MECHANICAL CHARACTERIZATION OF BIO-COMPOSITES FABRICATED FROM NATURAL COCONUT FIBRE AND LINEAR LOW DENSITY POLYETHYLENE

A thesis submitted to the Department of Chemistry, College of Science, Kwame Nkrumah

University of Science and Technology, Kumasi

in partial fulfillment of the requirements for the degree of

MASTER OF PHILOSOPHY (POLYMER SCIENCE AND TECHNOLOGY)

By:

Abasiwie Daniel-Luggard Akanzeriyomah, B.Sc. (Hons.)

June, 2015

CERTIFICATION

I hereby declare that this thesis is my own work towards the M.Phil. and that, to the best of my knowledge and belief, it contains no materials that has been accepted for the award of any other degree in any educational institution nor material previously published or written by another person, except where due acknowledgement has been made in the text.

Abasiwie Daniel-Luggard Akanzeriyomah

 (PG 6149811)   ……………………..   ……………………..

Student Name and ID   Signature   Date

Certified by:

Prof. Berko-Boateng Victor   ……………………..   ……………………..

Supervisor's Name   Signature   Date

Certified by:

Dr. Godfred Darko   ……………………..   ……………………..

Head of Department, Chemistry   Signature   Date

DEDICATION

To my Parents, Mr. and Mrs. Abasiwie & my lovely wife Priscilla

KNUST

ACKNOWLEDGEMENT

ABSTRACT

Fibre reinforced composite materials constitute an important class of engineering materials with outstanding mechanical properties, unique flexibility in design capabilities and ease of fabrication. Today, green, environmentally friendly, sustainable, renewable and biodegradable composites from natural fibres are among the most keenly required materials of choice. Coconut fibres can be used as environmentally friendly alternatives to conventional reinforcing fibres in composites. Composites consisting of linear low-density polyethylene (LLDPE) and coconut fibres with percent fibre loading of 10, 20, 30, 40 and 50 respectively were fabricated by extrusion. The extruded strands were pelletized, ground and test samples were injection moulded. The mechanical properties of composites were evaluated using standard American Society of Testing Methods (ASTM). Also, Fourier Transform Infrared Spectroscopy (FTIR) and Swelling Index studies were performed. Coconut fibre (CCF) was treated with sodium hydroxide (NaOH) (5% w/v) for 24 hours. The FTIR results revealed a partial removal of lignin and hemicellulose after the CCF treatment, manifested through the disappearance of the peak at 1740 cm^{-1}. The NaOH treatment increased the tensile strength and tensile modulus in the treated coconut fibre composites (TCFC) whilst slightly decreased the % elongation when compared to the untreated coconut fibre composites (UCFC) at similar % fibre loading, although both were lower than the pure LLDPE. For both the UCFC and TCFC, maximum or optimum ultimate tensile strength was attained at 30% fibre loading (w/w). Generally, the results showed that increasing percent coconut fibre content loading decreased the tensile strength and elongation at break but increased the young's modulus at similar fibre loading in all cases studied. The swelling index generally increases with increasing amount of fibre loading in the composites with a corresponding decrease in crosslink density.

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LIST OF ABBREVIATION

LLDPE	-	Linear Low Density Polyethylene
MMDA's	–	Metropolitan, Municipal and District Assemblies
CCF	–	Coconut Fibre
NaOH	–	Sodium Hydroxide
FRP	–	Fibre Reinforced Plastics
DP	–	Degree of Polymerization
MAPP	–	Maleated Polypropylene
MFI	–	Melt Flow Index
KBr	–	Potassium Bromide
ASTM	–	American Society of Testing Methods
FTIR	–	Fourier Transform Infrared
UCFC	–	Untreated Coconut Fibre Composites
TCFC	–	Treated Coconut Fibre Composites
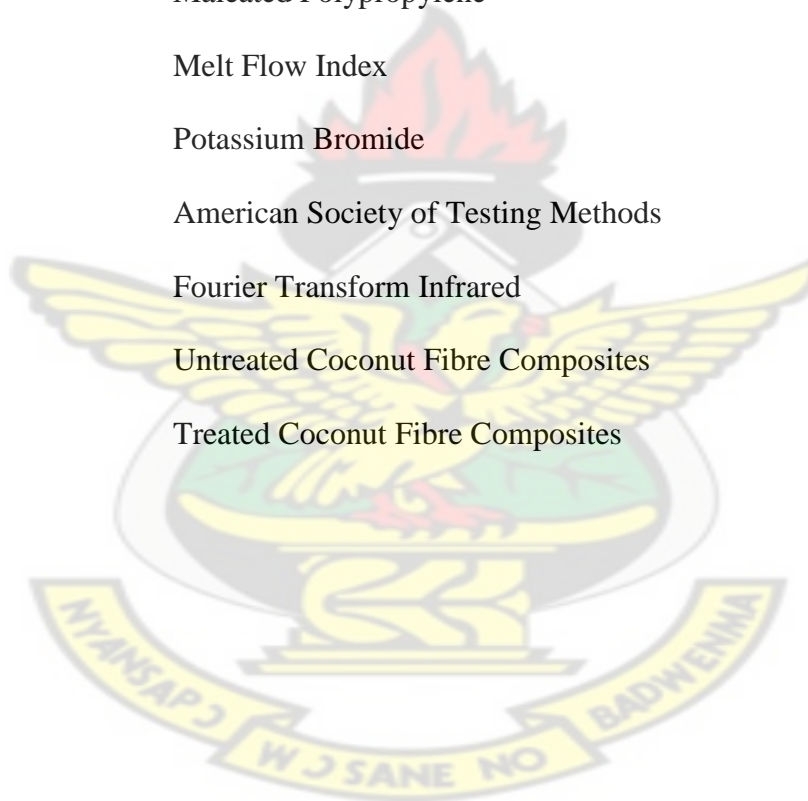
CHAPTER ONE

1.0 INTRODUCTION

Fibre reinforced composite materials constitute an important class of engineering materials. These materials offer outstanding mechanical properties, unique flexibility in design capabilities and ease of fabrication. The potential of plant fibre as reinforcement in composite materials have been well recognized since the Egyptians, some 3,000 years ago, used straw reinforced clay to build walls. However, the current application of plant fibre in composites is mainly non-structural components with a random fibre orientation used by the automotive and building industry (Broge 2000; Clemons 2000; Karus *et al*., 2002; Parikh *et al*., 2002).

Composites made of high strength fibres such as graphite, aramid and glass are commonly used in broad range of applications from aerospace structure to automotive parts and from building materials to sporting goods (Arib *et al*., 2006). However, the development of natural fibre reinforced composites becomes an attractive research area and a possible substitute for synthetic fibre composites due to the non-recyclability, high density and health hazards associated with composites reinforced with synthetic fibres such as glass, carbon and aramid fibres (Corrales *et al*., 2007). Besides, the greatest problem of using synthetic fibre reinforced materials is how to conveniently dispose of them once they have come to the end of their useful life span (Bodros *et al*., 2007). As a result, there has been growing interest in the use of natural cellulosic fibres as reinforcement for polymeric matrix (Hassan *et al*., 2011). Several natural fibres such as sisal (Chow *et al*., 2007), jute (Bledzki *et al*., 2007), flax (Baley *et al*., 2006), bamboo (Kumar *et al.,* 2010), kenaf (Tawakkal *et al*., 2012), bagasse (Vilay *et al*., 2008) fibres have been studied as a reinforcement and filler in polymer composites.

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Linear Low Density Polyethylene (LLDPE), a thermoplastic, is selected as the matrix material for this investigation or study, and this is in agreement with the general trend for industrially fabricated plant fibre composites where thermoplastics are increasingly being used in preference to thermosettings (Clemons, 2000; Karus *et al*., 2002). A thermoplastic matrix composite offers several advantages over its thermosetting counterparts. Some of these merits include: (i) they are easier to recycle, (ii) they are faster to process (i.e. no extra time for curing), (iii) they are fabricated by a cleaner process technique (e.g. less toxic by-products), and (iv) they are less expensive. However, there are a number of disadvantages of thermoplastics, which are more technically oriented, and are directed in particular towards their use in plant fibre composites. These include among others: (i) their high viscosity, (ii) their high melting temperature, and (iii) their low polarity. As a result, in the fabrication of plant fibre composites with a thermoplastic matrix, special attention must be paid to the effect of; (a) composite porosity, (b) process temperature, and (c) fibre-matrix compatibility.

Polymer composites based on natural fibres are currently attracting great interest/attention as alternative materials to glass/synthetic fibre reinforced plastics in several applications, mostly automotive, building and packaging products.

LLDPE has become popular in the food packaging industry because it is a relatively cheap thermoplastic with superior mechanical properties such as outstanding impact strength compared to other forms of PE. Also, the ease of processability, rescalability and recyclability have made LLDPE the material of choice for various applications in the packaging industry such as heavy duty sacks, refuse sacks, carrier bags and for general packaging needs (Brydson, 1999). Some of the properties which make polymers attractive for package manufacture are lightness, flexibility,

chemical resistance, versatility and a wide range of formulation that allow the development of new designs to meet specific packaging requirements.

1.1 PROBLEM STATEMENT AND JUSTIFICATION

Polymeric materials have provided a wide range of products in response to the increasing demand and the ever growing market for new materials. In the past, polymer products demand has been based on synthesis of new polymers, however, the focus has now shifted to other approaches due to governmental restrictions, environmental and societal concerns. Material scientists and researchers have shifted their focus to natural/biodegradable blends and composite materials.

Composites made of conventional materials such as glass, aramid and carbon are non-recyclable, have high density and health hazards as well as disposal problems at the end of their useful lifespan (Bodros *et al*., 2007; Hassan *et al*., 2011). The problem of safe plastic waste disposal is very paramount, especially in developing countries like Ghana where the safe disposal of plastic waste is posing serious challenges to sanitation and development in the various Metropolitan, Municipal and District Assemblies (MMDA's). Plastics disposal problem in Ghana is overwhelming. Plastic wastes cause environmental problems such as blockage of water ways, clogging of sewer systems, choking of animals to death when they feed on them, affecting the fragile eco-systems and aesthetic deterioration of landscapes.

Biodegradable polymers, however, could be instrumental in offering scientists and researchers a possible solution to pollution and waste disposal problems stemming from plastics disposal. Rising oil prices, environmental and energy concerns have also stimulated more interest in biodegradable and bio- derived polymers (Bledzki *et al*., 2009).

The utilization of natural fibre in composite fabrication has gained attention due to the potential reduction of waste disposal problems especially in agricultural fields, environmental pollution (Nishino, 2004) , finds various applications in engineering, electronic and automotive fields (Goda *et al*., 2006) and also in packaging, paneling, fencing and furniture (Zaman *et al*., 2011). Green, environmentally friendly, sustainable, renewable, biodegradable composites from natural fibres are among the most keenly required materials of choice in the 21st century (Mohanty *et al*., 2002; Nishino, 2004; Bledzki *et al*., 2007). Undoubtedly, most cellulosic fibres are harvested yearly and the supply should be inexhaustible compared to the limited supply of oil reserve from which many synthetic fibres are derived (Arib *et al*., 2006).

Natural fibre reinforced polymers also exhibit numerous advantages such as high mechanical properties, low weight, low cost, low density, high specific properties (Zaman *et al*., 2011), possess better electrical resistance, good thermal and acoustic insulating properties and higher resistance to fracture (Goda *et al*., 2006). Additionally, the natural fibres reinforced composites can decrease wearing of machines due to its low abrasiveness and absence or little of health hazardness during processing, application and upon disposal (Goda *et al*., 2006).

Unfortunately, the incompatibility between lignocellulosic materials and many polymer matrices affect the degree of dispersion of the fibres in the matrix and the overall homogeneity of the composite (Kumar *et al*., 2010, Suradi *et al*., 2010, Mir *et al*., 2012).

 Thus, studies on the effectiveness of various coupling agents/compatibilizers and fibre surface modification mechanisms are required to improve the interfacial adhesion and consequently, leads to the fabrication of fibre reinforced composites with better properties for various applications.

Another challenge to overcome is the control of fibre orientation (i.e. alignment of the fibres), to ensure that the fibre mechanical properties are most efficiently utilized, and to obtain maximum fibre content.

By applying coconut plant fibre for composite reinforcement, the full potential of plant fibres can be explored, and also form the necessary basis whereupon the prospects of plant fibres in both structural and non-structural composite components can be identified. Various aspects of the use of coir fibres as reinforcement in polymer–matrix composites are described in literature (Enriquez *et al*., 2010; Zaman *et al*., 2011; Mir *et al*., 2012).

Coconut fibre is an abundant, versatile, renewable, cheap, and biodegradable lignocellulosic fibre used for making a wide variety of products. Coir has also been tested as filler or reinforcement in different composite materials. Furthermore, it represents an additional agro-industrial non-food feedstock (agro industrial and food industry waste) that should be considered as feedstock for the formulation of eco-compatible composite materials.

This study therefore seeks to fabricate a LLDPE / Coconut fibre biocomposite with potential application as a packaging material.

1.3 OBJECTIVES OF THE STUDY

1.3.1 General Objective

This study seeks to develop bio-composites (LLDPE-coconut fibre composite) to explore the potential of coconut fibre as a reinforcing material.

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1.3.1 Specific Objectives

This project seeks:

➢ To characterize, compare and optimize the surface morphology of coconut fibres for use as reinforcement in LLDPE matrix.

➢ To fabricate LLDPE/coconut fibre bio-composites via single screw extrusion and injection moulding techniques.

➢ To evaluate and compare the effect of fibre treatment using sodium hydroxide (NaOH) on the properties of LLDPE/Coconut fibre bio-composites.

➢ To determine the mechanical properties (such as: tensile strength, young's modulus and % elongation at break) of LLDPE/Coconut fibre bio-composites.

➢ To study the effect of coconut fibre loading on the material properties of LLDPE/Coconut fibre bio-composites.

➢ To compare the mechanical properties of treated coconut fibre composites and the untreated coconut fibre bio-composites

➢ To study the swelling index behaviour of fabricated LLDPE- Coconut Fibre bio-composites.

1.4 SCOPE OF STUDY

The overall goal of this research is to produce a polymer bio- composite consisting of Coconut fibre (CCF) (ie. coconut palm fruit fibre) and linear low density polyethylene (LLDPE) that will be suitable for packaging and other applications.

Untreated CCF-LLDPE and Alkali (NaOH)-Treated CCF –LLDPE materials would be compounded using a single -screw extrusion technique.

This study would emphasize the mechanical properties of the treated and untreated bio-composite systems. In order to achieve these objectives, the work would be divided into various scopes. Firstly, the effect of the chemical treatment on CCF would be evaluated by comparing the NaOH treated CCF and Untreated CCF–LLDPE Composites. Secondly, to determine the effect of fibre loading on CCF-LLDPE composites, various percentages of fibre loading by weight (10%, 20%, 30%, 40% and 50%) would be employed. The comparison between untreated and treated composites would be done to study the change in trend in mechanical behaviour of the composites to be fabricated. Thirdly, in order to study the influence of fibre length and orientation on the composite, CCF would be chopped up and sieved to obtain whiskers which would be employed in this work. In the final scope, the fabricated CCF-LLDPE composites would be subjected to various solvents in order to evaluate their swelling behaviour in such solvents.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Composites

Composites are materials that comprise strong load carrying material (known as reinforcement) imbedded in weaker material (known as matrix). Reinforcement provides strength and rigidity, thus helping to support structural load. The matrix or binder (organic or inorganic) maintains the position and orientation of the reinforcement. Significantly, constituents of the composites retain their individual, physical and chemical properties; yet together they produce a combination of qualities which individual constituents would be incapable of producing alone (Hull and Clyne, 1996). The reinforcement may be platelets, particles or fibres and are usually added to improve mechanical properties such as stiffness, strength and toughness of the matrix material.

Although composite materials are widely perceived as being a modern development, composites have in fact been around for over 5000 years-since the construction of Babylon with bitumen reinforced with straw and horse hair. Indeed, composites can theoretically be called the oldest engineering concept, as nature has been exploiting them since the dawn of time. Modern and ancient applications all make use of the fact that composites can possess enhanced strength, stiffness and fracture toughness whilst not exhibiting an increase in weight.

Historical examples of composites (Chawla, 1987) are abundant in literature. Significant examples include the use of reinforcing mud walls in houses with bamboo shoots, glued laminated wood by Egyptians (1500 BC) and laminated metals in the forging of swords (1800 AD). In the 20th century, modern composites were used in 1930s, where glass fibres reinforced resins. Boats and aircrafts were built out of these glass composites, commonly called fibre glass. Since the 1970s, the application of composites has widely increased due to development of new

fibres such as carbon, boron and aramids, and new composite systems with matrices made of metal and ceramics.

In recent years, composites made of natural fibres have received increasing attention in light of the growing environmental awareness. Also because of their low density, good mechanical performance, unlimited availability and problem-free disposal, natural fibres offer a real alternative to the technical reinforcing fibres presently available. Natural fibres can compete with glass fibres especially with respect to the specific strength and specific stiffness. Composites, the wonder material with light weight, high strength-to-weight ratio and stiffness properties have come a long way in replacing the conventional materials like metals, wood etc. The material scientists all over the world focused their attention on natural composites reinforced with jute, sisal, coir, pineapple etc. primarily to cut down the cost of raw materials.

2.2 Fibre reinforced composites

Fibre reinforced composites consist of fibres of high strength and modulus embedded in a matrix with distinct interfaces between them. Fibre reinforcement improves the stiffness and the strength of the matrix. In the case of polymers that are not tough in the non-reinforced form, the toughness may also increase (De and White, 1996).

The fibre reinforced composites exhibit anisotropy in properties. The maximum improvement in properties is obtained with continuous fibre reinforcement. However, short fibre reinforced composites offer many advantages like ease of fabrication, low production cost and possibility of making complex shaped articles, over continuous fibre reinforcement. The performance of the composite is, however, controlled by the fibres and depends on factors like aspect ratio, orientation of fibres and fibre-matrix adhesion.

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Discontinuous fibre reinforced composite form an important category of materials used in engineering applications. The use of fibre reinforced plastics (FRP) composites for the production of rebars and prestressing tendons in civil engineering and transportation applications are becoming increasingly important in recent years (Kalamkrov *et al*., 1998).

Major constituents in a fibre reinforced composite material are the reinforcing fibres and a matrix, which act as a binder for the fibres. Coupling agents such asmaleated polypropylene and maleated polyethylene are used to improve the wettability of the fibre with the matrix as well as fillers used to reduce the cost and improve the dimensional stability, are the other commonly found constituents in a composite.

2.3 Role of matrix materials in composites

The role of matrix in a fibre-reinforced composite is to transfer stress between the fibres, to provide a barrier against an adverse environment and to protect the surface of the fibres from mechanical abrasion. The matrix also plays a major role in the tensile load carrying capacity of a composite structure. The binding agent or matrix in the composite is therefore of critical importance (Saira *et al*., 2007, Verma *et al*., 2013). Also the matrix should be chemically and thermally compatible with the reinforcing fibres. Another requirement of the matrix is to be compatible with the manufacturing methods which are available to fabricate the desired composite components.

Four major types of matrices have been reported: Polymeric, Metallic, Ceramic and Carbon. Most of the composites used in industry today are based on polymer matrices. Polymer resins have been divided broadly into three categories namely; thermosetting, thermoplastic and elastomers.

2.3.1 Thermoset polymer matrices

A thermoset is a hard and stiff cross-linked material that does not soften or become mouldable when heated. Thermosets are therefore stiff and do not stretch the way that elastomers and thermoplastics do. Several types of polymers have been used as matrices for natural fibre composites. Most commonly used thermoset polymers are epoxy resins and other resins (Unsaturated polyester resins (as in fibreglass), Vinyl Ester, Phenolic Epoxy, Novolac and Polyamide) (Hull and Clyne, 1996; Chawla, 1987; Bledzki *et al.*, 1998; Tawakkal *et al.*, 2012). The reinforcement of polyesters with cellulosic fibres has also been widely reported. Polyester-jute (Roe *et al.*, 1999), Polyester-sisal (Pal *et al.*, 1988; Alvarez *et al.*, 2004), polyester-coir (Owolabi *et al.*, 1985; Verma *et al.*, 2013), polyester-banana-cotton (Satyanarayana *et al.*, 1983), polyester-straw (White and Ansell, 1983, Baiardo *et al.*, 2004), and polyester-pineapple leaf (Devi *et al.*, 1997), are some of the promising systems.

2.3.2 Thermoplastic polymer matrices

Thermoplastics are polymers that require heat to make them processable. After cooling, such materials retain their shape. In addition, these polymers may be reheated and reformed, often without significant changes in their properties. Some of the thermoplastics which have been used as matrix for natural fibre reinforced composites are as follows: High density polyethylene (HDPE) (Maiti and Singh, 1986; Woodhams *et al.*, 1984; Enriquez *et al.*, 2010), Low density polyethylene (LDPE) (Raj *et al.*, 1990; Tan *et al.*, 2010), Chlorinated polyethylene (CPE) (Maldas and Kokta, 1995), Polypropylene (PP) (Woodhams *et al.,* 1984; Simpson and Selke,1991; Sain and Kokta, 1994; Arib *et al.*, 2006; Bodros *et al.*, 2007), Normal polystyrene

(PS) (Kokta *et al.*, 1983; Maldas *et al.*, 1989; Zakaria and Poh, 2002), Poly (Vinyl chloride) PVC) (Maldas *et al.*, 1989; Maldas and Kokta,1993), Mixtures of polymers (Hedenberg and Gatenholm, 1995; Suradi *et al.*, 2010),   Recycled Thermoplastics (Yam *et al.*,1990; Sain *et al.,* 1993).

Mostly, the thermoplastics which are utilised for natural fibre reinforced composites possess processing temperature (temperature at which fibre is incorporated into polymer matrix) not exceeding 230°C since most natural fibres thermally undergo degradation at temperatures above 200°C. These are usually polyolefins like polyethylene and polypropylene. Technical thermoplastics, like polyamides, polyesters and polycarbonates often require processing temperatures greater than 250°C and are therefore not suitable for such composite processing without fibre degradation.

2.3.2.1 Linear low-density polyethylene (LLDPE)

LLDPE has side chains similar to those of LDPE but with proper catalysts and coreactive agents, the chains are dramatically reduced in length (Crawford and Throne, 2000). LLDPE has a density range of 910 kg/m^3 to about 940 kg/m^3, and is 65% to 75% crystalline at room temperature. Competitive with LDPE, the 'linear low' materials have found rapid acceptance because of their high toughness (at low, normal and high temperatures), improved stiffness, chemical resistance, tensile strength, elongation at break and puncture resistance. However, it has somewhat poorer impact strength when compared with LDPE and MDPE.

In Lee and Joo's study (Lee and Joo, 1999; Gu, 2009), a thermoplastic LLDPE resin was used as the matrix for fibre composites. Its low processing temperature (less than 130°C) made composite fabrication possible without partial melting or annealing of the fibres. The high

toughness of LLDPE yielded a good impact-resistant composite and had advantages of thermoplastic composite processing, such as short processing time, unlimited storage time and solvent free processing.

2.4 Reinforcements used in composites

The structural load applied to composites is primarily carried by the reinforcement. As a result, the strength and stiffness of the composite is mainly determined by the nature of reinforcement. Composite reinforcement may be in the various forms including fibres, particles or whiskers.

2.4.1 Types of fibres

A fibre is defined as a unit of matter characterised by flexibility, fineness, and high ratio of length to thickness (Farnfield, 1975). Fibres are a class of hair-like materials which are in discrete elongated pieces, similar to pieces of thread and can be spun into filaments, thread or rope. They can be used as a component of composite materials.

A fibre can be categorized into two main groups, namely man-made fibre and natural fibre. In general, natural fibres can be subdivided based on their source of origin such as plants, animals, or minerals; whereas man-made fibres can also be subdivided into synthetic and natural polymers.

Natural fibres such as cotton, wool, silk, flax, hemp and sisal were among the first fibres used by man. However, the first man-made fibre was probably glass (Cooke, 1989). Presently, both natural and synthetic fibres (commonly known as man-made fibres) are readily available and are being used as fillers or reinforcements in composites.

Reinforcing fibres in a single-layer composite may be short or long compared to its overall dimensions. The long fibres and short fibres are called continuous fibres and discontinuous fibres, respectively (Agarwal and Broutman, 1990).

The continuous fibres in a single-layer composite may be all aligned in one direction to form a unidirectional composite, which are very strong in the fibre direction but are generally weak in the direction perpendicular to the fibres. The continuous reinforcement in a single layer may also be provided in a second direction to provide more balanced properties. However, the orientation of short or discontinuous fibres cannot be easily controlled in a composite material. In most cases, the fibres are assumed to be randomly oriented in the composite (Agarwal and Broutman, 1990).

Alternatively, short fibres, sometimes referred to as chopped fibre may be converted to a lightly bonded preform or mat that can be later impregnated with resin to fabricate single-layer composites. Chopped fibres may also be blended with resins to make a reinforced moulding compound. These fibres tend to become oriented parallel to the direction of material flow during a compression or injection moulding operation and thus get a preferential orientation.

Figure 2.1 below represents an accepted classification of single layer alignments.
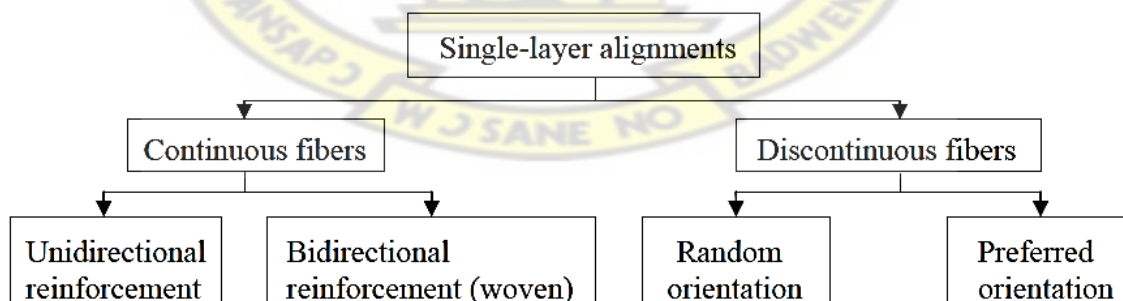
Figure 2.1: Single – layer alignments (Agarwal and Broutman, 1990)

2.4.2 Synthetic fibres

A large number of synthetic fibres with a variety of properties have been produced from polymers by various spinning techniques, including melt, dry, wet and emulsion spinning. Before synthetic fibres were developed, artificial (manufactured) fibres were made from cellulose, from plant sources. At the beginning of the twentieth century, synthetic fibres started supplementing and replacing natural fibres. The first truly synthetic fibre was nylon, followed by polyesters, polyacrylics and polyolefins. Also synthetic elastomeric, glass and aramid fibres became important commercial products (Cooke, 1989; Saira et al, 2007).

Synthetic fibres are now readily available, ranging in properties from the high elongation and low-modulus elastomeric fibres, through the medium-elongation and medium-modulus fibres such as polyamides and polyesters, to the low-elongation, high modulus carbon, aramid and inorganic fibres. With such a wide variety of synthetic fibres available, the volume of synthetic fibres consumed worldwide is now greater than that of natural fibres. Glass fibre is the dominant synthetic fibre and is used in 95 % of cases to reinforce thermoplastic and thermoset composites (Mohanty *et al.*, 2005).

2.4.3 Natural fibres

Natural fibres are subdivided based on their origins into vegetable/plants, animals, or minerals. Figure 2.5 below shows the classification of natural fibres. Vegetable or plant fibres include bast or stem fibres, leaf or hard fibres, seed, fruit, wood, cereal straw and other grass fibres (Alexander *et al.*, 2005). Structural materials in animals are mainly made of proteins such as collagen, elastin and keratin in combination with various polysaccharides, calcium minerals (in bone and teeth) or complex phenolic compounds (in hard insect cuticles). Mineral fibres are

naturally occurring fibre or slightly modified fibre obtained from minerals. Mineral fibres such as asbestos fibres had been used historically for insulating houses. However, to provide protection for workers and consumers, the manufacture and transformation of asbestos fibres have been forbidden (Bilba *et al*., 2007).
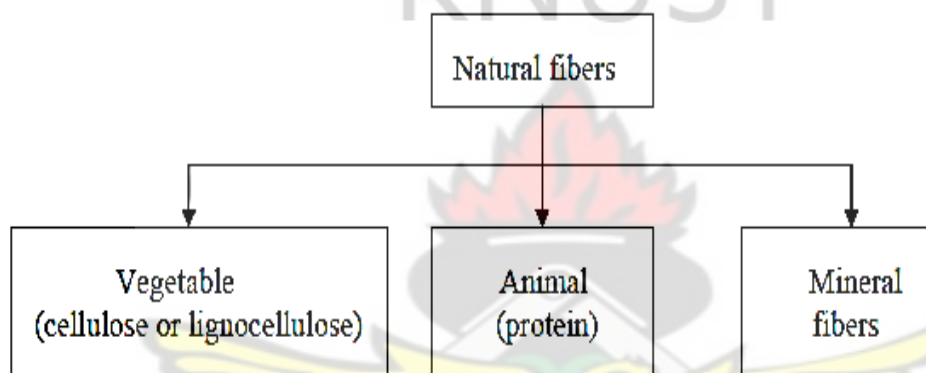
Figure 2.2: Classification of natural fibres (Alexander *et al*., 2005).

Natural fibres are now emerging as viable alternatives to glass fibres especially when combined in composite materials for various applications. The advantages of natural fibres over synthetic or man-made fibres such as glass are their relatively high stiffness which is a desirable property in composites, low density, recyclable, biodegradable, renewable raw materials, and their relatively low cost (Mohanty *et al*., 2005; Frederick and Norman, 2004; Joseph *et al*., 2002). Besides, natural fibres are expected to give less health problems for the people producing the composites. Natural fibres do not cause skin irritations and they are not suspected of causing lung cancer (Bos, 2004). Some disadvantages of natural fibres are their relatively high moisture

sensitivity and their relatively high variability of diameter and length. Notwithstanding these limitations, the abundance of natural fibres combined with the ease of their processability is an attractive feature, which makes them a covetable substitute for synthetic fibres that are potentially toxic (Pothan *et al*., 2006).

An important factor that controls the different types of natural fibres is their species. This is because the properties of fibres are different between different species. In addition, the properties of fibres within a species vary depending on area of growth, climate and age of the plant. Lastly, the properties of natural fibres vary greatly depending on the processing method used to extract the fibres.

2.5 Main components of natural fibres

The main or major chemical component of plants is water. However, on a dry weight basis, all plant cell walls consist mainly of sugar-based polymers (carbohydrates) which are combined with lignin with lesser amounts of extractives, protein, starch and inorganics. These chemical components are distributed throughout the cell wall, which is composed of primary and secondary wall layers. Chemical composition varies from plant to plant as well as geographical locations, ages, climatic and soil conditions (Saheb and Jog, 1999; John and Thomas, 2008). According to Sain and Panthapulakkal (2004), the plant age, climatic conditions and fibre processing techniques are factors that influence the structure of fibres as well as their chemical composition. Bledzki and Gassan (1999) also summarized that component or composition comprises values of plant fibres such as cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances, of which cellulose, hemicellulose and lignin are the major components, with

regard to the physical properties of the fibres. Therefore, the percentages and properties of these components contribute to the overall properties of plant fibres (Sain and Panthapulakkal, 2004).

2.5.1 Cellulose

Cellulose is the vital component of all plant fibres. The cell walls of large numbers of plants consist of the same substance called "cellulose" (Bledzki and Gassan, 1999). According to Nishino (2004), cellulose is a natural linear homopolymer (polysaccharide), in which D-glucopyranose rings are connected to each other with β-(1-4)-glycosidic linkages. Cellulose is thus considered as a 1,4-β-D-glucan (Bledzki and Gassan, 1999). According to Sain and Panthapulakkal (2004), the basic chemical structure of cellulose in all plant fibres is the same whiles the cell geometry of each type of cellulose varies with the fibre. The cell geometry is one of the factors which contribute to the mechanical properties of plant fibres. The molecular structure of cellulose is shown in Figure 2.3 below (Edwards *et al*., 1997).

From the molecular structure of cellulose, it can be seen that cellulose contains alcoholic hydroxyl groups. These hydroxyl groups form intermolecular and intra molecular hydrogen bonds with the macromolecule itself and also with other cellular (cellulose) macromolecular substances. As a result, natural fibres are generally hydrophilic in nature (Mohanty *et al*.,2005; Herrera and Valadez, 2005).
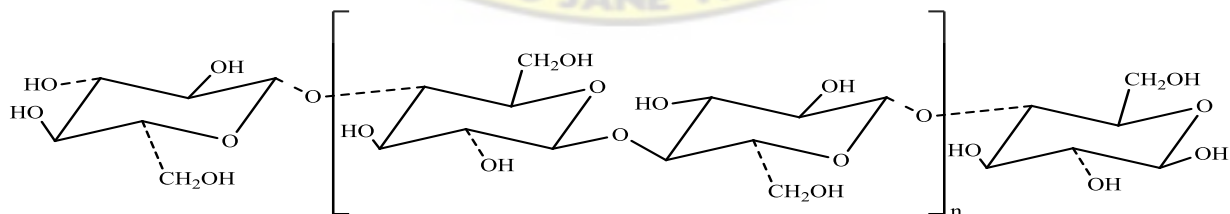
Figure 2.3: Molecular structure of cellulose (Edwards et al., 1997).

Even though the chemical structure of cellulose from different natural fibres is the same, the degree of polymerization (DP) varies. The mechanical properties of a fibre are largely dependent on the DP (Mohanty *et al.,* 2005). The number of glucose units in a cellulose molecule is referred to as degree of polymerization (DP). Most plants generally consist of approximately 45 - 50 % cellulose, on a dry weight basis.

2.5.2 Hemicelluloses

Another essential chemical component of plant fibres is the hemicellulose. Hemicelluloses are polysaccharides composed of a 5- and 6-ring carbon ring sugars (Alexander *et al*., 2005). Figure 2.4 below shows a partial structure of hemicelluloses with a combination of 5-ring carbon ring sugars (Bledzki and Gassan, 1999).
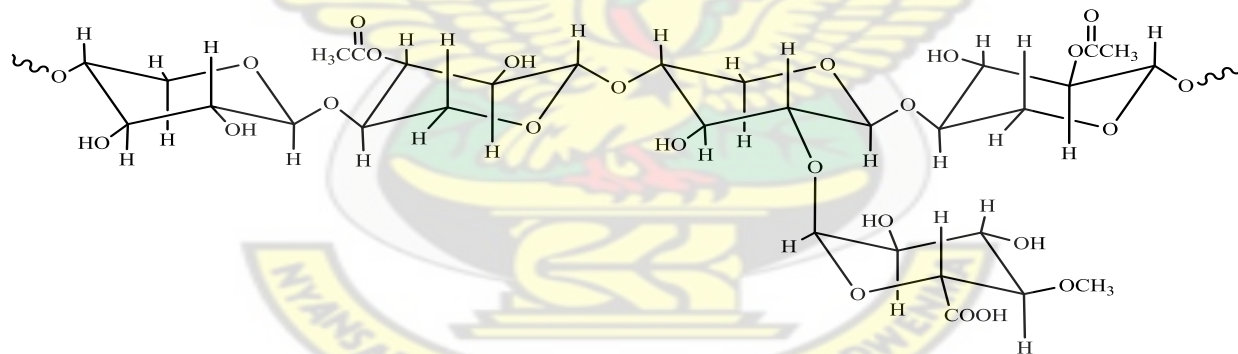
Figure 2.4: Partial structure of hemicelluloses (Bledzki and Gassan, 1999)

Hemicelluloses has a random, amorphous structure with little strength, highly branched polymer compared to the linearity of cellulose, and has a degree of polymerization lower than that of cellulose (Sain and Panthapulakkal, 2004). They are also classically defined as alkali soluble

material after removal of pectin substances, very hydrophilic and easily hydrolysed in acids (Alexander *et al.*, 2005).

Unlike cellulose, which contains only a 1, 4-β-glucopyranose ring, hemicellulose contains different types of sugar units such as D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor amount of other sugars. These monomers of hemicelluloses are shown in Figure 2.5 below**.** Usually, all of the monomers are present.
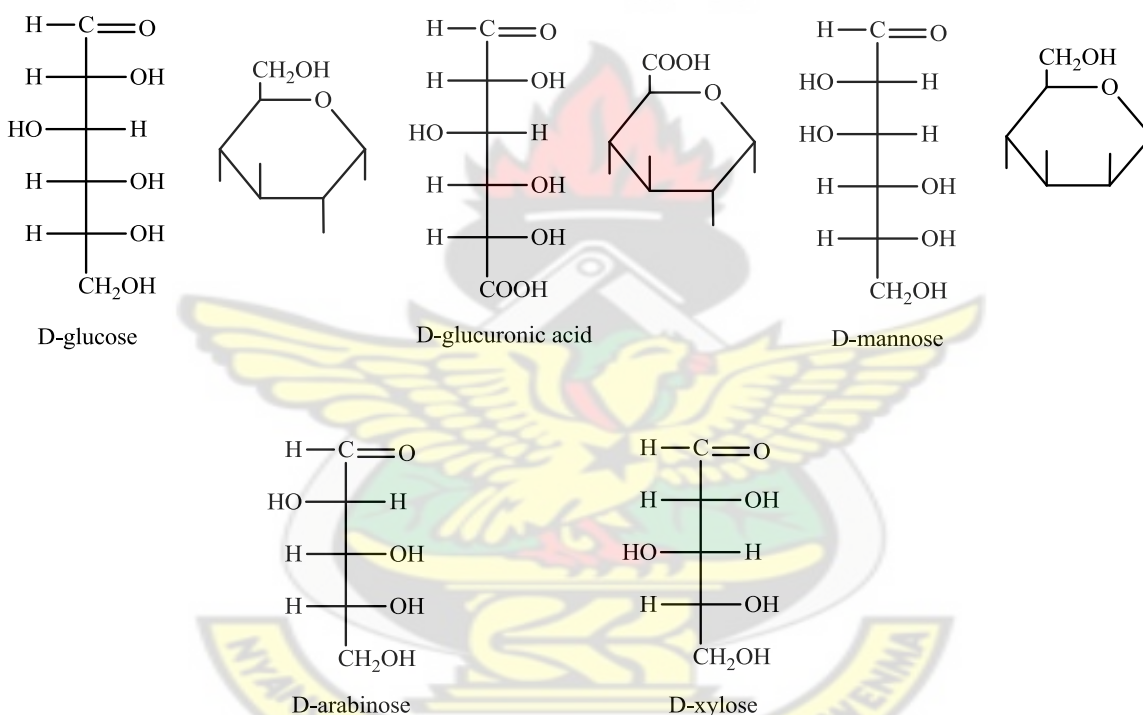
Figure 2.5: Monomers of hemicelluloses (Bledzki and Gassan, 199; John and Thomas, 2008).

Bledzki and Gassan (1999) have concluded that hemicelluloses differ from cellulose in three aspects. First, it contains several different sugar units whereas cellulose contains only 1, 4-β-D-glucopyranose units. Second, it exhibits a considerable degree of chain branching, whereas cellulose is a linear polymer. Third, the degree of polymerization of native cellulose is 10-100 times higher than that of hemicelluloses.

2.5.3 Lignin

Lignin is a complex chemical compound most commonly derived from wood and an integral part of the cell walls of plants. Lignin is the compound that gives rigidity to the plants. It is thought to be a complex, three-dimensional copolymer of aliphatic and aromatic constituents with very high molecular weight. Lignin is amorphous and hydrophobic in nature (Alexander *et al*., 2005; Mohanty *et al*., 2005; Habrant *et al.,* 2009). The partial structure of lignin can be seen in Figure 2.6 below.
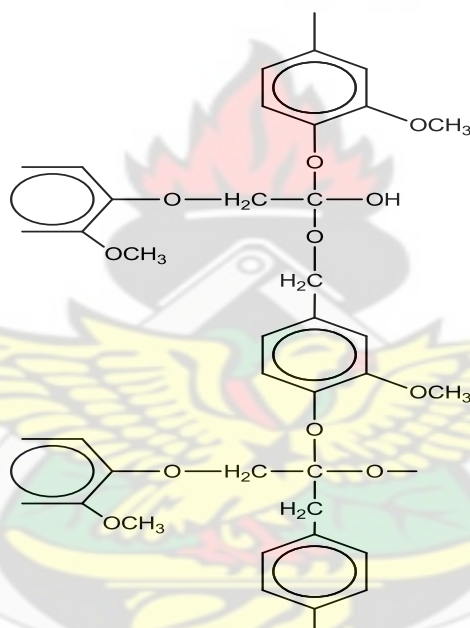
Figure 2.6: Partial structure of lignin (Bledzki and Gassan, 1999).

Lignin can be classified in several ways but they are usually divided according to their structural elements. All plants lignin consist mainly of three basic building blocks of guaiacyl, syringyl, and p-hydroxyphenyl moieties, although other aromatic type units also exist in many different types of plants, which forms a randomized structure in a 3-dimensional network inside the cell walls (Habrant *et al*., 2009).

Figure 2.7 below shows building blocks of lignin. There is a wide variation of structure within different plant species. The function of the lignin in plants is as an encrusting agent in the cellulose/hemicelluloses matrix or called plant cell wall adhesive. Therefore, lignin acts as a structural support material in plants by filling the spaces between the polysaccharide fibres, which hold the natural structure of the plant cell walls together (Sain and Panthapulakkal, 2004). Lignin stiffens the cell walls and acts as a protective barrier for the cellulose. The properties of lignin vary with the fibre type, but it always has the same basic composition (Mohanty et al., 2005; Sain and Panthapulakkal, 2004).

Phenylpropane unit   Guaiacyl   Syringyl
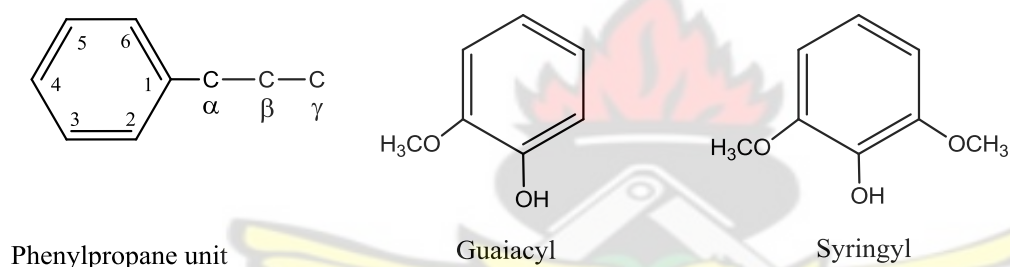
Figure 2.7: Building blocks of lignin (Habrant _et al_., 2009).

2.5.4 Pectin

Pectin is a collective name for hetero polysaccharides which consists essentially of polygalacturon acid and is soluble in water only after partial neutralization with alkali or ammonium hydroxide (Gassan and Bledzki, 1999).

2.5.5 Waxes

Waxes make up the part of the fibres, which can be extracted with organic solvents. These waxy materials consist of different types of alcohols which are usually insoluble in water as well as in acids such as palmitic acid, stearic acid (Gassan and Bledzki, 1999).

Various studies have been carried out to determine the chemical composition of some natural fibres as shown in table 2.1 below.

Table 2.1: Chemical constituents of some plant fibres (Saira et al., 2007)

Fiber	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)	Extractives (%)	Ash (%)	Pectin (%)	Wax (%)
BAST							
Jute	61-71.5	13.6-20.4	12-13	-	-	0.2	0.5
Flax	71-78.5	18.6-20.6	2.2	2.3	1.5	2.2	0.7
Hemp	70.2-74.4	17.9-22.4	3.7-5.7	3.6	2.6	0.9	0.8
Ramie	68.6-76.2	13.1-16.7	0.6-07	-	-	1.9	0.3
Kenaf	31-39	15-19	21-5	3.2	4.7	-	-
LEAF							
Sisal	67-78	10-14.2	8-11	-	-	10.0	2.0
PALF	70-82	-	5-12	-	-	-	14.0
Henequen	77.6	4-8	13.1	-	-	-	-
SEED							
Cotton	82.7	5.7	-	-	-	-	0.6
FRUIT					-		
Coir	36-43	0.15-0.25	41-45	-	-	3-4	-
WOOD							
Soft	40-44	25-29	25-31	5	0.2	-	-
Hard	43-47	25-35	-	16-24	2-8	0.4	-

2.6 Major drawbacks of natural fibres

2.6.1 Moisture absorption of fibres

The ligno-cellulosic natural fibres are hydrophilic and thus absorb moisture. The swelling behaviour of natural fibres is generally affected by their morphology as well as physical and chemical structures. Plant fibres change their dimensions with varying moisture content because the cell wall polymers contain hydroxyl and other oxygen containing groups, which attract moisture through hydrogen bonding (Saheb and Jog, 1999).

The hemicelluloses are mainly responsible for moisture absorption. The waxy materials present on the surface help to retain the water molecules on the fibre. The porous nature of the natural fibre accounts for the large initial uptake at the capillary region. The hydroxyl group (-OH) in the cellulose, hemicellulose and lignin build a large amount of hydrogen bonds between the macromolecules in the plant fibre cell wall (Joly *et al*., 1996).

The schematic representation of swelling process in cellulose is given in figure 2.8 below.
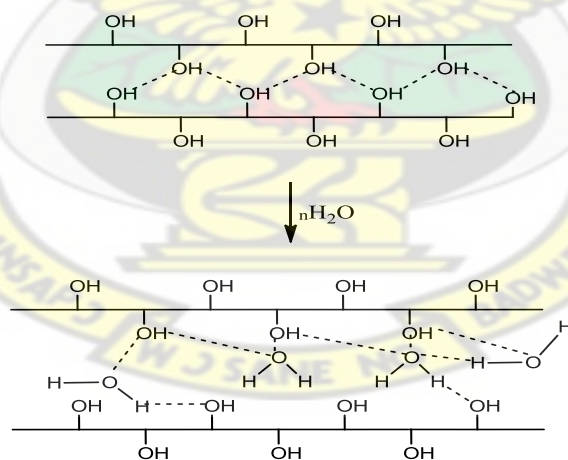
Figure 2.8: Schematic representation of water absorption of cellulosic fibres (Mwaikambo and Ansell, 2002).

Generally moisture content in natural fibres varies between 5-10%. This can lead to dimensional variations in composites and also affect the mechanical properties of composites. As a result, the removal of moisture from fibres is very critical before the preparation of the composites. The moisture absorption of natural fibres can also be minimised through proper surface modification systems.

2.6.2. Thermal stability of natural fibres

Thermal treatment of natural fibres results in a variety of physical and chemical changes since they are complex mixtures of organic materials. The limited thermal stability of natural fibres is one of their drawbacks. As mentioned earlier, natural fibre is composed of mainly cellulose, hemicellulose and lignin. Each of these components has its own characteristic properties with respect to thermal degradation when used in polymer composites. However, the microstructure and the three dimensional nature of natural fibre are variables, that also play important roles in terms of their effects on combustion behaviour. Thus, the individual chemical components of the fibre behave differently if they are isolated or if they are intimately combined within each single cell of the fibre structure (Schniewind, 1986; Zaman et al., 2011).

The thermal degradation of cellulose based fibres is therefore greatly influenced by their structure and chemical composition. Natural fibre begins degrading at about 240°C. Thermal degradation pattern of cellulosic fibres like oil palm, sisal, banana, coir, hemp, jute etc. was also reported (Baiardo *et al*., 2002). It was reported that chemical modification improved the thermal stability of their composites. Chemically modified fibres showed a satisfactory thermal stability at processing temperatures for potential composites.

Thermal degradation of natural fibres is a two stage process; one in the temperature range 80-180°C and other in the range 280-380°C. The low temperature degradation (80-18O°C) process is associated with degradation of lignin, whereas the high temperature degradation (280-380°C) process is due to cellulose. The degradation of natural fibres is a crucial aspect in the development of natural fibre composites and thus plays a critical role on the curing temperature with regard to elastomers and thermosets processing and extrusion temperature in thermoplastic composites processing (Ge *et al*., 2005; Alvarez *et al*., 2004).

2.6.3. Biodegradation and Photodegradation of natural fibre

The ligno-cellulosic natural fibres are degraded biologically by very specific enzymes capable of hydrolysing the cellulose, especially hemicellulose present in the cell wall into digestible units (Hatakeyama *et al.,* 2005). Ligno-cellulosics exposed outdoors also undergo photochemical degradation caused by ultraviolet light.

Biodegradation of cellulose brings about weakening of the strength of natural fibres. Photo degradation primarily takes place in the lignin component which is responsible for the colour changes (Saheb and Jog, 1999). The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet degradation.Resistance to biodegradation and ultraviolet radiation, however, is improved by bonding chemicals to cell wall or by adding polymer to the cell matrix.

2.7. Factors influencing the properties of fibre reinforced composites

2.7.1 Strength, modulus and chemical stability of fibre and matrix

In fibre reinforced composites, the fibres act as the main load carrying agents whilst the matrix keeps them in the desired orientation and location. The final properties of fibre-reinforced composite therefore depend on the strength and modulus of the reinforcing fibre (Saira *et al*., 2007). The choice of the matrix depends on the final requirements of the product and other factors such as cost, fabrication process, environmental conditions and chemical resistance of the matrix. The function of the matrix varies depending on how the composite is stressed. For instance, in compressive loading, the matrix prevents the fibres from buckling and provides a stress transfer medium, so that when an individual fibre breaks, it does not lose its load carrying capacity. The physical properties of the matrix that influence the behaviour of the composites are shrinkage during cure, modulus of elasticity, ultimate elongation, tensile and flexural strength and compression and fracture toughness.

2.7.2. Fibre length, loading and orientation

The mechanical properties of the composites are depended on several factors such as fibre length, loading and orientation in the matrix. There are several studies on the effect of fibre length and fibre orientation on the tensile strength of the short fibre composites (Saheb and Jog, 1999).When a load is applied to the matrix, stress transfer occurs by shear at the interface along the fibre length and ends of the fibre. The extent of load transfer is a function of the critical fibre length (aspect ratio), the direction and orientation of fibre and the compatibility between fibre–matrix interfaces.

For short fibre reinforced composites, there exists a critical aspect ratio at which the properties are maximised. This critical aspect ratio depends on the volume fraction of the fibre and also on the ratio of the modulus of the fibre and matrix. At low volume fraction, the fibres play no major role and the strength of the composite is matrix dominated. However, above a certain critical volume fraction of the fibre the strength of the composite increases. The critical volume fraction depends on the fibre aspect ratio and found to decrease with increase in aspect ratio. At low fibre content, the critical aspect ratio remains almost constant and show sharp decrease at higher volume fraction. A critical fibre length may be defined as the minimum fibre length at which the maximum allowable fibre stress can be achieved. The increase in fibre length above critical fibre length does not contribute to the increase in composite strength. However, a decrease in fibre length below the critical fibre length results in a decrease in composite strength. When all the fibres are below critical length, the fibres act only as filler and the strength of the composite decreases. The critical aspect ratio depends on the efficiency of stress transfer from the matrix to fibre and it decreases with improvement in fibre-matrix adhesion.

Depending on the fibre orientation at the matrix, three types of composite are prepared. Firstly, longitudinally aligned fibre composites generally have higher tensile strength but lower compressive strength (due to fibre buckling). Secondly, transversely directed fibres undergo very low tensile strength, which is lower than the matrix strength.

Finally, randomly orientated short fibre composites have different mechanical properties. This is due to the complexities of load distribution at different direction along the interfaces, consistent mechanical properties of these composites are far more difficult. Therefore, by controlling factors such as the aspect ratio, the dispersion and orientation of fibres, considerable

improvements in the properties can be accomplished (Fakirov and Bhattacharyya, 2007; Mwaikambo and Ansell, 1999 and Joseph *et al*., 2003).

2.7.3. Presence of voids

During the incorporation of fibres into the matrix, or in the manufacture of laminates, air or other volatiles may be trapped in the material. The trapped air or volatiles exist in the cured laminates as micro voids and may consequently affect the mechanical properties of the composites significantly. There are two types of voids in composite materials namely: (a) voids formed along individual fibres and (b) voids formed between lamina and in resin-rich regions. Some factors such as shrinkages during cure of the resin and the cooling rate play important role in void formation (Joseph *et al*., 2003). A high void content (over 20% by volume) usually leads to lower fatigue resistance, greater susceptibility to water diffusion and increased scattering or variation in mechanical properties (Bowles and Frimpong, 1992; Vaxman *et al*., 2004). The volatiles produced during the curing cycle in thermosetting resins and during melt processing operation in thermoplastic polymers may also result in the production of voids. Most studies have reported that composites at higher fibre content display more risk for void formation (Vaxman *et al*., 2004).

2.7.4. Moisture absorption of fibres

The lignocellulosic fibres are hydrophilic and absorb moisture. Many hydrogen bonds (hydroxyl groups -OH) are present between the macromolecules in the fibre cell wall. When moisture from the atmosphere comes in contact with the fibre, the hydrogen bond breaks and hydroxyl groups form new hydrogen bonds with water molecules. The cross section of the fibre becomes the main

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access of water penetration. The interaction between hydrophilic fibre and hydrophobic matrix causes fibre swelling within in the matrix. This results in weakening the bonding strength at the interface, which leads to dimensional instability, matrix cracking and poor mechanical properties of the composites (Zakaria and Poh, 2002). Therefore, the removal of moisture from fibres is an essential step for the preparation of composites. The moisture absorption of fibres can be reduced by eliminating hydrophilic hydroxyl groups from the fibre structure through different chemical treatments (Wang *et al*., 2007).

2.7.5 Fibre-matrix interface

Interface refers to the boundary region between two phases in contact. The composition, structure and properties of the interface may vary across the region and may also differ from composition, structure or properties of either of the two contacting phases fibre and matrix. This interfacial region exhibits a complex interplay of physical and chemical factors that exert a considerable influence in controlling the properties of reinforced composites. The interfacial interaction depends on the fibre aspect ratio, strength of interactions, fibre orientation and aggregation etc. (Sreekala *et al.,*1997; Alvarez *et al*., 2005). Extensive research has been done to evaluate the interfacial shear strength (ISS) of man-made fibres (Hristov *et al*., 2004) and natural fibres (Khalil *et al*., 2001) by using methods such as fibre pull out tests, critical fibre length and micro bond tests.
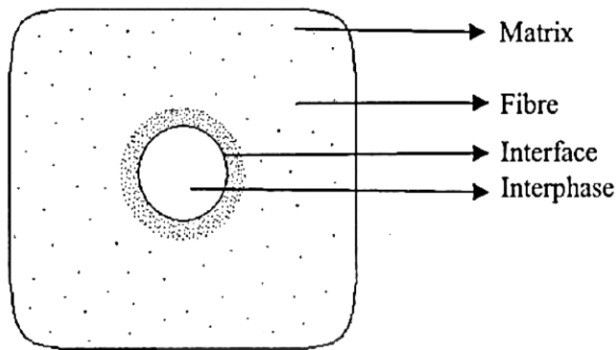
Figure 2.9. A schematic diagram of Interface/Interphase in a fibre reinforced composite

In fibre composites, stresses acting on the matrix are transferred to the fibre across the interface. To achieve efficient stress transfer, the fibres have to be strongly bonded to the matrix. Composite materials with weak interface have relatively low strength and stiffness but high resistance to fracture whereas materials with strong interface have high strength and stiffness but are very brittle. The effects are related to the ease of debonding and pull out of fibres from the matrix during crack propagation.

2.8. Mechanisms of fibre-matrix adhesion

The fibre-matrix interface adhesion can be explained in terms of five main mechanisms.

a) Adsorption and wetting

This is due to the physical attraction between the surfaces, which is better understood by considering the wetting of solid surfaces by liquids. Between two solids, the surface roughness prevents the wetting except at isolated points. When the fibre surface is contaminated, the effective surface energy decreases. This hinders a strong physical bond between fibre and matrix interface (Saira et al., 2007).

b) Interdiffusion

Polymer molecules can be diffused into the molecular network of the other surface, say fibre, as shown in Figure 2.10(a) below. The bond strength will depend on the amount of molecular conformation, constituents involved and the ease of molecular motion.

c) Electrostatic attraction

This type of linkage is possible when there is a charge difference at the interface. The electrostatic interaction at the interface is shown in Figure 2.10 (b) & (c) below. The anionic and cationic species present at the fibre and matrix phases will have an important role in the bonding of the fibre-matrix composites via electrostatic attraction. Introduction of coupling agents at the interface can enhance bonding through the attraction of cationic functional groups by anionic surfaces and vice versa (Saira *et al*., 2007).

d) Chemical bonding

Chemical bonds can be formed between chemical groups on the fibre surface and a compatible chemical group in the matrix as shown in Figure 2.10 below. The type of bond formed determines the strength. Interfacial chemical bonding can increase the adhesive bond strength by preventing molecular slippage at a sharp interface during fracture and also increasing the fracture energy by increasing the interfacial attraction (Mir et al., 2012).

e) Mechanical adhesion

Mechanical interlocking at the fibre-matrix interface is possible as given in Figure 2.10 (e) below. The degree of roughness of the fibre surface is very significant in determining the mechanical and chemical bonding at the interface. This is due to the larger surface area available on a rough fibre. Surface roughness can increase the adhesive bond strength by promoting wetting or providing mechanical anchoring sites.
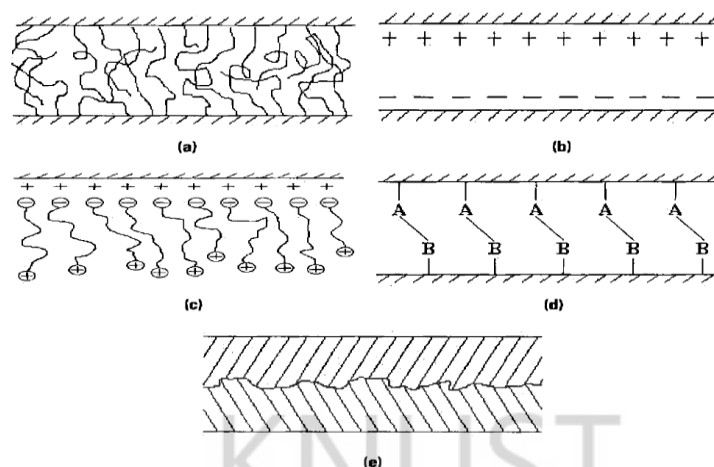
Figure 2.10. Schematic diagrams representing various fibre-matrix adhesions.

2.9 Fibre-matrix interface modifications

Natural fibres are hydrophilic in nature and as a result are incompatible with the hydrophobic polymer matrix and therefore have a tendency to form aggregates. The hydrophilic nature of the fibres makes them very sensitive to moisture absorption. In order to minimise the challenges related to high water absorption, treatment of fibres with hydrophobic reagents has been exploited. These reagents usually contain reactive functional groups that are capable of bonding to the reactive groups in the matrix polymer. The modification of natural fibres is therefore carried out to make fibres hydrophobic and to improve the interfacial adhesion between the fibre and the polymer matrix (Bledzki and Gassan, 1996; Kumar *et al*, 2010).

In addition to the surface treatments of fibres, use of a compatibilizer or coupling agent for effective stress transfer across the interface are also being explored (Lu *et al*., 2005; Harper and Wolcott, 2004). The compatibilizer may be a polymer with functional groups grafted into the chain of the polymer. The coupling agents are generally tetrafunctional organometallic compounds based on silicon, called silanes (Saheb and Jog,1999). Brief descriptions of some important fibre chemical modifications methods are given below.

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2.9.1. Alkali treatment

Alkali treatment of cellulosic fibres, also called mercerization, is the usual method to produce high quality fibres (Ray *et al*., 2001). Alkali treatment improves the fibre-matrix adhesion due to the removal of natural and artificial impurities (Mishra *et al*., 2001a). Moreover, alkali treatment leads to fibrillation which causes the breaking down of the composite fibre bundle into smaller fibres. In other words, alkali treatment reduces fibre diameter and thereby increases the aspect ratio. Therefore, the development of a rough surface topography and enhancement in aspect ratio offer better fibre-matrix interface adhesion and an increase in mechanical properties (*Joseph et al.,* 2000). Alkali treatment increases surface roughness resulting in better mechanical interlocking and the amount of cellulose exposed on the fibre surface. This increases the number of possible reaction sites and allows better fibre wetting. The following reaction takes place as a result of alkali treatment:

Fibre-OH + NaOH → Fibre-O-Na + H_2O
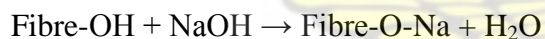
Jähn et al., (2002) found that the cellulosic fine structure of flax fibres was directly influenced by mercerization treatment. Moreover, alkali treatment influenced the chemical composition of the flax fibres, degree of polymerization and molecular orientation of the cellulose crystallites due to cementing substances like lignin and hemicellulose which were removed during the mercerization process. Consequently, mercerization or more general alkali treatment had a lasting effect on the mechanical behavior of flax fibres, especially on fibre strength and stiffness (Gassan and Bledzki, 1999). Several other studies were conducted on alkali treatment (Mishra *et al*., 2002; Joseph *et al*., 2000; Sreekala *et al*., 2000). They reported that mercerization led to the increase in the amount of amorphous cellulose at the expense of crystalline cellulose and the removal of hydrogen bonding in the network structure.

2.9.2. Silane treatment

Coupling agents usually improve the degree of cross-linking in the interface region and offer a perfect bonding result. Silane coupling agents were found to be effective in modifying the natural fibre-matrix interface. Various silanes were effective in improving the interface properties of wood-polypropylene (Coutinho *et al.*, 1997), mineral-filled elastomers (González *et al.*, 1997), fibre-reinforced epoxies (Culler *et al.*, 1986) and phenolics composites (Ghatge and Khisti 1989). Alkoxy silanes are able to form bonds with hydroxyl groups. Coupling agents such as toluene dissocyanate and triethoxyvinyl silane were tested in fibre treatment in order to improve the interface properties. Silanes undergo hydrolysis, condensation and bond formation stage. Silanols can form polysiloxane structures by reaction with hydroxyl group of the fibres. The reaction schemes are given in Figure 2.11 and 2.12.

In the presence of moisture, hydrolyzable alkoxy group leads to the formation of silanols.
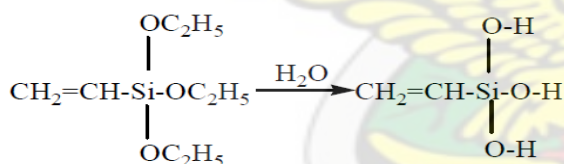
Figure 2.11 Hydrolysis of silane (Sreekala *et al.* 2000).
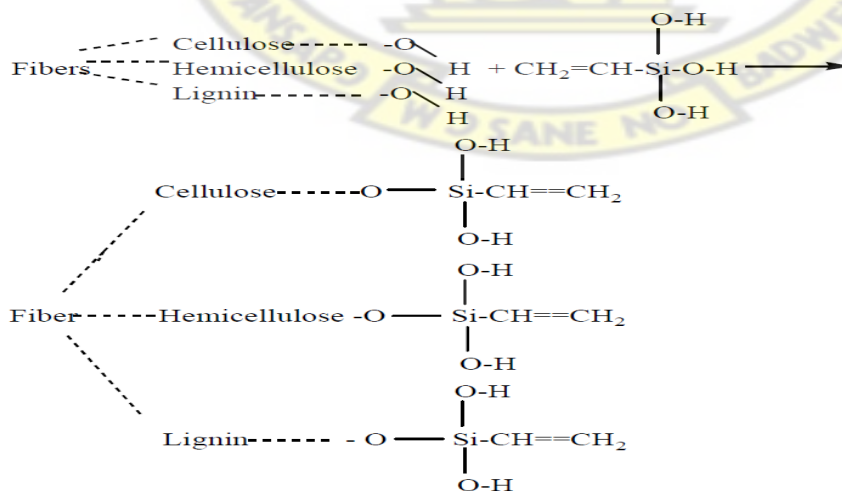
Figure 2.12 Hypothetical reactions of fibre and silane (Sreekala *et al.*, 2000).

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González *et al.* (1997) investigated the effect of silane coupling agent on the interface performance of henequen fibre-reinforced high-density polyethylene composites. The fibre-surface silanization resulted in better interfacial load transfer efficiency but did not improve the wetting of the fibre. Hydrogen and covalent bonding mechanisms could be found in the natural fibre-silane system. It was assumed that the hydrocarbon chains provided by the silane application influenced the wettability of the fibres, thus improving the chemical affinity to polyethylene. Silane treatment of cellulosic fibres can increase the interfacial strength and therefore the mechanical properties of the composite (George *et al.*, 1998; Bataille *et al.*, 1989). Silane treatment also enhanced the tensile strength of the composite (Joseph *et al.*, 2000).

2.9.3 Benzoylation

Manikandan *et al.*, (1996) reported that benzoylation of the fibre improved fibre matrix adhesion, thereby, considerably increasing the strength of composite. Joseph *et al.*, (2000) studied the benzoylation treatment on the surface of fibres. A fixed amount of washed fibre (35g) was soaked in 18% NaOH solution for 0.5 h, filtered and washed with water. The treated fibre was suspended in 10% NaOH solution and agitated with 50 ml benzoyl chloride. The reaction between the cellulosic –OH group of sisal fibre and benzoyl chloride is shown in Figure 2.13 as follows:

Fiber —— OH + NaOH ⟶ Fiber —— O⁻Na⁺ + H₂O

Fiber —— O⁻Na⁺ + ClC(=O)—⟨benzene⟩ ⟶ Fiber—— O —— C(=O)—⟨benzene⟩ +NaCl
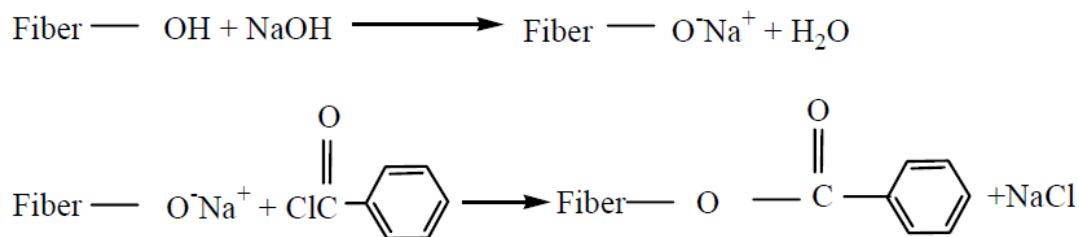
Figure 2.13 A possible reaction between cellulosic-OH groups and benzoyl chloride (Joseph *et al*. 2000).

2.9.4 Other chemical treatment methods

Several interface modification methods were also reported in literature. Acetylation of natural fibres is a well-known esterification method to introduce plasticization to cellulosic fibres. Acetylation has been extensively applied to wood cellulose to stabilize the cell wall, improving dimensional stability and environmental degradation. One of the modification techniques employed by the Okura Company in Japan was to produce esterified woods (Mohanty *et al*., 2001), which would be molded into plastic sheets by hot pressing.

Another effective method of surface chemical modification of natural fibres is graft copolymerization. Optimized vinyl grafted natural fibres, consisting of the orderly arrangement of grafted moieties, act as compatible reinforcing fibres with several resin systems to obtaining better fibre-matrix adhesion of the resulting biocomposites (Mohanty *et al*., 2001; Ghosh and Ganguly, 1993).

Isocyanate has a functional group -N=C=O which is very susceptible to reaction with the hydroxyl group of cellulose and lignin in the fibres and forms strong covalent bonds, thereby creating better compatibility with the binder resin in the composites. Kokta *et al*., (1990a) and Raj *et al*., (1988) pointed to the performance of isocyanate as a coupling agent. Isocyanates provided better interaction with thermoplastics resulting in superior properties. Isocyanates could

act as a promoter or as an inhibitor of interaction. The radical enhances the chemical interlocking at the interface.

Permanganate treatment was carried out to improve the bonding at the fibre-polymer interface. Joseph *et al*., (2000) and Sreekala *et al*., (2000) investigated the fibres which were pre-treated with alkali and then dipped in permanganate solution in acetone. Tensile strength values of the composite showed a marginal increase with permanganate treatment.

Acrylation treatment, maleated polypropylene/maleic anhydride treatment and titanate treatment of cellulosic fibres have also been reported (Sreekala *et al*., 2000; Mohanty *et al.,* 2001). Acrylation treatment resulted in high strain values of the composites. The composites ability to withstand the applied flexural stress is manifested by higher strain values, which indicate the elastic nature of the material.

Maleated polypropylene or maleic anhydride grafted polypropylene (MAPP) has been widely used as a coupling agent or a compatibilizer in natural fibre reinforced polypropylene composites. The treatment of natural fibres with MAPP copolymer provides covalent bonds across the interface. Through such treatment, the surface energy of the fibres is increased, thereby providing better wettability and high interfacial adhesion. Many other compounds such as chromium complexes and titanates can be used as coupling agents.

Systematic studies on the chemical modification of various natural fibres like sisal, coir, oil palm, banana and pineapple and its reinforcing effect on various thermosets, thermoplastics and rubbers have also been reported. In all cases, it was observed that the composite properties have greatly improved by using treated fibres due to better fibre-matrix interaction (Park *et al*., 2004; Sreekala and Thomas, 2003; and Joseph *et al*., 2002). However, there is limited information

available concerning the effect of duration or treatment time required by these surface modification methods on the mechanical properties of composites.

2.10Effects of Fibre Surface Modifications on Fibres

The chemical modification directly influences the cellulosic fine structure of natural fibres. The effects of fibre modification on the tensile properties of fibres are briefly reviewed here.

2.10.1 Tensile properties of fibres

Sreekala *et al*. (2000) measured the tensile properties of untreated and modified fibres, such as tensile strength, Young's modulus and elongation at break. Many of the modifications decreased the strength properties due to the breakage of the bond structure, and also due to the disintegration of the non-cellulosic materials. Some of the treatments, like silane and acrylation, led to strong covalent bond formation and thereby the strength was enhanced marginally. Optimum mechanical performance was observed for silane-treated and acrylated fibre. The reinforcing ability of the fibres did not just depend upon the mechanical strength of the fibres but on many other features, such as polarity of the fibre, surface characteristics and presence of reactive centers. These factors control interfacial interaction. The Young's modulus of the fibres improved upon acrylation, alkali and silane treatment. The improved stiffness of the fibres was attributed to the crystalline region (cellulosic) of the fibre. The fibre also showed very good elongation properties, with values increasing upon modifications. Lower elongation of the untreated fibre may be due to the three dimensionally cross-linked networks of cellulose and lignin. The various treatments broke this network structure giving the fibre higher elongation and lower strength properties.

Mishra *et al*. (2001b) also investigated the tensile properties of untreated, chemically modified and AN-grafted sisal fibres. Chemically modified fibres showed an appreciable decrease in the tensile properties. This decrease was attributed to the substantial delignification and degradation of cellulosic chains during chemical treatment. The extension at break of these fibres did not change much. In all the cases of grafting, it has been found that the tensile strengths were higher than that of untreated fibre.

2.11. Effects of Fibre Surface Modifications on Composite Properties

Several studies have been carried out on the influence of various types of chemical modifications on the properties of natural fibre-reinforced thermoplastic composites. Here, the effects of fibre modification on the mechanical properties are reviewed.

2.11.1 Mechanical properties of composites

The mechanical properties of a natural fibre-reinforced composite depend on many parameters, such as fibre strength, modulus, fibre length and orientation, in addition to the fibre-matrix interfacial bond strength as stated earlier. A strong fibre-matrix interface bond is, therefore, critical for high mechanical properties of composites. A good interfacial bond is required for effective stress transfer from the matrix to the fibre whereby maximum utilization of the fibre strength in the composite is achieved (Karnani *et al*., 1997). Surface modification to the fibre also improves resistance to moisture-induced degradation of the interface and the composite properties (Joseph *et al*., 2000). In addition, factors like processing conditions/techniques have significant influence on the mechanical properties of fibre reinforced composites (George *et al*., 2001).

Sapieha *et al*., (1989; 1990) have found that by the addition of a small amount of dicumyl peroxide or benzoyl peroxide into the cellulosic fibre-polymer (LDPE) systems during processing significantly improved the mechanical properties of the composite. Kokta *et al.,* (1990a; 1990b) have extensively studied the effect of different chemical modifications, such as silane treatment and grafting, on the mechanical properties and dimensional stability of cellulosic fibre-thermoplastic composites. They found that the chemically modified cellulosic fibre-reinforced thermoplastic composites offered superior physical and mechanical properties under extreme conditions even after recycling**.**

However, some studies have also reported decrease in mechanical properties of composites after surface modification of fibres. Georgopoulos et al., (2005) have investigated that the loading of LDPE with natural fibers leads to a decrease in tensile strength of the pure polymer. On the other hand, Young's modulus increased due to the higher stiffness of the fibers. Also, the tensile strength of the PP-wood-based composites decreased significantly with increasing wood fiber content and no significant change in modulus of elasticity was found for any weight fraction of wood fiber. Fiber pullout was observed on most of the PP composite fracture surfaces examined using SEM. These results indicate a lack of adhesion between PP and wood fiber (McHenry and Stachurski, 2003).

2.12 Fabrication of composites

The fabrication and shaping of composites into finished products are often combined with the formation of the material itself during the fabrication process. The formation of the composite involves the combination of the matrix and fibre such that the matrix impregnates, surrounds and wets the fibres. The important processing methods for thermosetting polymers involve hand lay-

up, bag moulding process, filament winding, sheet moulding, resin transfer moulding whereas thermoplastics processing methods include rotational moulding, compression moulding, injection moulding and extrusion.

2.12.1 Extrusion

The extrusion process basically consists of continuously shaping a fluid polymer through the orifice of a suitable tool (die), and subsequently solidifying it into a product. In the case of thermoplastics, the feed material, in powder or pellet form, is most commonly heated to a fluid state and pumped into the die. Oladipo et al. (1999) investigated the composite (aspen wood fibre/HDPE) manufacturing process. The components were fed at pro-determined mass flow rates, based on the desired wood fibre mass fraction in the composite, into a ZSK-30 Werner & Pfleiderer extruder (Werner & Pfleiderer Ltd., Marple, Cheshire, UK) having 28 mm co-rotating twin screws. The extruder was operated at a working temperature of 150ºC and a screw speed of 100 rpm. This temperature ensured that while the polymer was fully melted (melting point is 120-135ºC), the wood fibres were not burned.

2.13 Current Industrial Applications of Composites

Reinforced fibre composites have gained popularity over conventional materials because of their: High strength to weight ratio and rigidity, Wide range of manufacturing techniques, Ease of fabrication, Versatility in design and Low cost. Due to these overwhelming advantages, there is wide range of applications of fibre reinforced plastics. Some important applications are:

1. Transportation*:* Manufacture of vehicle bodies, cooling system components etc

2. Material handling*:* Pharmaceutical trays and boxes, storage tanks etc.

3. Sporting goods*:* Fishing rods, Tennis racquets, Hockey sticks etc.

4. Construction*:* Structured shapes, panelling, sliding etc.

5. Aerospace and Military*:* Rocket motor cases, nozzles, nose cones, blades, pressure bottles, assault boat and rifle stocks, bullet proof helmet, bridge sections, ladders etc.

The studies so far reported proved that the utilization of natural fibres in polymeric matrices offer economic and environmental advantages. Owing to the uncertainties prevailing in the supply and price of petroleum based products, it is highly important to rely on the naturally occurring alternatives. Proper utilization of indigenous available raw materials will open up new markets for these natural resources. Hence, the importance of studies on composites containing natural fibres cannot be overemphasized.
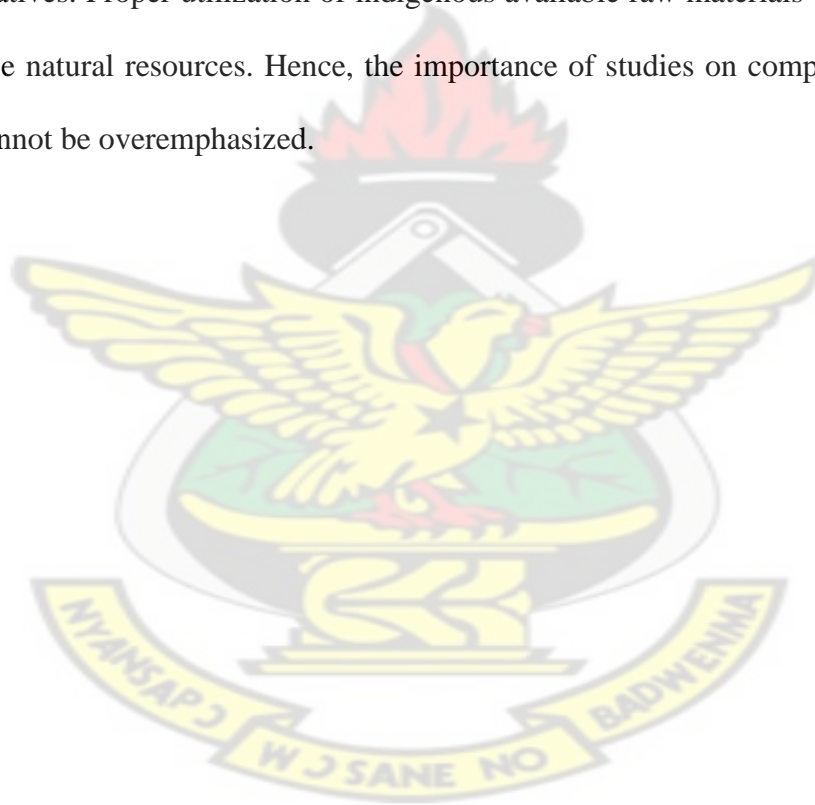
CHAPTER THREE

3.0 MATERIALS, METHODOLOGY AND CHARACTERISATION

3.1 Materials

3.1.1. Coconut fibre

Coconut fibre was obtained from the ripe coconut husk collected from Kumasi Metropolis, by retting in water for 3 months. After retting, the husks were then beaten with a hammer. Coconut fibres were then removed from the shell and separated with a comb, washed thoroughly with distilled water and dried at 25 ^{O}C. The process of obtaining the coconut fibres are shown below in figure 3.1.

(a)   (b)   (c)
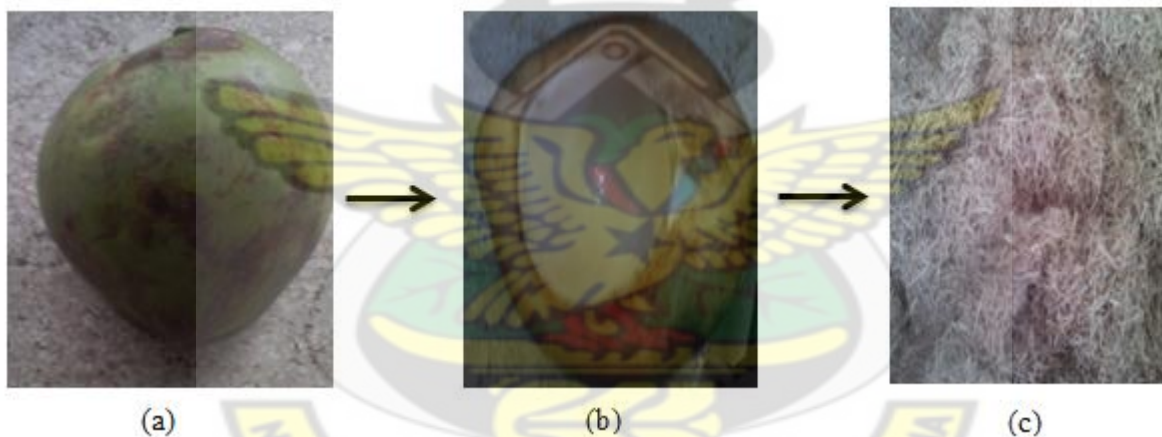
Figure 3.1: From coconut fruit to coconut fibre (a) coconut fruit, (b) half coconut fruit and (c) fibre strands

3.1.2 Linear Low Density Polyethylene

Linear Low Density Polyethylene (LLDPE) with 0.9 g/10 min MFI and 0.92 g cm^{-3} density was purchased from Poly Tank Ghana Limited in the powdered form, white in colour and has a commercial name as Exxonmobil LLDPE.

3.1.3 Chemicals

a. Sodium hydroxide (NaOH) (reagent grade) was used for the coconut fibre surface modification. NaOH has a molecular weight of 40.00, an assay of 97.0 − 100% and was manufactured by Park Scientific limited, Northampton, UK.

b. Toluene (Methylbenzene − $C_6H_5CH_3$, reagent grade) was used for the swelling index study. It has a molecular weight of 92.14, an assay of 95% and manufactured by Phillip Harris Limited, Shenstone, England.

c. Cyclohexane (Analar grade) was used for the swelling index study. It has a molecular weight of 84.16, an assay of 99.8% and manufactured by Fisons Scientific Equipment, Loughborough, England.

3.2 Equipment

    a. Single screw extruder used for the extrusion of the material was manufactured by J.B Engineering (Chippenham) Ltd, England, with a model number- extruder 1.20. (Fig. 3.2 a) and presently found at the Metrology Laboratory, Mechanical Engineering Department, KNUST - Kumasi.

    b. Injection moulding machine used for the moulding of test specimen was manufactured by J. B Engineering (Chippenham) Ltd, England, with a model number - 14-34. (Fig. 3.3 a) and presently found at the Metrology Laboratory, Mechanical Engineering Department, KNUST - Kumasi.

    c. Hounsfield Universal Tensile Strength Testing Machine used to determine the tensile properties of composites was manufactured by Hounsfield Test Equipment Ltd, UK with a model number of H50KS and a load cell of 50N capacity. (Fig. 3.6)

d. Interspec 200-X used for the FTIR spectroscopic analysis was manufactured by Spectronic Camspec Ltd, UK with a model number 200-X. (Fig. 3.5)

3.3. Fibre preparation and surface modification

3.3.1. Fibre preparation

Ripe coconut husks collected from various locations within the Kumasi Metropolis, Ghana, were soaked in tap water in containers for 3 months. This process is called retting, which partially decomposed the pulp on the shell, thereby allowing the fibre to be removed from the husk easily. After retting, the husks were then beaten with a hammer. Coconut fibres were then removed from the shell and separated with a comb. After drying at 25 ^{O}C, the coconut fibres were combed to further separate the fibres into an individual state, or as close to that as possible. Then a sifter was finally employed to remove impurities. The derived fibres were then washed thoroughly in distilled water, dried at 25 ^{O}C and designated as untreated coconut fibre (UCF).

3.3.2. Surface modification via alkali treatment

Some of the untreated coconut fibres were treated with sodium hydroxide (NaOH) aqueous solution (5% w/v) for 24 h at 25 ^{o}C(Gu, 2009). The alkali-treated fibres were immersed in distilled water after the treatment for 24 h expecting to remove the residual NaOH. Then, it was washed with distilled water until all the sodium hydroxide was removed, and the waste water tested neutral with a pH meter. Subsequently, coconut fibres were dried at 25°C until constant weight was obtained and designated as treated coconutfibre (TCF). All the coconut fibres, both alkali-treated and untreated, were then cured in an oven, then conditioned under the environment of relative humidity of 65% and temperature at 25 °C for 24 h before further processing. Both

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untreated and treated coconut fibre were then chopped into smaller sizes and sieve analysis performed with a 2 mm sieve. The sieved coconut fibres of length of about 2 mm or less than 2 mm, which passed through the sieve, were then used to prepare the bio-composites.

3.4 Preparation of composites and test specimen

3.4.1 Composite fabrication via extrusion

The chopped pre-treated and untreated coconut fibres were oven dried at 80°C for 24 h to reduce the moisture content. Mixtures of thermoplastic (LLDPE) powder and (10, 20, 30, 40, and 50) % by weight of coconut fibres were then prepared by using a food blender in a dry blending process. This aided in the homogeneous mixing of the coconut fibres and LLDPE matrix during the extrusion process. The dry blend was then fed into the single-screw extruder (J.B Engineering (Chippenham) ltd, England, Model number- extruder 1.20). Barrel temperatures (of the three zones) used were 75, 130 and 180 ºC respectively. The screw speed used was 120 rpm and feed rate to the extruder of 50g/hr. Blends prepared were extruded using a one-hole strand die.Extruded strands were then pelletized.

Figure 3.2a The single screw extruder in use

A schematic representation of the extruder is shown below
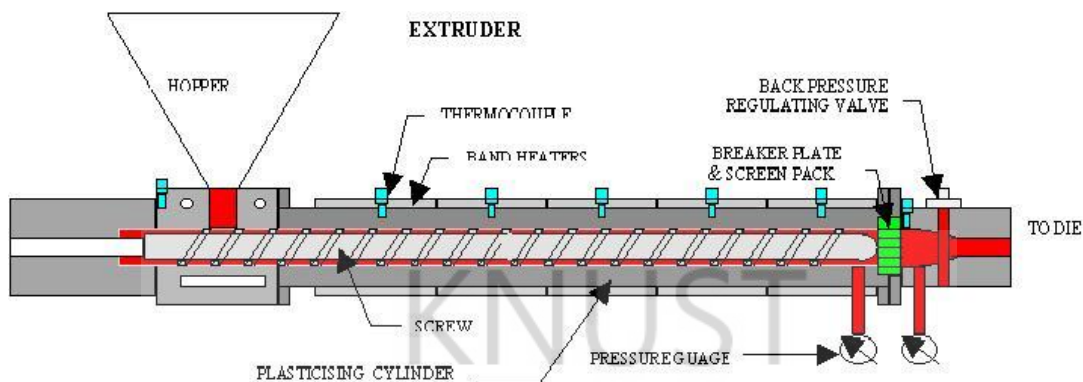
Figure 3.2b A schematic diagram of a single screw extruder

The pellets were further chopped into very small granules before being used in injection moulding to ensure homogeneity in composites formed. Composites were moulded into tensile test specimen by using an injection moulding machine (J. B Engineering (Chippenham) Ltd, England, Model number - 14-34) at 170 ^{o}C with a retention time of 5 minutes. After moulding test specimen were conditioned at 23 ^{o}C, with 50% relative humidity for at least 40 h according to ASTM D618-99.

Figure 3.3 a. The injection moulding machine used

A schematic representation of the injection moulding process is also shown below.
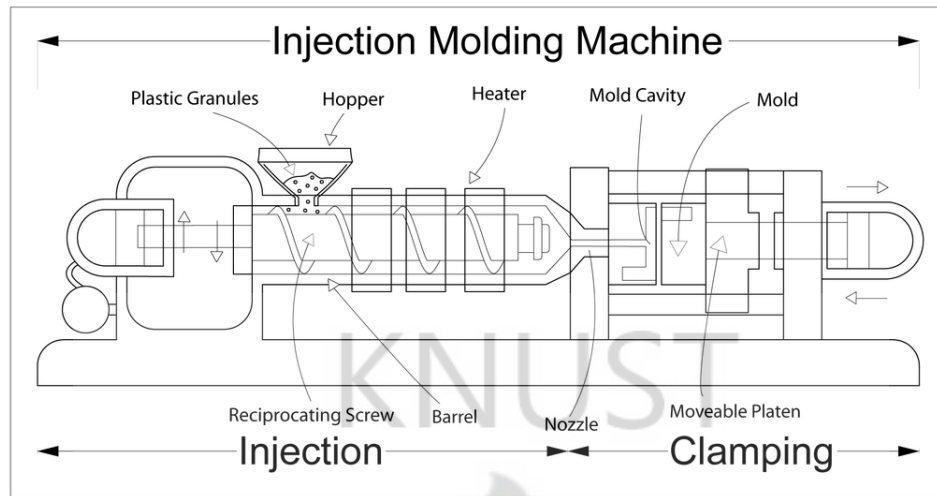
Figure 3.3 b A schematic diagram of a typical injection moulding machine

3.4.2 Tensile test specimen

Test specimen obtained according to the ASTM D638-99 (ISO-527-99) were cylindrical in shape (popularly referred to as dogbone shape) with a diameter of 4.98mm and a gauge length of 40mm as shown below.

$L_1 = 60$ mm

$L_2 = 40$ mm

$D = 4.98$ mm

Figure 3.4 A test specimen

3.5. Testing and characterisation methods

3.5.1 Fourier transform infra-red spectroscopy analysis

Infrared spectra of untreated and treated coconut fibre were obtained with Fourier Transform Infrared Spectrophotometer (Spectronic Camspec Ltd, UK, Model- Interspec 200-X) by using solid KBr pellet technique. Fibre samples and composites fabricated were cut into small pieces and ground well before mixing with KBr. The spectrometer was used in the transmission mode with a resolution of 2 cm^{-1} in the range of 4500 – 500 cm^{-1}. The samples were tested after being pressed with 2.5wt% of KBr to form a disc.
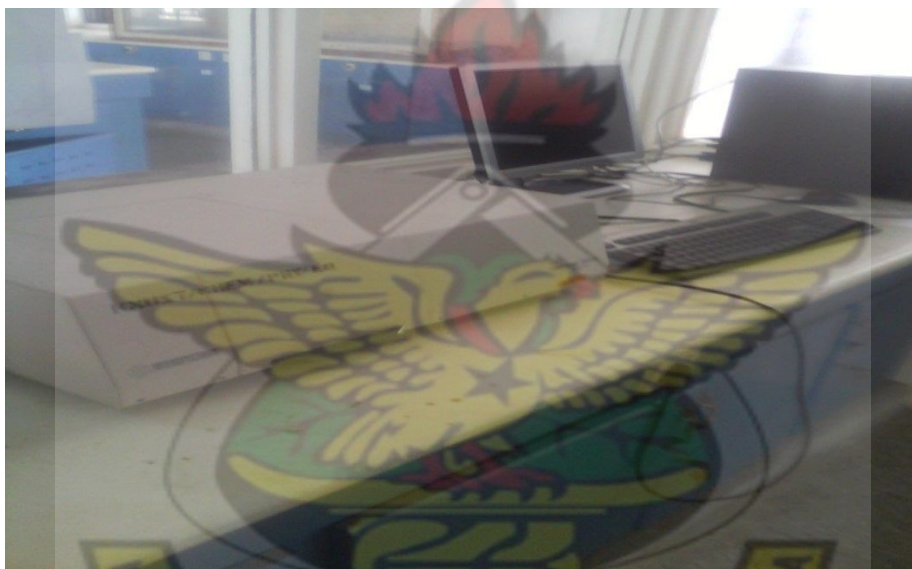
Figure 3.5 The FTIR spectrometer

3.5.2 Tensile properties

The tensile properties of the specimens were determined using cylindrical shaped samples with a Hounsfield Universal Tensile Strength Testing Machine (Hounsfield Test Equipment Ltd, UK, Model number - H50KS) with a load cell of 50N capacity. The gauge length between the jaws at

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the start of each test was adjusted to 40mm and the measurements carried out at a crosshead speed of 5mm/min according to ASTM D638-99 (ISO-527-99). Average of at least five sample measurements was taken to represent each data point. The test was performed under controlled environment (20 ^{o}C, 65% RH) according to the standard test method for tensile properties of plastics (ASTM D638 – 99). The stress-strain curves were then plotted and the ultimate tensile strength, Young's modulus and % elongation at break were determined for the various composites.

Figure 3.6: Universal tensile testing machine

3.5 Swelling index studies

Swelling behaviour was determined by the change in mass. For swelling test, ASTM D 3616 was followed.Test pieces of known weight (W_d) of the fabricated bio-composites were immersed in toluene and cyclohexane for 24 hr at 25 ^{o}C. The surface of the swelled samples was then immediately blotted with tissue paper and re- weighed (W_s). The swelling index (S.I) of composites was calculated by using the swelling data obtained. Swelling index (SI) was calculated by the equation:

S . I = $\frac{Ws}{Wd}$

where,

W_d = dry weight.

W_s = swollen weight.

Consequently, the cross linking density was determined as the inverse of the swelling index.

Cross link density = $\frac{1}{S.I}$

<center>**CHAPTER FOUR**</center>

4.0 RESULTS AND DISCUSSION

4.1 Fourier Transform Infra-Red Spectroscopy

4.1.1 Untreated coconut fibre (UCF)

A fourier transform infra-red spectroscopy analysis was performed on the untreated coconut fibre. The FTIR spectrum for the untreated coconut fibre is shown in figure 4.1 below. The FTIR spectrum obtained shows an absorption peak at 1740 cm^{-1}, which is the characteristic band for carbonyl stretching, associated with the carbonyl groups present in lignin and other cellulosic components. The strong broad peak at 3500-3400 cm^{-1} is the characteristic hydrogen-bonded – OH stretching vibration as well as the hydroxyl groups present in carbohydrate. The peaks at 2940 cm^{-1} and 760 cm^{-1} corresponds to the C-H and C-O stretching vibrations respectively. A band at 1600 cm^{-1} is due to the C-C stretching of the aromatic ring in the lignin components, while a strong peak at 950 cm^{-1} arises from the glycosidic linkages. The bands at 1370, 1330 and 1310 cm^{-1} are due to the -CH deformation, -OH in plane bending and -CH$_2$ wagging respectively. The band near 1260 cm^{-1} is due to the -C-O-C bond in the cellulose chain. Similar observations were made by other researchers (Mir *et al.*, 2012; Haque *et al.*, 2010).

<center>53</center>
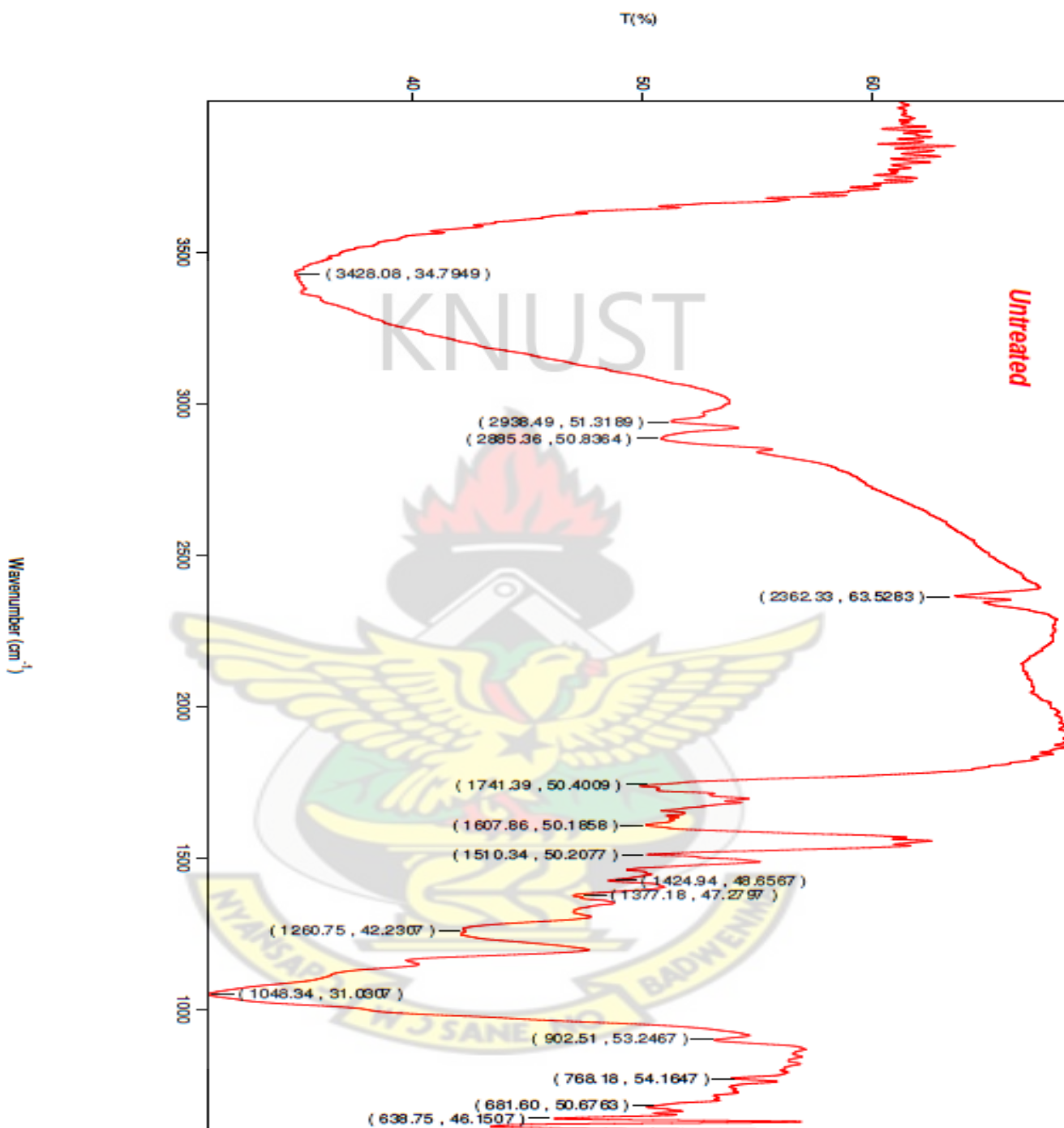
Figure 4.1 FTIR spectrum of Untreated Coconut Fibre (UCF)

4.1.2 Alkali treated coconut fibre (TCF)

The FTIR spectrum for the treated coconut fibre is shown below in Figure 4.2. Most of the peaks

exhibited by the UCF were also found in the TCF. However, for the alkali treated coconut fibres

the 3400 cm^{-1} band assigned to the alcohol group was reduced due to the removal of the hemicellulose component. Also, another important change observed as a result of alkali treatment is the removal of the hydrogen bonding in the network. This is evident from the increased intensity of the -OH peaks at 3300cm^{-1}. Furthermore, on mercerization, the peak at 1740 cm^{-1} in the spectrum of the raw fibre disappeared. This could be attributable to the fact that a substantial amount of uranic acid, a constituent of hemi-cellulose is removed from the fibre, resulting in the disappearance of the peak. Similar observations were made by various studies (El-Shekeil *et al*., 2012; Herrera-Franco and Valdez-Gonzalez, 2005; Janna *et al*., 2009).

Also, the result of FTIR shows that fatty acid and waxy material on the surface of the coir fibre were disposed of by alkali solution. This was observed through the deep brown colouration of the waste water obtain from TCF after the treatment as compared to the UCF which was not treated.
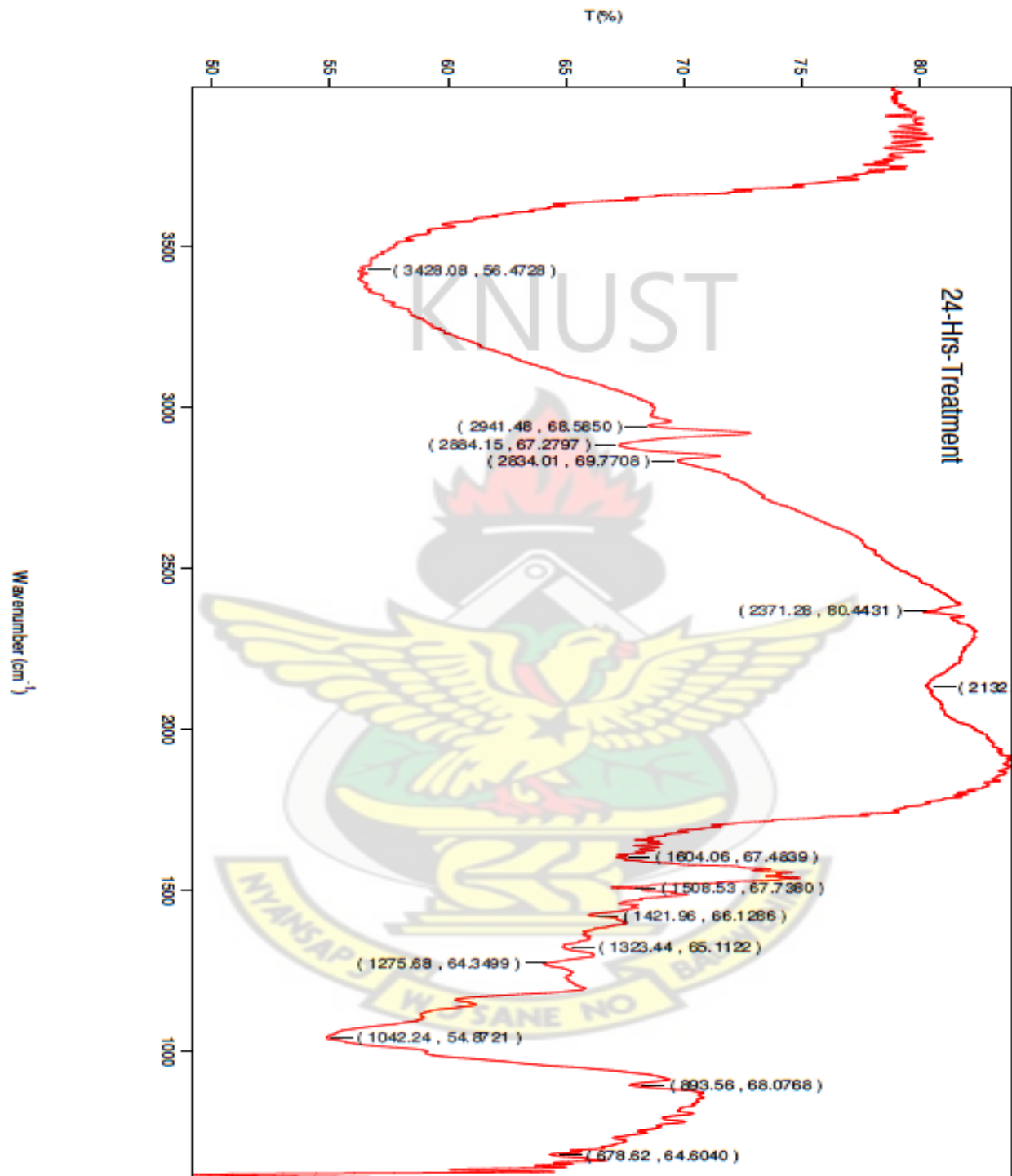
Figure 4.2 FTIR spectrum of Treated Coconut Fibre (TCF)

4.1.3 Composites

Figures 4.3 and 4.4 below represent the FTIR spectra of the untreated coconut fibre composites (UCFC) and the treated coconut fibre composites (TCFC) respectively. After the formation of the bio-composites, the characteristic absorption peaks of the LLDPE/CCF groups are as follows: $3500 – 3400$ cm^{-1} attributed to the stretching vibration of the O-H band; 2920 cm^{-1} attributed to the stretching vibration of the C–H band; 2851 cm^{-1} attributed to the stretching vibration of the CH$_2$ band; 1471cm^{-1} attributed to the C-H deformation and 719 cm^{-1} attributed to the inner rocking vibration of methylene (-CH$_2$).

From these characteristic absorption peaks observed, it can be seen that the LLDPE/CCF biocomposites spectrums show all the characteristic peaks for both the pure LLDPE and CCF. However, a slight shift in the peaks is observed. Also, it is expected that an interaction between the LLDPE carbonyl group and the CCF hydroxyl group may influence the position and intensity of the carbonyl peak in the composite spectrum. However, there is no observable increase in intensity of this peak, contrarily to one's expectations and therefore does not seem to suggest any change in peak position. As a result it could be seen that there are no observable interactions between the LLDPE and CCF from the FTIR results.

It is generally observed that the intensity of the 3400 cm^{-1} peak assigned to the stretching vibrations of the hydroxyl groups decreased with the alkali treatment of the fibre as depicted in UCFC and TCFC respectively. However, no significant differences were observed in both intensity and position of peaks with increased in percent fibre loading in all fabricated bio-composites. Therefore, after comparison among the spectrums of CCF, LLDPE and LLDPE/CCF bio-composites, it reveals that no new bonds are formed due to the mixture of CCF with the LLDPE.
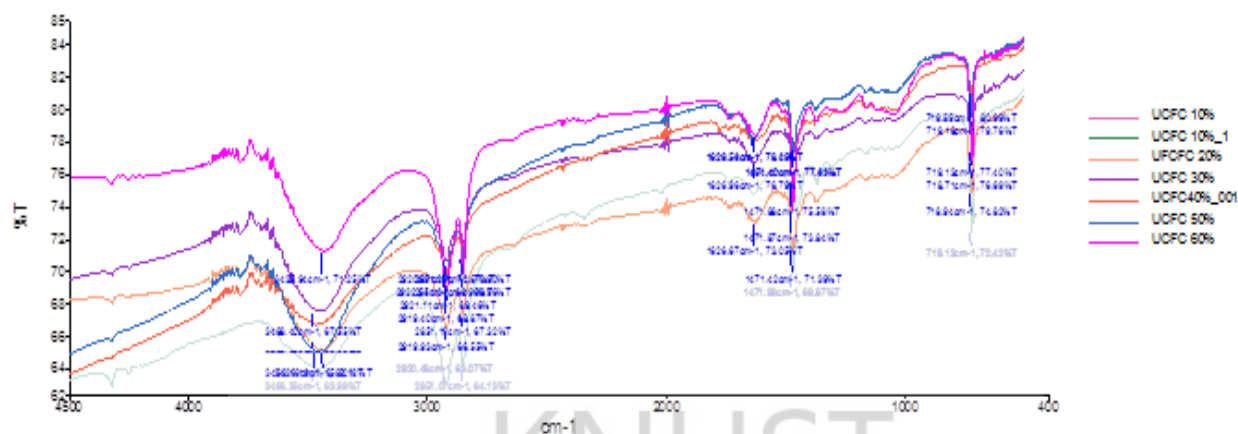
Figure 4.3 FTIR Spectra of UCFC
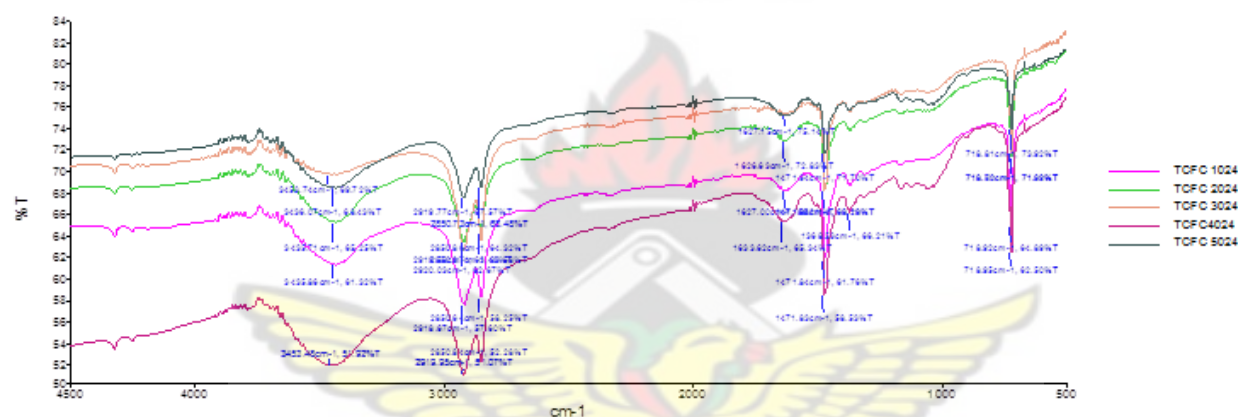
Figure 4.4 FTIR spectra of TCFC

Table 4.1 Summary of main FTIR peaks

Chemical structure	Peak location	UCF	TCF	LLDPE	COMPOSITES
O-H[a]	3500-3400	3428	3428	-	3453
C-H[a]	3100-3000	2938	2941	2920	2920
CH$_2$, CH$_3$ [a]	3000-2800	2885	2884	2851	2851
C=0	1740	1741	-	-	-
C=C[a]	1600	1607	1604	1633	1633
CH$_2$, CH$_3$ [b]	1500-1300	1510	1508	1471	1471
C-O[a]	1300-1000	1260, 1048	1275, 1042	-	-
C-0-C		768	678		

[a]streching ; [b]bending

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4.2 Mechanical properties of biocomposites

The most critical factors that influence the mechanical properties of fibre-reinforced materials are usually the volume fraction and fibre-matrix interfacial adhesion. The degree and quality of interfacial bonding is also determined by a number of factors mainly the nature of fibre and matrix (polymer) components, the fibre aspect ratio, the processing method and the treatment mechanism of the fibre (Gomes *et al*., 2007; Pracella *et al*., 2006). Therefore, in this study, the adhesion between the LLDPE/coconut fibres composite without treatment was expected to be poor as compared to the LLDPE/coconut fibre composite with alkali treatment before fabrication. The effects of fibre content and surface modification on the tensile properties of composites fabricated as well as their stress-strain behaviour are discussed below.

4.2.1 Stress-Strain behaviour of LLDPE/coconut fibre composites

The tensile test is one of the most widely used testing standards for measuring the mechanical properties of a polymeric material. This test determines the stress-strain curves in tension. This is done by continuously measuring the force that develops as the test specimen is elongated at a constant rate of extension. Thus, to better understand the effect of the extensional flow on the LLDPE/CCF bio-composites, stress –strain curves are plotted below in Figure 4.5, 4.6, and 4.7 with curves showing individual behaviour at appendix.
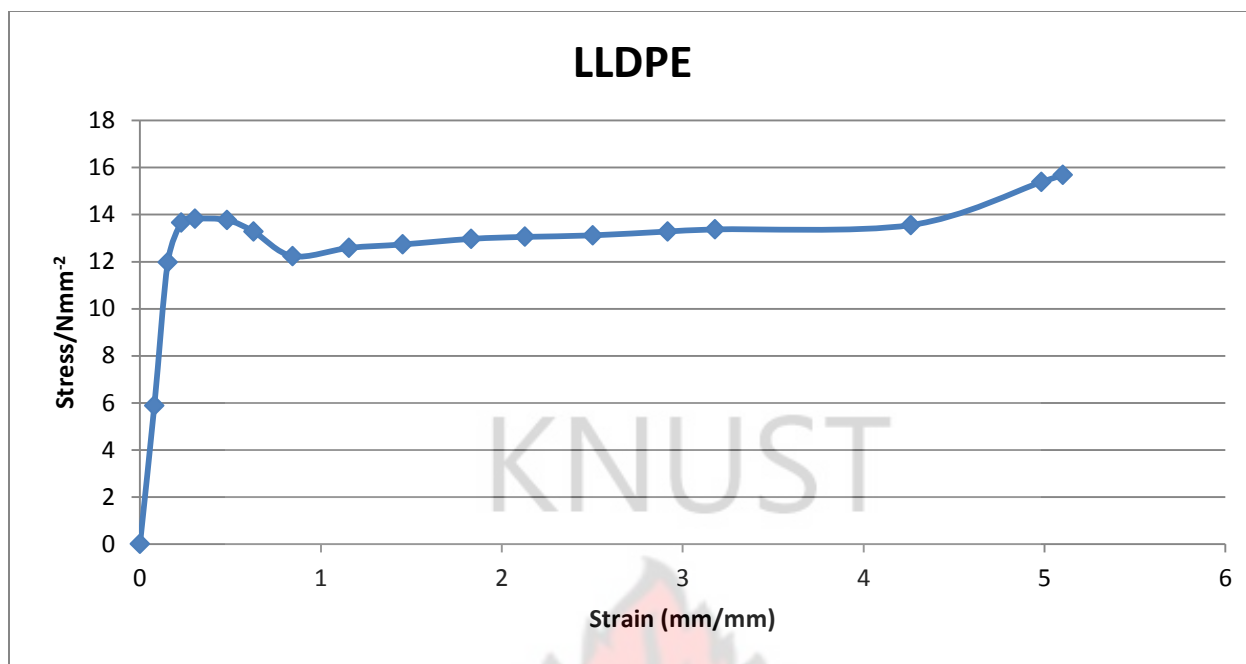
Figure4.5 Tensile stress versus strain behaviour of pure LLDPE
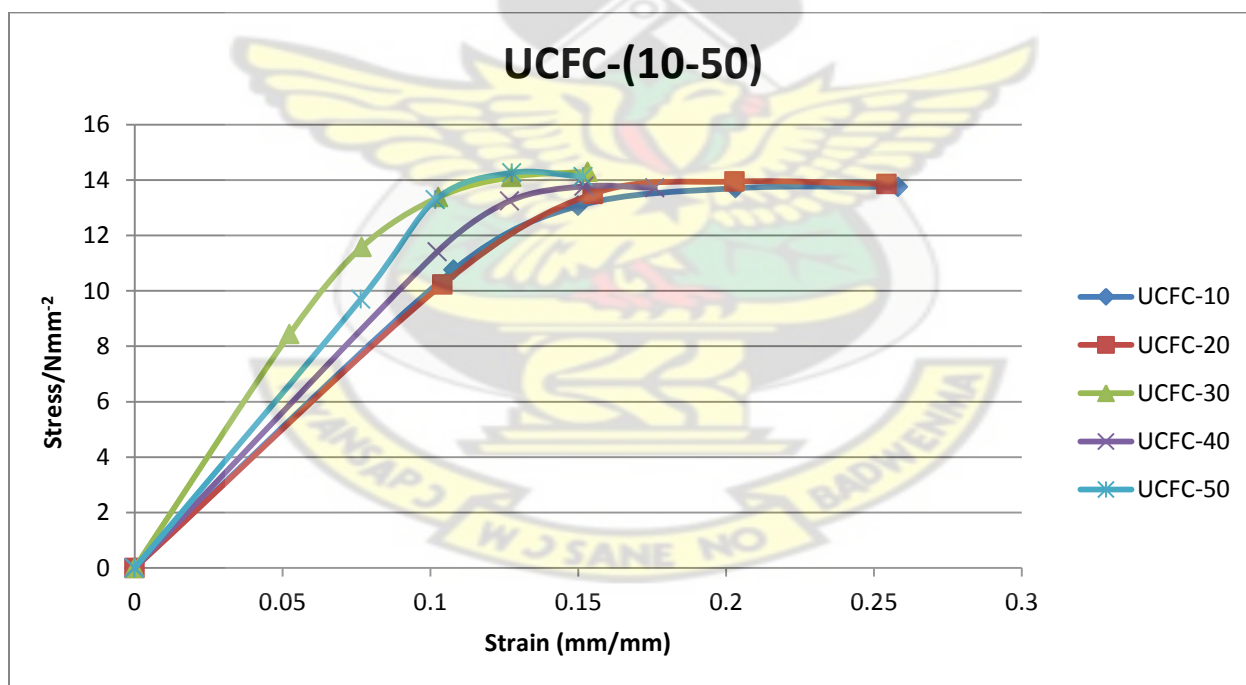
Figure 4.6 Tensile Stress versus Strain behaviour of LLDPE/CCF Biocomposites
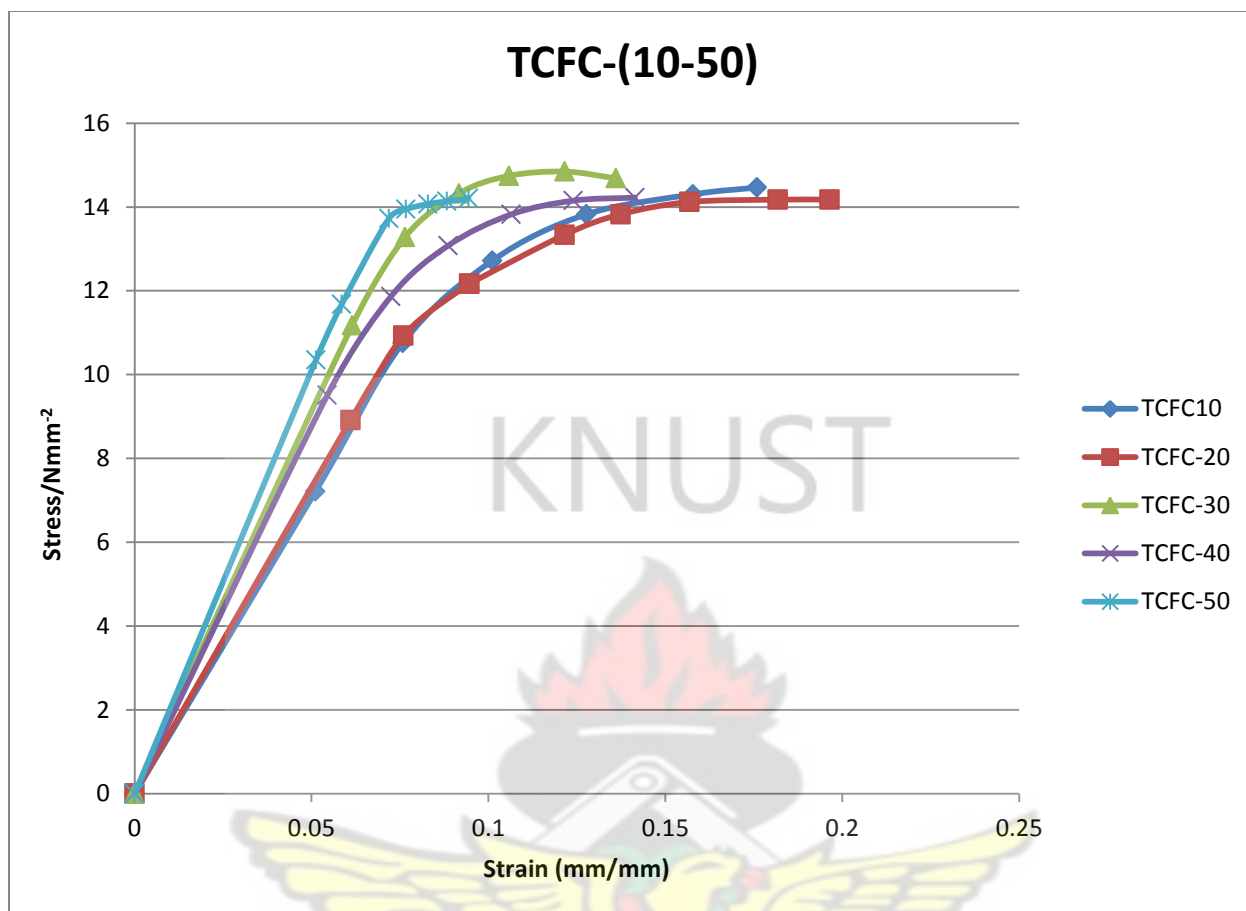
Figure 4.7 Tensile Stress versus Strain behaviour of LLDPE/CCF Biocomposites

In both UCFC and TCFC, the tensile stress is found to increase gradually with fibre loading and a maximum stress was attained at the 30% fibre loading (w/w). Also, the curve for the pure LLDPE exhibited a ductile character with extensive deformation as compared to the composites. However, with the addition of the CCF into the polymeric matrix (LLDPE), the curves show that the composites exhibit a bit of brittleness in character since they failed after a maximum point with a small amount of deformation.

The dependence of tensile properties of LLDPE/CCF biocomposites with standard deviations are provided in tables 4.2, 4.3 and 4.4 below. Also, the variation of tensile strength, young's modulus and % elongation at break with fibre loading is also shown below in figure 4.10, 4.11 and 4.12 respectively.

4.2.2 **Mechanical failure/Morphology of fractured surface of LLDPE/coconut fibre**

composites

A visual observation of the fractured surfaces of the bio-composites after tensile failure reveals poor adhesion between the CCF reinforcement and the LLDPE matrix. This is due to the presence of voids resulting from fibre pull out that were noticed from the fractured surface. A further inspection of the morphology of the fractured surface showed the fibrils as being poorly dispersed in the LLDPE matrix with very little crosslinking observed. A picture of the fractured surface of biocomposites is shown in Figure 4.8 below.

Figure 4.8: A fractured surface after tensile failure

The biocomposites failed in a ductile manner and this is evident in the way the part of failure shows beach marks signifying a degree of plastic deformation was experienced before fracture. The material therefore went through appreciable amount of plastic deformation before fracture. A failure mode mechanism for the bio-composites is schematically shown below in figure 4.9.
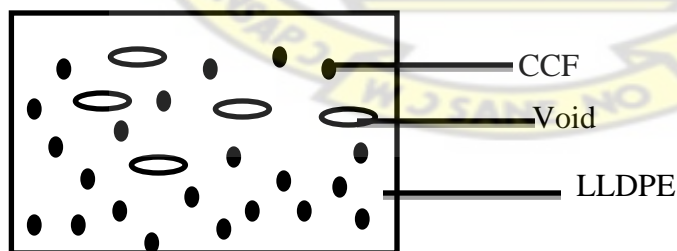
Figure 4. 9: A schematic diagram depicting possible adhesion between CCF and LLDPE

4.2.3 Effect of alkali treatment on tensile properties of LLDPE/coconut fibre composites

The NaOH treatment as exhibited in TCFC generally resulted in an increase in the tensile strength and tensile modulus; however, it slightly decreased the % elongation as compared to the UCFC at similar % fibre loading as shown in figure 4.10, 4.11 and 4.12 below.

In UCFC, the fibres were untreated, and the fibre bundles were still strongly bonded to each other with high stacking. The fibre surface is smooth as a result of oils and waxes present. Thus, mixing the fibres with LLDPE led to interfacial bonding with the surface without reaching the inside of the structure of the fibre bundles. The strength of the UCFC was therefore most likely a result of the natural cohesion of the untreated fibre bundles.

However, in TCFC the fibres were treated with NaOH, which cleaned them and provided a rougher surface. Lignin, pectin and other impurities within the coconut fibre are considered as hindrances for proper adhesion with the LLDPE during composite fabrication. The alkali treatment of the coconut fibre was therefore done in order to improve the adhesive character of the coconut fibre and consequently lead to an improved or better interfacial bonding between the LLDPE-CCF biocomposites fabricated.

The treatment, however, appears to have softened the inter-febrillar matrix, which negatively affected the stress transfer in the fibres (Thomas and Pothan, 2009). Thus, alkali treatment leads to fibrillation which causes the breaking down of the composite fibre bundle into smaller fibres. In other words, alkali treatment reduces fibre diameter and thereby increases the aspect ratio. Alkali treatment uncovers the fibrils and gives the fibres a rough surface topography (Mwaikambo and Ansell, 2002). Alkali treatment also changes the fine structure of the native cellulose I to cellulose II by a process known as alkalization (John and Anandjiwala, 2008). The reaction of NaOH with cellulose is shown in equation (1) below.

Fibre – OH + NaOH → Fibre – O–Na + H_2O + (Surface impurities)   (1)
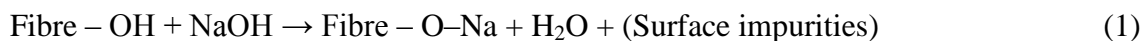
From this reaction, it implies the alkali sensitive hydroxyl (OH) groups present among the molecules are broken down, which then react with water molecules and move out from the fibre structure. The remaining reactive molecules form the fibre–cell–O–Na groups between the cellulose molecular chains (John and Anandjiwala, 2008). As a result of this mechanism, hydrophilic hydroxyl groups are reduced increasing the fibres moisture resistance.Alkali treatment also appears to take out a certain portion of hemicelluloses, lignin, pectin, wax and oil covering materials. Similar trends were reported in various studies on alkali modification of natural fibres (Li *et al*., 2007; Mwaikambo *et al*., 2007 and Ray *et al*., 2001).As a result, the fibre surface becomes clean. In other words, the fibre surface becomes more uniform due to the elimination of microvoids and thus the stress transfer capacity between the ultimate cells improves. In addition to this, it reduces fibre diameter and thereby increases the aspect ratio (length/diameter). This increases effective fibre surface area for good adhesion with the matrix (Joseph *et al*., 2003).

The treatment therefore removes a certain amount of hemicellulose, lignin, wax, oils, and other impurities, and thereby causing the surface to become rough. Similar observations were found in various studies (Liu and Dai, 2007,Li et al, 2007; Mwaikambo *et al*, 2007 and Ray *et al*, 2001) where they observed an increased in mechanical properties of composites after alkali treatment.This is evident in the improved tensile strength and modulus recorded for the alkali treated biocomposites (TCFC) as compared to the untreated ones (UCFC).

However, notwithstanding this, a possible deterioration in the fibre strength due to the alkali treatment, might have accounted for the generally low values in tensile strength of composites fabricated when compared to the pure LLDPE.

4.2.4 Effect of fibre loading on tensile strength of coconut fibre/LLDPE composites

The tensile strength of coconut fibre/LLDPE composites generally decreased with increasing of fibre loading in all the composites fabricated (i.e UCFC and TCFC). This reduction in strength properties with increasing the fibre loading could be largely attributed to factors such as the effective matrix cross-section reduction and stress concentration increase. Similar results have been observed by several researchers (Sobhy and Tammam, 2010;El-Shekeil *et al.,* 2012).

The tensile strength of the pure LLDPE (i.e. 0% fibre loading) was found to range from 15.565– 15.846 (mean = 15.690 ± 0.113, n = 5). Figure 4.7 below shows the comparison in tensile strength properties of UCFC and TCFC reinforced LLDPE composites. The overall tensile strength of all types of composites fabricated was lower when compared to pure LLDPE. This could be attributed to poor interfacial adhesion due to the hydrophilic CCF and the hydrophobic LLDPE. Similar observations were made by other researches (Kumar *et al.*,2010).

However, for both the UCFC and TCFC, maximum or optimum ultimate tensile strength was attained at 30% fibre loading (w/w).The range, mean and standard deviation of the ultimate tensile strength of UCFC and TCF Care given in table 4.2 below.

Table 4.2: Range, Mean and Standard Deviation of Ultimate Tensile Strength

Fibre loading (%)	UCFC			TCFC		
	Range	Mean	Standard Deviation	Range	Mean	Standard Deviation
0	15.655-15.846	15.690	0.113	15.655-15.846	15.690	0.113
10	13.730-13.827	13.755	0.040	14.435-14.530	14.465	0.037
20	13.820-13.895	13.857	0.028	14.135-14.225	14.175	0.039
30	14.265-14.348	14.298	0.037	14.795-14.885	14.845	0.044
40	13.630-13.850	13.716	0.082	14.182-14.255	14.224	0.036
50	13.695-14.650	14.112	0.301	14.185-14.225	14.205	0.018

From the UCFC results, it was found that the tensile strength of composites increased gradually, up to a maximum at 30% of fibre loading (w/w) and then dropped back till the 50% fibre loading(w/w). This observation in trend of ultimate tensile strength of UCFC is depicted in Figure 4.10 below. For instance, at 10% fibre loading (w/w), its tensile strength ranges from 13.730 – 13.827 (mean =13.755$\pm$ 0.040, n= 5) and gradually increased up to 14.265-14.348 (mean = 14.298$\pm$0.037, n=5) for the 30% fibre loading (w/w).

On the other hand, the ultimate tensile strength of TCFC decreases gradually with increasing fibre loading also attaining a maximum tensile strength at 30% fibre loading(w/w). This is also shown in Figure 4.10 below. Here, at 10% fibre loading (w/w), ultimate tensile strength ranges from 14.435 – 14.530 (mean = 14.465$\pm$0.037, n= 5) reaching a maximum tensile strength once

again at 30% fibre loading (w/w) which ranges from 14,795-14.885 (mean = 14.845±0.045, n = 5).

Generally the tensile strength of alkali treated composites (TCFC) is higher compared to composites without alkali treatment (UCFC) at similar coconut fibre loading, although both are lower than the pure LLDPE.This indicates that the chemical modification of coconut fibres with the alkali (NaOH) has resulted in an improvement of interfacial bonding and dispersion between the CCF and LLDPE. This is in agreement with most researches which observed increase in tensile strength with surface modification of fibres after alkali treatment (Zaman *et al*., 2011; Kumar *et al*., 2010). Also a significant difference was reported in the tensile strength between alkali-treated and –untreated coir fibre compositesin a study on tensile behaviour of coir fibre and related composites after NaOH treatment (Gu, 2009). This increase in ultimate tensile strength of composites with alkali treatment implies that most of the fats, lignin and pectin covering the fibre surface have been removed and thereby creating a rough surface topography as stated earlier.

This led to a slight improvement in the adhesive character of the coconut fibres as compared to the untreated coconut fibres and hence the slight increase in tensile strength of the TCFC over the UCFC reported in this study. Similar observations were made in various studies by other researchers (Li *et al*., 2007; Mwaikambo *et al*., 2007 and Ray *et al*., 2001).

The result of the FTIR also shows that fatty acid and waxy material on the surface of the coconut fibre were disposed of by the alkali treatment. Therefore, the alkali treatment improves significantly the compatibility between the coconut fibre and LLDPE, and this may be largely accountable for the slight rise in the mechanical performance of the TCFC over the UCFC

composites. This is, however, in contrast with some researches that reported a decline in mechanical performance of composites after alkali treatment was carried out (Tan *et al*., 2010). Also in both cases (i.e UCFC and TCFC), at higher loading of fibres, it was observed that the tensile strength further slightly decreased. This could be due to the probability of inter-fibre contact and thus yielding some extent of aggregation in the composites. Thus, the decrease in the tensile strength as the percentage of coconut fibre loading is increased could be due to the fact that the coconut fibres probably tend to cling together in bundles and thereby resisting dispersion of the individual fibres as fibre content increases (Sobhy and Tammam, 2010).However, the relatively higher tensile strength exhibited by the composites at lower fibre loading of coconut fibre may be attributed to greater interfacial bonding of coconut fibre with LLDPE matrix. Similar observations were reported in literature(Kumar *et al*., 2010; Enriquez *et al*., 2010).
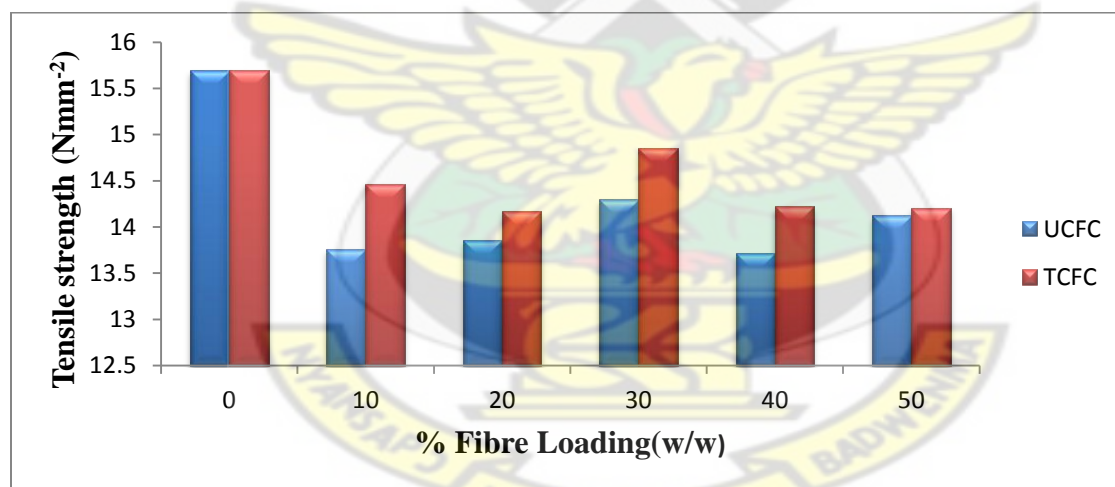
Figure 4.10: A graph showing the effect of fibre loading on tensile strength of composites

Furthermore, the addition of the coconut fibres to the LLDPE did not contribute greatly to an increase in tensile strength values of the composites (both TCFC and UCFC) as compared to the pure LLDPE due to lack of efficient adhesion between the CCF and LLDPE. An observation of

the fractured surfaces of the composites reveals this lack of adhesion with the presence of voids resulting from fibre pull- outs. The potential surface morphology looks like fibrils dispersed in the LLDPE matrix. Evidence of poor interaction between CCF and LLDPE was generally observed, with the presence of the fibre pull outs in both the UCFC and TCFC, confirming that the chemical treatment was not totally effective in improving the adhesion between the reinforcement and the matrix. This is schematically shown in figure 4.9.

Another factor that may be accountable for the decline in tensile strength property of the composites is probablya possible deterioration of the coconut fibres due to the duration of treatment of the fibresas well as the retention time during the extrusion process. This could have probably resulted in fibre degradation.

Finally, statistical analysis was also carried out on the tensile strength of both the UCFC and TCFC. Significant difference is noticed in the tensile strength between the alkali treated(TCFC) and –untreated(UCFC) coconut fibre composites($P < 0.01$).

4.2.5 Effect of fibre loading on Young's Modulus of coconut fibre/LLDPE composites

The young's modulus of coconut fibre / LLDPE composites increased with increasing of fibre loading for all composites fabricated. This trend in property is expected since the addition of fibre increases the relative stiffness of the composites. This in turn, however, led to a decrease in the elongation at break of composites. The Young's modulus is a measure of the relative stiffness of composites (Shash V, 1983). The range, mean and standard deviation of the young's modulus of UCFC and TCFC are given in table 4.3 below.

Table 4.3: Range, Mean and Standard Deviation of Young's modulus

Fibre loading (%)	UCFC			TCFC		
	Range	Mean	Standard Deviation	Range	Mean	Standard Deviation
0	77.875-78.015	77.929	0.053	77.875-78.015	77.929	0.053
10	99.680-99.720	99.695	0.017	140.985-141.140	141.076	0.067
20	98.245-98.355	98.291	0.054	145.95-146.205	146.099	0.094
30	161.002-161.100	161.027	0.041	181.695-181.766	181.740	0.027
40	111.478-111.495	111.485	0.008	174.524-174.615	174.568	0.043
50	126.815-126.840	126.825	0.011	199.405-200.018	199.573	0.253

The Young's modulus of the treated LLDPE/coconut fibre composites with NaOH (i.e. TCFC-24 and TCFC-48) isslightly higher when compared to the untreated LLDPE/coconut fibre composites (UCFC) at similar percent fibre loading. This can be attributed to the fact that, the alkali treatment had resulted in an increase in mechanical properties of the TCFC bio-composites by improving adhesion across the interface to a certain degree. This has also led to the reduction or minimization of inadequate dispersion associated with fibre buckling. A similar trend in behaviour of modulus has been reported in LDPE/PKSbio-composites study (Romisuhani *et al*., 2010).

Also, statistical analysis performed on the results shows significant difference in young's modulus between the alkali –treated (TCFC) and –untreated (UCFC) bio-composites.

Figure 4.11 shows the effect of fibre loading on Young's modulus of untreated and treated coconut/LLDPE composites.
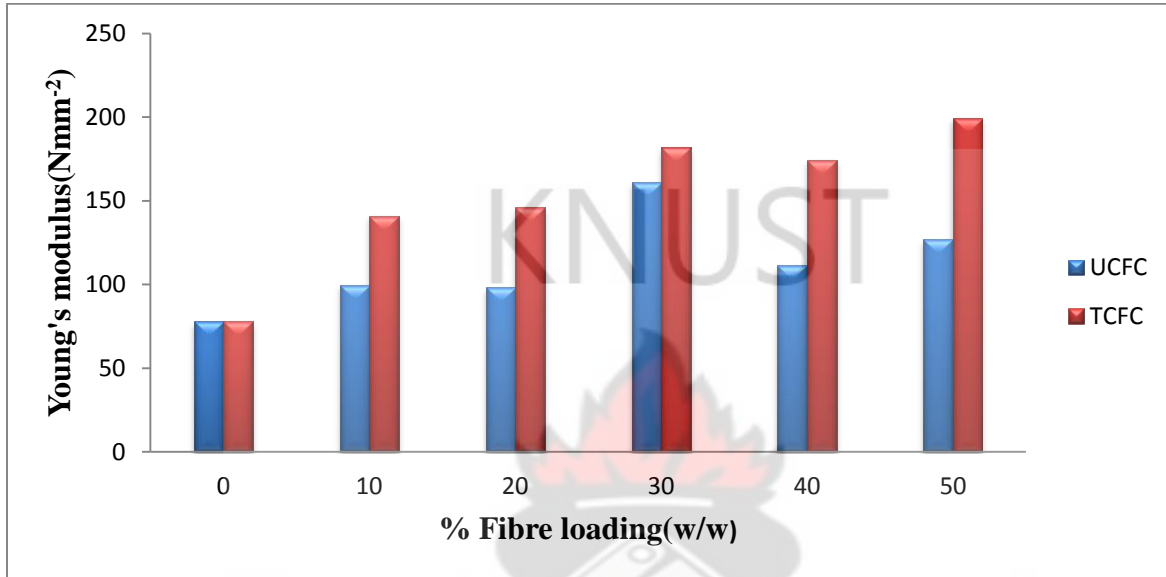
Figure 4.11: A graph showing the effect of fibre loading on Young Modulus of composites

4.2.6 Effect of fibre loading on elongation at break of coconut fibre/LLDPE composites

The increase in fibre loading leads to a reduction in the elongation at break for all LLDPE/coconut fibre composites fabricated. The elongation at break of the composites therefore decreases steadily with the increasing of fibre loading in all cases. The decrease in elongation at break in filled polymer composites is largely due to the fact that the deformation of the fibre is generally much less than that of the polymer matrix. Therefore, the fibre forces the matrix to deform more than the overall deformation of the composite (Qiu *et al*., 2003).

Elongation at break of the composites also decreased significantly compared to the pure LLDPE. The ductility of the composites thus decreased with increment of the fibre content. This decrease can be attributed to poor interfacial adhesion. Similar observations were made by Enriquez *et al*.,

2010. The range, mean and standard deviation of the elongation at break of UCFC and TCFC are given in table 4.4 below.

Table 4.4 Range, Mean and Standard deviation of the elongation at break

Fibre loading (%)	UCFC			TCFC		
	Range	Mean	Standard Deviation	Range	Mean	Standard Deviation
10	25.78-25.86	25.816	0.036	17.50-17.65	17.586	0.063
20	25.39-25.50	25.434	0.045	19.58-19.68	19.642	0.038
30	15.25-15.40	15.326	0.061	13.56-13.64	13.600	0.032
40	17.54-17.64	17.588	0.041	13.98-14.22	14.140	0.097
50	15.14-15.20	15.166	0.024	9.26-9.58	9.444	0.119

Also, the significant decrease in % elongation at break as the CCF was incorporated into the LLDPE in both cases was reported. This may be attributable to the increase in the discontinuity of the matrix with subsequent increase in disperse phase of the CCF. The higher content of CCF, thus reduced the compatibility between the CCF and LLDPE due to possible agglomeration of fibres.

The results also indicate that at similar fibre loading, elongation at break of untreated LLDPE/coconut fibre composites (i.e UCFC) is higher than treated LLDPE/coconut fibre composites (TCFC). The lower% elongation at break for the alkali treated coconut fibre composites indicates that the removal of the lignin and pectin did not lead to an improvement in the elasticity of the coconut fibre (Gu, 2009). Instead, a more brittle character was introduced into the biocomposites after the alkali treatment. This accounted for the decline in % elongation

at break of TCFC as compared to the UCFC. Therefore, the lower % elongation at break of TCFC than the UCFC at similar fibre loadings indicates that the composites with better interfacial adhesion resulted in a decrease in % elongation at break. Similar observations were made by Romisuhani *et al*., (2010).

Once again, statistical analysis was performed on the results obtained. Significant difference was noticed for the % elongation at break values between the composites fabricated by using the alkali –treated (TCFC) and –untreated (UCFC) bio-composites (P < 0.01)

Figure 4.12 shows the effect of fibre loading on elongation at break of untreated and treated LLDPE/coir composites.
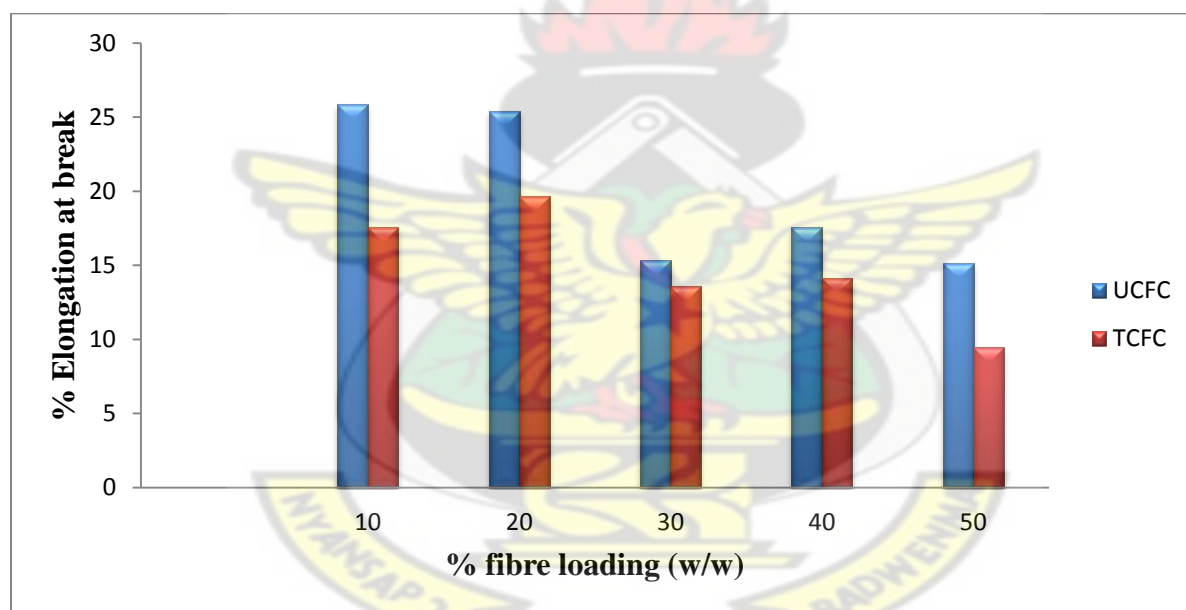
Figure 4.12: A graph showing the effect of fibre loading on % elongation at break of composites

4.3 Swelling index studies

The swelling measurement was performed on the LLDPE/coconut fibre composites fabricated at different blend ratios. Toluene and cyclohexane solvents were used for the analysis. The choice

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of these solvents solely depended on the difference between them. Whilst toluene is an aromatic solvent; cyclohexane is aliphatic and therefore exhibit different abilities to dissolve or swell the fabricated composites. It was, however, observed that the uptake of the toluene is slightly higher than the cyclohexane. Similar observations were made by Khalil *et al*., (2012). Thus, the aromatic reaction between the toluene and the composite is accountable for the higher solvent absorption.

The swelling index generally increases with increasing amount of fibre loading in the composites. The mean values of the swelling index and crosslinking density are provided in table 4.5 below where W_d- dry weight, W_s- swollen weight, and S.I –Swelling index.

Table 4.5: Swelling index and crosslinking density parameters of CCF/LLDPE bio-composites

composite	TOLUENE				CYCLOHEXANE			
	W_d	W_s	S.I	1/S.I	W_d	W_s	S.I	1/S.I
LLDPE	0.46	0.49	1.065	0.939	0.47	0.49	1.043	0.959
UCFC10	0.11	0.12	1.091	0.917	0.12	0.13	1.083	0.923
UCFC20	0.10	0.11	1.100	0.909	0.10	0.11	1.100	0.909
UCFC30	0.12	0.14	1.167	0.857	0.10	0.11	1.100	0.909
UCFC40	0.09	0.11	1.222	0.818	0.11	0.12	1.091	0.917
UCFC50	0.1	0.13	1.300	0.769	0.12	0.14	1.167	0.857
TCFC10	0.11	0.12	1.091	0.917	0.14	0.15	1.071	0.934
TCFC20	0.10	0.11	1.100	0.909	0.12	0.13	1.083	0.923
TCFC30	0.13	0.15	1.154	0.867	0.11	0.12	1.091	0.917
TCFC40	0.12	0.14	1.167	0.857	0.10	0.11	1.100	0.909
TCFC50	0.11	0.13	1.182	0.846	0.12	0.14	1.167	0.857

For instance, swelling index increases from 1.065 (i.e. pure LLDPE) to 1.300 and 1.182 at 50% fibre loading for the UCFC and TCFC respectively with toluene as a solvent. However, with the cyclohexane as a solvent, swelling index also increased from 1.043 for pure LLDPE to 1.67 for both composites at the 50% fibre loading. This means that there is less cross linking at higher percent fibre loadings leading to an increased in solvent absorption.

Also, the alkali treated (TCFC) composites recorded slightly lower swelling index as compared to the untreated(UCFC) biocomposites at similar % fibre loading. For instance, at 30% fibre loading, swelling index of the treated coconut fibre/LLDPE composites (TCFC) is 1.083 which is lower than the untreated composites UCFC which recorded 1.167 as shown in table 4.5 above. The relatively lower swelling index reported by the alkali treated composites (TCFC) could be attributable to the fact that the chemical modification of the coconut fibre surface employed was effective to some extent and hence might have minimized the absorption of moisture by these composites.

However, the general increase in swelling index of the composites with percent increase in fibre loading is due to insufficient LLDPE-CCF adhesion upon fibre loading. This is, however, in contrast with Azizan *et al*., (2002) who observed that swelling index decreases with filler loading due to polymer-filler interaction in natural rubber/ LLDPE blends. This behaviour reported is due to differences in polymer-fibre interaction. The greater the interaction, the lesser the absorption of solvent and vice versa.

On the other hand, crosslinking density generally decreases with increasing percent fibre loading. This indicates that there is less polymer-fibre interaction due to possible fibre agglomeration. When this happens, the absorption of the solvent increases, resulting in more and more composites swelling (Leblanc, 2002; Dahlan *et al*., 2002a).

The increase in swelling index and decrease in crosslinking density are also attributable to the slightly decline in tensile stregth of the UCFC as compared to the TCFC. The effect of fibre loading on the swelling index and crosslinking density of composites are shown below in figures 4.13, 4.14, 4.15 and 4.16.
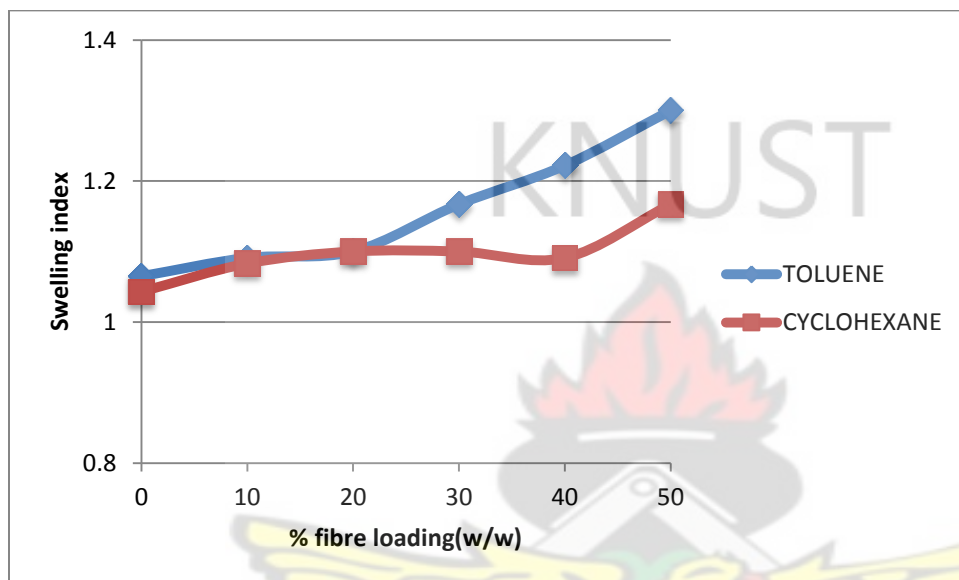

Figure 4.13: Graphs showing the effect of fibre loading on swelling index of UCFC
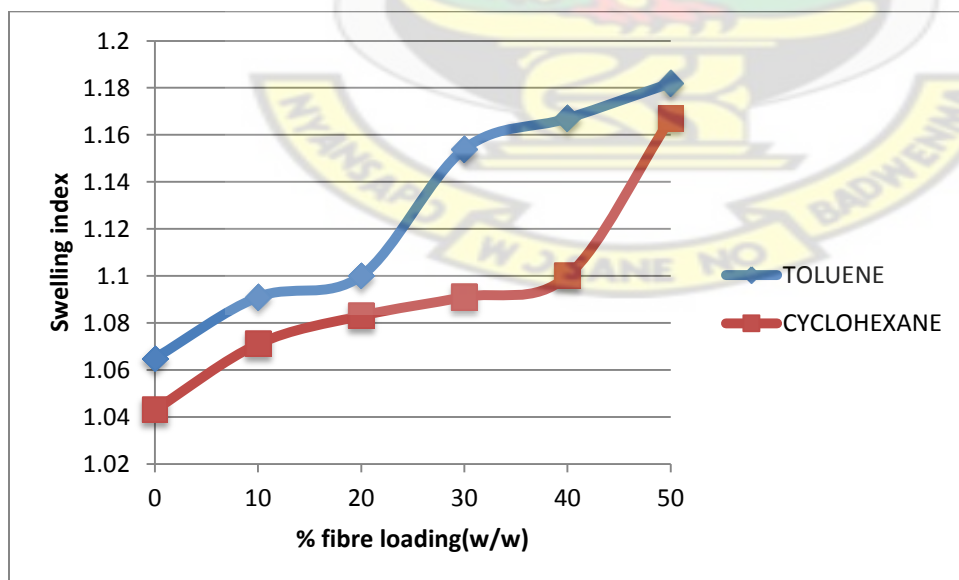
Figure 4.14: Graphs showing the effect of fibre loading on swelling index of TCFC
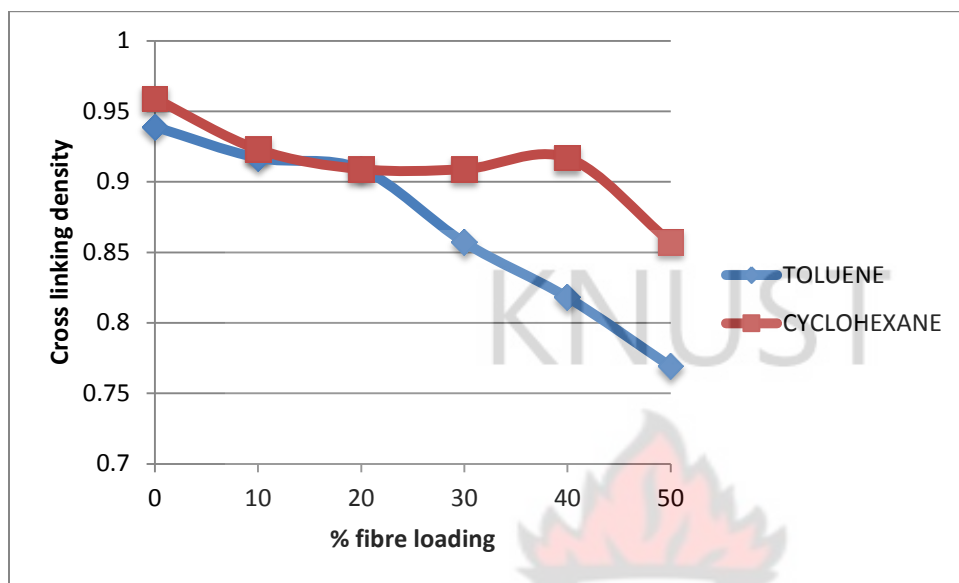

Figure 4.15: Graphs showing the effect of fibre loading on crosslinking density of UCFC
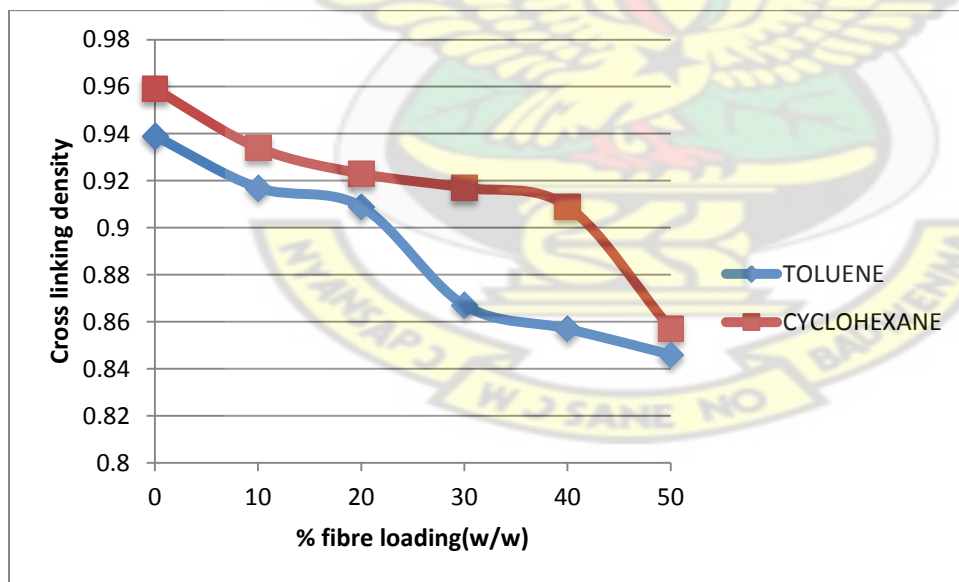
Figure 4.16: Graphs showing the effect of fibre loading on crosslinking density of TCFC

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The scientific world is facing a serious challenge of developing new and advanced technologies and methods to treat solid wastes, particularly plastic waste. The processes to decompose these wastes are actually not cost-effective and do subsequently produce harmful chemicals. Owing to this, reinforcing polymers with natural fibres is the way to go. Natural fibres are low cost, recyclable, low density and eco-friendly materials.

In this study, the effect of alkali treatment on coconut fibre and fibre loading on mechanical properties of LLDPE/coconut fibre bio-composites were evaluated. The NaOH treatment as exhibited in TCFC generally resulted in an increase in the tensile strength and tensile modulus; but slightly decreased the % elongation as compared to the UCFC at similar % fibre loading. The alkali treatment of the coconut fibre thus improved or enhanced the adhesive character of the coconut fibre and consequently led to an improved or better interfacial bonding between the LLDPE-CCF biocomposites fabricated.

In both UCFC and TCFC, the tensile strength is found to increase gradually with fibre loading and a maximum stress was attained at the 30% fibre loading (w/w). From the stress-strain curves, the pure LLDPE exhibited a ductile character with extensive deformation. However, with the addition of the CCF into the polymeric matrix (LLDPE), the curves showed that the composites exhibited a bit of brittleness in character by failing with a small amount of deformation.

Also, it was found that the tensile strength and elongation at break of the composites (UCFC and TCFC) generally decreased with fibre loading as compared to the pure LLDPE. However, maximum tensile strength was achieved with the 30% fibre loading for the UCFC and TCFC.

The results also indicated that, at similar fibre loading, elongation at break of untreated LLDPE/coconut fibre composites (UCFC) is higher than treated LLDPE/coconut fibre composites (TCFC). This implies the composites with alkali treatment have better interfacial adhesion that decreases the elongation at break. The young's modulus of coconut fibre/LLDPE composites, however, increased with increasing fibre loading in both cases (i.e UCFC and TCFC).

However, notwithstanding this, the addition of the coconut fibres to the LLDPE did not contribute greatly to an increase in tensile strength values of the composites (both TCFC and UCFC) as compared to the pure LLDPE due to insufficient adhesion between the CCF and LLDPE. An observation of the fractured surfaces of the composites reveals this lack of adhesion with the presence of voids resulting from fibre pull- outs. Additionally, the decline in tensile strength property of the composites is probably a possible deterioration of the coconut fibres due to the duration of treatment of the fibres as well as the retention time during the extrusion process.

The swelling index generally increases with increasing amount of fibre loading in the composites. This increase in swelling index of the composites with percent increase in fibre loading is due to insufficient interfacial bonding upon fibre loading. Consequently, cross-link density decreased with increasing % fibre loading.

Based on the above deductions, it could be concluded that coconut fibre has a very promising future as reinforcement in natural fibre composites and could offer us with an alternative in plastic waste management when used in packaging materials.

Furthermore, although there was no opportunity to study other mechanical properties like flexural and compressive as well as impact and hardness, the modulus as obtained from the

tensile test was very high as compared to the pure LLDPE. This suggests the fabricated bio-composites could be good for various packaging purposes.

5.2 Recommendation

Natural fibre-reinforced composites should be developed and characterized so as to produce cost-competitive bio-composites for industrial applications. A thorough study is needed to evaluate the optimum levels and to make general conclusions to commercialize the use of bio-renewable fibres like coconut fibres. In future works, combination of modern testing techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM) and a mixture of fibre surface modification techniques could lead to a better understanding of desirable properties. Also, to understand and measure properly the role of the reinforcement (coconut fibre), processing conditions and surface treatments need to be further optimized to achieve improved properties of fibre-reinforced composites. Finally, an attempt should be made to injection mould a large sample of the bio-composites from this study on an industrial scale to determine its potential commercial use based on current known properties.

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APPENDIX

Stress strain curves of individual biocomposites

UCFC-10

UCFC-20

UCFC-30

UCFC-40

UCFC-50

TCFC-10

TCFC-20

TCFC-30

TCFC-40

TCFC-50