as well as in South America and Africa will lead to an increased amount of *jatropha* in future. The shells of the seeds (hulk) are promising to be an alternative fuel for these countries, because they appear as a byproduct during the processing of *jatropha* oil and cannot be used for any other application until now. On the other hand, the byproduct such as seed shell contains fixed carbon that can be an alternative to make carbonized filler. There is limited information in the literature regarding the use of *jatropha* seed shell for the purpose of energy.

During the processing of plant oil from *jatropha* seeds the whole seed (kernel and seed shell) can usually be used. The press cake which accrues as a byproduct is rich in protein and could be used after a detoxification process as animal

food. However, through the height of the shell content of press cake, crude fiber content is also high. This could be a disadvantage for being used as animal food. Therefore, the production of high-value, protein-rich animal food from *jatropha* seed press cakes without the skin is preferred. *Jatropha* seeds are cracked by desheller and separated by using separator air into the kernel and shell. The shells of the *jatropha* seed from the deshelling process are free flowing materials comparable to rice husks.

Although materials scientists have studied filled polymer systems for many years, surprisingly little basic understanding exists regarding how the size, shape, distribution, surface chemical nature, and concentration of the filler particles affect the mechanical and rheological behavior of polymers during the curing process. Filler dispersion quality affects the properties of the finished product. Large ones tend to form agglomerates that cause the failure. Reduction of particle size depends on the properties of the fillers (i.e. size, shape, structure, military, etc.) as the intensity and duration of stress applied hydrodynamic stress.

The use of composite polymer matrices in applications has become attractive because of the many advantages offered by composite materials. This advantage is the excellent resistance to corrosion, and strength-to-weight ratio is high. However, the environment contains several pounds of elements that undermine the organic polymers, humidity, acid rain, temperature cycling, and ultraviolet radiation (UV). Of all the environmental pressure, UV radiation is potentially the most damaging for polymer materials.

In this study, carbonized *jatropha* seed shell will be used as filler in vinyl ester composites by affecting carbonized particle size and carbonized particle loading. The durability of environment study for vinyl ester composites filled with carbonized *jatropha* seed shell also investigates the thermal degradation, accelerated

weathering, and chemical corrosive media. A series of tests will be conducted to investigate the respective properties and change of properties of vinyl ester composites filled with carbonized *jatropha* seed shell.

1.3 Objectives of the Research

The purpose of this study is to determine the potential of carbonized from biomass waste (seed shell of *jatropha*) as filler in vinyl ester composite and durability of environment for carbonized *jatropha* seed shell filled vinyl ester composites. The filler is widely used in polymer materials to provide appropriate characteristics of specific commercial applications. For example, a polymer composite material (vinyl ester composites) filled with carbonized is characterized by high mechanical strength and dimensional stability. The principal objectives of this research were as follows:

5 To analyze and characterize of carbonized *jatropha* seed shell as filler in vinyl ester composites.

6 To study the effect of particle loading and particle size on the physical, mechanical, morphology and thermal properties of carbonized *jatropha* seed shell filled vinyl ester composites.

7 To investigate the effect of accelerated weathering and chemical corrosion media on the physical, mechanical, and morphological properties the vinyl ester composites filled carbonized of *jatropha* seed shell.

1.4 Organization of Thesis

There are altogether five chapters in this thesis. Chapter 1 (Introduction) presents an overview on introducing and background, scope of study and objectives

of study. The overall content of this thesis are summarized in the last section of this chapter.

Chapter 2 (Literature Review) focused on literature review of present study. Review of composites, *jatropha* seed shell as potential filler for carbonized black process, durability of environment in degradation of composites.

Chapter 3 (Materials and Method) explain about materials that used in this study and methodology of production of carbonized *jatropha* seed shell, fabrication and characterization of carbonized *jatropha* seed shell filled vinyl ester composites and methodology of degradation of carbonized *jatropha* seed shell filled vinyl ester.

Chapter 4 (Results and Discussion) provide the results and discussion of characterization of carbonized production of *jatropha* seed shell, characterization of carbonized *jatropha* seed shell filled vinyl ester composites and explanation of characteristic change of carbonized *jatropha* seed shell filled vinyl ester composites.

Chapter 5 (Conclusion and Recommendation) summarizes the overall the findings from the present research. The conclusions reflect the achievements of the listed objectives, which obtained throughout the study. Finally, recommendations for the research future are listed. These recommendations are presented in their interests and the importance of research related to the present for the composites in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Biocomposite

Nowadays, governments, industries, and scientists are concerned to develop sustainable materials from renewable resources to find alternatives new resource to replace the used of crude oil, because they have specific advantages as compared to synthetic fibers or conventional resources. Therefore a new innovation in the areas of biocomposite is the substitution of oil-derived polymers and polymer of bioresources (bio-based polymer matrix) as a component of a term which indicates that overall biocomposite (both matrix and reinforcement) comes from bioresources. Biocomposite materials are composites that are one of the good phase matrix (polymer) or strengthening/filler comes from bioresources. Plant fibers, including timber and non-timber or by-products from plants come under bioresouces and acts as a reinforcement or filler biocomposite materials are renewable resources. Bioresources resin from vegetable oils and starch gradually replaces polymer generally used fossil fuels synthetic based. Biocomposites is a composite material consisting of one or more phase(s) derived from biological origin. In terms of the reinforcement, this could include the fibers of plant, such as flax, cotton, bagasse, hemp, bamboo, oil palm, kenaf, jute, coconut and the like, or fibers from recycled wood or waste paper, or even by- products from food crops (Abdul Khalil et al., 2013).

Biocomposites polymers have been widely used in many applications. One of the key to achieving this is a composite high-performance interfacial angle interaction between polymer matrix and filler. It is well known that polymer

biocomposites between materials in industry, most important and is much used in chemical engineering, sporting goods, the car aircraft and weapons, etc.

For decades, many biocomposites polymer has been prepared and is combined with different types of synthetic reinforcing filler to improve the mechanical properties and acquire traits that are demanding in the actual application. Polymer composite material reinforced bioresources has appeared in a wide spectrum of areas of polymer science. The resulting composite material of low density, low cost, non-corrosive, and non-toxicity of certain property, comparable, and most importantly they are eco-friendly (Manti et al., 2005; Hassan et al., 2010). Depending on the origin of bioresources (left, bast, seed, and fruit, wood, stalk and grass/reeds (Jawaid and Abdul Khalil, 2011)), leaf and bast are more commonly used in biocomposite applications than others. The used bioresources reinforcement to composites have many advantageous attributes such as high specific strength and modulus, low density, relative non-abrasivenss, wide avaliability and ease to modification of fiber surface (Ribot et al., 2011).

Many researchers have developed their biocomposites with bioresource. They looked for bioresources because of wide availability, abundant resources are available and the futuristic ways to alleviate the commercialization, a comprehensive study has outlined biocomposite materials (Hassan et al., 2010). They have developed biocomposites with reinforce both of thermoplastic and themoset matrixes. Many investigations have been made on bioresources as potential reinforcements for composites and in some cases the results show that the composite biological resources themselves good stiffness, but composites do not achieve the same level of strength glass fiber composite (Ojha et al., 2012).

2.2 Constituents of Composites

Composites are materials consisting of strong load carrying material (known as the amplifier) embedded in a weak material (known as matrix) consisting of two or more component (phase) which is not soluble in each other. In a composite, reinforcement provide strength and rigidity, and help to support the structural loading. Binder or Matrix, there are organic or inorganic, can maintain the position and orientation of the reinforcement. It is clear that the constituents of composite retaining their individual properties, physical and chemical; but together they produce a mix of quality constituent individuals would be able to produce their own (Taj et al., 2007).

By simplicity, however, composite can be grouped into categories matrix by virtue of having each kind. A method of fabricating also vary according to physical and chemical properties matrix and strengthen fiber. Most common advanced composites is a polymer matrix composite. Composite consists of polymers thermosetting or thermoplastic reinforced by natural fiber or boron. These materials can be made into various shapes and sizes. They give it enormous strength and stiffness with resistance to corrosion. The reason for this most common is low cost, high principles their strength and simple manufacturing.

2.2.1 Matrices

The matrix is material that summarizes two or more than two components in itself. In case of natural materials, composite fiber reinforced binding matrices fibers together. Transfer loads applied this fiber and also protect this fiber from harmful environmental impact (Thakur and Singha, 2010).

The role of basic matrix on bioresources-reinforced composite is to transfer the stress between the fibers, to provide a barrier against environmental harm and to

protect the surface of the fibers from mechanical abrasion. Matrix plays a major role in the combined structure weight pull capacity. Binding agent or matrix in composite is extremely important.

Mainly four types of matrices have been reported: Polymeric, Metallic, Ceramic and Carbon. There are three groups of materials that can be grouped to infuse the matrix phase:

3 Polymers: thermoplastics, thermosets, and elastomers

4 Metals: magnesium, aluminum, titanium, and steel, (among others)

5 Ceramics: silicon nitride, silicon carbide, carbon, and aluminum oxide (among others)

Polymer matrix composites (PMCs) which consists of various short or continuous fibers are bound together by an organic polymer matrix. Composite part used in the industry today is based on a polymer matrix. Traditional composite matrices are the most common consists of either thermoplastic or thermosetting polymers.

Metal matrix composite (MMC) is a composite material with at least two constituent parts, one metal. In structural applications, the matrix is usually light metals such as magnesium, aluminum, titanium, or and provides appropriate support for reinforcement. In high temperature applications, cobalt and cobalt-nickel alloy matrices are common.

Matrix ceramic composite (CMCs) are a subgroup of the technical subgroup and the composite materials of ceramics. They consist of a ceramic fibers embedded in a ceramic matrix forming a ceramic material ceramic fiber reinforced. Matrix and fibers may consist of ceramic material where carbon fiber and carbon can also considered ceramic material.

In the last few years, there has been a rapid growth in the development and application of strengthened fibers composite polymer thermosetting resin as vinyl ester, epoxy, and polyester (Ku et al., 2012). Some types of polymers have been used as a matrix for composite biological resources. The most common thermoset polymers used are other resins and epoxy resins (saturated polyester resins such as fiber glass, vinyl ester, novolac phenolic, epoxy and polyamide). This is because of their awareness of good strength, low density and high performance-cost ratio quickly clean processing (Suresha and Kumar, 2009).

Thermoset materials are hard and stiff crosslink that do not soften or be moldable when heated. Thermosets are stiff and not stretch the way that elastomers and thermoplastics are doing. Saturated polyesters very versatile in application and property and has been popularly used as thermoset polymer matrix in composites. They are widely produced in the industry because it has many advantages compared to other thermosetting resin curing capabilities including room temperature, good mechanical properties and transparency.

However, matrix materials also play an important role as it does for thermoset resin matrix composite that can be designed for certain applications properly selecting polymers. Vinyl ester resin is stronger and cheaper than polyester resins and epoxy resins. Polymers and composites are find an ever increasing usage for a variety of industrial applications such as bearings, seals, roller materials, cams, gears, wheels, belts transmission, and clutches etc. (Suresha and Kumar, 2009).

A thermoplastic is a polymer that requires heat during processing. After cooling, the materials retain their shape. In addition, the polymer can be heated and reformed, often without a significant change in their properties. Polymers that have been used as thermoplastic matrix composite reinforces are follows; low density

polyethylene (LDPE), high density polyethylene (HDPE), poly (vinyl chloride) (PVC), polypropylene (PP), normal polystyrene (PS), chlorinated polyethylene (CPE), mixtures of polymers, and recycled thermoplastics. The advantage of using biological resources in a thermoplastic composite bioresources is that of low cost, non abrasive, sustained, widely available, high levels of charge possible, lower density per weight of the raw materials, high specific properties, flexible and recyclable (Rowell, 2007). In lieu of conventional synthetic fibers such as aramid and glass fibers, are increasingly used for filler lignocellulosic reinforcement in thermoplastics because they are low density, good mechanical properties and thermal insulation, low prices, reduced wear tools, limited availability, and trouble-free disposal (Ayrilmis and Kaymakci, 2013).

As elastomer, natural rubber are used as the matrix and studied extensively because of its use in many engineering applications. Natural rubber is an attractive material with commercial success due to the physical nature of excellent mechanical strength, the low heat buildup, especially the high resistance to impact and tear, excellent flexibility, and above all the renewability (Onyeagoro, 2012). However, the dry raw rubber is rarely used in its original state for engineering and domestic applications. As a result, the manufacture of rubber products involves adding a lot of extra ingredients called additive to all rubber compounds to satisfy treated and vulcanized to improve application properties of rubber compounds. Additives used in the manufacture of rubber products vulcanizing agents, include accelerators, activators and/or retarders, fillers, anti-degradants, among others.

2.2.1.1 Vinyl ester as a matrix

One of thermosetting polymer is vinyl ester resin. Vinyl ester resin was first introduced commercially in the early 1960s (Ku et al., 2012). Vinyl ester resin has been widely recognized as materials with highly resistant to a wide range of common environmental chemistry. Vinyl ester resins used to fabricate a reinforced structure of pipes, tanks, cleaners and ducts. They are a prime candidate for use in composites for transportation and/or infrastructure. Such applications include fabrication of parts for automobiles and other transportation vehicles, fascia for buildings, reinforcements for bridges, etc. In addition to these applications, vinyl ester is also being used in adhesives, molding compounds, coatings, electrical applications, the structural laminate, and military/aerospace applications (Young, 1976).

Vinyl ester resin which closely chemically combine the best properties of unsaturated polyesters and epoxies are partly a compromise between the two (Ku et al., 2012). They can easily be handled at room temperature and has mechanical properties similar to epoxy resins. They have a better chemical resistance than polyester resins and cheaper, especially the hydrolytic stability, and at the same time offering greater control over the curing condition levels and reaction of epoxy resins. Pure vinyl ester resins is brittle and one approach to improve performance and minimize the cost of resin is to strengthen with filler. Structural products such as cast into shape, the best options for strengthening the vinyl ester resin is to mix it with particulate fillers (Ku et al., 2012). Vinyl-ester resins consist of styrene and a vinyl-ester prepolymer monomer. The chemical structures of these compounds are shown in Figure 2.1.

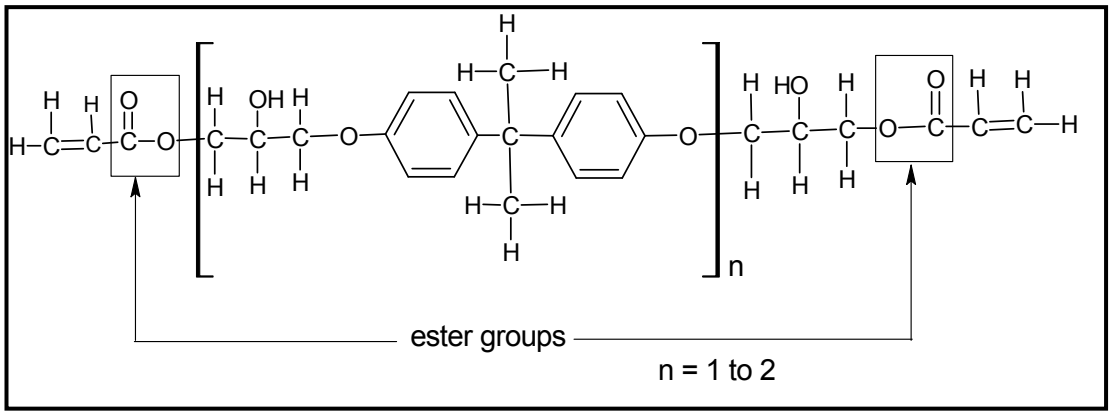

Figure 2.1 Structure of vinyl ester matrix (Sandals et al., 1988)

The vinyl ester provides the important polymer properties such as modulus, transsition glass temperature, toughness, and durability. The styrene monomer is reactive diluents. The main purposes of the styrene are to control the viscosity, improve the wetting behavior of the resin, and lower the cost of the overall resin system (Fink et al., 2002).

There are far fewer studies cited in the literature of vinyl ester resin in comparison with studies on unsaturated polyesters and epoxy resins, especially the study of the formation of structure-properties-vinyl ester resins. Most of the information focuses on the behavior of the drug and the morphology of free radical curable resin unsaturated polyester resin. Today, as a vinyl ester resin is becoming more and more important in industry, research on vinyl ester resin expands. The development and application of vinyl ester resin including a new synthesis of vinyl ester resin with new structural properties in an effort to increase the toughness, to reduce viscosity, to reduce shrinkage, and so on. Understanding the mechanisms of drug reactions, and gain better control of the properties of these materials has also attracted many researchers (Young, 1976). Vinyl ester resin which is used extensively as a matrix for liquid-molding composite structure. Vinyl ester shows

many attractive attributes, including low viscosity (allowing space-temperature infusion to do), room temperature curing, properties that are comparable to other resins are often used, and are relatively inexpensive. Unfortunately, however, the response of vinyl ester resin thermochemical at low temperature is not well understood (Fink et al., 2002).

Interfacial crystallization has been tremendous interest in recent decades, not only because of the significance of crystallography, but also due to the fact that it might be a new strategy to improve the interfacial adhesion and realize the full potential of filler to strengthen mechanical performance composite. Clearly, the formation of interfacial crystalline layer can offer good interfacial combination between the filler and the polymer matrix. Due to the nature of the action between the polymer filler for other modes of connecting network, such as the interfacial macro-molecules wrappers, covalent bonding and attachment of different tissue grafts or also identified the positive role, a combination of these interfacial physical or chemical on the load transfer efficiency improvement is anticipated. Properties of polymer/filler hook arising from interfacial crystal structure, however, it is difficult to clearly elucidate, and there is still the question of whether interfacial crystallization can be more effectively enhanced interfacial ulti carries or not has been argued for a long time. The obvious contradictions in experimental works have been reported by different researchers in the literature. Micrometer scale for filler-reinforced composites, some studies show the interfacial crystallization.

These are several general review related to the improvement of interfacial mechanical reinforcement and composites polymers fillers through interfacial crystallization, though there are several public reviews related to mechanical reinforcement in composites polymers fillers. Thus, this report is based on a review

of the latest developments in composite polymer crystallization interfacial filler and it is organized according to the following topics: a hybrid crystal structure/morphology is the presence of micro-and/or nano-fillers, the factors that control the hybrid crystal structure/morphology, the establishment of the mechanism of hybrid crystal structure/morphology, increase in interfacial and mechanically caused by interfacial crystallization, and conclusions and future perspectives (Ning et al., 2012).

Chandradass et al., (2007) has employed vinyl ester glass fiber reinforced composite filled with organoclay at room temperature have been successfully made using hand layup technique. Increased natural frequency and damping factor observed in organo clay filled hybrid of vinyl ester glass fiber reinforced composite. Suresha and Kumar, (2009) has investigated on mechanical performance and two-body abrasive wear of carbon vinyl acetate and vinyl ester glass-composite.

Ku et al., (2012), in their study of fracture toughness sawdust reinforced vinyl ester resin composite cured in the microwave get sawdust particles with larger size distribution have a better efficiency in increasing fracture toughness of composite. Vautard et al., (2009), in their studies, had mentioned the carbon fiber reinforced vinyl ester interfacial adhesion improvement by using layers of epoxy. In order to highlight that these parameters are the most influential in the case of carbon fiber vinyl ester composite, influence the adsorption of constituents of the matrix on the surface of carbon fiber and the impact of the cure volume shrinkage is also evaluated.

2.2.2 Reinforcement bioresource in composites

The use of reinforcement in biocomposites are basically additives. They are used to modify optical, mechanical or surface properties of the matrix material,

mainly for reduction in material cost, performance, improvements in properties, achieving ease of processing, service life of end product, reduction in processing cost and minimizing degradation during process over a period of usage (Shaikh and Channiwala, 2010). Strengthening provide the strength and stiffness; helping to support a structural load (Zaman et al., 2011; Fowler et al., 2006). The mechanical and physical properties of reinforcement of bioresource composites depend on many factors, effect of which has been the subject of many studies. Mainly, the effect of content, species, particle size and coupling agent has been investigated (Gozdecki et al., 2012). The physical and mechanical properties of bioresource composites are largely depending on the type of matrix, content and properties of the reinforcement bio-filler and bio-filler–matrix interaction (Hardinnawirda and Aisha, 2012).

Bioresources is primarily being sought since the production of composites using natural substances as reinforcing the bioresources are not only cheap but also able to reduce the environmental pollution caused by biodegradability properties, which allow this composite plays an important role in solving environmental problems of the future (Yang et al., 2004; El-Tayeb, 2008). Composite made of bioresources offers the opportunity for broad applications in areas such as consumer goods, cheap housing and civil, and other common for many applications where the cost of expensive reinforcements at present limit the use of conventional lightweight reinforced composite. Another disadvantage of natural fiber composites that make them less attractive is the poor resistance to moisture absorption. Therefore, the use of natural fibers in a polymer matrix are not alone sufficient in satisfying all the needs of the technical handling of fiber reinforced composite. In an effort to develop a superior, yet economical composites, biological resources can be combined with

synthetic fibers in the same matrix material to take best advantage of the fiber and matrix properties (Jayabal et al., 2011).

2.2.2.1 Bio-filler

Fillers are particulate or fibrous materials that are used to reinforce polymer composites for enhanced physical properties (Osarenmwinda and Abod, 2010; Circiumaru et al., 2011). To overcome the limitations of clear polymers, for example, low power and low stiffness, and to expand their applications in various sectors, inorganic particulate fillers, such as glass, micro-/nano-SiO_2, $CaCO_3$ particles, Al_2O_3, carbon black, and $Mg(OH)_2$, layered silicates and carbon nanotubes, are often added to process the polymer composite, which typically combines the advantages of their constituent phase (Fu et al., 2008). Many researcher concern to replacement conventional sintetic or inorganic particulate filler to bio-filler because lignocellulosic filler (bioresources) are increasingly used for reinforcement in biocomposites because they are low density, good thermal insulation and mechanical properties, tool wear is reduced, limited availability, low prices, and free disposal problems (Ayirimis et al., 2012).

Bioresources as bio-filler has been the focus of attention because they have shown excellence attracting low cost and low density per unit volume, using the tools of certain strength is reduced and accepted their renewable characteristics and side relegated. There are various types of bioresources which can be applied as a filler or reinforcement. Bio-fiber is in many cases cheaper than synthetic fibers and cause less environmental hazard, health problems, and for the people who produce the composite glass fiber-based compared to composite (Majeed et al., 2013). Particulate fillers are generally used in the polymer industry to reduce costs, and to improve

processing capabilities, electrical properties, fire retardancy and mechanical properties. Effect of fillers on the properties of the composite depends on their concentration, their interactions with the matrix, the size and shape of the filler and filler dispersion. Hence, visualize and characterization filler distribution is essential to understanding and optimize processes microstructure-property relationships of composites.

2.2.2.2 Carbonized particulate filler

Carbonized particulate is a very important ingredient used as filler into polymers. This is a form of amorphous coal, which usually consist of particles of carbon sphere. The size of the molecules is less than a few dozen nanometers. Particle agglomeration spatial configuration with the makes a different. The structure and configuration of particles affect the properties of carbon black.

The origins of obtaining carbon black is mainly based on incomplete combustion of material carbonaceous. The main precursor including: wood, coal, natural gas and hydrocarbons. Basic production methods to include material: furnace method, lamp method, and is now more widely used method of plasma. (Stabik, 2012; Okieimen and Imanah, 2005).

Carbon black is a general term for a family of important products that are used primarily for reinforcement of rubber, as black pigment and electrically conductive due to the nature. It's very smooth fine powder with large surface area and essentially consists of carbon elements. Black carbon is one of the most stable chemical products. Generally, it is the most widely used nano material and aggregated dimension that ranges from tens of thousands to a few hundred nanometers (nm); it imparts special properties for composite part.

Therefore, these needs to develop filler from another source; especially from renewable resources (bioresources), to replace some values of carbon black. The waste products of agriculture (corn cobs, peanut husks, peeled cassava, cocoa pod husk, peel a banana, rubber shell seeds, bamboo, coconut shell, cherry stones, sugar cane, oil palm wastes generated (including oil palm trunks, empty fruit bunches, oil palm shell), and rice husk (Abdul Khalil et al., 2007) are some of the raw materials is known to have a commercial advantage to replace man-made carbon, which can be directly used or modified by a simple process for high value-added materials (Okieimen and Imanah, 2005).

Bioresources for the manufacture of filler particle carbonization is strategically located worldwide to supply rubber tire industry, which consumes 70% of filler particles produced carbonization. About 20% are used for other rubber products and 10% used for various non-rubber applications. At 2005, world capacity of filler particle carbonized is estimated at over 10 million tons (Auchter, 2005). The value of more than 40% used by rubber industry alone. Extra value much marketed to non-application of rubber (Voll and Kleinschmit, 2002; Wang et al., 2003).

Some of the profit from its use as a UV stabilizer for carbon, weather-resistant, electrical conductivity, and modify the mechanical properties of carbon filled composites. For example, the particle-filled polyethylene composite filler carbonization was used as pipes in extreme weather conditions, while polypropylene geotextiles composite filler particles practically carbonization for strengthening land and many development goals. Particle composite filler carbonization also can survive thermal width Range, making them valuable in thermo-mechanical applications such as automotive industry (Abdul Khalil et al., 2007; Abdul Khalil et al., 2010).

Carbon black particulate fillers are for example is widely used as fillers in polymer industry reinforcement. These fillers are added to polymers to achieve desired service and improve the quality of the product. Carbon black is commercially available that are obtained from the thermal cracking of natural gas and produce black furnace by incomplete combustion from the oil feed stock (Abdul Khalil et al., 2010).

Filler carbonization commercial particles used as filler and has its own characteristics and values. The properties of carbon used in the composite depends mainly on the origin, processing conditions and chemical treatments. Particle size, surface activity, the level of interactions with the polymer, chemical composition, and the level of irregularity form fillers are factors that affect the behavior of the composite. However, a high carbon content (90-99%) of the carbon fillers results in a material that is hydrophobic nature and prone to aggregation when dispersed in water (Abdul Khalil et al., 2007).

Carbon black can be used for the manufacture of dry cells in industry electrical, in the manufacture of paints and varnishes, or the pharmaceutical industry (Stabik, 2012). Carbon black can be broadly defined as the aggregate particles have extremely fine molecular structure of graphitic carbon amorphous quasi. The Structure of carbon black show in Figure 2.2.

Elemental of Carbon is the most universal element of the periodic table and marked as C in this table. Carbon in the chemical compound has hybridized sp, sp2, sp3 and create one or more covalent bonds with other carbon atoms or with heteroatoms. Carbon atoms with sp2 or sp hybridized have non p orbital hybridization is capable to form a bond between the p orbitals are two carbon atoms. Basically provide, together with the sigma bond is formed by the sp2 or sp orbit

some of the bonds, which allow creating a variety of chemical compounds (Stabik, 2012).

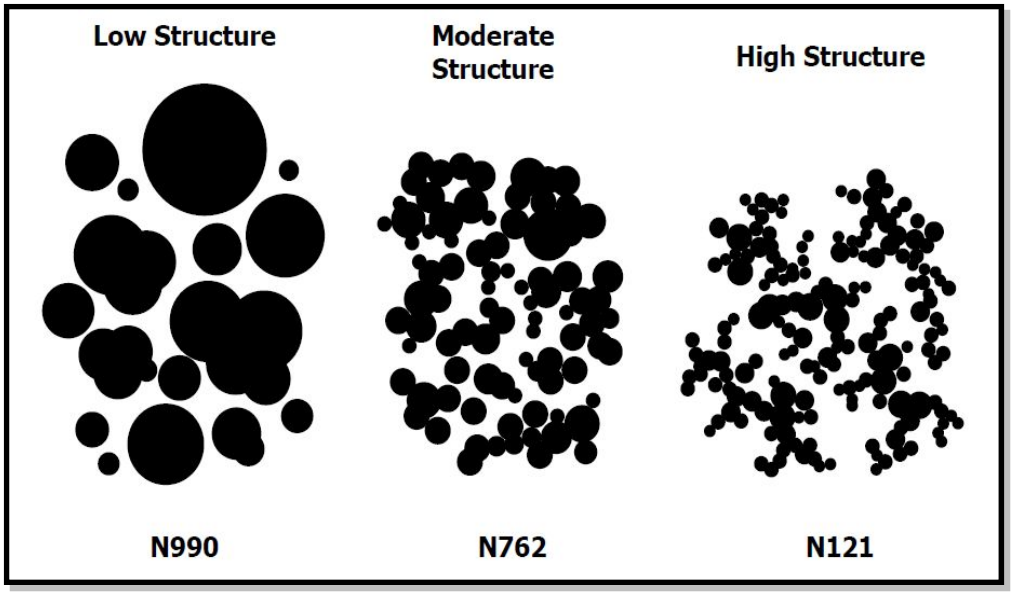

Figure 2.2 Carbon black structure comparison (Thompson, 2010)

Amorphous form of element C is widely used in industry, especially as a filler in rubber components during processing of rubber and paints. This element also allows for the creation of the multidimensional structure of the substances which have very different physical and chemical properties. Characteristic properties of carbon are presented in Table 2.1.

Table 2.1 Basic properties of elemental carbon (Stabik, 2012)

Symbol, atomic number	C-6	Melting point	3820 ^{o}K/3546 ^{o}C
Atomic mass	12.0107 u	Specific heat	710 J/(kg.K)
Standard atomic weight	70 (67) pm	Density	Depend on a variety

It should be noted that the mechanical strength of the atoms in the C-C bond is the largest of the known in nature. This allows for the creation of natural and