CHEMICAL TREATMENTS OF BAGASSE NATURAL FIBRE AND APPLICATION FOR USE AS FILLER IN UNSATURATED POLYESTER COMPOSITE

BY

Josephine Taiye OMOLE, B.SC. TEXTILE SCIENCE

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JANUARY, 2016

DECLARATION

I declare that the work in this dissertation entitled "CHEMICAL TREATMENTS OF BAGASSE NATURAL FIBRE AND APPLICATION FOR USE AS FILLER IN UNSATURATED POLYESTER COMPOSITE" has been carried out by me in the Department of Textile Science and Technology. All information contained in the literature are duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

OMOLE, Josephine Taiye

_____	_____	_____
Name of student	Signature	Date

CERTIFICATION

This dissertation entitled "CHEMICAL TREATMENTS AND APPLICATION OF BAGASSE NATURAL FIBRE FOR USE AS FILLER IN UNSATURATED POLYESTER COMPOSITE" by Josephine Taiye, OMOLE meets the regulation governing the award of the degree of masters of science in textile science and technology of Ahmadu Bello University, and is approved for its contribution to knowledge.

Dr. B.M. Dauda

_____	_____	_____
Chairman, Supervisory Committee	Signature	Date

Dr. A. S. Lawal

_____	_____	_____
Member, Supervisory Committee	Signature	Date

Dr. A. Danladi

_____	_____	_____
Head of Department	Signature	Date

Prof. K. Bala

_____	_____	_____
Dean, School of Postgraduate Studies	Signature	Date

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ABSTRACT

This work has investigated the effect of various chemical treatments on the properties of bagasse fibre for use as filler in unsaturated polyester composite. Bagasse is a natural fibre obtained as a by-product of the sugarcane milling process. As with other natural fibres it has the setback of being hydrophilic; this research tried to explore the use of chemical modification of the fibre surface as a way of remedy. Four different chemicals, namely, Sodium hydroxide, Acetic acid, Acrylic acid and Potassium permanganate were used in carrying out the treatments. Mechanical properties such as tensile strength and modulus, flexural strength and modulus were carried out. The treatments were carried out for 3hours at 70^{o}C except for Sodium hydroxide treatment that was done at room temperature using 2wt% concentration. The Fourier Transform Infrared Spectroscopy (FTIR) analysis of the fibre revealed that the Potassium permanganate treatment had more effect as most of the OH group visible at a peak of around 3400cm^{-1} were reduced. Also the peaks showing lignin, pectin, and hemicelluose at peaks of 1250-1260cm^{-1}, 1600-1650cm^{-1}, and 1720-1750cm^{-1} respectively were also removed which were all present in the untreated fibre. The Scanning Electron Microscope (SEM) studies of Potassium permanganate treated fibre composite revealed the roughness of the fibre increased as a result of the various chemicals which also showed that Potassium permanganate treated fibre became rougher as compared to the untreated fibre and also had more micropores. The tensile strength of Potassium permanganate treated fibre composite was found to be 77.85MPa as compared to 68.50MPa of the untreated fibre composite. The water absorption level was found to be lower at 2.2% maximum than the untreated fibre composite except for the unsaturated polyester composite which is as expected and was at an average of 5%. The hardness and impact strength were also improved for all chemically treated samples. However, in the case of flexural strength not much effect was seen and in fact the flexural modulus of KMnO4 treated fibre composite dropped to

21.1MPa and NaOH treated fibre composite was 25.60MPa, Acetic acid (CH_3COOH) treated fibre composite 20.91MPa and $CH_2=CHCO_2H$ treated fibre composite 15.90MPa, all of which were lower than the untreated fibre composite. SEM studies on the composites indicated that higher interaction was found in $KMnO_4$ treated fibre composite although little debonding was observed.

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LIST OF ABREVIATIONS

UPC - Unsaturated polyester composite

UNTFC – Untreated fibre composite

SHTFC – Sodium hydroxide treated fibre composite

AATFC – Acetic acid treated fibre composite

ACTFC- Acrylic acid treated fibre composite

PPTFC – Potassium permanganate treated fibre composite

MEKP – American society for testing materials

CHAPTER ONE

1.0 INTRODUCTION

The use of natural fiber composite is wide and immeasurable in terms of quality, ease of use and good mechanical properties (Nishito *et al*., 2003). These materials have been widely used in the systems for comfortable driving and to reduce the energy consumption. It is used in automotive, construction, furniture and building industries and also packaging (Satayanarayana *et al*., 2009; and Inuwa 2013). Natural fiber composites have many advantages over synthetic ones as result of their low cost, recyclability, biodegradability, environmental friendliness, low density, high specific strength and stiffness; excellent absorbance properties and high impact energy absorption (Lu Na *et al.*, 2012; Mohanty *et al*., 2003; Munawar *et al*., 2007; and Mwaikambo and Ansell 2002). Environmental issues have resulted in considerable interest in the development of new composite materials based on biodegradable resources (Maldas *et al*., 2007); the renewed interest of natural fibers was a result of non-renewable problems coupled with the disposal of the synthetic petroleum – based products (Sain *et al*., 2005). Short fibres are used in rubber compounding to considerably improve processing advantages, improvement in certain mechanical properties and for economic consideration (Gonzalez and Ansell 2009; and Gu 2007). The reinforcement of biofibers rubber composites has been well documented by Mark (2011). Though natural fibers have been largely appreciated and appraised, they have their limitations. Their hydrophilic property poses a serious challenge in their effective use and so is not well compatible with polymer matrix which is hydrophobic. To overcome this, the fibre surface has to be modified (Thamae *et al*., 2007; Dittenber and Gangarao 2012; and Bledzki *et al*., 1996). The modification could be physical or chemical and has various types, this treatment

process removes non cellulosic substance, e.g. impurities, waxes, pectin, hemicelluloses, lignins which cover the cellulose fibrils and bind these fibrils together (Wu *et al.*, 2000). These contribute to ineffective fibre – matrix interaction and poor surface wetting. Removal of these substances also gives rise to a rougher fibre surface resulting in an increase in surface contact of the fibre and the matrix. This causes an improvement of mechanical interlocking between the polymer and the fibre, leading to enhanced mechanical properties (Sulawan *et al.,* 2012).

The vast number of natural fibres used for making composite includes wood, Jute, Bamboo, Sisal, Hemp, Flax, Oil palm, Kenaf, and of recent Bagasse fiber. These fibers were reinforced with various matrixes such as polyester, epoxy, vinyl ester, thermosets, LDPE, phenol-formaldehyde e.t.c. (Xue *et al.*, 2006; Maya *et al.*, 2007; Sain *et al.*, 2005; Nural and Ishak 2012; Xie *et al.*, 2010; Alvarez and Vazquez 2006; Sever 2010; Seki 2009; Saw *et al.*, 2011 and Srubar *et al.*, 2012).

1.1 Composites

Composites are materials formed in form of a blend. That is, they contain at least two different materials with varying traits and properties. However, in the blend (composite), their properties are improved. The intent of a composite is to obtain desirable traits, features and characteristics that cannot be obtained when these materials are used individually. The individual materials in the composite still retain their distinct properties. A composite comprises of the reinforcement and the matrix; the reinforcement (that imparts rigidity) is held in place by the matrix which is usually the weaker component (Hull and Clyne 1996).

The majority of composites are fibre-reinforced plastics, in which the fibres are embedded in a

matrix. Essentially, stiff composite parts consist of a textile material that is “frozen” into the shape of a polymer matrix that also protects the fibres against degradation due to external factors such as moisture, chemicals, and UV-radiation.

The fibres in the matrix may consist of individual fibres or they may have been cross-linked in a specific textile structure, such as a yarn, a woven, knitted fabric or a nonwoven structure.

The fibres in the matrix may be oriented in one or more directions. The fibre orientation, length, stiffness and fiber volume fraction will determine to a large extent the mechanical properties of the final composite.

1.1.1. Classes of composite

Broadly, composites may be classified into three groups on the basis of matrix. They are:

Polymer Matrix Composites (PMC)

Ceramic Matrix Composites (CMC)

Metal Matrix Composite (MMC)

Ceramics Matrix Composite (CMC):

These may be of low density (although some are very dense). They have great thermal stability and are resistant to most forms of attack (abrasion, wear, corrosion). Although intrinsically very rigid and strong because of their chemical bonding, they are all brittle and can be formed and shaped only with difficulty. These composites are therefore of good strength and stiffness.

Metal Matrix Composites (MMC):

They are mostly of medium to high density - only magnesium, aluminum and beryllium can compete with plastics in this respect. Many have good thermal stability and may be made

corrosion resistant by alloying. They have useful mechanical properties and high toughness, and they are moderately easy to shape and join. It is largely a consequence of their ductility and resistance to cracking that metals, as a class, became the preferred engineering materials. On the basis of even so superficial a comparison it can be seen that each class has certain intrinsic advantages and weaknesses, although metals pose fewer problems for the designer than either plastics or ceramics.

Polymer Matrix Composites (PMC):

These are composites in which their matrices are polymers and are the most common. They are of low density. They have good short-term chemical resistance but they lack thermal stability and have only moderate resistance to environmental degradation (especially that caused by the photo-chemical effects of sunlight). They have poor mechanical properties, but are easily fabricated and joined. More so, their manufacturing equipments are simpler and easier to handle and operate. This is further classified into;

Fibre – Reinforced Polymer (FRP)

Particulate - Reinforced Polymer (PRP)

Fibre – Reinforced Polymer (FRP): Common fibre - reinforced composites are composed of a fibre and a matrix. Fibres are used as reinforcements; they serve as the main source of strength while the matrix glues all the fibres together in shape and transfers stresses between the reinforcing fibres. The fibres carry the loads along their longitudinal directions. Sometimes, filler might be added to aid the manufacturing process, imparting special properties to the composites, and / or reduce the cost.

Common fibre reinforcing agents include asbestos, carbon/graphite fibres, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminum oxide, glass fibres, polyamide, natural fibres

etc. similarly, common matrix material includes epoxy, phenolic, unsaturated polyester, polyurethane, polyetheretherketone (PEEK), vinyl esters, etc. epoxy is widely used and has good adhesion properties. However its cost has greatly limited its use.

Particulate - Reinforced Polymer (PRP): Particles used for reinforcement include ceramics and glasses such as small mineral particles, metal particles such as aluminum and amorphous materials, including polymers and carbon black. Particles are used to increase the modules of the matrix and to decrease the ductility of the matrix. Reinforcements and matrices can be common, inexpensive materials and that are easily processed. Some of the useful properties of ceramics and glasses include high melting point temperature, low density, high strength, stiffness, wear resistance, and corrosion resistance.

Many ceramics are good electrical and thermal insulators. Some ceramics have special properties; some ceramics are magnetic materials; some are piezoelectric materials; and a few special ceramics are even superconductors at very low temperatures. However, ceramics and glasses have one major setback: they are brittle. A good example of a particle reinforced composite is the thread of an automobile tire which has carbon black particles in a matrix of rubber polymer (Owen 2014).

1.1.2 Components of a typical composite

The major components are:

Matrix; and

Reinforcement

The Matrix**:** Matrix is continuous, ductile, more flexible and plastic substance. it distributes the load among reinforcing units.

1.1.2.1 Functions of the matrix

The matrix binds the fibres together, holding them aligned in the important stressed directions. Loads applied to the composite are then transferred into the fibers, the principal load-bearing component through the matrix; enabling the composite to withstand compression, flexural and shear forces as well as tensile loads. The ability of composites reinforced with short fibres to support loads of any kind is dependent on the presence of the matrix as the load-transfer medium, and the efficiency of this load transfer is directly related to the quality of the fibre/matrix bond.

The matrix must also isolate the fibers from each other so that they can act as separate entities. Many reinforcing fibers are brittle solids with highly variable strengths. When such materials are used in the form of fine fibers, not only are the fibers stronger than the monolithic form of the same solid, but there is the additional benefit that the fiber aggregate does not fail catastrophically. Moreover, fibre bundle strength is less variable than that of a monolithic rod of equivalent load-bearing the ability. But these advantages of the fibre aggregate can only be realized if the matrix separates the fibres from each other so that cracks are unable to pass unimpeded through sequences of fibres in contact, which would result in completely brittle composites.

The matrix should protect the reinforcing filaments from mechanical damage (eg. abrasion) and from environmental attack. Since many of the resins which are used as matrices for glass fibres permit diffusion of water, this function is often not fulfilled in many GRP materials and the environmental damage that results is aggravated by stress. In cement the alkaline nature of

the matrix itself is damaging to ordinary glass fibres and alkali-resistant glasses containing zirconium have been developed in an effort to counter this.

For composites like MMCs or CMCs operating at elevated temperature, the matrix would need to protect the fibres from oxidative attack.

A ductile matrix will provide a means of slowing down or stopping cracks that might have originated at broken fibres: conversely, a brittle matrix may depend upon the fibres to act as matrix crack stoppers.

Through the quality of its 'grip' on the fibres (the interfacial bond strength), the matrix can also be an important means of increasing the toughness of the composite.

By comparison with the common reinforcing filaments most matrix materials are weak and flexible and their strengths and moduli are often neglected in calculating composite properties. But metals are structural materials in their own right and in MMCs their inherent shear stiffness and compression rigidity are important in determining the behavior of the composite in shear and compression. The potential for reinforcing any given material will depend to some extent on its ability to carry out some or all of these matrix functions, but there are often other considerations.

1.1.2.2 Reinforcement**:** Discontinuous, hard and firm component

Styles of reinforcements

Many reinforcing fibres are marketed as wide, semi-continuous sheets of 'prepreg' consisting of single layers of fibre tows impregnated with the required matrix resin and flattened between paper carrier sheets. These are then stacked and allowed to cure with time, the orientations of each 'ply' being arranged in accordance with design requirements, and hot pressed to consolidate

the laminate. This process is able to cope with curved surfaces, provided the degree of curvature is not too great, but there may be a possibility of local wrinkling of the fibres when prepregs are pressed into doubly curved shapes.

One means of overcoming this problem is to use the reinforcement in the form of a woven cloth. Many of the fine filamentary reinforcing fibers like glass, carbon and Silicon can be readily woven into many kinds of cloths and braids, the fibres being effectively placed by the weaving process in the directions required by the designer of the final composite structure.

In simple designs, this may call for nothing more elaborate than an ordinary plain weave or satin weave, with fibres running in a variety of patterns but in only two directions, say 0° and 90°, but weaving processes to produce cloths with fibres in several directions if the plane of the cloth are readily available. Fibres of different types have also been intermingled during the weaving processes to produce mixed-fibre cloth for the manufacture of fabrics.

We have considered expensive raw materials, and it is often only the fact that the overall cost of a product may nevertheless be lower than a manufactured composite, conventional materials by more costly processes that makes a competing product made from composites design solution gives an attractive alternative. Thus, although large quantities of glass fibres are supplied in chopped form for compounding with both thermoplastic and thermosetting matrix polymers, it may not seem economical to chop the more expensive types of reinforcement. Nevertheless, there are some advantages in using even these fibers in chopped form, provided they can be arranged in the composite in such a way as to make good use of their intrinsically high strengths and stiffness. The process for producing both chopped fibres, like glass and carbon, and naturally short filaments, like whiskers or asbestos fibres, in the form of prepreg sheets with fibres that were very well aligned in either unidirectional or poly-directional patterns is advantageous.

These prepregs also have excellent ‘drapability’ and can be used to form complex shapes, long as the short fibres are well above some critical length, which for carbon, for example, may be of the order of only a millimeter, they are able to contribute a high fraction of the intrinsic properties to the composite without the loss that occurs with woven reinforcements as a result of the out-of-plane curvature of the fibres

Composite materials are usually classified by the type of reinforcement they use. For example, in a mud brick, the matrix is the mud and the reinforcement is the straw. Common composite types include random-fiber or short-fiber reinforcement, continuous-fibre or long-fibre reinforcement, particulate reinforcement, flake reinforcement, and filler reinforcement.

In the composite material, the structural reinforcement is held in place by matrix. In the case of fibre reinforced polymer (FRP) composites, structural fibre is surrounded by a matrix adding rigidity. Most often this matrix is a thermoplastic or a thermosetting resin. A matrix alone is not structural and brittle while the reinforcement alone is flimsy. But together, they form a strong composite. A matrix is therefore the resinous phase of a reinforced plastic material which the fibres or filaments of a composite are embedded.

Fibre-matrix interface is the area which separates the fibre from the matrix and differs from them chemically, physically and mechanically. This region in most composite materials has a finite thickness because of diffusion and / or chemical reactions between the fibre and the matrix.

1.1.3 Benefits of composites

a. Light weight: In comparing composites to materials like ceramic, metal, and wood; then, composite can be said to be very light typically a composite material will weigh ¼ that of a steel structure of the same strength. Hence, a car or motorcycle made from composite

will weigh much lesser that when made from steel or other alloy metals. It has also been proven that fuel consumption is greatly reduced.

b. High strength: One major reason of blending materials is to obtain certain desired characteristics based on end use. Increase in strength is one of such and composite materials are extremely strong, particularly per unit weight. Composite materials like Aramid and S-glass which are used widely for making body armor. Soldiers have more protection from blast and fire threats due to high strength composite materials.

c. Corrosion and chemical resistance: Composites are highly resistant to chemicals and will never rust or corrode. This explains the much use of composites in marine applications, they were also among the very first to discover composite as salt water is corrosive and can lead to rusting. Composite is therefore a big advantage to the marine industry.

d. Elastic: Fibre reinforced composites have excellent elastic properties. When metals or steel are bent, they yield but in the case of composite, they almost immediately snap back into place a phenomenon that is ideal for springs. Thus, composites are used in car leaf springs.

e. Non-conductive: Certain composites are non-conducting. For example, ladders are meant to be strong and rigid but not conduct electricity when made from composite, but those made from aluminum can conduct electricity. Although, most electrical companies such as the Power Holding Company of Nigeria (PHCN) still use aluminum which is not safe for workers, a number of developed countries now use composite ladders which are safer.

1.2 Fibres

These are flexible macroscopically homogeneous body having a ratio of length to width and a small cross-section.

Fibres are classified as either natural or synthetic

Natural fibres: These can be mineral based e.g. asbestos; animal based e.g. wool, silk, mohair, e.t.c or vegetable which are classified as part of the plant from which the fibre is obtained e.g. seed hairs (cotton, kapok), stem or bast fibres (hemp, jute, ramie, Kenaf), fruit (coir) and leaf (sisal, pineapple, palm, henequen, bagasse). Ugbolue (1999).

1.2.1 Agricultural fibres

There is an increasing interest in using agricultural fibres for building components, either to complement or replace wood. Many of these lingocellulosics have been used to successfully produce particleboards, fibreboards, inorganic bonded products, and other building components. Building components made from agricultural materials fall into the same product categories as other wood-based composition products. Low-density insulation boards, medium-density fibreboards, hard-boards, particleboard, and other building system components, such as walls and roofs, are being produced. Binders may be synthetic thermosetting resins, modified naturally occurring resins like tannin or lignin, starches, thermoplastics, inorganic, or no binder at all. There seems to be little restriction to what has been tried and what may work.

1.2.2 Sugarcane bagasse fibre

Sugarcane, a renewable agricultural resource from which bagasse fibre is obtained is largely grown in three major countries namely; Brazil, India, and China in decreasing order. It is also

grown in other parts of the world which includes northern Nigeria but in relatively small quantities as compared to the above mentioned countries. From literature, there are over 10 varieties of sugarcane grown around the world identified using numbers, each with its distinguishing characteristics ranging from color, size, taste, time of maturity, crystallinity, tensile and flexural properties, to soil adaptability.

Bagasse is an organic waste product produced during the pressing of sugar cane to extract sugar and the extraction of juice from sorghum that is used to make alcoholic beverages. While it was originally seen to have no commercial value, it is now used as a source of cellulose to make ethanol fuel, shaped into disposable table ware, paper production in nations with climates where only few trees can be grown; it is also inculcated into building materials. Using bagasse in this manner is seen as beneficial to the environment and as a significant reduction in the waste stream. In some other instances, bagasse is burned to supply heat to the sugar refining operation; some is returned to the fields; and finds their way into various panel products. Bagasse is composed of fibre and pith. The fibre is thick walled and relatively long (1 to 4mm). It is obtained from the rind and fibro vascular bundles dispersed throughout the interior of the stalk. For the best quality bagasse fibre and particle boards, only the fibrous portion is utilized.

Another name for bagasse is megass, from a root term that originally meant “rubbish”. Instead of creating air pollution by burning it, however, new uses for it continue to flourish daily. It has become an essential ingredient in pressed construction materials used in the building trade, in the manufacture of acoustical tile, and as a source fibre in animal feed. Brazil has the world leading economy for bagasse production from sugarcane, followed closely by India. It was estimated in 2004 that Brazil produced 12% of its own electricity needs by using it to generate alchohol–based fuel such as ethanol, or through burning the waste in pellet form directly. The Brazilian

Sugarcane Industry Association (UNICA) noted in 2011 that the harvest was projected to be around 595.89million tons which is a 10% increase from the previous year.

1.3 Statement of the Research Problem

The good potential of natural fibres as a suitable substitute for synthetic fibres in reinforced composites is now in vogue. Synthetic fibres are non-biodegradable, expensive to process, and require expatriates in handling equipments. A number of natural fibre advantages have been identified; these include: low weight, environmental friendliness, non-toxicity, availability, low cost, and non-requirement of technical know-how to obtain the fibres. However, its hydrophilic nature which creates poor adhesion between the fibre and polymer matrix is one factor that has limited its full utilization – hence the research problem. Fibre modification using chemical or physical treatment has been developed as a way of remedy; although a number of these treatments exist some are more compatible to certain fibers than others (Haque *et al*., 2010). It would therefore be considered in this work the readily availability of the fibre of choice (Bagasse) and polymer to be used for the production of this composite and to see how best or to what extent the fibre–matrix interphase can be improved by carrying out various chemical treatments on the fibre and observing its effect on the finished composite produced.

1.4 Research Aim and Objectives

Aim:

The aim of this study is to state the likely suitable chemical modification method for the variety of bagasse fibre used as far as the four chemical used (acetic acid, acrylic acid, sodium hydroxide, and potassium permanganate) is concerned.

Objectives:

i. To utilize waste sugarcane as a reinforcement in composite production.
ii. To evaluate the effect of different chemical treatments of the bagasse fibre by carrying out SEM studies.
iii. To prepare the fibre-polymer reinforced composite using the hand lay-up technique and study its mechanical properties.
iv. To evaluate its water absorption properties as a function of immersion time.

1.5 Justification

Although a hand full of research has been carried out on fibre reinforced composites from the view of improving the hydophobicity of the fibre through fibre modification; this research used four chemicals for its treatments as oppose to the usual one or two. The treatment ought to improve adhesion, compatibility and interaction between the fibre and the polymer matrix. Sugarcane is readily available hence the fibre is in abundance. This research is aimed at

exploring the possibilities and opportunities available for the use of Bagasse fibre - polymer composite for use in place of ply woods in construction and other building applications. Unsaturated polyester has been chosen as the polymer because of not just its availability but its low cost and compatibility. In this part of the world the sugar industry is growing and a lot of sugar cane stem from which Bagasse fibre is obtained is left as waste. The world is campaigning for zero waste as much as possible. The idea is from *"waste to wealth"*.

1.6 Scope of the Study

The study is limited to the following areas:

i. Analysis of the physical properties of only Bagasse fibre after chemical treatments.
ii. FTIR analysis of the treated fibres.
iii. SEM studies of fibres and also of the produced composites.
iv. Analysis of the mechanical properties of the composite.

CHAPTER TWO

2.0 LITERATURE REVIEW

This chapter gives an account of previous works, thesis accepted and published whose methods and findings are pivotal to chemical treatment and modification, polymer matrix type, and mode of composite preparation with emphasis on the physical and mechanical properties of natural-fibre composites.

Over the years, varieties of natural fibres which includes hemp, jute, kenaf, okro, pineapple leaf, sisal, flax, ramie, oil palm, wood, maize cob, rice husk, coir, and bagasse have been used as fillers in fibre-reinforced polymer matrix composite. The limitation of these natural fibres been hydrophilic has led to the treatment of the fibre prior to their use in the composite.

Vilay *et al*., (2008) studied the effect of surface treatment and fibre loading on the properties of bagasse fibre-reinforced unsaturated polyester composite and obtained significant increase in mechanical properties as well as reduction in water absorption level; this was is agreement with Bledzki *et al*., 1993; Jannah *et al*., 2009; and Mylsamy and Rajendran 2011). Asegekar and Joshi (2013) studied different varieties of bagasse fibre and came out with the conclusion that, flexural strength and modulus varied within varieties and was generally found to be low, the tensile strength also varied and was different between varieties. Their water absorption level varied between 13 – 18%. Their fibre fineness as a function of Tex value differs with varying irregularities even between the same variety, this can affect processing, workability, and use.

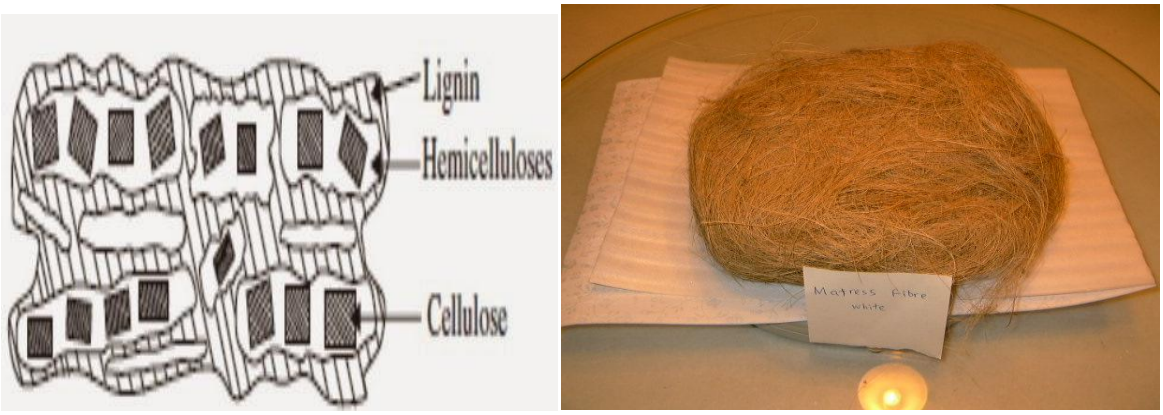
Xie *et al*., (2011) studied the properties of natural fibre composites made by pultrusion process varying the matrix found out that in terms of cost, availability, and processing polyesters was the best. However, their overall mechanical properties were found to be similar. Lu Na *et al*., (2013);

Niu *et al*., (2011); and Yusuf *et al*., (2010) studied thermal stability and thermos-mechanical of high density hemp fibre/polyethylene composite, propylene/hemp fibre composite and Polylacti acid/Kenaf fibre composites respectively as. This study indicated a decrease in thermal stability with increase in fibre loading, an increase in storage modulus, but above 40% fibre loading it began to drop. Brahmakumar *et al*., (2005) studied the effect of waxy substances on coconut fibre surface and how it limits interfacial bonding and strength of composite. According to Brahmakumar et al., these substances hinders interfacial bonding and causes a reduction in strength and hardness except otherwise removed to improve their properties. Cao *et al*., (2006) studied the mechanical properties of biodegradable composites reinforced with bagasse fibre after chemical treatment and found that these mechanical properties increased. This means that the chemical treatments led to a modification of the bagasse fibre, similar results were obtained by Sreenivasan *et al*., 2012; Sreekumar *et al*., 2009; Rosa *et al*., 2009; Rout *et al*., 2001; Mwaikambo *et al*., 2006; and Kushwaha and Kumar 2010.

Gopalakrishnan, *et al*., in 2010 when analyzing bagasse fibre, gave its major constituents as follows:

Table 2.1: Percentage constitution of bagasse components

Constituent	**%**
Moisture	49
Fibre	48.7
Soluable solids	2.3



a b

Figure 2.1: (a) inner structure of bagasse fibre; (b) bagasse fibre mass

a b

Figure 2.2: (a) bagasse pellets and (b) baggasse stem respectively

These bagasse pallets and stems are useful even in this form, the pallets are used in the production of cigarettes while the stems could be crushed and used in the production of animal feed. Other uses of bagasse include:

i. Fuel

Bagasse is often used as a primary fuel source for sugar mills. When burned in sufficient quantity, it produces sufficient heat energy to supply all the needs of a typical sugar mill with energy to spare. To this end, a secondary use for this waste product is in cogeneration, the use of a fuel source to provide both heat energy, used in the mill and electricity which is typically sold to the consumer electricity grid. The resulting CO_2 emissions are equal to the amount of CO_2 that the sugar cane plant absorbed from the atmosphere (photosynthesis) during its growing phase. Sugar factories significantly contribute to green power in electricity supply. For example, Florida Crystals Corporation, one of America's largest sugar companies owns and operates the largest biomass power plant in North America; Hawaiin Electric Industries also burns bagasse for cogeneration.

Ethanol produced from the sugar in sugarcane is a popular fuel in Brazil. The cellulose – rich bagasse is being widely investigated for producing commercial quantities of cellulose ethanol. For example, BP is operating a cellulosic ethanol demonstration plant based on cellulosic materials in Jennings, Louisinana.

ii. Pulp, Paper, Board and Feed

Bagasse is commonly used as a substitute for wood in many tropical and subtropical countries for the production of pulp, paper and board such as India, China, Colombia, Iran, Thailand and Argentina. It produces pulp with physical properties that are well suited for

generic printing, writing papers as well as tissue products but it is also used for boxes and newspaper production. Bagasse can also be used for making boards resembling plywood or particle board, called bagasse board and Xanita board, and is considered a good substitute for making partitions, furniture etc.

Many industries have presented a method of converting bagasse into cattle feed by mixing it with molasses and enzymes (such as bromelin) and fermenting it. A South African company mixes 30 % bagasse cellulose fibres with recycled kraft paper fibre to make ultra-light composite boards. These are sold as an environmentally – friendly, formaldehyde free alternative to most MDF and particle board.

iii. As fillers in composite production

This is the new trend for the use of agricultural fibres. Bagasse, as one of such can be used too although its feasibility is not yet at its peak and is therefore still been researched and has contributed largely to the automotive, construction and marine industries.

Health hazards of bagasse

Workplace exposure to dusts from the processing of bagasse can cause the chronic lung condition pulmonary fibrosis more especially referred to as bagassosis.

2.1 Surface Treatments and Fibre Modification

Synthetic fibres are natural organic polymers, synthetic organic polymers or inorganic substances which do not create the maximum compatibility between it and the matrix and natural fibres are now taking over. (Bledzki *et al*., 2010; Boynard *et al*., 2003; Felix and Gatenholm 1991; and Fraga *et al*., 2006).

The compatibility between the natural fibre and the polymer can be further improved via fibre surface modification, matrix modification or adding compatibilizer. A good number of works have been done on chemical modification of fibre (Li *et al*, 2004; Bisanda and Ansell 1999; Bessadok *et al*., 2007; Gulati and Sain 200; George *et al*., 2001; and Gassan and Bledzki 1997). The studies of fibre and/or polymer modification have been focused on both physical and chemical methods.

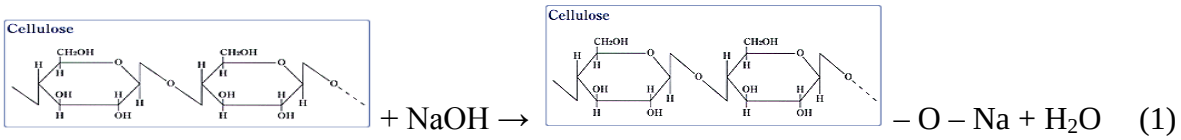
The physical methods include;

I. Heat treatment
II. Plasma treatment
III. Corona treatment

The chemical treatment includes

2.1.1 Alkaline treatment

Alkaline treatment or mercerization using mostly Sodium hydroxide is one of the most used chemical treatments of natural fibres when used to reinforce thermoplastics and thermosets. The important modification done by alkaline treatment is the disruption of alkaline treatment in the network structure thereby increasing the roughness of the surface. Xue Li *et al*., (2007). This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fibre cell wall, depolymerizes cellulose and exposes the short length crystallites. Addition of aqueous Sodium hydroxide (NaOH) to natural fibre promotes the ionization of the hydroxyl group to the alkoxide.



$$+ NaOH \rightarrow \quad - O - Na + H_2O \qquad (1)$$

Equation 2.1: Probable reaction of cellulose with Sodium hydroxide

Thus, alkaline processing directly influences the cellulosic fibril, the degree of polymerization and extraction of lignin and hemicellulosic compounds.

Experiments carried by researchers have shown that alkaline treatment has two major effects on the fibre:

(1) It increases surface roughness resulting in better mechanical interlocking; and

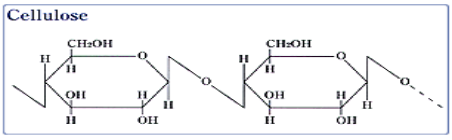
(2) It increases the amount of cellulose exposed on the fibre surface, thus increasing the number of possible reaction sites. Alkaline treatment therefore has a lasting effect on the fibre strength and stiffness (Xue Li *et al.*, 2007; and Lu Na *et al.*, 2012). However, at higher alkaline concentration, excess delignification of natural fibre occurs resulting in a weaker or damaged fibre; therefore the concentration must be kept under control. The mechanical treatment and water absorption properties of coconut fibre was also carried out using alkaline treatment (Nural and Ishak 2012).

2.1.2 Silane treatment

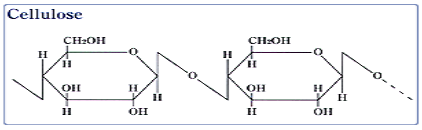
Silane is a chemical compound with the chemical formula SiH_4. Silanes are used as coupling agents to let glass fibres adhere to a polymer matrix, stabilizing the composite material. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fibre-matrix interphase. In the presence of moisture, hydrolazeable alkoxy group leads to the formation of silanols which then reacts with the hydroxyl groups in the fibre forming stable covalent bonds to

the cell wall that are chemisorbed onto the fibre surface. Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fibre by creating a cross linked network due to covalent bonding between the matrix and the fibre. Xue Li *et al*., (2007).

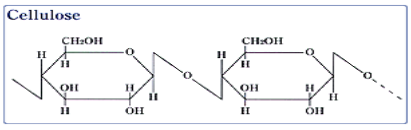
The reaction is as follows:



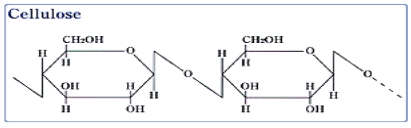
$CH_2CHSi \quad (OC_2H_5) \rightarrow$



$CH_2CHSi(OH)_3 + 3C_2H_5OH$ (2)



$+ \quad CH_2CHSi(OH)_3 \rightarrow$



$CH_2CHSi(OH)_2O + H_2O$ (3)

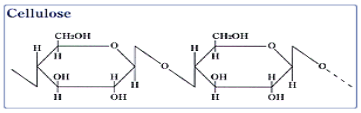
Equation 2.2: Probable reaction of cellulose with Silane

Many researchers applied silane treatment in surface modification of glass fiber composites (Sain *et al.*, 2005). Silane coupling agents were also found to be effective in modifying natural fiber – polymer matrix interface and increasing the interfacial strength (Srikanth *et al*., 2012).

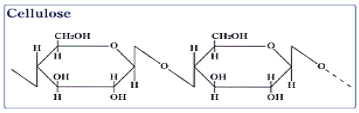
2.1.3 Acetylation of natural fibres

Acetylation describes a reaction introducing an acetyl functional group (CH_3COO^-) into an organic compound. Acetylation of natural fibres is a well known esterification method causing plasticization of cellulosic fibres. Chemical modification with acetic anhydride or acetic acid substitutes the polymer hydroxyl group of the cell wall with acetyl groups, thus, modifying the

properties of these polymers e.g.unsaturated polyester they become hydrophobic. Xue Li *et al*., (2007). The reaction of acetic anyhydride with fibre is shown below:



$+ CH_3 – C (=O) – O – C (=O) – CH_3 \rightarrow$



$– OCOCH_3 + CH_3COOH$ (4)

Equation 2.3: Probable reaction of cellulose with Acetic anhydride

Acetylation can reduce the hygroscopic nature of natural fibres and increase the dimensional stability of composites. Acetylation was used in surface treatment of fibres for use in fibre – reinforced composites.

2.1.4 Benzoylation treatment

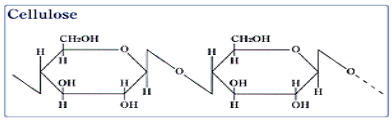
This is an important transformation in organic synthesis. Benzoyl chloride includes benzoyl ($C_6H_5C=O$) which is attributed to the decreased hydrophilic nature of the treated fiber and improved interaction with the hydrophobic polymer matrix. Benzoylation of fibres improves fiber matrix adhesion, thereby increasing the strength of the resulting composite, decreasing its water absorption and improved its thermal stability.

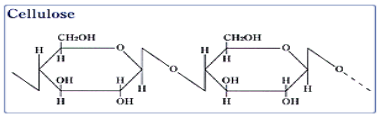
Several works have carried out using benzyl chloride and it was observed that the thermal stability of the treated composites were higher than for the untreated ones. A better result is obtained when the fibres are first alkaline pre-treated (Xue Li *et al*., 2007).

2.1.5 Acrylation and acrylonitrile grafting

Acrylation reaction is initiated by free radicals of the cellulose molecules. Cellulose can be treated with high energy radiation to generate radicals together with chain scission.

Acrylic acid (CH_2=CHCOOH) can be graft polymerized to modify glass fibres as well as natural fibres, the procedure usually follows mixing the fibres with a certain percentage of sodium hydroxide (NaOH) for about 30 minutes and then treated with a solution of acrylic acid at 50 – 60^0C for an hour at various concentrations. The reaction follows the path below:



+ CH_2 = CHCN → 

– OCH_2CH_2CN

(5)

Grafting reduces the hydrophilic nature of the fibres.

Equation 2.4: Probable reaction of cellulose with Acrylic acid

2.1.6 Maleated coupling agents

Maleated coupling agents are widely used to strengthen composites containing fillers and fibre reinforcements. The difference with other chemical treatments is that maleic anhydride is not only used to modify fiber surface but also the polymer matrix to achieve better interfacial bonding and mechanical properties in composites. Mechanical properties such as Young's modulus, flexural modulus, hardness and impact strength of plant fiber-reinforced composites increased after maleic anhydride treatment.

2.1.7 Permanganate treatment

Permanganate is a compound that contains permanganate group MnO^-_4. Permanganate treatment leads to the formation of cellulose radical through MnO^-_3 ion formation. Then, highly reactive Mn^{3+} ions are responsible for initiating graft copolymerization. Most permanganate treatments are conducted by using Potassium permanganate solution in different concentrations with

soaking duration from 1 to 3 minutes after alkaline pre-treatment. This treatment reduces the hydrophilic nature of the fibre improving surface roughness thereby resulting in increased fiber/matrix interaction.

$$C_6H_{10}O_5 + KMnO_4 \rightarrow C_6H_{10}O_6 + K^+ + MnO^{3-}$$

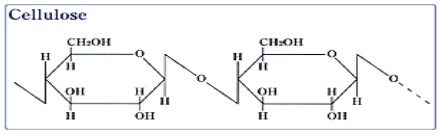
Equation 2.5: Probable reaction of cellulose with Potassium permanganate

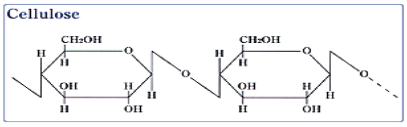
2.1.8 Peroxide treatment

In organic chemistry, peroxide is a specific functional group or a molecule with the functional group ROOR containing the divalent ion O-O. Organic peroxides tend to decompose easily to free radicals of the form RO; RO then reacts with the hydrogen group of the matrix and cellulose fibers. For example, the peroxide initiated free radical reaction between PE matrix and cellulose is shown by the equation below:

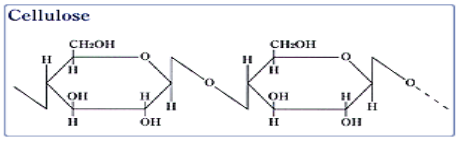
$$RO - OR \rightarrow 2RO \qquad (1)$$

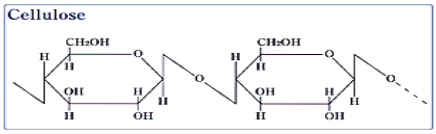
$$RO + PE - H \rightarrow ROH + PE \qquad (2)$$

RO + 

– H → ROH + 

(3)

PE + 

→ PE – 

(4)

Equation 2.6: Reaction of cellulose with Perioxide

2.1.9 Isocyanate treatment

An Isocyanate is a compound containing the Isocyanate functional group, –N=C=O, which is highly susceptible to reaction with the hydroxyl groups of cellulose and lignin in fibres and has been reported to work as a coupling agent in fibre reinforcement (Xue Li.*et al*., 2004). The reaction between fiber and Isocyanate coupling agent is shown below:

R-N=C=O +HO-Fibre →R-NH-C(=O)-O-Fibre

Equation 2.7: Probable reaction of cellulose with isocyanate

Where R could be different chemical groups.

2.1.10 Graft copolymerization

The reaction is initiated by free radicals of the cellulose molecule. The molecule is then treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Then the cellulose molecule cracks and radicals are formed. Afterwards, the radical sites if the cellulose are treated with a suitable solution (compatible with the polymer matrix), for example, vinyl monomer, acrylonitrile, methyl methacrylate, and polystyrene. The resulting copolymer possesses properties characteristic for both, fibrous cellulose and grafted polymers. A typical example is the polypropylene – maleic acid copolymer (MAH – PP) (Gassan and Bledzki 2000).

Generally, there are a host of chemicals that are available for chemical modification if only their affinity and susceptibility for various fibres will be tested and researched. Although, many people are comfortable with the convectional chemicals particularly Sodium hydroxide but others too may give even better adhesion depending on the fibre in question.

2.2 Polymeric Materials

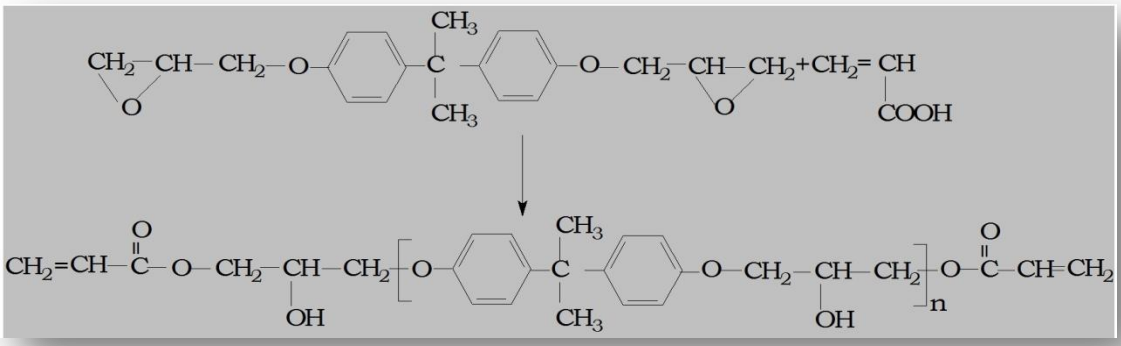
Few polymers are thermally stable by comparison with metals or ceramics and even the most stable, like the polyimides, or poly(ether ether ketone) (known as PEEK) are degraded by exposure to temperatures above about 300°C. There is nothing that reinforcement can do to combat chemical degradation, but the associated fall in strength and increase in time-dependent (creep or visco-elastic) deformation, a feature common to all polymers, though less serious in cross-linked resin systems than in thermoplastics, can be delayed by fibre reinforcement.

A more serious problem in polymers is their very low mechanical strength and stiffness in bulk form and, like metals, the weakest plastics tend to be ductile but the strongest tend to be brittle, although there are exceptions. Polymers are traditionally insulators and in their application as such strength is usually a secondary consideration. The electrical conductivity of plastics reinforced with carbon fibres is of importance in many aeronautical applications, however, where protection of avionics systems from external electrical activity (eg. lightning strike) is of importance. Most polymers are already low-density materials, and the addition of fibres confers no density advantage. It is in the reinforcing of polymers that most developments have been made so far, and it is likely that there is still scope for improvement. There is a thriving, international reinforced plastics Industry, for which both the science and technology are highly advanced. And although the level of awareness of the merits of reinforced plastics on the part of designers in general engineering seems to be low, the same is not true of the aerospace industry for which the potential benefits of very high strength and stiffness, combined with low density are easily recognized.

2.2.1 Unsaturated polyester

Unsaturated Polyester is of the thermosetting resins group produced by dissolving a low-molecular-weight unsaturated polyester in a vinyl monomer and then copolymerizing the two to form a hard, durable plastic material. Unsaturated polyesters, usually strengthened by fibreglass or ground mineral, are made into structural parts such as boat hulls, pipes, and countertops (Suh *et al*., 2000).

Thermosetting resins results in a three-dimmensional network. At this point, the intermolecular bonding is strong, hence for dissociation to occur the polymer must be permanently degraded. Application of heat will allow the polymer to go through a softening stage to make moldings easy. Whereas in thermoplastic, the polymer is fully polymerized in the raw state, the reaction is purely physical. Therefore application of heat allows the material to be heated and molded very easily and the procedure (that is, molding and remolding) can be repeated several times until the accumulated effect of the applied heat causes the polymer to degrade, (Pravednikov *et al.*, 1981, Kardash *et al.*, 1971; Kaas 1981; Dine-Hart and Wright 1967; and Orwall *et al.*, 1981).



Equation 2.8: Reaction of a low molecular weight unsaturated polyester with a vinyl monomer to give a high weight unsaturated polyester.

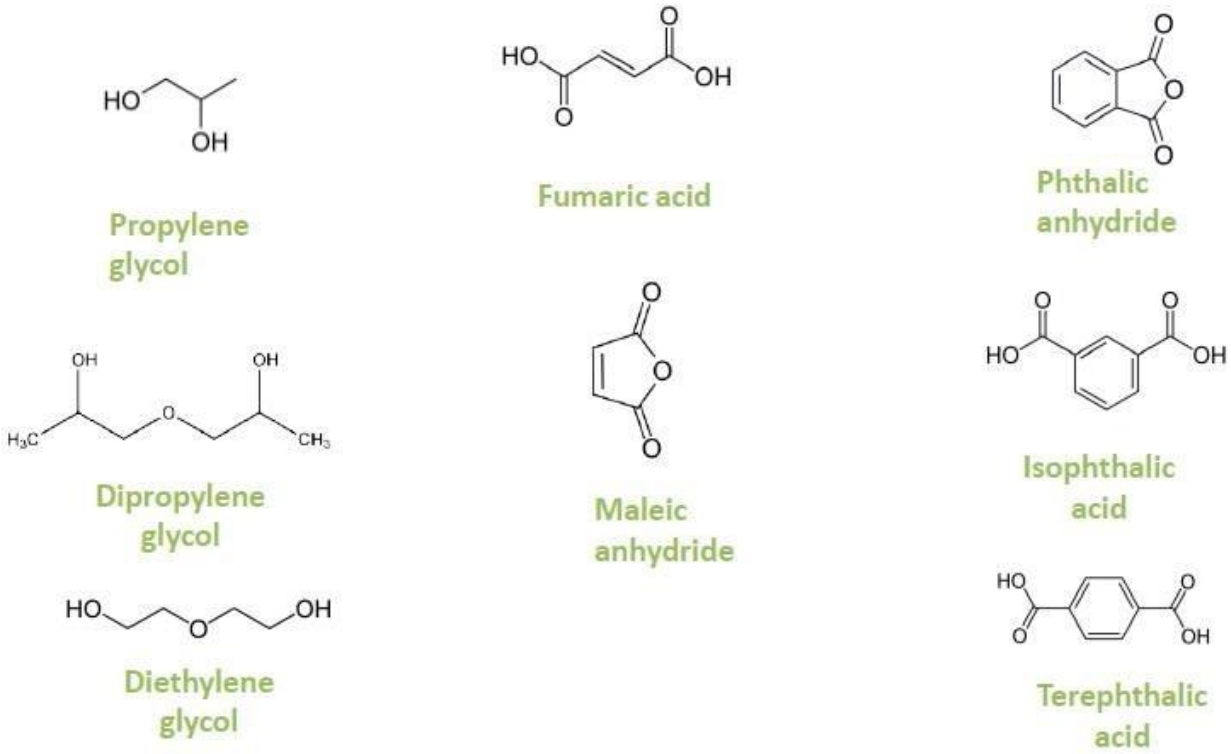


Figure 2.3: Examples of vinyl monomers used in the production of high molecular weight unsaturated polyester.

Unsaturated polyesters are copolyesters, that is, polyesters prepared from a saturated dicarboxylic acid or its anhydride (usually phthalic anhydride) as well as an unsaturated dicarboxylic acid or anhydride (usually maleic anhydride). These two acid constituents are reacted with one or more di-alcohols, such as ethylene glycol or propylene glycol, to produce the characteristic ester groups that link the precursor molecules together into long, chainlike, multiple-unit polyester molecules. The maleic anhydride units of this copolyester are unsaturated because they contain carbon-carbon double bonds that are capable of undergoing further

polymerization under the proper conditions. These conditions are created when the co-polyester is dissolved in a monomer such as styrene and the two are subjected to the action of free-radical initiators. The mixture, at this point usually poured into a mold, then copolymerizes rapidly to form a three-dimensional network structure that bonds well with fibres or other reinforcing materials. The principal products are boat hulls, business machines, automobile parts, automobile-body patching compounds, tubs and shower stalls, flooring, translucent paneling, storage tanks, corrosion-resistant ducting, and building components. Unsaturated polyesters filled with ground limestone or other minerals are cast into kitchen countertops and bathroom vanities. Bowling balls are made from unsaturated polyesters cast into molds with no reinforcement (Suh *et al.*, 2000; Ahmad *et al*., 2007; and Kutz 2011).

Recently there has been a global focus on greener processes and technologies. This is where unsaturated polyesters have the most potential over their metallic counterparts. Production of metals continues to deplete our natural resources and consumes most of our fossil fuels. Unsaturated polyesters although previously synthesized from fossil fuels can now be manufactured from biological resources instead. Starches, plant oils and other naturally derived building blocks have been discovered that can be used to prepare unsaturated polyester resins (John and Anandjiwala 2008; Kalia *et al.*, 2009; and Kazayawoko *et al.*, 1999). Collectively, there is an ever increasing potential for unsaturated polyester resins. Their low cost, ease of use and weight advantages make them prime candidates for a wide variety of structural and decorative applications. Imagine a world where all metal components are replaced with thermosets composite components manufactured from unsaturated polyester resins –these are the possibilities of "pure science".

2.2.2 Chemical properties of unsaturated polyester

Unsaturated polyester resins are the most commonly used thermosets resins in the world. More than 2 million tons of unsaturated polyester resins are utilized globally for the manufacture of a wide assortment of products, including sanitary-ware, pipes, tanks, gratings, high performance components for the marine, automotive industry, and in the manufacture of composites.

Unsaturated polyester resins form highly durable structures and coatings when they are cross-linked with a vinyl reactive monomer, most commonly styrene. The properties of the cross-linked unsaturated polyester resins depend on the types of acids and glycols used and their relative proportions (Marrati 2002).

Unsaturated polyester resins are further classified into the following categories:

a. Ortho-phthalic polyesters: resins made from ortho-phthalic anhydride are generally cheaper than the other two classes of unsaturated polyester resins. They are usually used to manufacture general purpose composite laminates where only moderate structural properties are required.
b. Isophthalic polyesters: resins made from Iso-phthalic acid. These resins are much more structurally competent than the ortho-phthalic resins. They also have superior corrosion resistance and are used for more demanding applications
c. Terephthalic polyesters: Tere-phthalate resins are made from tere-phthalic acid. These resins are currently made in small volumes and are considered a specialty resin. Although they tend to have better thermal and chemical resistance than iso-phthalic resins they are difficult to manufacture.

Propylene glycol is the predominant alcohol used in producing various types of unsaturated polyester resins. Other alcohols like neo-pentyl glycol (NPG), di-ethylene glycol (DEG) and ethylene glycol (EG) are also used used in the production of unsaturated polyester resins. Each of these alcohols contributes to the final polymer characteristics, which includes heat distortion temperature (HDT), physical strength, and water uptake and weather resistance.

The addition of styrene and other monomers are to optimize properties and to minimize environmental impact. Their effect includes:

a. Inhibitors: Because of the tendency of unsaturated polyesters to self-polymerize inhibitors are added to both the monomer and the formulated resin. Inhibitors slow the curing reaction by reacting with free-radicals before they cause crosslinking between the polymer and the monomer. Common inhibitors include Quinones (HQ, MTBHQ, PBQ, or THQ) and p-tert-butylcatechol (TBC).
b. Promoters: Sometimes referred to as accelerators, these materials facilitate effective room temperature curing. The promoter reacts with the initiator at the time of molding. Promoters include cobalt compounds, used with MEKP initiators; and aniline compounds, used for co-promoters in a MEKP system and as the primary promoter in ambient conditions with BPO initiators. Polyester resins are available in pre-promoted form, where the resin manufacturer includes the promoter in the product; or in unpromoted formulations where the molder adds promoter prior to processing.
c. Initiators: Sometimes incorrectly referred to as catalyst. When added to polyester resin the initiator reacts with the resin and decomposes, forming free radical molecules. These

free radicals overcome the inhibitor and begin a cascading polymerization reaction, also known as curing.

d. Functional additives: Resin characteristics and performance can be modified with the addition of a number of additives. These include: Fire retardant additives, thixotropes, pigments, vapor suppressants, and other additives.

Their versatility in use allows unsaturated polyester resins to be used in a myriad of composite applications. Composite parts can be made at temperatures as low as 15°C to as high as 150°C depending on the processing requirement of the application. Unsaturated polyester resins also have excellent service temperatures. They have good freeze-thaw resistance and can be designed for use in many low to moderate temperature applications ranging from refrigerated enclosures to hot water geysers.

When it comes to weight for cost comparisons, unsaturated polyester resins are much favored over their metallic counterparts. With the current fuel and processing costs, the increasing prices of steel and aluminum are pushing more fabricators to use unsaturated polyester resin composites instead. Another major advantage is the increased productivity potential. While metals involve the use of specific smelters, expensive tooling and processing requirements, unsaturated polyester resins are far cheaper and afford the use of low cost tooling. An unsaturated polyester resin can be molded at ambient temperature whereas metals need to be heated to well over 2000°C before they are melted and poured into mould cavities. Although the perception is that metals are generally structurally superior, there has been much advancement in the development of technologies for producing higher strength composites made from unsaturated polyesters resins.

Adding beauty to structure is easily attained with unsaturated polyester resins. Easily pigmented resin systems can be employed to produce parts with aesthetic appeal without compromising structural properties. Natural stone can be simulated with granite like effects in solid surface features made with special NPG based unsaturated polyester resins. These products are advantageous over their natural stone counterparts in that they offer non porous surfaces which allow them to be used in hygienic environments like kitchens, hospitals and biological laboratories. High gloss blemish free parts can also be produced in-mould using pigmented gel-coat technologies. In the case of glass-fiber boats a smooth and attractive high gloss surface is achieved that need not be sprayed or finished with a paint.

While this family of plastics goes under the name "polyesters," they are quite distinct from the polyesters described above. In fact, they are thermosets, and are probably most familiar to the public for their role in fibre-glass reinforced plastics. These materials were introduced to military use (i.e., naval craft) in 1942. After World War II, their characteristics proved extremely appealing to such non-military markets as automotive, marine, corrosion-resistant structures, building, electrical applications, and consumers' goods such as luggage, fishing poles and cases and housings of every type and description. These thermosetting resins are made by the condensation reaction between dysfunctional acids and glycols. The resulting polymer is then dissolved in styrene [$C_6H_5CHCH_2$] or other vinyl unsaturated monomers. The structures of the acids and glycols used and their proportions, especially the ratio of the unsaturated versus the saturated acid, and the type and amount of monomer used, are all tailored for each resin to balance economy, processing characteristics, and performance properties. ("Unsaturated polyester" 2015).

The use of unsaturated polyester as matrices in most natural fibre composite is common and a hand full of research are available, these include: polyester – sisal (Admavathi, *et al*., 2012), polyester – jute (Akil, *et al.*, 2005), polyester – coir (Owolabi, *et al.,* 1985), polyester – pineapple leaf (Devi, *et al*., 1997), polyester – kenaf (Aziz, *et al*., 2004), and polyester – palm (Al-kaabi *et al*., 2005).

2.2.3 Advantages and disadvantages of unsaturated polyester

Advantages:

Easy to use

Lowest cost of resins available

Low energy (temperature) requirements during processing in terms of composite production

Disadvantages:

Only moderate mechanical properties

High styrene emissions in open moulds

High cure shrinkage Limited range of working times

2.3 Fabrication Methods

There are numerous methods for fabricating composite components. Some methods have been borrowed (injection moulding, for example), but many were developed to meet specific design or

manufacturing challenges. Selection of a method for a particular part, therefore, will depend on the materials, the part design and end-use or application. Composite fabrication processes involve some form of molding, to shape the resin and reinforcement. A mold tool is required to give the unformed resin /fibre combination its shape prior to and during cure.

The most basic fabrication method for thermosets composites is *hand- layup*, which typically consists of laying dry fabric layers, or "plies," or prepreg plies, by hand onto a tool to form a laminate stack. Resin is applied to the dry plies after layup is complete (e.g., by means of resin infusion). In a variation known as wet layup, each ply is coated with resin and "debulked" or compacted after it is placed. Nural and Ishak (2012) used hand lay-up method, John *et al*., (2008) used a two –roll miller in the production of its composite, Vilay *et al*., (2008) prepared its composite using vacuum bagging technique. Other methods include, pultrusion, injection molding, etc.

Several curing methods are available. The most basic is simply to allow cure to occur at room temperature. Cure can be accelerated, however, by applying heat, typically with an oven, and pressure, by means of a vacuum. For the latter, a vacuum bag, with breather assemblies, is placed over the layup and attached to the tool, then evacuated using a vacuum pump before cure. The vacuum bagging process consolidates the plies of material and significantly reduces voids due to the off-gassing that occurs as the matrix progresses through its chemical curing stages.

Hand layup and spray- up methods are often used in tandem to reduce labor. For example, fabric might first be placed in an area exposed to high stress; then, a spray gun might be used to apply chopped glass and resin to build up the rest of the laminate. Balsa or foam cores may be inserted

between the laminate layers in either process. Typical glass fiber volume is 15 percent with spray- up and 25 percent with hand layup.

Spray-up processing, once a very prevalent manufacturing method, is becoming outdated; Federal regulations in the U.S. and similar rules in the EU have mandated limits on worker exposure to, and emission into the environment of VOCs and hazardous air pollutants (HAPs). Styrene, the most common monomer used as diluents in thermoset resins, is on both lists. Because worker exposure to and emission of styrene is difficult and expensive to control in the spray-up process, many composites manufacturers have migrated to closed mold, infusion-based processes, which better contain and manage styrene. Although open molding via hand layup is being replaced by faster and more technically precise methods, it is still widely used in the repair of composite parts.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Experiment

Three point bending (flexural) test	-	ASTM – D790-08
Tensile strength test for composites	-	ASTM – D638-06
Impact strength of composites	-	ASTM – E23
Hardness test for composites	-	ASTM – D2240
FTIR analysis for fibres	-	ASTM – E2224-10

3.2 Materials

- The Sugarcane used was of the variety NG57-258 of the classification “chewing canes”, from a sugarcane plantation in Hunkiyi – Zaria, Kaduna state; Nigeria.
- Aluminum Foil

3.2.1 Chemicals and reagents

a. The polymer is Unsaturated Polyester obtained from NYCIL NIG. LTD, Ikeja – Lagos state

b. Methyl Ethyl Ketone Peroxide (MEKP- initiator)

c. Cobalt Naphthalene (Accelerator)

d. Sodium Hydroxide

e. Acetic Acid

f. Permanganate

g. Acrylic Acid

h. Distilled water

i. Potassium bromate (KBr)

3.3 Equipment

Digital Weighing Balance

Phenom Scanning Electron Microscope (Model: Pro X)

Universal Testing Machine (TIRA model 4204)

Charpy Impact Tester (model SI-IC3)

Indentec Universal hardness testing machine, shore A. model no. 5019 B.

Laboratory glassware such as volumetric flask, beakers, measuring cylinder, conical flask, stirring rod, desiccators, etc.

Glass mould of 15cm x 10cm x 4cm dimension

FTIR spectroscopy machine NICOLET iS10

Milling machine Retsch 400

3.4 Methods

i. Fibre preparation

ii. Treatment of fibres

iii. Composite preparation

iv. Testing and characterization

3.4.1 Fibre preparation

3.4.1.1 Extraction of sugarcane fibres

The sugarcane obtained fresh from the farm was subjected to extraction of the juice from the stalk by sucking the juice and the remains collected. The residue called bagasse was collected for fibre extraction. The soft-core part pith was removed from the bagasse manually to get outer hard rind. The rind was then cut across the length so that the cut portions are free from the nodes. Asagekar and Joshi (2013) and Collier and Collier (1998).

The samples were then subjected to hot water treatments (material: liquor ratio 1:50). In this process, the samples were kept in hot water around 90^{o}C for 1hour for removal of coloring matters and sugar traces. The samples were then dried under the sunlight.

The baggasse fibres were then washed with clean water and then distilled water then dried overnight before use. The washed untreated fibers were named "UFs" (untreated fibers). The average fibre length was determined to be between 5 to 5.3cm.

Treatment of the UFs with a 2 wt % sodium hydroxide, acrylic acid, acetic acid, and potassium permanganate respectively was carried out for three hours at 70^{o}C after which the fibers were washed severally to neutralize the PH and dried first by sun drying for one hour then at room temperature for 24hours and finally at 60^{0}C for five (5) hours. Kaewkuk *et al*., (2013) and other works varied between concentration, temperature and the timing. For example, Gassan and Bledzki (1999) used 26wt% NaOH for 20minites at 20^{o}C on jute/epoxy and obtained a significant increase in mechanical properties, Syndenstricker *et al*., (2003) used 2% NaOH for 1hour at room temperature on sisal/polyester and obtained an increase in shear strength.

3.4.2 Treatment of fibres

i. Alkylation using Sodium hydroxide

The fibers having been washed with distilled water was treated with 2wt% NaOH, after which it was treated with acetic acid for 3-5 minute for neutralization effect and then thorough rinsing.

ii. Acetylation using Acetic acid

Treatment was also done with 2wt% acetic acid followed by an after treatment in Sodium hydroxide solution for 3–5 minutes for neutralization and then severe rinsing with distilled water.

iii. Permanganate treatment using Potassium permanganate

First, pre-treatment in Sodium hydroxide for 1-3 minutes, followed by Treatment with 2wt% potassium Permanganate

iv. Acrylation using Acrylic acid

Treatment was done with 2wt% acrylic acid followed by an after alkaline treatment using Sodium hydroxide and rinsing several times.

3.4.3. Determination of fibre volume fraction (V_f)

This is the percent or amount of fibre contained within the composite, that is, a volume of the composite. This helps in determining the required amount of fibre that would exactly fill the mold after the polyester has occupied its volume. This helps prevent wastage and ensures accuracy in terms of content and weight. It was calculated using the formula below:

$$V_f = (W_f/\rho_f)/ (W_m/\rho_m) + (W_f/\rho_f)$$

Where:

V_f = Fibre Volume Fraction

W_f = Weight of Fibre

W_m = Weight of matrix

p_f = Density of Fibre

p_m = Density of Matrix

Thus, based on the calculation, the fibre volume fraction was 20% which is same for all sample composites produced. According to Vilay *et al.*, (2008), the maximum mechanical property was found to be at 20% fibre volume for bagasse/unsaturated polyester composite. However, other works (sisal fibre/polypropylene composite, Kaewkuk *et al.*, (2012) have proven that above 20% fibre content not much change was observed and in fact more water was absorbed compared to the untreated fibre.

3.5 Composite Preparation

The fibres after treatment were carefully arranged within the mold such that they are parallel to one another and spread as evenly as possible, then the unsaturated polyester was poured to spread and fill the mold as much as possible. Five samples each of various treatments was produced using hand lay-up method.

Plate 3.1**:** Image of the glass mold used in the composite fabrication.

In a typical open mold application, the mold is first waved and sprayed with gel coat, then cured in a heated oven at about 50-60^{o}C. Fiber content can be increased by up to 50 percent by curing the parts in a vacuum bag. This is then followed by curing.

Plate 3.2: Samples of composite produced

3.6 Characterization

3.6.1 Functional group determination

Assessment of the fibres functional groups before and after the fibre treatment was carried out using Fourier Transform Infrared Spectroscopy (FTIR). This revealed the functional groups present and to what extent they were available particularly after treatment. This is with particular reference to the hydroxyl (OH) group which enhances moisture absorption in the fibre.

3.6.2 Determination of the tensile strength and modulus

Tensile properties of treated and untreated fibre composites were carried out following ASTM D638 using a universal testing machine (TIRA test 2810). The specimen was tested on a load cell 10KN, a crosshead speed of 10mm/min, and a guage length of 80mm. the test was done at the Science Complex, Sheda – Abuja.

Plate 3.3**:** Universal testing machine.

Plate 3.4: Dumpbell shaped samples for tensile test

The tensile strength was calculated using the equation below:

$$\text{Tensile strength} = \frac{Breaking\ force\ (N)}{Original\ Crossectional\ Area\ (m^2)}$$

The flexural strength and modulus were also calculated using the formula below:

$$\text{Flexural strength} = \frac{3PL}{2bt^2}$$

$$\text{Flexural modulus} = \frac{PL^3}{4bt^3w}$$

Where,

L = Span length of sample

P = Applied load

b and t = Sample width and thickness respectively

w = Deflection.

3.6.3 Impact test

Charpy impact testing machine following ASTM – E23 standard was used in carrying out this test at the Metallurgical and Materials Department of the Engineering Faculty, Ahmadu Bello University, Zaria - Nigeria. It was subjected to a 15joule energy impact at 3.21m/s suspended with a pendulum whose mass was 25kg.

Plate 3.5: Samples for impact testing

Plate 3.6: Charpy impact tester.

3.6.4 Hardness testing

This test was carried out on a DIN 53505 EN ISO 868 machine that measures in Shore A using ASTM D2240 standard. The testing was done at the Chemical and Leather Technology Laboratory, Zaria – Nigeria.

Hardness test helps to determine the resistance of the material to indentations and all other forms of deformity. The test was based on the rate of penetration by an indenter into the sample. The test was done at various points on the sample to obtain an average.

Plate 3.7: Hardness machine

3.6.5 Morphological analysis

The longitudinal and cross – sectional characteristics of fibres as well as the produced composites were studied by microscopic analysis using the scanning electron microscopic (SEM). SEM is a surface analytical technique used to generate magnified topographical images of a material surface 20x to over 100,000x.

The hair fibre to be studied is first made electrically conductive by ion sputtering with platinum. The examination is typically done along the fibre axis. SEM studies for fibres have been carried

out to examine the degree of micro damage resulting from combing, brushing, bleaching, perming, and heating from curling ions, UV exposure, and other chemical treatments.

The SEM uses a focused beam of high energy electrons to generate a variety of signals at the surface of the solid specimens. The field emission cathode in the electron gun of a SEM provides narrower probing at low as well as at high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. The signals that derive from electron sample interaction reveals information about the sample including external morphology (texture), chemical composition, crystalline structure, and orientation of material making up the sample.

Coatings applied to hair fibres can be detected as well as evidence of surface damage such as cracking, pitting, and cuticle lifting resulting from exposure to chemicals or environmental conditions.

3.6.6 Water absorption

Water absorption of the composite as a function of immersion time was determined following ASTM D570 standard test. Then, the test specimen was immersed in distilled water at room temperature. The percentage increase in weight during immersion was then calculated using the following equation:

$$\text{Water absorption (\%)} = [\ (w - w_o)/w_o\ ] \times 100$$

Where w is the wet weight and w_o is the dried weight.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Surface Treatment of Fibres

4.1.1 Alkaline treatment using Sodium hydroxide

From unaided visual examination of the fibres after alkaline treatment, the bundle of fibres looked whiter and fluffy. A similar inference was observed by Vilay *et al*., (2008) and Xue Li *et al*., (2007). This result implies that most of the semi-cellulosic substances such as pectin, lignin, wax, hemicellulose, etc as earlier mentioned have been removed to a reasonable extent.

The reaction likely to have occurred is as follows:

$$\text{Fibre} - OH + NaOH \rightarrow \text{Fibre} - O^{-} - Na^{+} + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{eqn 4.1}$$

Equation 4.1: Probable reaction mechanism during NaOH, treatment of the bagasse fibres

4.1.2 Permanganate treatment using Potassium permanganate

It was observed that the colour of the fibres changed from white to purple, and the fibres became crispy to touch.

$$C_6H_{10}O_5 + KMnO_4 \rightarrow C_6H_{10}O_6 + K^{+} + MnO^{-}_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{eqn 4.2}$$

Equation 4.2: Probable reaction mechanism during, KMnO4 with bagasse fibre

4.1.3 Acetylation using Acetic acid

Physical observation of the treatment shows that it imparted a little of yellow colour unto the fibres. The fibres after drying became more crispy to feel and a little stiffer, that is, its flexibility reduced.

$C_6H_{10}O_5 + CH_3COO^- \rightarrow C_6H_9O_5 + CH_3COOH$ ……..4.3

Equation 4.3: Probable reaction mechanism during CH_3COOH treatment of bagasse fibre

4.1.4 Acrylation using Acrylic acid

This treatment made the fibres whiter and crispy to feel. They initially looked swollen but after drying became normal.

$C_6H_{10}O_5 + CH_2 = CHCO_2H \rightarrow C_6H_{10}O_5 – OCH_2OCH_2CH$……..4.4

Equation 4.4: Probable reaction mechanism during $CH_2=CHCO_2H$ treatment of bagasse fibre

4.2 **FTIR Spectroscopy**

In order to see the effect of the chemicals on the fibre, that is, to see what has actually happened to the OH group present, FTIR examination was carried out. The FTIR of the individual samples was run to reveal the functional groups present and help determine to what extent they have been replaced.

Analyzing the FTIR spectra for the untreated fibre (plate 4.1), we see that the traces of the OH group is very visible and appears broad, comparing with the treated fibres (plates 4.2 – 4.5) the OH group is reduced (that is, only few traces are found) as the peaks (3400 -3650cm^{-1}) are found in the regions due to noise and interference.

However, the FTIR machine uses KBr powder to form the thin transparent pallets. That is, the powdery fibre substance is mixed with the KBr powder to form the pallets which is prepared by putting little of each in a small pestle and mortar and then meshed together to form the pallets. On running the FTIR of just the KBr, it was observed that the OH group was found. This is due to the fact that KBr is highly anhydrous and begins to absorb moisture as soon as it is exposed;

hence, during the period of mixture and pallet formation, the sample may have become a little moist. This is why the OH group trace is found in the region that results due to the noise in the untreated fibres.

The FTIR spectroscopy machine is a very sensitive one such that no matter how insignificant the trace of OH group that lingers it picks the resolution giving the resultant peak. This means that FTIR analysis does not show the extent to which a functional group is present, for instance, it does not tell us if the peak was due to 10molecules of water or just one molecule as long as the molecule is present it picks the resolution and gives the resultant peak.

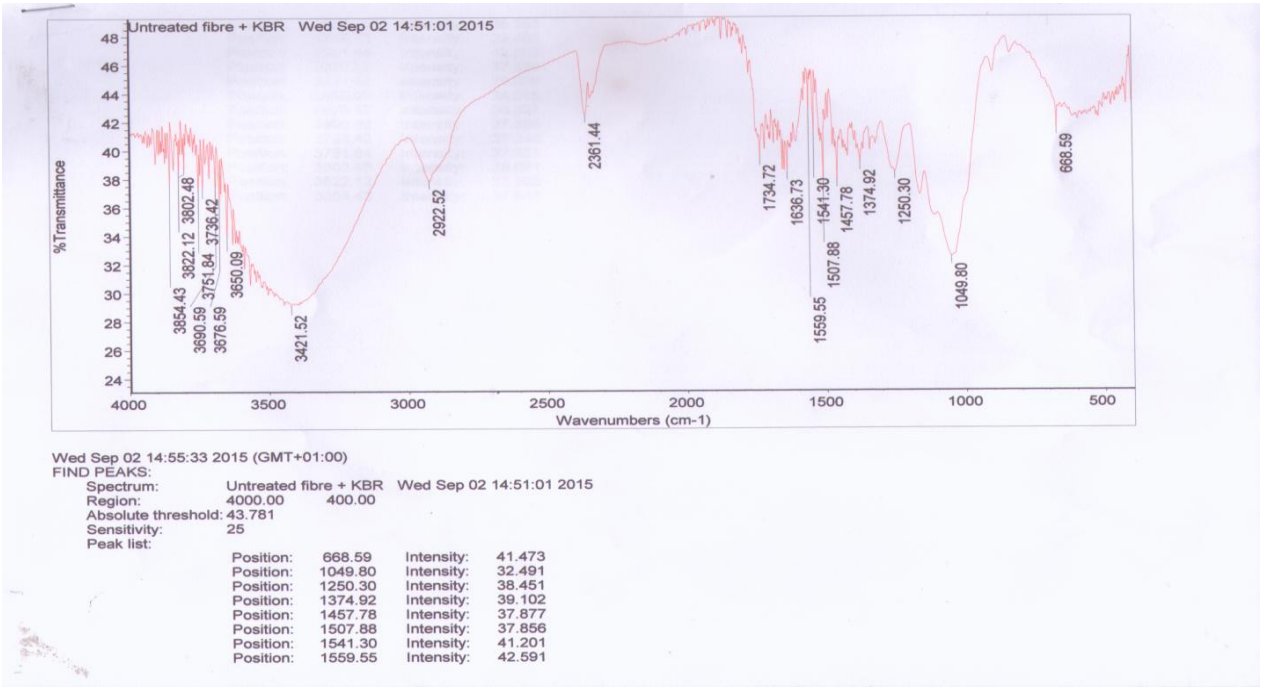
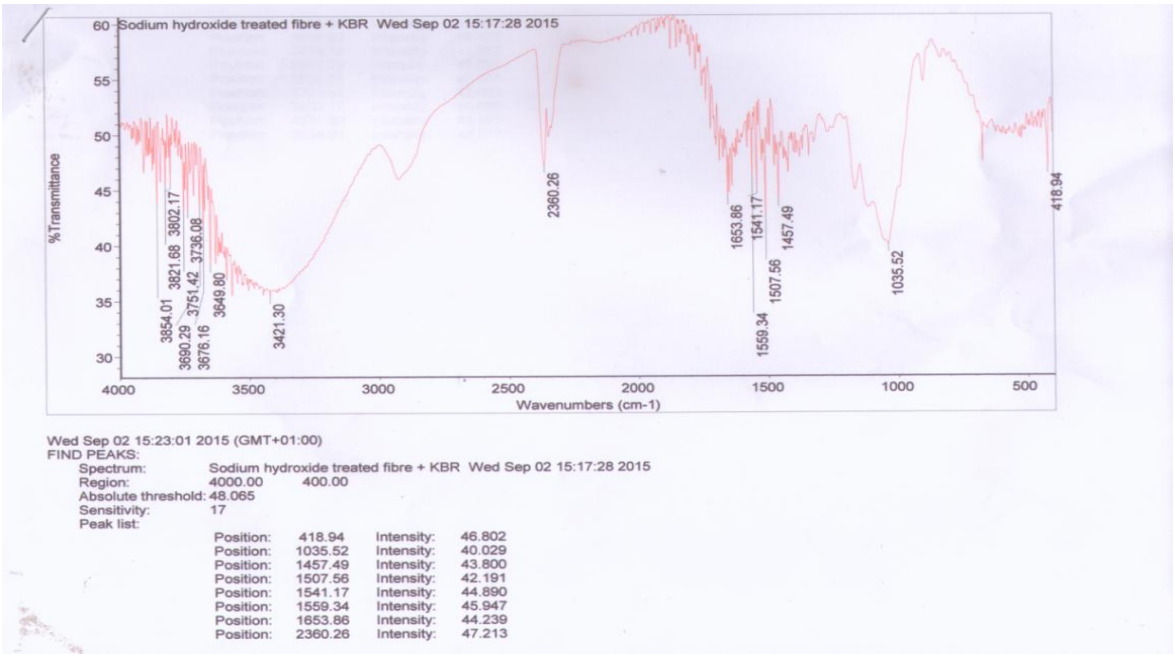


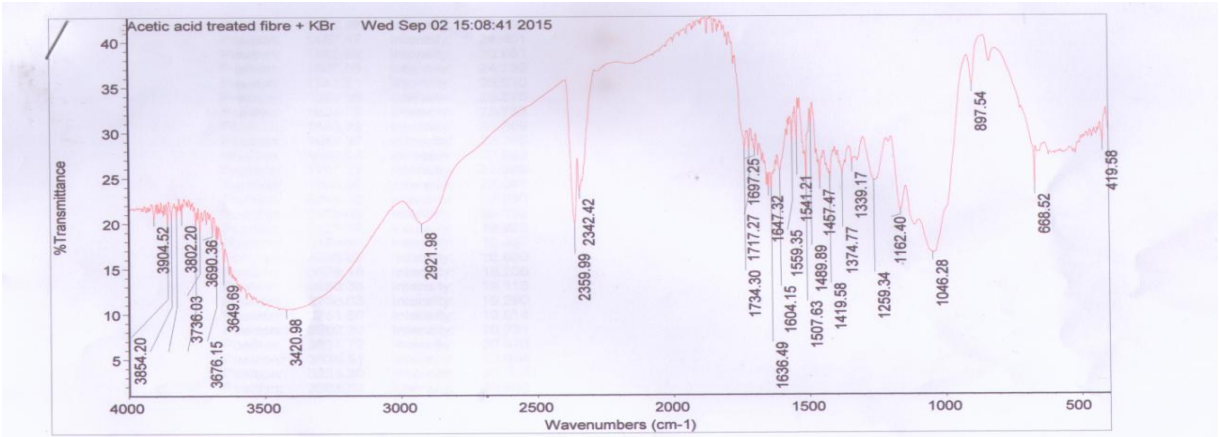
Plate 4.1: Spectrum of Untreated fibre.



Wed Sep 02 15:23:01 2015 (GMT+01:00)
FIND PEAKS:

Spectrum:	Sodium hydroxide treated fibre + KBR Wed Sep 02 15:17:28 2015		
Region:	4000.00	400.00	
Absolute threshold:	48.065		
Sensitivity:	17		
Peak list:			
Position:	418.94	Intensity:	46.802
Position:	1035.52	Intensity:	40.029
Position:	1457.49	Intensity:	43.800
Position:	1507.56	Intensity:	42.191
Position:	1541.17	Intensity:	44.890
Position:	1559.34	Intensity:	45.947
Position:	1653.86	Intensity:	44.239
Position:	2360.26	Intensity:	47.213

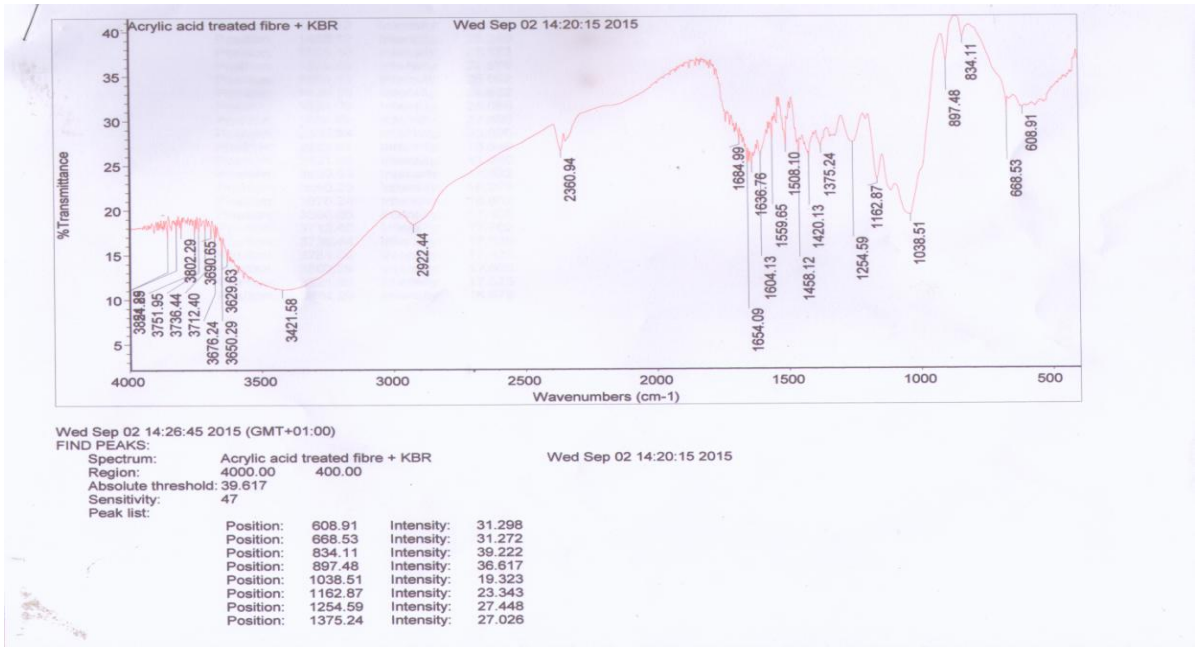
Plate 4.2: Spectrum of Sodium hydroxide treated fi bre



Wed Sep 02 15:14:03 2015 (GMT+01:00)
FIND PEAKS:

Spectrum:	Acetic acid treated fibre + KBr Wed Sep 02 15:08:41 2015		
Region:	4000.00	400.00	
Absolute threshold:	37.959		
Sensitivity:	45		
Peak list:			
Position:	419.58	Intensity:	28.657
Position:	668.52	Intensity:	23.815
Position:	897.54	Intensity:	35.279
Position:	1046.28	Intensity:	16.625
Position:	1162.40	Intensity:	21.356
Position:	1259.34	Intensity:	24.632
Position:	1339.17	Intensity:	26.413
Position:	1374.77	Intensity:	25.353

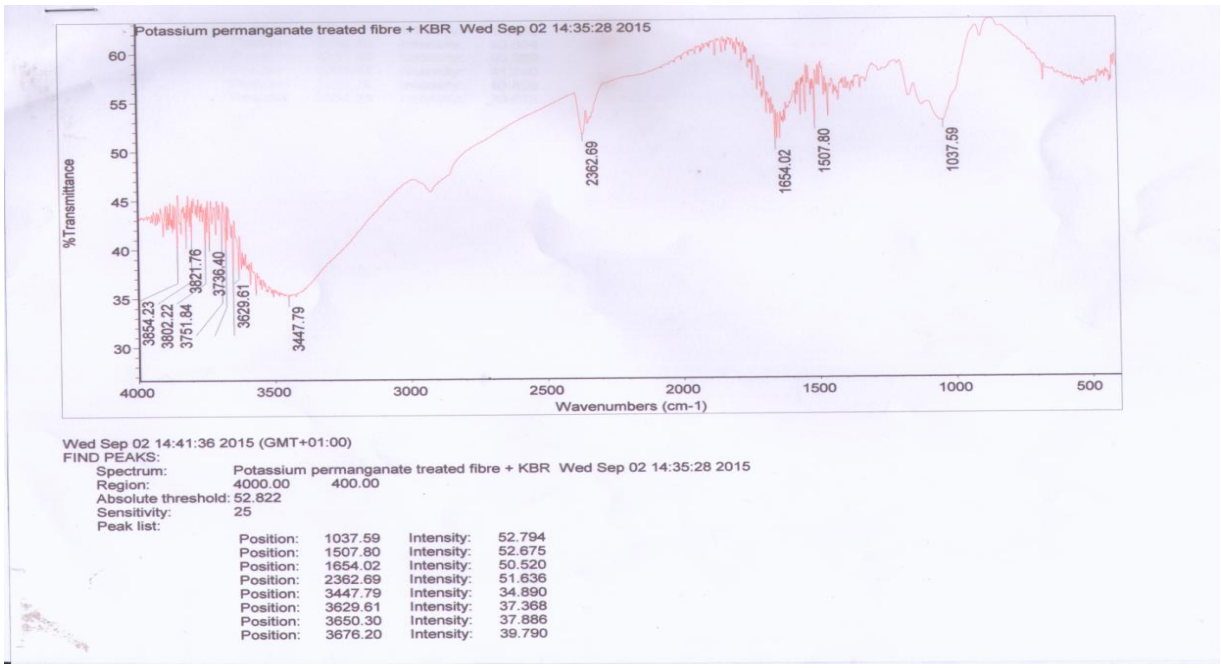
Plate 4.3: Spectrum of Acetic acid treated fibre



Wed Sep 02 14:26:45 2015 (GMT+01:00)
FIND PEAKS:
Spectrum: Acrylic acid treated fibre + KBR Wed Sep 02 14:20:15 2015
Region: 4000.00 400.00
Absolute threshold: 39.617
Sensitivity: 47
Peak list:

Position:	608.91	Intensity:	31.298
Position:	668.53	Intensity:	31.272
Position:	834.11	Intensity:	39.222
Position:	897.48	Intensity:	36.617
Position:	1038.51	Intensity:	19.323
Position:	1162.87	Intensity:	23.343
Position:	1254.59	Intensity:	27.448
Position:	1375.24	Intensity:	27.026

Plate 4.4: Spectrum of Acrylic acid treated fibre



Wed Sep 02 14:41:36 2015 (GMT+01:00)
FIND PEAKS:
Spectrum: Potassium permanganate treated fibre + KBR Wed Sep 02 14:35:28 2015
Region: 4000.00 400.00
Absolute threshold: 52.822
Sensitivity: 25
Peak list:

Position:	1037.59	Intensity:	52.794
Position:	1507.80	Intensity:	52.675
Position:	1654.02	Intensity:	50.520
Position:	2362.69	Intensity:	51.636
Position:	3447.79	Intensity:	34.890
Position:	3629.61	Intensity:	37.368
Position:	3650.30	Intensity:	37.886
Position:	3676.20	Intensity:	39.790

Plate 4.5: Spectrum of Potassium permanganate treated fibre

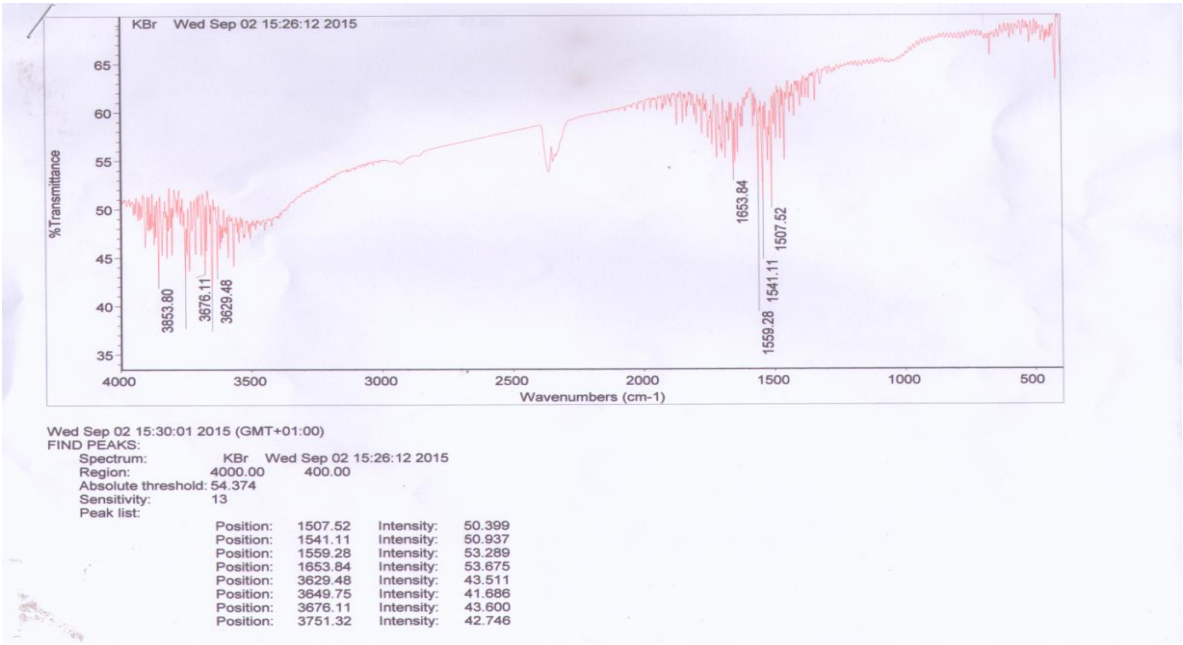


Plate 4.6: Spectrum of Potassium bromide (KBr)

Table 4.1: Band wavelengths of various visible chemical groups for the treated and untreated fibres

Band wavelength (cm^{-1})	Associated chemical group	Untreated bagasse	Sodium hydroxide treated bagasse	Acetic acid treated bagasse	Potassium permanganate treated bagasse	Acrylic acid treated bagasse
3200- 3650	-OH stretching	Dominant	Low	Low	Very low	Low
1250-1260	Lignin peak	Predominant	Removed	Reduced	Removed	Quite dominant
1600-1650	Hemicelulose peak	Predominant	Removed	Reduced	Removed	No change
1720-1750	Pectin wax	Present	Removed	No change	Removed	Removed

To further see what changes has occurred within the fibre morphology due to the chemical effect, Scanning Electron Microscope (SEM) of the fibres was carried out. Back Scattered Images were obtained at a magnification of 500x and 1000x as shown in the plates below:

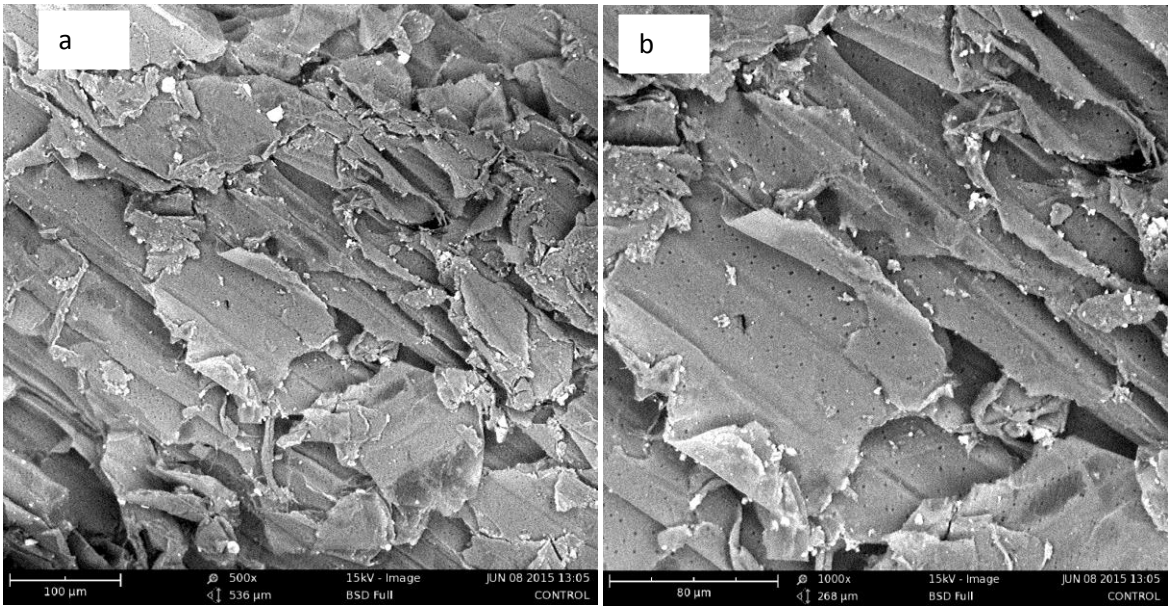


Plate 4.7: SEM micrographs of the untreated fibre at 500x (a) and 1000x (b) respectively.

The SEM of the untreated fibre above (plate 4.7) shows significant amount of flake-like structures sticking to the surface of the fibres, while these flakes may improve mechanical interlocking between the fibre and matrix, they are loosely held unto the fibre and will thus only serve as barrier between the fibre and the matrix.

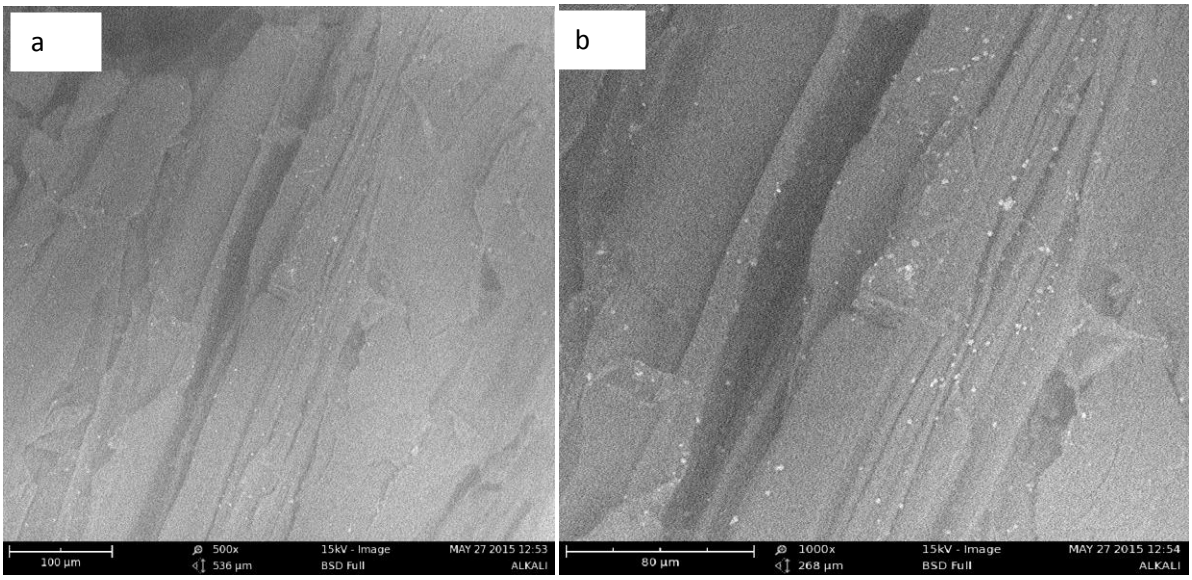


Plate 4.8: An SEM micrographs of the Sodium hydroxide treated fibre at 500x (a) and 1000x (b) magnifications respectively.

In the plate 4.8 above, the flake – like structures have collapsed closing up the pores, the surface roughening has also reduced extensively. All these contribute to the reason why in subsequent characterization of the composite produced, Sodium hydroxide treated fibre composite had poor results.

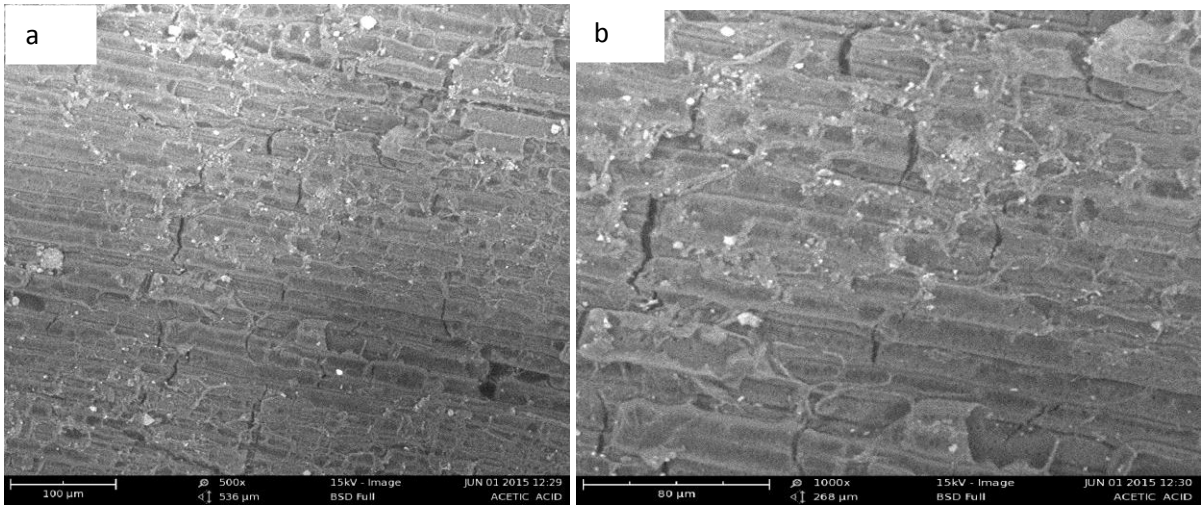


Plate 4.9: SEM micrographs of the Acetic acid treated fibre at 500x (a) and 1000x (b) magnifications respectively.

Here, the roughening has reduced and fewer micropores can be seen, hence the aim of modifying this fibre with acetic acid was not achieved. The flake- like structure has collapsed closing up the pores.

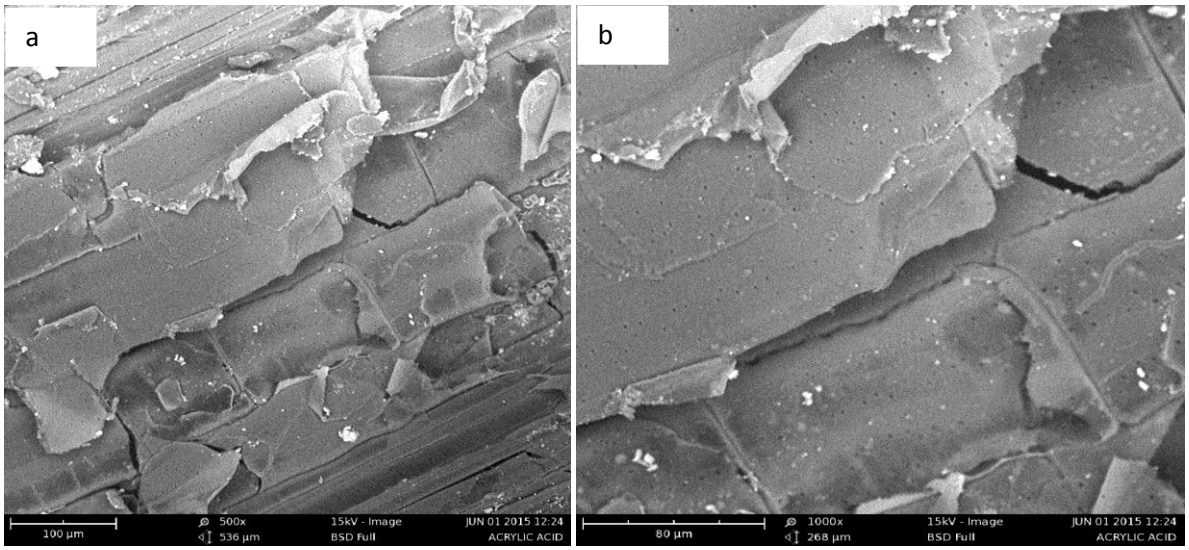


Plate 4.10: SEM micrographs of the Acrylic acid treated fibre at 500x and 1000x magnifications respectively.

We could also see in plate 4.10 that the fibre surface has also become less rough compared to the untreated sample (plate 4.7). This has reduced the pores available for adhesion and better interaction within the composite.

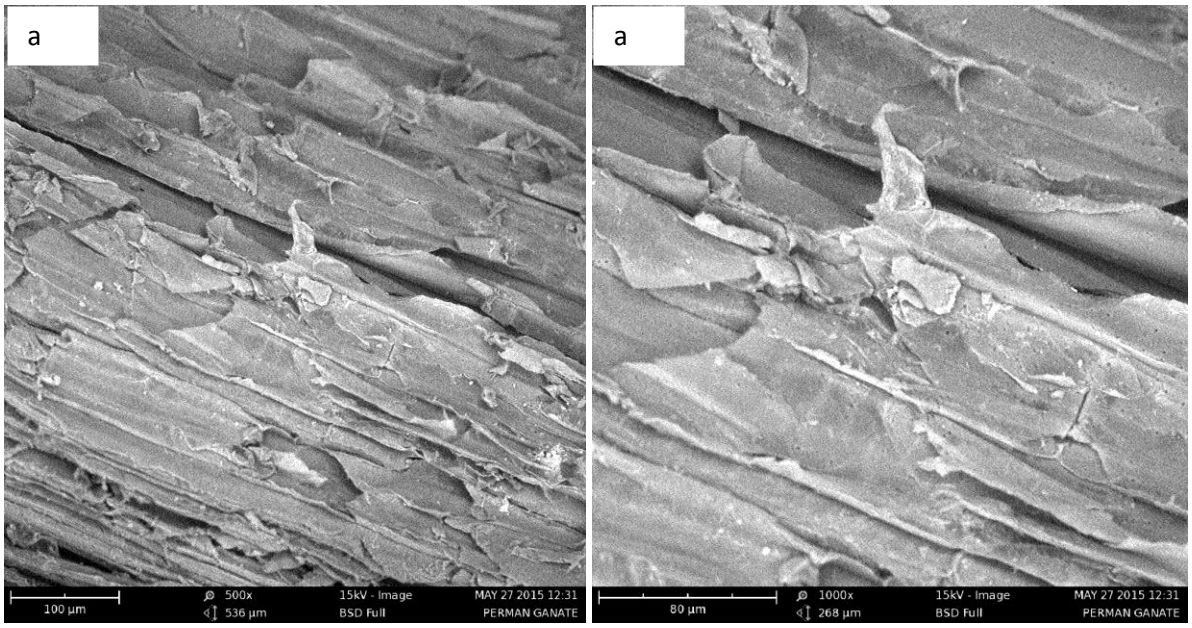


Plate 4.11: SEM micrographs of the Potassium permanganate treated fibre at 500x (a) and 1000x (b) respectively.

This shows more visible micropores compared to the untreated fibre, these micropores provide sites for mechanical interlocking that is, the treatment destroyed the cellular structure of the bagasse fiber, hence reduces void content of the fiber. Although the flake-like structure have been reduced, they are still present but this time not as loosely held as when compared to the untreated fibre in plate 4.7. It also revealed a compressed cellular structure compared to the untreated fibre. In other words, the treatment destroyed the cellular structure of the bagasse fibre (Vilay *et al*., 2008).

Generally, cellulose is unreactive to many chemicals and the OH groups of the microfibrils have very low accessibility (Ahmed *et al*., 2012). The untreated fibre (plate 4.7), shows that the fibre surface itself even before treatment is a little rough; this maybe due to handling and processing (that is rinsing, boiling, and rinsing again before drying to remove soil particles and coloring matter as much as possible). However, plates 4.8, 4.9, and 4.10 showing for sodium hydroxide, acetic acid and acrylic acid respectively, it is observed that the roughening has actually reduced.

In plate 4.8 (Sodium hydroxide treated fibre) the chemical made the fibre more aligned (this causes an increase in crystallinity). This would have been very good if the fibre is to be used alone for some other purposes such as fuel source since water inhibits burning giving it good water absorption properties; but in this case it required to be more rough than crystalline as the roughening increases fibre–matrix interlocking which is the first aim of chemical modification. On plate 4.9 (Acetic acid treated fibre), the roughening also reduced but not as much as in the case of Sodium hydroxide treated fibre, the reduction may have been due to the concentration of the acetic acid used.

As for acrylic acid treated fibre (plate 4.11), there was also a reduction in surface roughening and the fibre's inner structure was made more compact. However, an increase in roughening combined with a little alignment was observed for Potassium permanganate treated fibre (plate 4.11). This is a very good plus as the fibre-matrix interlocking of the composite produced would be enhanced and its mechanical properties improved.

Generally, all natural cellulose fibres are multi-cellular, where a bundle of individual cells bound by natural polymers such as lignin and pectin; in this study, the fibres used depicts a bundle of individual cell which has a hollow cavity called lumen within the unit cells of the biofibers; the presence of which creates decreased bulk density of the fibres which act as acoustic and thermal insulators (Vilay *et al*., 2008).

The plates below also show the micropores in each fibre:

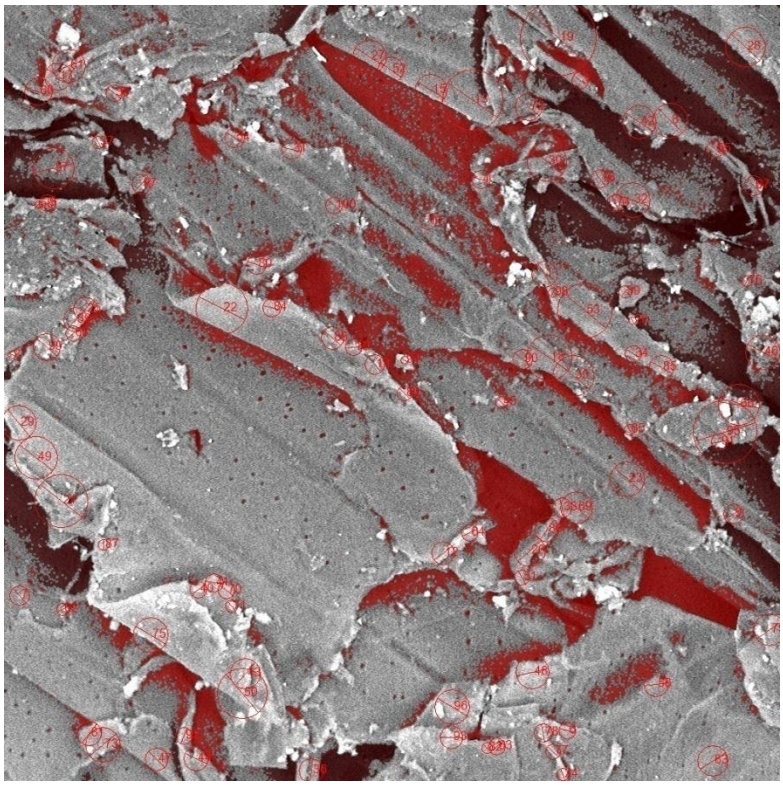


Plate 4.12: SEM micrograph of micropores for the untreated fibre.

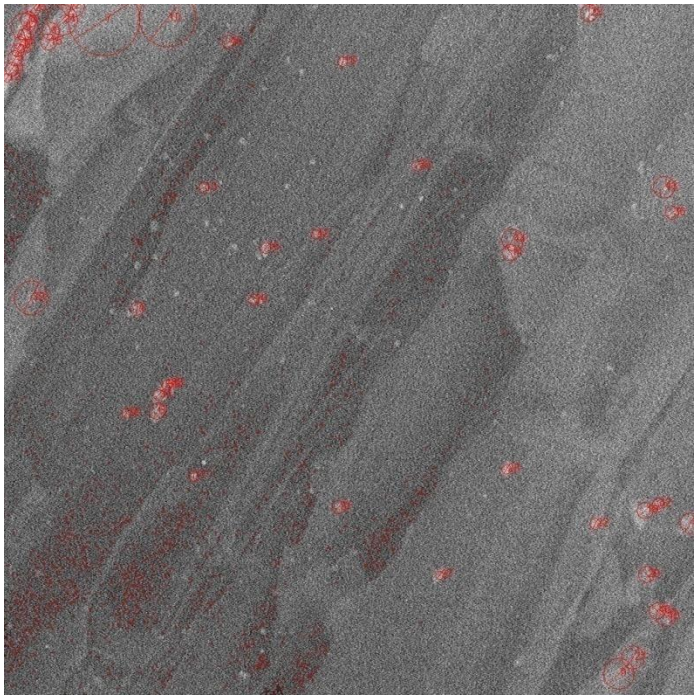


Plate 4.13: SEM micrograph of micropores for Sodium hydroxide treated fibre

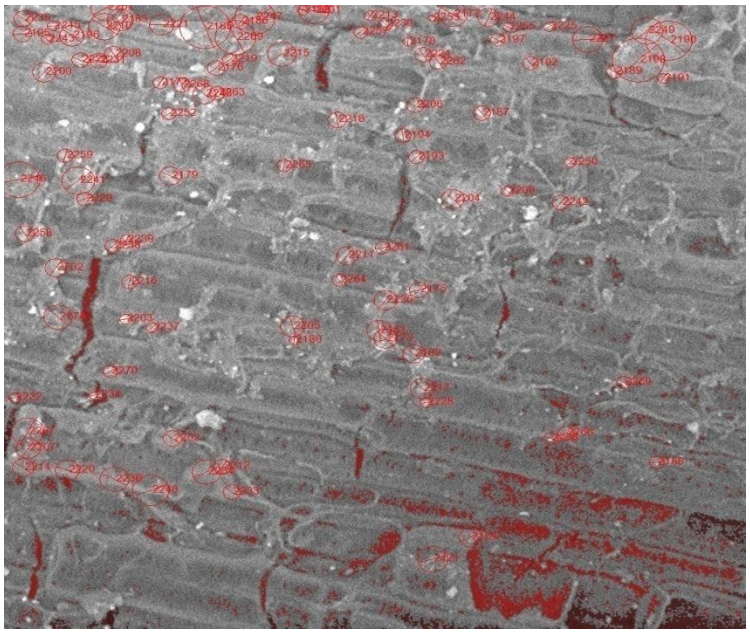


Plate 4.14: SEM micrograph of micropores for Acetic acid treated fibres

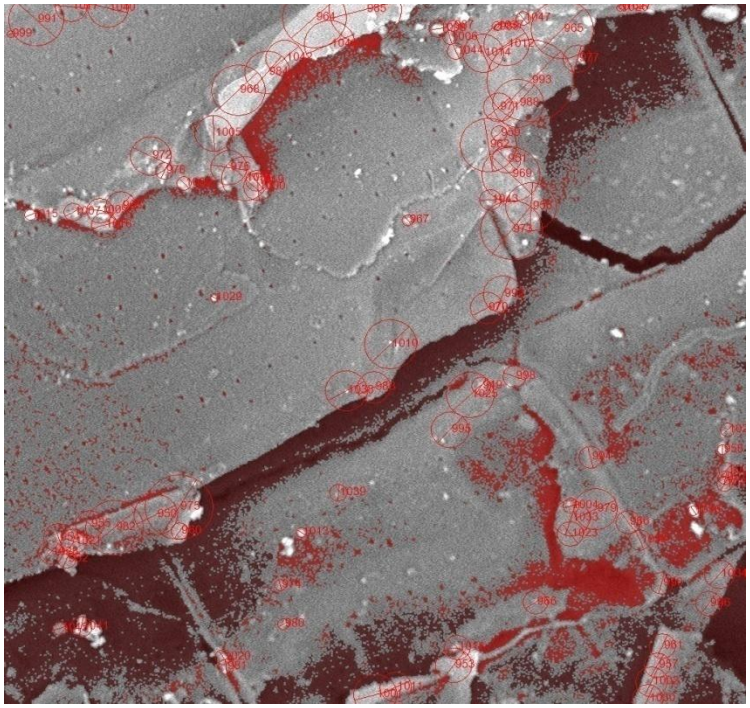


Plate 4.15: SEM micrograph of micropores for Acrylic acid treated fibre

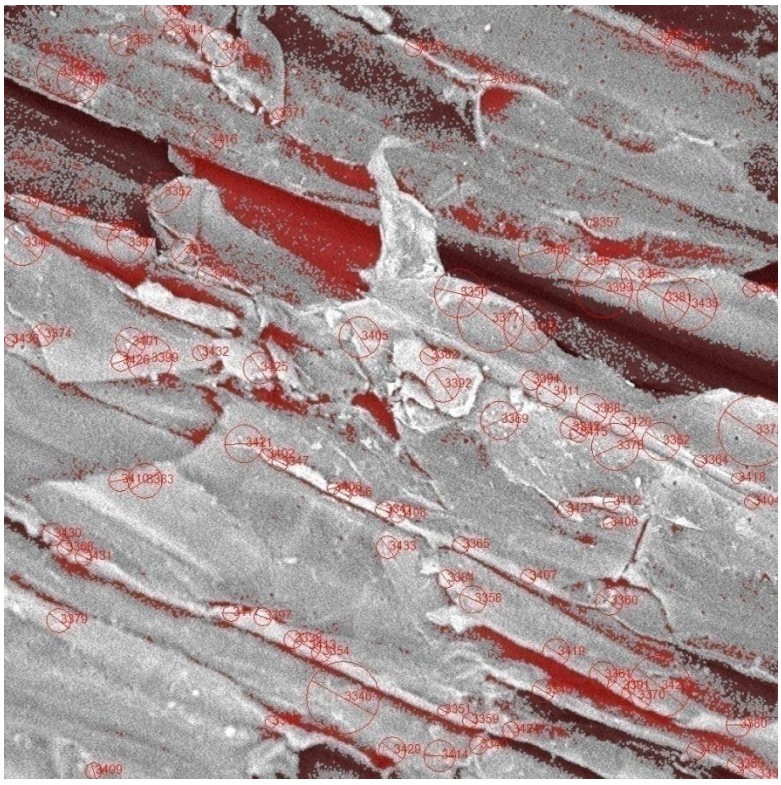


Plate 4.16: SEM micrograph of micropores for Potassium permanganate treated fibre

Looking at the pore micrographs, plate 4.12 shows that a good number of pore sites are available for interaction this is due to the fact that the untreated fibre is seen to be a little rough which as ealier stated may have been as a result of handling and processing. That of sodium hydroxide treated fibre (plate 4.13) is the fewer in number than that of the untreated (plate 4.12) indicating that the Sodium hydroxide had no effect on the fibre, hence, was not modified; this is not in conformity with the studies carried out by other researchers (Vilay, *et al*., 2008; and Xue Li *et al*., 2007) who have used sodium hydroxide as the chemical for fibre modification and obtained improved mechanical properties, this is most likely due to the type of fibre used and even in the case were bagasse fibre was used, the variety was different owing to the fact that there are over 10 verities of sugarcane grown all over the world. Acrylic acid and Acetic acid treated fibres (plates 4.15 and 4.14 respectively) also had reduced pores than the untreated fibre although

higher than that of sodium hydroxide treated fibre. Potassium permanganate treated fibre (Plate 4.16) showed improved pores and has proven to be the best chemical suitable for bagasse fibre modification as far as these four tested chemicals are concerned.

4.3 Water Absorption

5g each of the samples were immersed in water for 24hours, 120 hours, 240hours, 360hours, 480hours, 600hours, and720hours respectively. After which the samples were weighed again in order to calculate their increase or decrease in weight percentage.

Formula used was given as:

Water absorption (%) = $[W - W_O / W_O] X 100$

Where, W = final weight and W_O = initial weight

The result is shown in figure 4.1 below reveals that there was no significant effect on the water absorption level for the unsaturated polyester (1-2.2%) as there were no fibers carrying the OH group and other waxy substances such as lignin, pectin, and hemicelluloses to facilitate moisture absorption. The untreated fiber composite on the other hand absorbed water over time; between 5-7% while the chemically treated fibers also absorbed water but not as much as the untreated fibers in some cases like for acetic acid. Sodium hydroxide and acrylic acid treated fiber composite also absorbed water almost as much as the untreated fiber. The potassium permanganate treated fibre composite absorbed water between 4-5.2% within the thirty days of immersion in water. This contradicts previous works that has been carried out using sodium hydroxide and acetic acid; these variations may have been due to the fiber in question or even

variation within the same variety. As for bagasse fibre, there are over 10 varieties of sugarcane from which the fibre can be extracted.

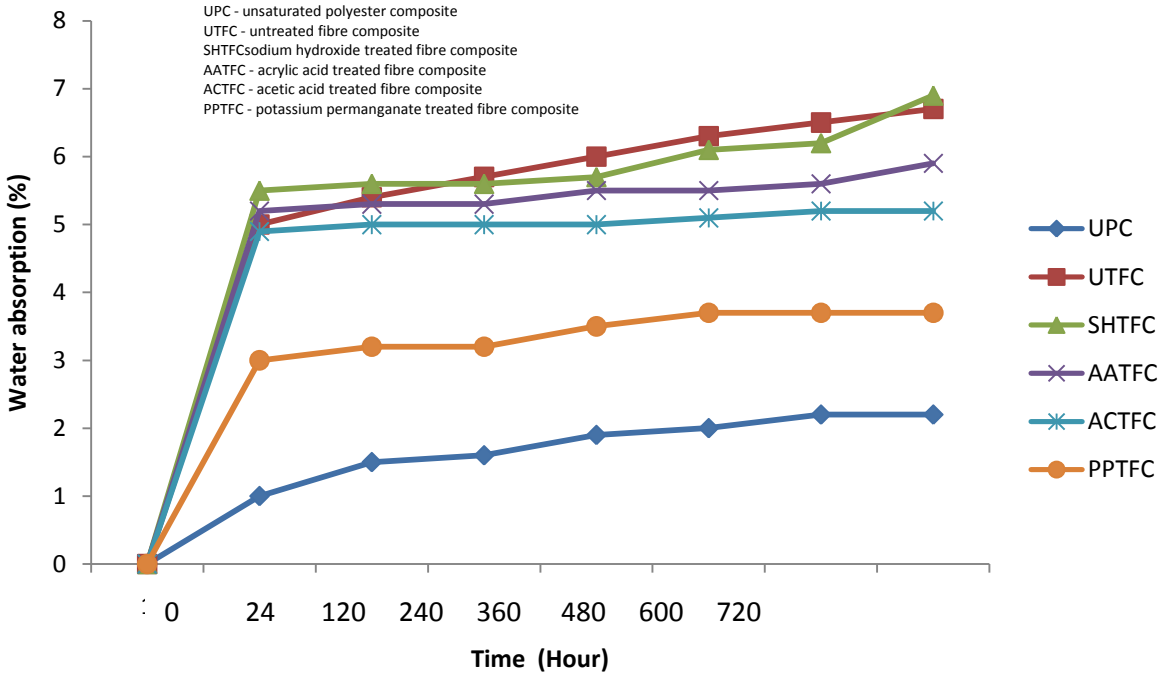


Figure 4.1: Line graph of the water absorption of composites

4.4 **Tensile Properties**

Tensile strength

Strength is a very important factor in terms of performance no matter the end use. The strength is a measure of the force required to stretch the composite up to its breaking point. The strength determines the amount of load it can carry and how far (durability) it can carry the applied load. From the figure below (Figure 4.6), the strength of PPTFC increased to 77.85Mpa which is about 40% higher than the untreated fibre. SHTFC decreased to 52.50Mpa which is lower than the untreated fibre, this indicates that the treatment did not modify the fibre, also in the case of

AATFC, no change was observed. The strength of the UPC at 68.50Mpa is quite worrisome as the fibres were expected to reinforce the UPC thereby improving the strength; but this was not the case as only the PPTFC increased in strength when compare to the UPC and UNTFC. The decrease in SHTFC may have been due to the fact that the time frame for treatment and treatment parameters were too harsh and may have lead to degradation of the lignocelulosic substance in the fibres and as such affected the expected end results. A similar effect was observed by Maya *et al*., (2007) using alkali and silane treatment. Another reason may have been due to the variety of the fibre used as previous studies in the work carried out by Asegekar and Joshi in 2013 showed that the general tensile strength of bagasse fibre is low and varies between the different variations.

The figure below gives a clear picture of the effect of the tensile strength obtained

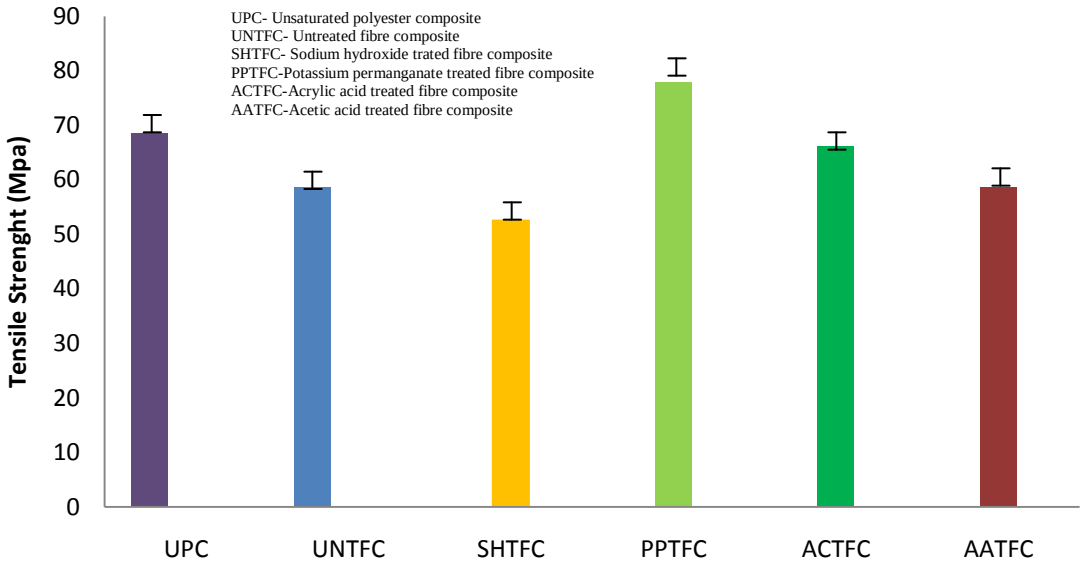


Figure 4.2: Effect of chemical treatment on the tensile strength of the composite.

Tensile modulus:

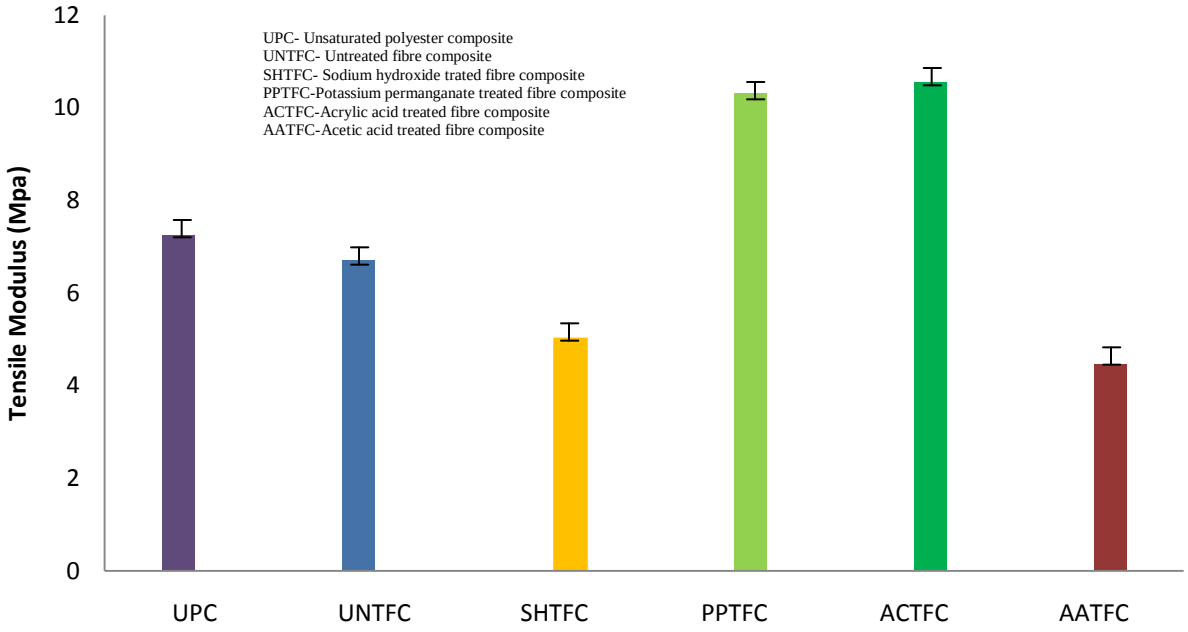


Figure 4.3: Effect of chemical treatment on the tensile modulus of the composite.

Modulus is a measure of stress over strain, that is, the amount of load the material can carry before catastrophic extension (strain) occurs. This is very vital as it determines to a great extent the end use for which the material can be put.

Alkali treatment using Sodium hydroxide has been known (Vilay *et al*., 2008 and Xue Li *et al*., 2007) to be very effective for surface modification of natural fibres used as reinforcement in composites, but so far, it has given rather an unexpected result (5.02Mpa); this maybe due to the variation in the bagasse fibre used, aside from the fact that there are various varieties; maturation period also affects the fibre properties to an extent (Asagekar and Joshi 2013). However, PPTFC with a value of 10.32Mpa and ACTFC with a value of 10.55Mpa were both higher than the UNTFC (6.70Mpa). This reveals the potential of Acetic acid if the concentration or treatment time is increased.

4.5 **Flexural Properties**

The results obtained is as shown in the figures below

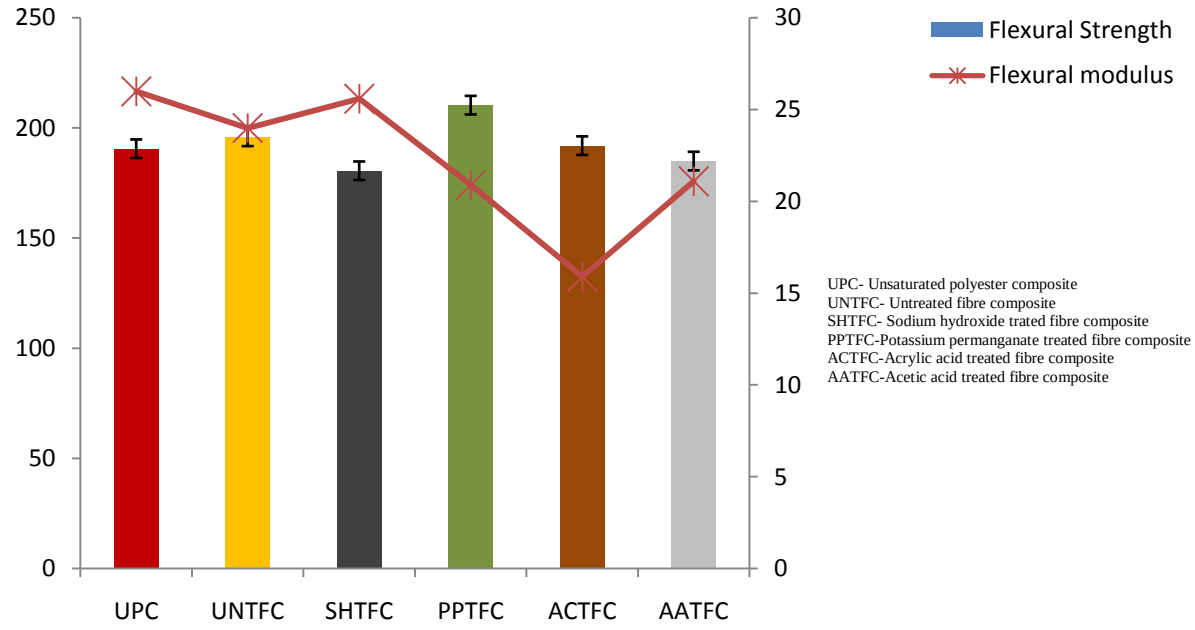


Figure 4.4 Effect of chemical treatment on the flexural strength and modulus of the composite

From figure 4.4, PPTFC increased in flexural strength (210.38Mpa) in flexural strength. While others decreased. However, the UPC at 190.6Mpa was found to be lower than the UNTFC at 195.22Mpa. It is observed that there is a significant drop in the modulus (figure 4.4), this is in agreement with studies on bagasse fiber carried in 2013 and the drop in modulus varies not just in different varieties but also by maturation time within the same variety. Asegakar and Joshi (2013).

4.6 Impact Test

The impact test measures the energy required to break the sample by a swing carrying a specified load under standard conditions. Polymeric materials have their impact energies related to their toughness which could be seen when they collide against other objects or materials. The charpy impact tester was used in carrying out this test and its results are as shown in figure 4.5 below:

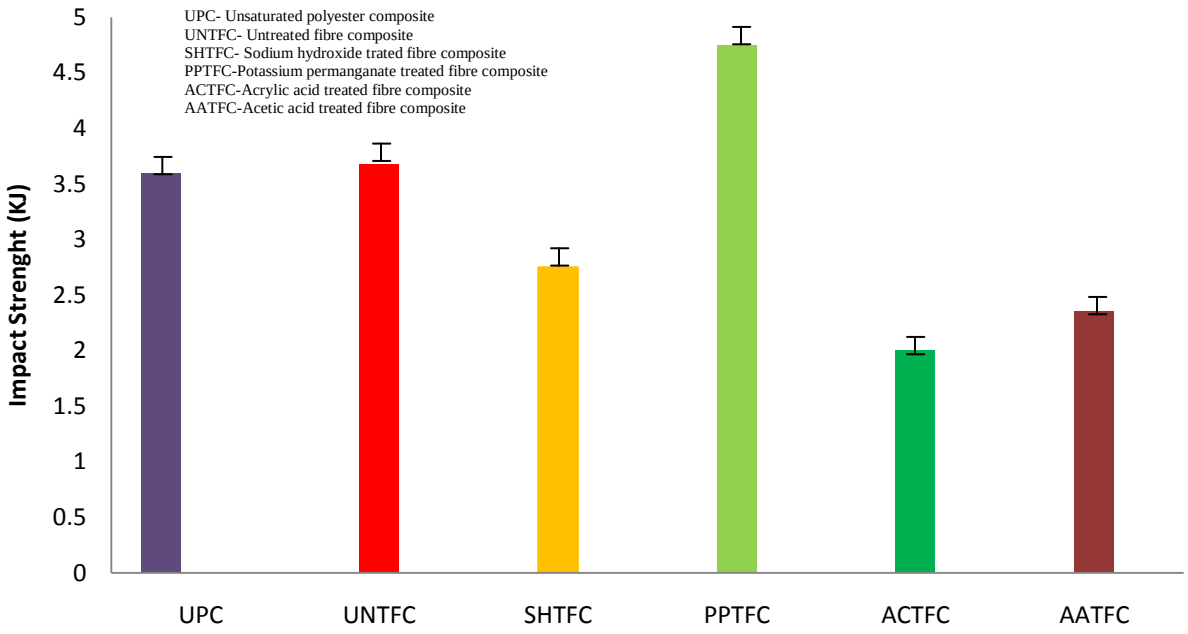


Figure 4.5: Effect of chemical treatment on impact strength of the composites

The impact strength of potassium permanganate treated composite was found to be higher at 4.95KJ than the unsaturated polyester which is 4.0KJ, the untreated fibre composite was a little higher than unsaturated polyester composite while all others had a significant decrease the least been acrylic acid treated composite at 2.0KJ. Again, the more open pores available in the open structure of potassium permanganate is most likely responsible for the excellent strength displayed.

4.7 Hardness Test

The hardness test is also to reveal the increase or decrease in strength of the composite; this is as shown in figure 4.6 below:

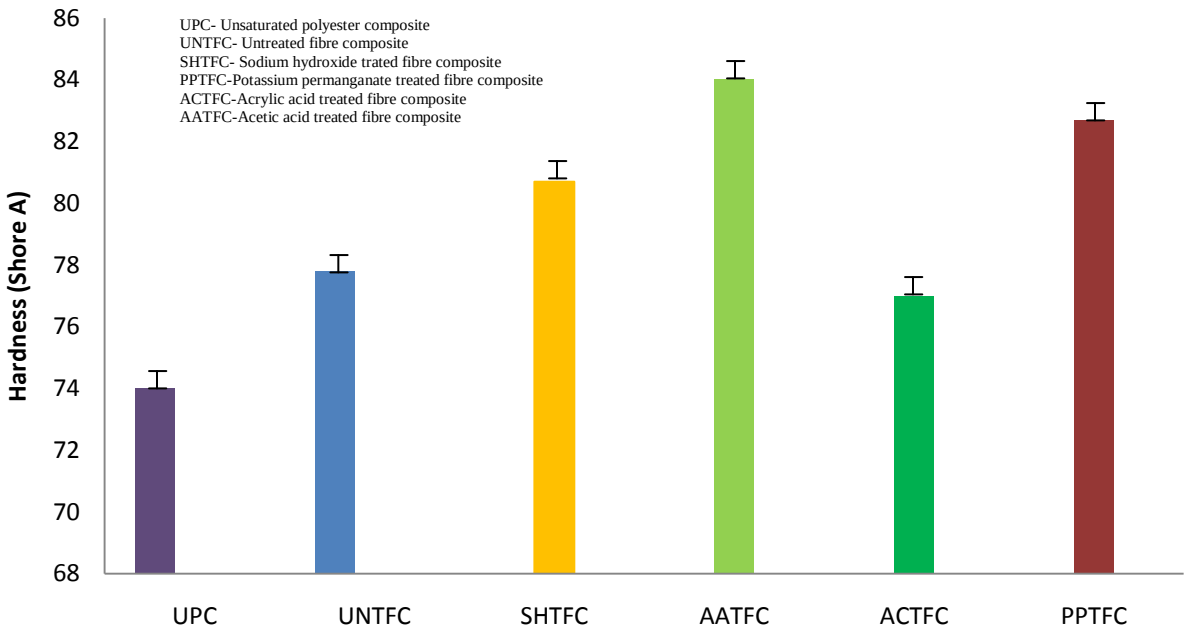


Figure 4.6: Effect of chemical treatment on the hardness of the treated composite

The figure 4.6 above shows that AATFC was the hardest with a value of 84 Shore A, PPTFC and SHTFC followed with values of 82.7 and 80.7 Shore A respectively. Although, all samples increased significantly, ACTFC reduced in hardness (77.0 Shore A) when compared to the UNTFC.

4.8 Morphological Analysis

It gives an image to show clearly the fibre–matrix interphase of the composites; both treated and untreated. The micrographs are given in the plates 4.1–4.6 below:

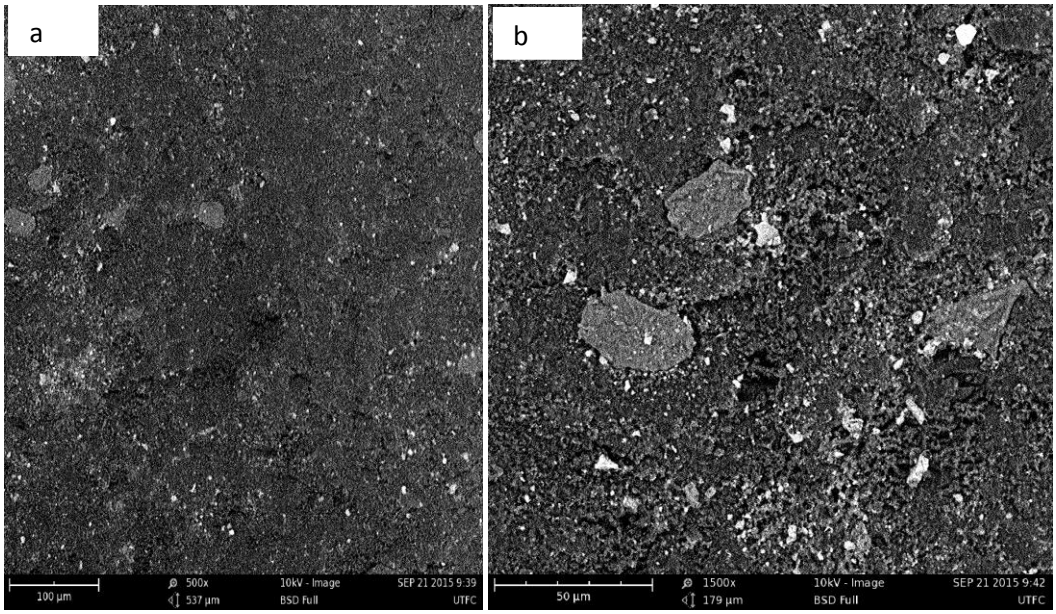


Plate 4.17: Micrograph of untreated fibre composite 500x (a) and 1500x (b) magnifications, respectively.

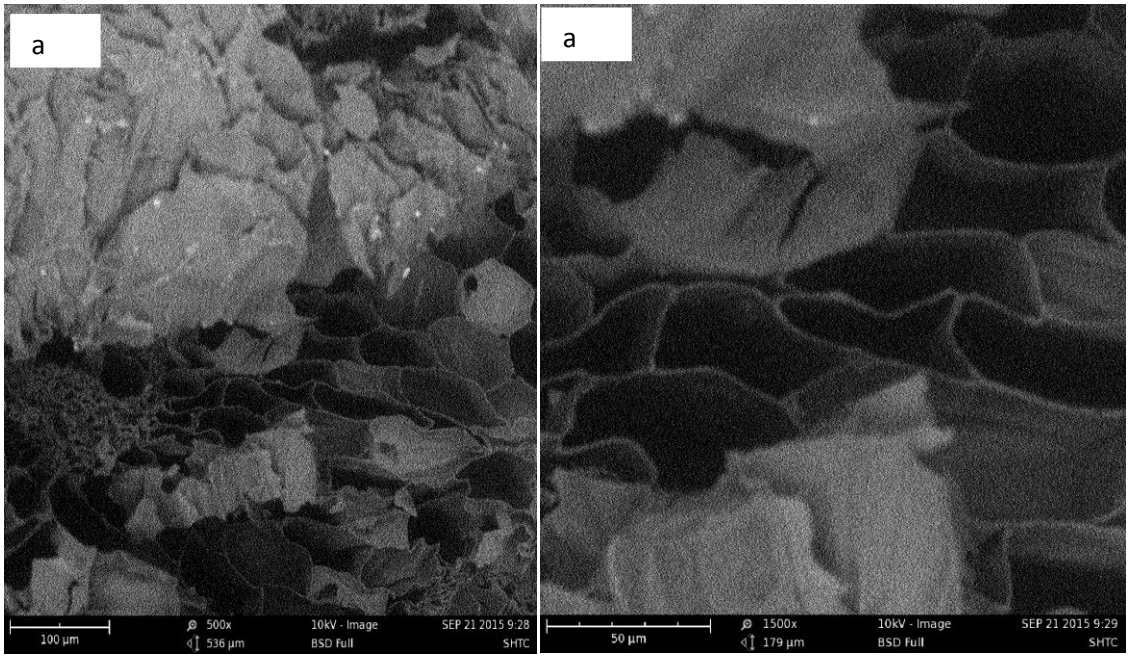


Plate 4.18: Micrograph of Sodium hydroxide treated fibre composite at 500x (a) and 1500x (b) magnifications, respectively.

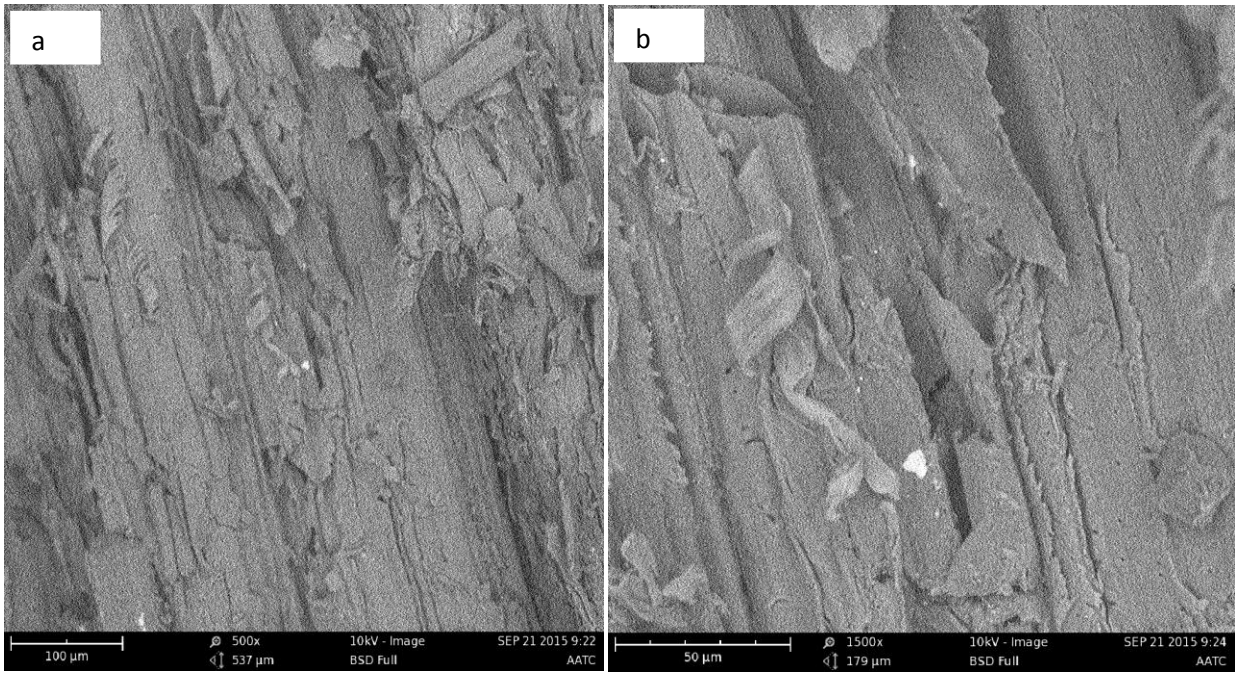


Plate 4.19: Micrograph of Acrylic acid treated fibre composite at 500x (a) and 1500x (b) magnifications, respectively.

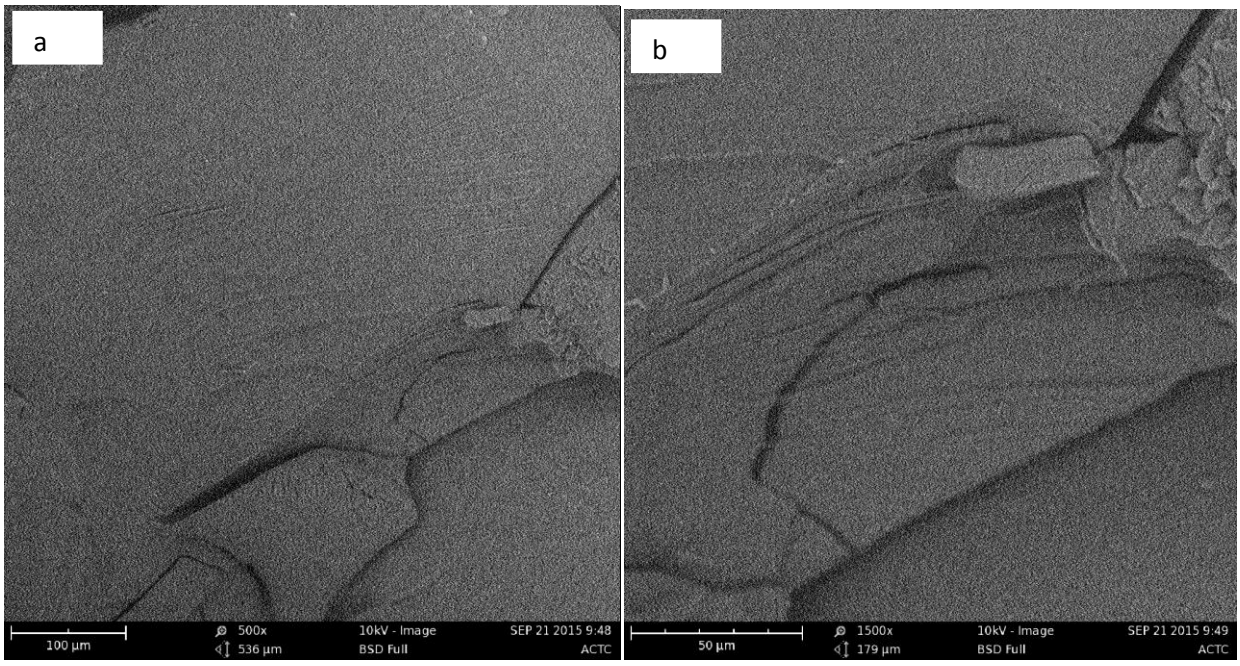


Plate 4.20: Micrograph of Acetic acid treated fibre composite at 500x (a) and 1500x (b) magnifications, respectively.

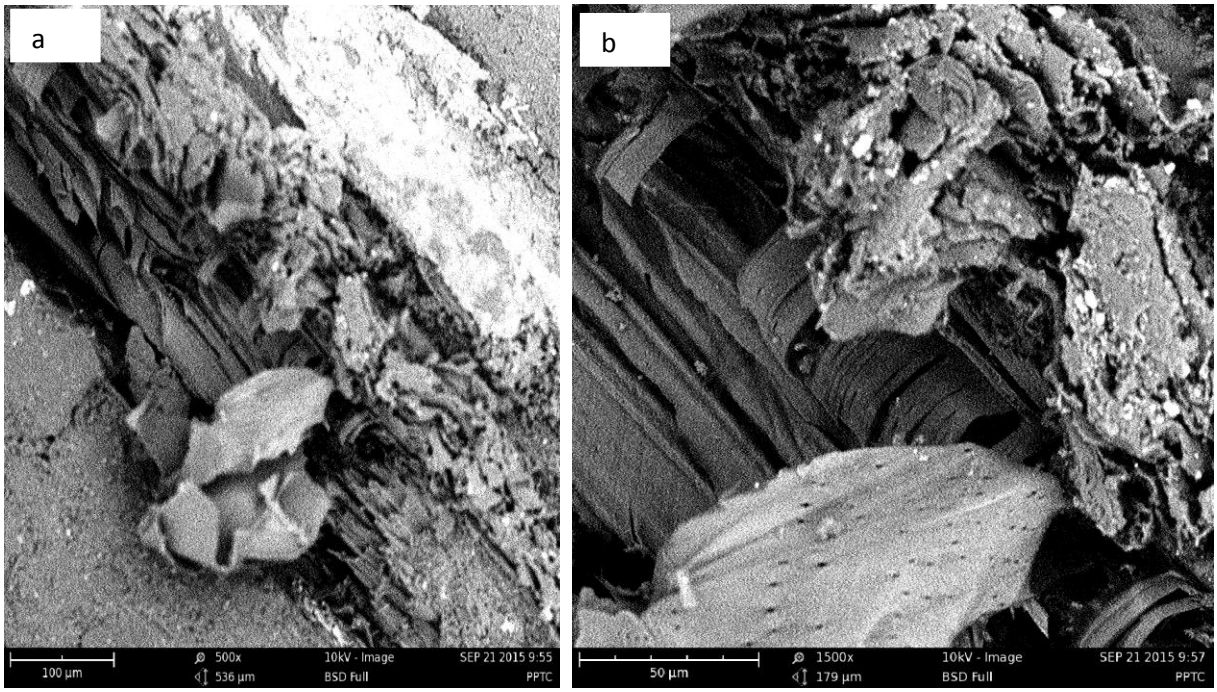


Plate 4.21: Micrograph of Potassium permanganate treated fibre composite at 500x (a) and 1500x (b) magnifications, respectively.

Looking at the plates (4.11 – 4.15) of composite micrographs above it is observed that plate 4.15 (potassium permanganate treated fibre composite) has a different internal morphology in which the matrix had a little of debonding due to fibre pullout, however, the $KMnO_4$ succeeded in modifying the fibre and hence the composite. Also it can be seen that the polyester resin adhered to the fibre surface owing to improved interaction; this has supported good adhesion between the potassium permanganate treated fibre and the polyester matrix and following the tensile strength result one would say it is reinforcing.

SHTFC (Plate 4.12) showed the presence of voids (empty spaces) even in the composite, this is most likely responsible for the high amount of water absorbed (up to 7%) by the composite as these openings are those of such through which water can easily pass through.

Plate 4.13 (ACTFC) showed in the micrograph that the fibre/matrix bonding is poor. While that of the AATFC showed no site of bonding at all, this implies that no improvement in interaction occurred between the fibre and the matrix.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

This research had its focal point on the investigation of the effect of various chemical treatments on bagasse natural fibre reinforced composites with the aim of pointing out the most effective chemical treatment of the fibre reinforced composite using unsaturated polyester as the polymer matrix.

Bagasse fibre was prepared from scratch. After milling of the juice from the sugarcane ; the pulp (inner part) was separated from rind (outer part) and then processed to obtain the fibre. The bundles of fibres were then divided into five different portions; one was kept in that form as control and the rest were then treated with the various chemicals. Scanning electron microscopic studies were carried out on the fibres to see what morphological changes had occurred within the fibres as a result of the chemical treatments. FTIR spectroscopy analysis was also carried out on the fibres to see the functional groups present after treatment which revealed the effect the chemicals had on the fibres. Various tests were carried out on the composites to see the effect of these treatments on their physical, mechanical and morphological properties. Comparisons were made based on the results obtained and the following summary is therefore obtained: On the physical properties, the treated fibres became more loose and there was change in color which was most visible in Potassium permanganate treated fibres.

The untreated fibre surface itself was observed to have been slightly rough and may have been as a result of handling and processing. It was observed that the surface area of Potassium permanganate treated fibre increased and roughened (Plate 4.5), creating more micropores (Plate 4.10) which improved fibre / matrix interaction for better adhesion. In the other chemically

treated fibres the roughening was not as much as the untreated fibre (Plate 4.1) and the micropores produced were fewer than expected (Plates 4.11 – 4.14).

On the hardness test carried out, the treatments had significant effect in increasing the hardness as all the treated samples (SHTFC, AATFC, ACTFC, and PPTFC) were higher with values of 80.7, 84.0, 77.0, and 82.7 Shore A respectively when compared to the controlled samples.

On the tensile strength, PPTFC had better tensile strength of 77.85Mpa. SHTFC had a poor tensile strength of 52.5Mpa which was found to be lower than the untreated fibre composite of 58.57Mpa. This shows that only the $KMnO_4$ treatment led to modification. The tensile modulus also followed similar pattern, but the ACTFC had better modulus of 10.55Mpa and PPTFC had a modulus of 10.32Mpa, it is observed that the difference of about 1% is negligible.

On the impact test, there was also a positive result. This is determined by the energy required to bring about the crack initiated as the impact strength reflects the energy for the propagation of the existing crack. An optimum interaction between the fibre and the matrix is essential to have good impact strength. Impact damages initiates' matrix cracking, fibre – matrix debonding and delamination at relatively low impact energies; and fibre fracture and fibre pull – outs at higher impact energies.

On water absorption test, the treated samples took in little amount of water over time with the unsaturated polyester absorbing less at 1-2.2%; the percentage increase is therefore reasonable. However, following the trend of the results obtained from the potassium permanganate and acetic acid treated composite samples shows that the water absorption should have all been lower than that of the untreated fiber composites significantly; that is, the volume of water before and after the experiment should have relatively remained the same implying that the hydrophilic

nature of the fibre had reduced and so water intake is also reduced. Reduction in water absorption due to chemical treatment was also recorded by Ramakrishma and Rai (2006); and Carrillo et al., (2010). The idea behind chemically treating these fibres is to make them more hydrophobic than hydrophilic so as to create a good adhesion environment, this was not so as the composite increased in its after weight although, the increase could be said to be insignificant depending on the realistic end use, hence, not very good for use as buildings materials in areas that are water logged.

On the s SEM studies, the lumens of the fibres that were chemically treated collapsed closing up most of the pore sites, except in potassium permanaganate treated fibre where more sites were created thus improving fibre – matrix adhesion as shown in plate 4.5. Fibre pullout is a common composite defect (Sydenstricker *et al*., 2003; and Sathishkumar *et al*., 2012).

5.2 **Conclusion**

This research work successfully produced bagasse reinforced composites of various chemical treatments using hand lay – up technique and the following conclusions were drawn:

Chemical treatment had very little effect on the fibre- matrix adhesion and the resulting mechanical properties of the composites produced as out of the four chemicals used, only PPTFC had improved tensile strength and modulus at 77.85Mpa and 10.32Mpa. Although, AATFC had a close modulus of 10.55Mpa. The flexural strength of PPTFC was 210.38 Mpa, which was about 15% higher than the UNTFC. In the case of flexural modulus, PPTFC decreased by about 10% with a value of 21Mpa as oppose to 25.40Mpa for the UNTFC. However, little variations were observed as in the water absorption test carried out; all samples absorbed more water than

the UPC which was between 1 – 2.2%. PPTFC absorbed less water between 3 – 3.7% after 30 days of immersion in water when compared to the UNTFC. The UNTFC and SHTFC absorbed more water between 5 – 7%. The drying helped in removing most of the water content which is reflected in the water absorption test. Handling and processing has great effect on the properties and final behavior on the fibre.

The SEM revealed that the Potassium permanganate treated fibre was modified by the chemical which led to improved compatibility, increase in adhesion and fibre/matrix interaction, less water absorbtion, resulting in better mechanical properties when used to produce the composite.

Therefore, it can be concluded that under the environmental conditions for which this research work was carried out, Potassium permanganate is a more suitable chemical treatment for bagasse fibre obtained from the sugarcane variety NG57-258 and can be used as reinforcement while others can only be used as fillers.

5.3 Recommendations

Bagasse fibre is readily available due to irrigation of sugarcane during off season. Hence, it is important to do a thorough research studies on this fibre in order to maximize its use, improve our economy, and create a waste free environment.

i. The resin used was unsaturated polyester, other resin such as epoxy, polyethylene, recyclable and biodegradable thermoplastics such as polyethylene teraphtelate etc can also be used with bagasse fibre.

ii. The time of treatment was three (3) hours, in subsequent research the time could be increased to see if more efficient result would be obtained.

iii. Hands full of chemicals are available, only four (4) has been chosen for this research. In subsequent research, other chemicals could be used so as to reach a standard as far as bagasse fibre is concerned.

iv. The bagasse fibre was used in strand form, it could be crushed and other forms of composite production such as injection molding used in producing the composites.

v. FTIR spectroscopy was used as the method of identifying OH functional group in the fiber, other methods of identifying this functional group in cellulosic fibres such as Isocyanate back titration could be used.

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APPENDICES

APPENDIX A: WATER ABSORPTION OF TREATED AND UNTREATED COMPOSITES

Table C 2: Effect of chemical treatment on the flexural modulus

s/no	composite type	water absorbtion (%)						
		1(d)	5(d)	10(d)	15(d)	20(d)	25(d)	30(d)
1	UPC	1.0	1.5	1.6	1.9	2.0	2.2	2.2
2	UNTFC	5.0	5.4	5.7	6.0	6.3	6.5	6.7
3	SHTFC	5.5	5.6	5.6	5.7	6.1	6.2	6.9
4	AATFC	5.2	5.3	5.3	5.5	5.5	5.6	5.9
5	ACTFC	4.9	5.0	5.0	5.0	5.1	5.2	5.2
6	PPTFC	3.0	3.2	3.2	3.5	3.7	3.7	3.7

APPENDIX B: TENSILE STRENGHT AND MODULUS OF COMPOSITES.

Table B1: Effect of chemical treatment on the tensile strength

Table B 1: Effect of chemical treatment on the tensile strength

s/no	composite type	tensile strength (Mpa)
1	Unsaturated polyester	68.50
2	Untreated fibre	58.57
3	Sodium hydroxide treated fibre	52.50
4	Acetic acid treated fibre	58.60
5	Acrylic acid treated fibre	66.20
6	Potassium permanganate treated fibre	77.85

Table B2: Effect of chemical treatment on the tensile modulus

s/no	composite type	tensile modulus (Mpa)
1	Unsaturated polyester	7.26
2	Untreated fibre	6.70
3	Sodium hydroxide treated fibre	5.02
4	Acetic acid treated fibre	4.46
5	Acrylic acid treated fibre	10.35
6	Potassium permanganate treated fibre	10.32

APPENDIX C: FLEXURAL STRENGHT AND MODULUS OF COMPOSITES

Table C 1: Effect of chemical treatment on the flexural strength

s/no	composite type	flexural strength (Mpa)
1	Unsaturated polyester	190.60
2	Untreated fibre	195.22
3	Sodium hydroxide treated fibre	180.60
4	Acetic acid treated fibre	185.00
5	Acrylic acid treated fibre	192.00
6	Potassium permanganate treated fibre	210.38

Table C 2: Effect of chemical treatment on the flexural modulus

s/no	composite type	flexural modulus (Mpa)
1	Unsaturated polyester	26.00
2	Untreated fibre	25.40
3	Sodium hydroxide treated fibre	25.60
4	Acetic acid treated fibre	20.91
5	Acrylic acid treated fibre	15.90
6	Potassium permanganate treated fibre	21.10

APPENDIX D: IMPACT STRENGHT OF COMPOSITES

Table D1: Effect of chemical treatments on the impact strength of the composite

s/no	Impact Strength (KJ)		
Composite type	1st reading	2nd reading	Average
1. Unsaturated polyester	3.00	4.20	3.60
2. Untreated fiber	3.40	3.95	3.68
3. Sodium hydroxide treated fiber	2.50	3.00	2.75
4. Potassium permanganate treated fiber	6.00	3.50	4.75
5. Acetic acid treated fiber	2.00	2.00	2.00
6. Acrylic acid treated fiber	2.70	2.00	2.35

APPENDIX : HARDNESS TEST OF COMPOSITES

Table D1: Effect of chemical treatment on the hardness of the composites

s/no	Composite	Hardness (Shore A)			
		1st reading	2nd reading	3rd reading	Average
1	Unsaturated polyester	63.0	81.0	78.0	74.0
2	Untreated fiber	72.5	78.6	82.4	77.8
3	Sodium hydroxide treated fibre	87.0	82.0	73.0	80.7
4	Acetic acid treated fibre	85.0	89.0	78.0	84.0
5	Acrylic acid treated fibre	78.0	76.0	77.0	77.0
6	Potassium permanganate treated fibre	80.0	86.0	82.0	82.7