PRODUCTION AND OPTIMISATION OF REINFORCED POLYMER COMPOSITE ROOFING TILES USING CARBONISED FIBRES (*Eucalyptus globulus* SAWDUST AND LOCUST BEAN POD HUSK) WITH CLAY

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ABSTRACT

The production of Hybrid Polymer Composite (HPC) roofing tile from polymer and agricultural wastes, with clay as additive was borne out of the desire to convert waste to wealth and to promote local content in the building industry. Used low density polyethylene (LDPE) popularly known as pure water sachet was reinforced with carbonised natural fibre produced from *Eucalyptus globulus* sawdust (EGS) and locust bean pod husk (LBPH) with clay. Sequential extraction of biomass analysis was used to determine the chemical compositions (cellulose, hemicellulose, lignin, extractives and ash) of the natural fibres. The natural fibres were then treated with sodium hydroxide at varying concentrations and time. The treated natural fibres with the optimum cellulose yield were carbonised at 500^{o}C for 2 h, which was then used as reinforcement together with clay for the hybrid polymer composite (HPC) production. The HPC was compounded and produced using two-roll mill and compression moulding machine, according to the component mixture- process experimental design of this work. Characterisation of the micro structural properties of all the precursors and HPC produced were carried out. Upon the mercerisation treatment process, EGS recorded an optimum cellulose yield of 74.6% at 3% NaOH for 2 h, while LBPH recorded a higher cellulose yield of 80% at 1.5% NaOH for 3 h. The HPC produced was subjected to mechanical test (tensile, flexural and hardness). Result shows that the component mixture with the formulation of 5 wt% EGSA, 40 wt% LBPA, 2 wt% clay and 53 wt% PE, processed at 160^{o}C was found to give the highest flexural strength of 19.23 MPa and tensile strength of 10.25 MPa, compared to all other HPCs. The maximum hardness value recorded was 35.27 MPa. Result from the Differential Scanning Calorimeter (DSC) analysis further shows that the HPC has high resistance to heat and flame due to its high glass transition temperature (63^{o}C), melting temperature (138.39^{o}C) and enthalpy of 148.68 J/g. Similarly, the water absorption capacity of the HPC is as low as 0.5%, which is 20 times lower than the acceptable standard value for general roofing tiles. Furthermore, a performance evaluation of the HPC roofing tile was carried out by exposing it to natural weathering condition for one year, in comparison with other control samples including a polycarbonate sample from the market. The outcome shows that the HPC has high resistance to weathering effects of photo-degradation, temperature, rain and humidity. The percentage rate of degradation in-terms of its mechanical properties for hardness (18.91%) and flexural strength (10.19%) is low when compared to the control samples and the polycarbonate sheet. This observation is further confirmed by its low carbonyl index parameter of 0.12, as a reflection of its promising reliable service life span. A low-cost hybrid polymer composite with outstanding properties suitable for roofing purpose was produced in this work.

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ABBREVIATIONS

Abbreviation	Description
HPC	Hybrid Polymer Composite
EGS	*Eucalyptus globulus*
LBPH	Locust Bean Pod Husk
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
UV	Ultra-Violet
SPM	Scanning Probe Microscopy
PE	Polyethylene
PVC	Polyvinyl chloride
VPE	Virgin Polyethylene
EDX	Energy Dispersive X-ray
DSC	Differential Scanning Calorimeter
ANOVA	Analysis of Variance
WAC	Water Absorption Capacity
LDPE	Low Density Polyethylene
ASTM	American Society of Testing Materials
CI	Carbonyl Index
PEEK	Polyether Ether Ketone
LBPA	Locust Bean Pod Ash
MMC	Metal Matrix Composite
CMC	Ceramic Matrix Composite
PMC	Polymer Matrix Composite
ICI	Imperial Chemical Industries
Abbreviation	Description

WPC	Wood Polymer Composite
HALs	Hindered Amine Light Stabilizers
MA	Maleic Anhydride
PMPPIC	Poly[methylene](polyphenyl isocyanate)]
HDPE	High Density Polyethylene
CCD	Central Composite Design
MDE	Mixture Design of Experiment
RLDPE	Recycled Low Density Polyethylene
EGSA	*Eucalyptus globulus* sawdust Ash
MT	Mixing Time

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Over three decades now, ceramics, plastics, composite materials, and natural fibre have become emerging materials of interest. This is evident in the geometric production volume of composite materials in the market space, owing to great demand in different areas of application (Parnas, 2001). Similarly, the attention of the field of material science and engineering is drawn and geared towards eco-friendly materials. In the early 1990s, composites produced from natural fibres were substituting both glass and carbon reinforced polymer composite (Parnas, 2001; Layth *et al*., 2015). Currently, most fabricated products for indoor, outdoor and load bearing purposes are composite inclined in composition (Nayak, 2009; Jabar, 2017).

Composites are materials composed of two or more constituents, mixed and bonded together to give superior properties better than each of its constituting material standing alone (Sathishkumar *et al*., 2013). According to Kopeliovich (2010), composite is classified into three groups: ceramic matrix based composite, metal matrix based composite and polymer matrix based composite. Metal is the parent material in metal matrix composite. Metal composite offers better performance engineering property compared to pure metals when in use, at elevated temperatures. Such properties are high specific strength and modulus which finds application in design of heat exchangers, space shuttle, and in combustion chambers. Similarly, ceramics matrix composite have ceramic as the parent material in the composite. Ceramic materials have the ability to function under high temperature environment due to the strong covalent bonds present in the crystal structure (Samotu, 2010). The interest of this work is on polymer based composite.

A polymer composite is a multiple-phased material in which a polymer matrix is reinforced with fibre, fillers or both to give better performance properties which is not possess by the individual constituting material (Chawla, 2013). In this case, natural fibres such as bamboo, hemp, jute, sawdust and locust bean husk, can be used to reinforce a particular polymer matrix of interest such as polyethylene. Similarly, fillers such as calcium carbonate, ash particulate and clay, can also be used as additives to reinforce polymer resins to obtain better improved mechanical properties. Some of the advantages and outstanding properties of polymer composite are; high strength, design flexibility, light weight, thermal resistance, and good corrosion resistance. These unique properties have necessitated the need for polymer composite to be widely adopted for use in diverse fields such as civil engineering constructions, aerospace, automobile, ship building and in military hardware (Parnas, 2001; Omoyeni *et al*., 2016). One of the components of civil engineering construction is housing, and this undoubtedly remains one of the most basic needs of man, and as such its demand is on the increase (Aguwa and Okafor, 2012). Example of some building materials used in the construction industry are cement, roofing sheet (Zinc and Aluminium), and polyvinyl chloride (PVC) ceiling. Some other durable machine and electronic parts produced from composite are brake-pad, tanks, car bumper, train coaches, engine shaft, pressure vessel and diode. In addition, wide array of materials having less susceptibility to wear, corrosion, high temperature and oxidation tendencies, are produced from composites for multipurpose application even in the biomedical industry (Kutz, 2000).

Furthermore, the production of polymer composite can be tailored to fit into a specific structural design requirement. To achieve this, the composite designer must have the technical mastery of choice of materials and how to manipulate these properties together, in order to obtain a finished product with the desired property of interest (Wallenberger and Weston, 2004). The production of hybrid polymer composite roofing tile is the focus of this work.

However, it is important to note that the quality of a polymer composite depends on the individual properties of the reinforcing materials and polymer matrix, the treatment technique, processing technology and the processing conditions/parameters used. While the use or application of composites in many instance depend on the skill and experience of the designer in tapping the optimum potentials of diverse materials for composite production (Nayak, 2009).

Furthermore, it is also pertinent to note that, the mechanical and physical properties of natural fibre/polymer composites depend on a number of factors, such as fibre content, concentration of chemical such as alkaline used for treatment, alkaline contact time with fibre, aspect-ratio of the fibres, and fibre orientation. Other factors include particle size of fibre, dispersion level in the polymer matrix, fibre–polymer adhesion, processing technology, mixing time/speed, temperature and the use of external coupling agent (Sastra *et al*., 2005). In line with these factors, the effect of alkaline treatment concentration and its contact time on sawdust and locust bean pod husk fibres for hybrid polymer composite was investigated. Similarly, the need to optimize the hybrid polymer composite production process in this work is paramount.

Research has also shown that the durability and property response of most composites fall short of their expected optimal capacity. This however can be traced to weak experimental and process design in the area of component formulation, material modification, and processing technology. To bridge this gap, an optimisation software referred to as design expert is adopted for use in this work, through a series of simulated experimental trials of the input factors. This approach brings to bear the effect of the input factors and the extent of interaction between the polymer matrix and the reinforcing fibre or filler within the composite space (Ojewumi, 2016).

Therefore, this research focused on the production of a suitable hybrid polymer composite for roofing purpose from used polyethylene (pure water sachet) to be reinforced with *Eucalyptus globulus* sawdust, locust bean pod husk and clay. In order to optimize the production process at experimental design stage, process–mixture design of experiment which is a dropdown of response surface methodology (RSM) was used to adequately reconcile all the variables and parameters together. In this case, both the process variables and component proportion variables which influence the final property of the composite was be considered and captured (Montgomery, 2001).

1.2 Statement of the Research Problem

It is an established fact that in most satellite towns, a chunk of the Nigerian population uses sachet water for drinking purposes. These empty water sachets made from low density polyethylene (LDPE) and agricultural waste such as sawdust constitute almost 50% of refuse found in the dumping sites of most satellite towns in Nigeria. Akinro *et al.* (2012) reported that in 2008, an estimated volume of 2,184,055 tonnes of polyethylene waste was generated in Nigeria with LDPE having the higher percentage compared to HDPE. This also contributed in polluting and rendering the environment unclean thereby increasing the tendencies of flooding during rainy season. Converting these polymeric and agricultural wastes into useful materials will help to reduce waste, pollution and keep the environment clean and eco-friendly (Samotu, 2010). In a similar vein, large volume of agricultural waste is also being generated yearly and burnt in dump site. All of these wastes put together can be channelled and converted into useful purpose and products for wealth creation. Furthermore, the need to replace the use of synthetic fibre with natural fibre for production of indoor and outdoor accessories, have become very imperative. This has gone a long way in bringing about ease of degradation of fibre and eco-friendliness.

1.3 Aim and Objectives of the Study

The aim of this study is to produce hybrid polymer composite (HPC) suitable for roofing tile. This research was accomplished through the following objectives:

i. Alkaline treatment and modification of the reinforcing materials
ii. Carbonisation and Characterisation of the raw and treated reinforcing materials
iii. Statistical evaluation and modelling of the effect of the process variables
iv. Development and characterisation of the new hybrid polymer composite (HPC) prototype
v. Determination of the mechanical properties (flexural strength, tensile strength and hardness), thermal properties and water absorption capacity of the developed hybrid polymer composite.
vi. Performance evaluation of the developed hybrid polymer composite using natural weathering degradation process.

1.4 Scope of the Study

The scope of this research work limited to the use of used low density polyethylene (pure water sachet) as matrix, to be reinforced with treated carbonised *Eucalyptus globulus* sawdust fibre and locust bean pod husk fibre with kaolin clay for hybrid polymer composite (HPC) production. Only NaOH was used for the mercerisation process. The mechanical analysis is restricted to flexural strength, tensile strength and hardness properties alone. The thermal property analysis covers only enthalpy change, melting temperature, glass transition temperature, degree of crystallization, heat capacity and oxidation onset temperature. The water absorption capacity test is limited to 70 HPCs and two other control samples from recycled and virgin low density polyethylene. The duration of the outdoor exposure of the HPCs to determine its resistance to degradation, caused by natural weathering effects of sunlight, rainfall, ultra violet ray and humidity, lasted for just a period of one year.

1.5 Justification of the Study

Large volume of wastes from agriculture and polymer materials have continued to accumulate in landfills and this poses a threat to the serenity and hygienic condition of the environment as surveyed by Samotu (2010). These wastes can be converted into useful materials for the building industry, in a bid to promote local content while converting waste to wealth. Further statistical Survey by Akinro *et al.* (2012) has it that, the housing sector in Nigeria alone is estimated to have a deficit of 16,000,000 houses. This deficit however, calls for concern through research and development of low-cost building materials.

In developing countries such as Nigeria, the increasing cost of building materials such as zinc roof sheet, cement, wood and iron rod is making it difficult for people to build and live in their own houses. This justifies the reason why Aguwa and Okafor (2012) investigated the preliminary use of locust bean pod as binder for production of laterite blocks for building. Omoyeni *et al*. (2016) studied the utilization of maize husk and recycled low density polyethylene (LDPE) waste material for composite board production, while Bed (2015), worked on the preparation and characterisation of wood plastic composite using recycled LDPE/high density polyethylene (HDPE) plastic and sawdust. These reveal the importance and relevance of composite which when properly tailored by design property specification, will be of great use in the building industry. In-depth survey of literature shows that research into the use of polymer matrix for roofing purpose in building over the years is very skeletal. In Nigeria, research has also shown that most of the roofing materials are made from metals such as zinc and aluminium. Judging from this limitation, the need to develop other alternative materials such as composite for roofing purpose is very imperative. Bolaji and Mosobalaje (2008) attempted the use of synthetic additives with virgin polyethylene in this area. Literature review to date reveals that virtually no polymer composite has been produced using locust bean pod ash (LBPA) as reinforcement for this purpose. Also the thorough investigation on the effect of varying alkaline concentration and contact time in the production of composite has also received little or no attention. It is on this premise that this study seeks to investigate the combine effect of sawdust, locust bean pod, clay as reinforcement into recycled polyethylene matrix for the production of hybrid composite material that will be suitable for roofing purpose.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Background of Polymer Composite

In recent years, engineers and material scientist have focused more on the outstanding properties of reinforced natural fibre polymer composite. This is because of the improved mechanical properties, eco-friendliness, dielectric, renewability and biodegradability properties obtained in natural fibre composites (Singha and Vijay, 2008). These unique properties are not obtainable in high degree with the conventional synthetic glass fibre, carbon fibre and petroleum based plastics. The renewability and eco-friendliness attributes of natural fibres have paved way for their application in the housing and construction sector. Other advantages of natural fibres over traditional synthetic reinforcing materials are low cost, corrosion resistance, low density, abundant availability and less abrasion to processing equipment (Joshi *et al.,* 2004; Singha and Vijay, 2008). It should be noted that the properties of natural fibres such as coir, jute, ramie, sisal, bamboo, pineapple peel and wood can vary based on their age, source and the fibre separating techniques (Joseph *et al*., 2002; Djidjelli *et al*., 2004; Mishra and Mishra, 2011; Peltola *et al.,* 2011).

2.2 Classification of Composites

Composites are materials possessing outstanding properties made up of two or more distinct constituents with distinct chemical properties to give a holistic unique interfacing characteristic, different from any discrete material when combined together (Sathishkumar *et al*., 2013). According to Kopeliovich (2010), composite materials can be classified into three groups based on the matrix material in use. These are:

i. Metal Matrix Composites (MMC)
ii. Ceramic Matrix Composites (CMC)
iii. Polymer Matrix Composites (PMC)

Metal is the parent material in metal matrix composite. Metal composite offers better performance engineering property compared to pure metals when in use, at elevated temperatures. Such properties are high specific strength and modulus which finds application in design of heat exchangers, space shuttle, and in combustion chambers (Samotu, 2010).

Ceramics matrix composite have ceramic as the parent material in the composite. Ceramic materials have the ability to function under high temperature environment due to the strong covalent bonds present in the crystal structure (Samotu, 2010). The development and production of polymer based matrix composite is the area of focus in this work.

2.3 Polymer

Monomers are repeating units that combine together to form a polymer chain. The bulk of the repeating units are hydrogen and carbon, and in some cases chlorine, oxygen, sulphur, nitrogen, silicon, phosphorus and fluorine are part of the constituting elements that forms the polymer chain. Many links known as “mers’ are polymerized and bonded together to form a long polymer chain. Basically, polymers are of two classes, namely: thermoplastics and thermoset (Painter and Coleman., 1997). The choice of polymer material for this work is polyethylene which falls under the category of thermoplastic.

2.3.1 Low density polyethylene

Low-density polyethylene (LDPE) is the first grade of thermoplastic produced from ethylene monomer by imperial chemical industries (ICI) in 1933, through a free radical polymerization process of high pressure (Dennis, 2010). This method is employed in the manufacture of an array of thermoplastic products (Dennis, 2010). Akinro *et al.* (2012) reported that in 2008, an estimated volume of 2,184,055 tonnes of polyethylene waste were generated in Nigeria with LDPE having the higher percentage compared to high density polyethylene (HDPE). The United State of America (U.S.A) environmental protection agency reported that only 5.7% of LDPE is been recycled in U.S.A, of which the recycling code is 4. Interestingly, LDPE worldwide market has grown to US$33 billion (Dennis, 2010). Some of its properties are listed in Table 2.1.

Table 2.1: Properties of Low Density Polyethylene

Properties	Unit	Value
Density	(g/cm^3)	0.9 – 0.94
Glass transition temperature	(^{o}C)	-110
Melting point	(^{o}C)	115
Flexural strength	(psi)	1,175
Tensile strength	(psi)	41615
Elongation in 50 mm break	(%)	1000-1015
Hardness shore	Shore (D)	55
Ultimate tensile strength	(MPa)	7 - 40

(Kalpakjian and Schmid., 2008)

2.3.2 Poly vinyl chloride

Pure polyvinyl chloride is known to be a solid, white brittle substance, which is slightly soluble in tetrahydrofuran but insoluble in alcohol. It has a recycling code of 3 for the purpose of sorting. Polyvinyl chloride (PVC) is employed in the manufacture of an array of plastic consumers' products, in so many areas such as building and construction. Some of the products in this area are vinyl ceiling, PVC pipes, windows, doors and roof sheets. The ease of the use and maintenance of PVC is effectively replacing the use of wood, metal and paper in several applications. For instance, ceiling panel made from PVC is progressively replacing the traditional ceiling board and gypsum ceiling. Some of the suitable working properties of PVC panel that makes it to gain acceptability are - it is totally free of maintenance, resistance to dampness and water, attractive physical appearance and pattern, excellent sound and heat insulation property, as well as high elongation property (www.foramfera.com). Some of the properties of PVC are listed in Table 2.2.

Table 2.2: Properties of Poly Vinyl Chloride

Properties	**Unit**	**Value**
Density	(g/cm^3)	1.3 - 1.45
Glass transition temperature	(^{o}C)	87
Melting point	(^{o}C)	212
Flexural strength	(psi)	10500
Thermal Conductivity	(W/m.k)	0.14 - 0.28
Elongation at break	(%)	20 - 40
Young modulus	(psi)	4500 - 8700
Ultimate tensile strength	(MPa)	7 - 55

(Kalpakjian and Schmid., 2008)

2.3.3 Polymer matrix composites

Plastic polymer is one of the commonly used matrices in composite production. However, the mechanical property of plastic does not measure up adequately for structural application. To be specific, their strength and stiffness are low in comparison to ceramics and metals (Kopeliovich, 2010). These inherent material weaknesses in plastics polymer are compensated by reinforcing them using other materials like natural fibre. The workability of polymer under low pressure and temperature makes it attractive as a matrix in polymer composite application. Also, plastic polymer processing machines are simple and easy to operate when use for polymer composite production (Kopeliovich, 2010). Though, the deployment of 3 dimension (3D) print version technology and machine for polymer composite production is being researched into (Azwa *et al.* 2013).

There are two types of polymer composite. These are:

i. Fibre reinforced polymer (FRP)
ii. Particle reinforced polymer (PRP)

2.3.3.1 *Fibre reinforced polymer*

Polymer matrices are reinforced with natural fibre to form polymer composite. In this case, the fibre which act as reinforcement give strength to the polymer composite, while the polymer matrix help to bind and keep the fibres together in their respective proper place, while helping to transfer stress or load between the reinforcing fibres. These stresses are transferred along longitudinal lines of fibres. Low cost fillers may be added to smoothen and ease the workability and interaction between the fibres and matrix during the manufacturing process of the polymer composite. Some common reinforcing fibres are carbon fibres, molybdenum, beryllium carbide/oxide, aluminium oxide, magnesium oxide and glass fibre. Similarly, some common polymer matrices widely in use are epoxy, polyethylene, polyester, phenols, polyurethane, vinylester, polyether ether ketone (PEEK).

Epoxy, which is second in wide industrial application is known to have better adhesion and less shrinking capacity (Kopeliovich, 2010).

2.3.3.2 *Particle reinforced polymer*

In order to decrease the durability of polymer matrix and increase its tensile/flexural modulus, mineral particles such as carbon black glasses, metal particles, and ceramics are used as reinforcement in composites. This however, will also help to reduce the production cost of polymer composites. Automobile tyre is an example of particle reinforced composite produced from poly-isobutylene elastomer as matrix which is reinforced with carbon black particles (Kopeliovich, 2010). This research concentrates on the use of natural fibres as the reinforcing material for the polymer matrix.

2.4 Natural Fibre

Natural fibres which are used as reinforcement in composites can be obtained from animals, plants, as well as from some geological processes. This greatly influences the resulting properties of composites through their reinforcing orientation. When plant fibres are in use as reinforcement, the cellulose component present in it, help to enhance strength and integrity, which can be improved upon by modification through chemical treatment. This has led researchers to explore the advantages that can be obtained from the modification of the chemical composition of plant fibre for specific purposes (Kadolph, 2002).

2.4.1 Chemical composition of natural fibre

The specie/nature of plant fibre, growth conditions and the methods of chemical composition determination are key factors that influence the chemical composition and properties of plant fibre. Even among fibres of the same kind, there are variations. This is because the overall structure and composition of plant fibre is fairly complex (Amar *et al.*, 2005, Rakesh *et al.*, 2011). According to Bledzki *et al* (2008), plant fibre by nature's design, are composite materials. With the exception of cotton, plant fibres are composed of cellulose, lignin, hemicellulose, extractives (waxes and oil) and some water soluble compounds. Nevertheless, the first three components are predominant in composition.

2.4.1.1 *Cellulose*

One example of a naturally occurring polymer is cellulose, which is made up of a repeating unit known as D-anhydroglucose ($C_6H_{11}O_5$). These repeating units are connected by β-1,4-glucopyranose at C_1 and C_4 along the carbon chain. Each of this reoccurring unit is also made up of three hydroxyl groups having the ability to form hydrogen bond that play a prominent role in crystalline lattice formation. The cellulose monomer however, has a polymerized capacity range of 500- 3,000 unit. Further, Cellulose is not susceptible to strong alkali and oxidizing agents, but can easily be hydrolysed to water soluble sugars by the action of hot acid. The hydrophilic nature of cellulose when used as a reinforcing material in polymer composite does not create a strong interfacial adhesion with the hydrophobic nature of polymer matrices. Similarly, its resistance to water absorption is poor (Maya and Rajesh, 2008). These limitations inherent in natural fibre can be reduced drastically by either using chemical modification agents such as sodium hydroxide, coupling agent/compactibiliser or by grafting the polymer matrix (Khalil *et al*. 2001). All of these treatments will positively improve the interfacial property of the natural fibre for polymer composite production through the following ways: reduction in its hydrophilic nature, improvement of interfacial bonding capacity, better dimensional stability and stress transfer (Bledzki *et al.* 2008; layth *et al.* 2015).

2.4.1.2 *Hemicellulose*

Hemicellulose are polysaccharides comprising of an aggregate of 5- and 6-carbon ring sugars. Its repeating unit is characterized by a high degree of chain branching with side attachments and groups resulting in its amorphous nature. Interestingly, part of the functions of hemicellulose matrix is to give support to the micro fibrils present in the cellulose polymer. The numerous repeating hydroxyl group units is responsible for the hydrophilic nature of the hemicellulose components, while the acetyl group in its monomeric unit is responsible for its partial solubility in water and solubility in alkali. In acids, it is easily hydrolysed (Frederick and Norman, 2004). According to Amar *et al.* (2005), the presence of hemicellulose in natural fibre is responsible for moisture absorption, thermal and biodegradation due to its less stability and resistance to environmental conditions.

2.4.1.3 *Lignin*

One of the major rigid constituent of natural fibre from plant is lignin which have complex hydrocarbon of aromatics and aliphatic compound that is practically insoluble in majority of solvents. This can be linked to the fact that lignin compound cannot be reduced into monomeric unit. However, each building block of lignin molecule comprise of five methoxyl, five hydroxyl and some carbonyl groups (Jabar, 2017). It was further reported by Jabar (2017) that lignin molecule is a derivative of 4-hydroxy-3-methoxy phenylpropane whose melting and glass transition temperatures are around 170^0C and 90^0C respectively. In comparison to cellulose and hemicellulose, Amar *et al.* (2005) and Jabar (2017) further presented some salient properties of lignin compound as it include:

i. Solubility in hot alkali
ii. Hydrophobic and amorphous in nature
iii. Readily oxidized
iv. Condense easily with phenol
v. Not hydrolysed by acids
vi. Thermally stable
vii. Susceptible to ultra-violet degradation.

The percentage compositions of some plant fibres are shown in Table 2.3.

Table 2.3: Chemical Composition of Some Natural Plant Fibre

Fibre	**Cellulose (wt%)**	**Hemicellulose (wt%)**	**Ligning (wt%)**	**Wax (wt%)**
Bamboo	26 - 43	30	21 -31	-
Oil palm	65	-	29	-
Wheat straw	38 - 45	15 - 31	12 - 20	-
Jute	61 -71	14 -20	12 -13	0.5
Rice husk	35 -45	19 -25	20	-
Kenaf	72	20.3	9	-
Hemp	68	15	10	0.8
Coir	32 -43	0.15 -0.25	40 - 45	-
Hardwood stem	40 -55	24 -40	18 -25	
Softwood stem	45 -50	25 -35	25 -35	

(Faruk *et al.*, 2012)

2.4.2 Mechanical properties of natural fibres

The physical and mechanical properties of natural fibres are largely dependent on the fibre growth condition, fibre type, structural and chemical composition (Amar *et al.,* 2005). Similarly, Lee *et al.* (2014) also observed that the mechanical property of a natural fibre is dependent on the micro fibril orientation (angle and length), cellulose content and average degree of polymerization of the cellulose molecules. The low density, stiffness property-to-density ratio and strength of natural fibre can compete favourably with that of glass fibre. It is of great interest to note that the final mechanical property of a finished polymer composite is majorly dependent on the constituting materials that makes up the composite. Other specific factors are fibre dispersion, shape and size of particles, fibre loading or content, fibre alignment, orientation, aspect ratio and the level of interaction between the polymer matrix and the fibre/filler (Lee *et al.*, 2014). These properties can be further strengthened through the use of compactibiliser and stabilizing additives. For example, the use of carbon fibre is appropriate in areas of composites production with high load bearing capacity (Wambua *et al.,* 2003). The interest of this research is on the use of plant fibres obtained from agricultural waste of sawdust and locust bean pod husk for hybrid polymer composite production.

2.5 Sawdust

Sawdust (wood dust) is a by-product gotten from the processing of wood by the use of sharp cutting tools in sawmill. It is made up of particles sizes of fine grains which can be burnt into ash (Neagu *et al*., 2006). Aside the uses of wood fibre (sawdust) in poultry farming, particle board production and other areas, they are presently being deployed as reinforcing materials in polymer composite. The low cost, density and improved mechanical properties offered by wood fibre makes it suitable for structural and composite engineering applications (Carroll *et al.*, 2001; Robert *et al.*, 2002). The high molecular polarity and hydroxyl group found in natural cellulosic fibre is responsible for its weak resistance to water. This negatively affects the dimensional stability and interfacial bonding of natural-fibre polymer composite. Though, the degree of adhesion of one fibre to a particular polymer differs from another fibre (Thwe and Liao., 2003). Another challenge with natural fibre is its hydrophilic incompatibility nature with the hydrophobic character of polymer matrix, as this may lead to agglomeration during processing of polymer composite. As such, the need to subject natural fibres to surface modifications prior to their usage as reinforcing materials has become necessary. In line with this observation, fibre-polymer adhesion and effective stress transfer can be improved through grafting of polymer, bleaching, chemical treatment, compactibiliser and acetylation (Singace, 2000; Bhattacharyya *et al.*, 2003).

According to Nunez *et al*. (2003) the attention of researchers on the use of sawdust for Wood-Plastic Composite (WPC) is due to some of the advantages of WPC over conventional materials. These include: a manufacturing process with minimal energy consumption, chemical resistance and ease of recycling after service life. Other advantages include eco-friendliness, high strength-weight ratio, corrosion resistance and light weight. Furthermore, the differences in the quality and properties of WPC is due to variation in fibre loading, wood specie and fibre size/dimension, density, aspect ratio and morphology. Neagu *et al*. (2006) asserted that the longitudinal modulus of WPCs is a function of the lignin content of the wood fibre. As part of the focus of this work, wood sawdust was burnt into ash and reinforced into polymer matrix to produce roofing sheet composite for building purpose.

2.5.1 Factors affecting the quality and quantity of wood sawdust ash

There exist a wide range of factors that plays important role in determining the quantity, property and quality of ash from combusted wood. Some of these factors are wood specie, combustion technology such as furnace and its hydrodynamics, as well as the combustion temperature. Primarily, the chemical composition of wood ash and its yield is influenced by the combustion temperature. However, studies have shown that agricultural waste produces more quantity of ash than wood when burnt. This, however necessitate the characterisation of any ash produced before it is used in any area of application (Chowdhury *et al*., 2014). The chemical composition of sawdust ash is presented in Table 2.4.

Table 2.4: Chemical Composition of Sawdust Ash

Constituent	CaO	Na_2O	SiO_2	Al_2O_3	K_2O	P_2O_5	Fe_2O_3	SO_3	TiO_2	MgO
%	44.11	2.48	26.17	4.53	10.83	2.27	1.82	2.05	0.4	5.34

(Vassilev *et al*., 2010)

Ban and Ramli (2011) reported that there is 45% reduction in the quantity of wood ash produced when combusted within a temperature range of 538°C to 1093°C. Further observation show a decrease in the alkalinity of the ash due to the decomposition of bicarbonate and carbonates at combustion temperatures above 1000°C. However, these compounds will predominate especially for calcium carbonate when incinerated at temperatures below 500°C. Similarly, a decrease in the composition of metallic elements such as zinc, potassium, and sodium is observed with increase in combustion temperature.

It is also important to note that the texture and particle size of ash being produced can also be influenced by the combustion technology. In this case, grate fired furnace have the capacity to produce coarse grain particle ash, while fluidized bed furnaces produces finer grain particle ash compared to grate furnace (Vissilev *et al.,* 2010). Another agricultural waste fibre worthy of relevance in this work that can be processed into ash is locust bean pod husk.

2.6 Locust Bean Pod Husk

Locust bean tree, scientifically called *Parkia biglobosa* is a leathery brown pod fruit popularly found in the northern part of Nigeria. The pod is made up of three basic components, namely: a yellow gummy sweet pulp, seed and brown husk. The use of the husk is of interest in this work. In most parts of the country, the seed is majorly used for seasoning of food, popularly known as *Iru* in Yoruba and *dawadawa* in Hausa (Aguwa and Okafor, 2012). Alabi *et al*. (2005) reported that the seed is rich in protein, ascorbic acid, lipid, soluble sugar, and carbohydrate. The high saponification value of the oil extract from the seed, makes it suitable for application in the soap industry. To be more specific, Aliero (2004) further reported that the seed portion contain 30% protein, 54% fat, vitamins and some other micro elements like phosphorus, potassium and calcium. Part of the interest of this work is in using the husk which is a by-product of agricultural processing of the locust bean seed to reinforced polymer matrix in its ash form. The chemical composition of locust bean pod ash is shown in Table 2.5.

Table 2.5: Chemical Composition of Locust Bean Pod Husk Ash

Constituent	Al_2O_3	CaO	SiO_2	MgO	Fe_2O_3	K_2O	Na_2O	Pb_2O_5	L.O.I
% Weight	13.05	15.71	39.01	2.01	11.51	5.62	1.21	5.82	6.00

(Adama and Jimoh, 2011)

2.6.1 Properties and uses of locust bean pod husk

Locust Bean Pod Husk (LBPH) is dark brown in colour with a density of l0.97kg/m^3 and pH of 6, indicating its weak level of organic acidity. Part of the chemical composition shows that it has a tannin content of 27- 44%. The liquid extract of LBPH has been used as a component formulation in the moulding of mud blocks (Aguwa and Okafor, 2012). Long before now, the husk are spread on mud walls in order to allow the liquid extract from it to drain and percolate into the wall at the onset of the rainy season. Investigation and reliable evidence from local dwellers have shown that such mud buildings are less susceptible to termite attack and deterioration. Furthermore, LBP concentrated extract are known to strengthen the water resistance of walls, ceramic pots and floors. In the ancient days, ash obtained from burnt LBP husk is used for dying and tanning of indigo clothes and for soap making (Aguwa and Okafor, 2012). It is interesting to note that LBPH ash can be used as additive or reinforcement in composite. Ndububa and Uloko (2015) ascertained the water absorption capacity and compressive strength of the production of concrete mortar, using LBPH ash as a partial replacement of cement in the concrete mix. Adama and Jimoh (2011) reported that LBPH ash can be used as a pozzolan, which is a cementitious stabilizing additive in weak laterite for road construction. This is due to the presence of silica, alumina and ferrite oxide in the chemical composition of LBPH ash as observe in Table 2.5. In this work, locust bean pod husk ash (LBPHA) was also used as an additive or reinforcement in the production of hybrid polymer composite. This is due to its anticipated fire retardant and ultra-violet (UV) inhibitory property presented by magnesium and Aluminium oxide.

Generally, in polymer composite reinforcement, additives are sometimes incorporated to perform a specific function within the composite, though in relatively small amount in comparison to the resin matrix. Some additives tailored for specific function are colorant, suppressant, releasing agent, fire retardant, stabilizers, ultraviolet (UV) inhibitors such as hindered amine light stabilizers (HALs) and thixotropes (www.compositelab.com). Hence, this work investigated the use and effect of LBPH ash as one of the reinforcing constituent material with clay as filler (additive) in the production of hybrid polymer composite for roofing tiles.

2.7 Clay as Fillers (Additives) in Polymer Composite

Fillers are used to improve performance in composites. They are of different sizes, types and shapes. In composite formulation, the need to select suitable filler that will provide the needed chemical and physical performance property, at a low affordable cost, is of great importance. A sound understanding of the role and application of filler will go a long way in saving material cost and creating value addition with a difference (www.foramfera.com). Nowadays, the application of fillers is tailored towards a particular purpose. For example, resins that are reinforced with fillers have better dimensional shrinking control than unreinforced resins. Some other impacting properties of mineral filler are surface smoothness, strength, temperature resistance, water resistance, hardness, conductivity and colour. Furthermore, filler improves the workability of resin during product manufacturing. Some common available fillers in use include titanium oxide, clay, calcium carbonate, alumina trihydrate (www.foramfera.com). Kaolin clay was used as the filler component needed for the production of HPC in this research. Coupling agents can be incorporated if need be, to further enhance the compactibilisation of all the constituting materials together in the hybrid polymer composite.

2.8 Coupling Agent (Compactibiliser) in Polymer Composite

Coupling agents is often used as pre-treatment for fibres such as wood in order to improve the mechanical properties of polymer composite. Maleic anhydride (MA) and poly [methylene (polyphenyl isocyanate)] (PMPPIC) are examples of coupling agents. Two pre-treatment methods predominate, which include: graft co-polymerization of both the polymer and wood fibre, and the coating of wood fibre with coupling agent (Lu *et al.,* 2000). The essence of the pre-treatment is to enhance compatibility. This process is characterized by reactions between the polar hydroxyl groups found in wood and the coupling agents. For example, MA and PMPPIC will initiates a chemical reaction with the polymer matrix on the basis that, they have a molecular structure that is linear and similar (Lu *et al.*, 2000). In wood fibre reinforced polymer composite, four categories of coating methods is in use. These are: spraying, compounding, soaking and blending. Compounding method is mostly deployed in melt-blend process where the coupling agent is mixed at high temperature. In blending, the surface of the wood fibre is coated with a coupling agent at high or low temperature in a magnetic stirrer or roll mill. In soaking method, the cellulose obtained from the wood fibre is impregnated with coating agents that contains additive initiators. In spraying method, emulsification of the coupling agent is followed by surface spraying of the wood fibre.

It is important to note that, both spraying and blending method is appropriate for pre-coating of polymer and wood fibre prior to mixing. For the purpose of coating, soaking and spraying method are preferable than blending and compounding. This is because the former permit a more effective and even distribution of the coupling agent at the interface, notwithstanding the fact that there is difficulty in controlling the amount of coupling agent to be impregnated. It is on this premise that there is need to know the amount of the process variables that control the production of a given polymer composite for quality, optimisation and cost effectiveness (Lu *et al.*, 2000).

2.9 Effect of Process Variables in Polymer Composite Production

The choice of process variables is an important factor to be considered in the production process of a composite. Some process variables under consideration in polymer composite production are: fibre/filler content, fibre treatment, fibre/filler length, shape and orientation, particle size distribution, mixing time, contact time, temperature, pressure and mixing speed. All these, in one way or the other influence the response properties and quality of a polymer composite.

2.9.1 Effect of fibre/filler content loading in polymer composite

Adhikary *et al*. (2010) stated that the amount of fibre/filler content used in polymer composite formulation plays a crucial role in determining its final property. The effect of the volume or amount used on the finished property is dependent on the inherent property of the fibre, particle and shape orientation. The fibre loading in some wood-polymer composite can be as high as 70wt%, using compression moulding process. This however can negatively affect the workability level of the melt viscosity. Adhikary *et al*. (2010) further observed that the flexural and tensile property of wood-plastic composite begins to decrease when fibre content loading exceeds 50wt%. Advance in composite technology shows that nowadays, nano-sized particles are produced from fibres, in order to reduce the component formulation of these fibres in polymer composite to as low as 5wt% with the desired property.

2.9.2 Effect of alkaline treatment (mercerisation) on natural fibres

The availability of abundant and cheap natural fibre alongside its ease of processing, for use as reinforcing materials in polymer composite, is currently of great interest to researchers. However, a major challenge with polymer reinforced composites with natural fibre is their incompatibility leading to weak interphase and uneven dispersion within the polymer composite. Polymer is hydrophobic in nature while natural fibres are hydrophilic. This difference in character can be narrowed by chemical or physical modification of the fibre or polymer, thereby improving their compatibility. The surface of natural sourced fibres can be chemically modified through processes like coupling agents, chemical treatment, and graft co-polymerization, with the essence of improving the mechanical properties of polymer composites (Kumar *et al*., 2018).

According to Malkapuram *et al.* (2008), all of the above treatment methods reduces the hydrophilic property of the natural fibre. Alkali treatment is a suitable and cheap chemical treatment method of modifying natural fibre. The use of alkaline such as sodium hydroxide, in this case increases the surface roughness of fibre and also help to eliminate the network structure of the hydrogen bonding present within the natural fibre (Lee *et al.,* 2009). Furthermore, this type of chemical treatment assist in removing the extractives (oils and wax) and lignin that forms a coating around the cell wall of the fibre to a reasonable degree. Exposition of the short length crystallites and depolymerisation of the native structure of the cellulose is also observed (Li *et al.*, 2009). On account of this, alkali treatment promotes more amorphous cellulose formation at the depreciation of crystalline cellulose. So, when the crystallinity decreases the thermal conductivity decreases also. The removal of hydrogen bonding within the structural network of the fibre is responsible for all of these, as earlier mentioned due to high alkaline concentration. The reaction which takes place between natural fibre (NF) and the alkaline (NaOH) treatment is shown in Equation 2.1.

$$Fibre - OH + NaOH \rightarrow Fibre - O^{-}Na^{+} + H_2O \qquad (2.1)$$

In general, alkaline treatment (mercerisation) impacts two basic effects on the natural fibre:

1. It promotes surface roughness of the fibre, giving rise to better interfacial adhesion effect with the polymer matrix.
2. Exposition of more amount of fibre cellulose as reaction sites for possible reactivity (Abdullah, 2011).

Other alkaline treatment stocks that can be used apart from NaOH are KOH and LiOH. It must be noted that alkali solution not only affect the cellulose component, but also the hemicelluloses, lignin and pectin content, and the extent of their concentration will also impact on the extent of lattice transformation and swelling of the cellulose (Rokbi *et al.*, 2011). The use of acrylic acid for chemical treatment was reported by Li *et al*. (2009) as an effective surface modifier of natural fibres. Alkaline treatment using NaOH so far, in most literatures, is within the range of 1 to 15%.

2.9.3 Effect of concentration and duration of mercerisation (alkalisation)

The duration or contact time of chemical treatment on natural fibre have significant effect on the response of the fibre in a polymer composite. According to Li *et al.*, (2009) many research work on fibre treatment shows that most alkaline treatment concentration are within the range of 1 to 15%, while the duration of treatment is within the range of 10 minutes to 48 hours depending on the fibre that is been treated.

2.9.4 Effect of particle size on wood plastic composite

The size and geometric orientation of wood particles affects the mechanical property and durability of wood polymer composite. Wood particles from sawmill are usually relatively large, but can be further subjected to size reduction by milling and screened to make them smaller at an added cost.

Mesh screen is often used to characterize particle size distribution. The number of openings in a 2.54cm^2 screen is referred to as mesh size. For instance, there are 100 openings in a 100- mesh screen. Meaning that, higher mesh number translate into smaller particle size.

In most cases, finished product of WPCs is also affected by particle size distribution, and in most cases within the range of 10-80 mesh (Patterson, 2001; Clemons, 2002). Particle size effect on the mechanical properties of wood-reinforced- polypropylene composites was investigated by Stark and Rowlands (2003). In this experiment, wood particles of mesh sizes within the range of 35- 235 was used. It was found that more stress concentration which affects impact energy was observed with WPCs with larger particle sizes. Interestingly, the aspect ratio (length-to- diameter ratio) had greater effect in promoting effective load transfer within the polymer composite for improved mechanical property (Schwarzkopf and Muszynski, 2015). Wang (2007) used measurements from optical micrographs to investigate particle size distribution. The median value of the aspect ratio of all the particles was found to be 2.8. Similarly, fillers from wood fibres with aspect ratio of 10-20 impact better mechanical property on WPCs, though, there may be challenges when feeding and quantifying fibres into the extruder (Patterson, 2001).

2.10 Response Properties of a Polymer Composite

The response property of a polymer composite depends to a very large extent on the process variables of the production process at the experimental design stage. This is why great attention is devoted to selecting suitable upper and lower limits for the design of the experiment. Some of the desired response properties of polymer composite are excellent mechanical strength, resistance to thermal degradation and flame, resistance to ultraviolet radiation, resistance to water absorption, ultrasonic resistance. Other response properties depend on the specific desired engineering property of the polymer composite based on area of application.

2.10.1 Mechanical properties

Good mechanical property is one of the basic requirements of most polymer composites. These include tensile strength, flexural strength, hardness, modulus, elongation, and stiffness. It must be noted that flexural properties is critical to any structural element in consideration. This is because composite materials when used for structural purposes may easily be susceptible to failure due to bending. Therefore, the need to develop hybrid composite with improved flexural properties is pertinent (Suyash 2012).

Lee *et al*. (2009) reported that at optimum natural fibre loading, the tensile strength and young modulus of polymer reinforced composite increases to its maximum, but begins to drop as fibre content loading increases beyond optimum content. However, there are contrary views by some other researcher suggesting the opposite. Reasons are: fibre degradation due to high processing temperature, weak and faulty manufacturing technology and incompatibility between fibre and polymer matrix. These challenges can be overcome to obtain polymer composites with improved tensile strength by the use of coupling agents, improved processing technology and surface chemical modification (Santos *et al.*, 2009).

2.10.2 Thermal sensitivity and linear expansion

Both natural fibre and thermoplastics are sensitive to high temperature during processing. The high temperature requirement for the processing of some thermoplastic may have adverse effect in denaturing the wood fibre used for reinforcement in polymer composite. This however may not occur if processing temperature is kept below 200^oC. Based on this fact, the processing of wood-polymer-composite have been narrowed down to plastic polymers with lower temperature processing requirement. Some of these plastic polymers are: polystyrene, low density polyethylene (LDPE), polypropylene, high density polyethylene (HDPE), and polyvinylchloride (Bed, 2015). In this case, there is need to always reconcile the melting temperature of a polymer matrix with that at which a given fibre denatures, as this influences the interaction and adhesion between them for a better composite quality.

Thermoplastics respond more to variations in temperature than humidity. It has been observed that the incorporation of wood fibre as reinforcement in WPCs reduces its linear expansion capacity. The modulus of elasticity of WPCs decreases with increase in temperature (Bed, 2015).

2.10.3 Water absorption capacity (WAC) of wood-fibre polymer composite

The hydrophilic nature of wood fibre gives it the capability of absorbing and desorbing water, leading to changes in its dimensional structure (Kord 2011).

The outdoor and indoor application of WPCs in homes and office buildings exposes them to water and rain. The need to investigate the variation in the water absorption capacity of WPCs, based on wood fibre type and content loading is very paramount. This, to a large extent determines the durability and life span of WPCs (Najafi *et al.,* 2007). The hygroscopic nature of fillers and the weak interfacial bonding between fillers and matrices have adverse effect on the quality of WPCs due to high water absorption capacity. Similarly water absorption in WPCs is also affected by particle size distribution. Larger particle size promotes higher water absorption (Mosadeghzad *et al.,* 2009).

It has been established that WAC is affected by particle size distribution by a direct linear proportionality relationship. Meaning that, small particle size equals low water absorption in polymer composite. The water absorption that occurs in agro-fibre polymer composites is a cumulative effect of the absorption mechanism occurring in each and individual cellulosic fibre particle. In addition, the various micro gaps at the interfacial adhesion points of the fibre- polymer matrix also retain water when expose to moisture. Similarly, voids that are created as a result of vapour loss during the melt heating and curing manufacturing process, present the polymer composite with micro openings that can also hold water (Azad and Tajvidi, 2009). The rate of WAC within a polymer composite can be dependent on the processing temperature, fibre dispersion level, fibre type, matrix type and possible water reaction sites with the composite (Bledzki and Faruk 2004).

It has been observed over time that low fibre-wettability by molten polymer matrix is obtained with larger particle distribution. Similarly, there is this high possibility of inter particle-particle alignment and agglomeration resulting from incomplete plastic polymer encapsulation. Furthermore, the low water diffusion coefficient possessed by smaller particle distribution and its high surface area at optimum fibre loading is also responsible for its positive effect in polymer composite (Najafi *et al*., 2013).

It is obvious that high moisture absorption capacity in natural fibre is not desirable in WPCs, as this affect its dimensional stability as well as its mechanical property (Leu *et al.,* 2012). This of course, weakens the interfacial adhesion between the polymer and natural fibre with the swelling of the fibre. When WPCs are exposed to moisture over a given period of time, degradation of its mechanical properties such as flexural strength, tensile strength and harness is noticeable. Nevertheless, the onset and extent of this degradation process can be delayed and minimize through the use of surface modification agents such as peroxide, saline, isocyanate, maleic anhydride permanganate and sodium hydroxide (Cui *et al.,* 2008; Cui *et al.,* 2011).

Studies have shown that the initial rate of absorption and transport of moisture in WPCs is slow, coupled with an uneven distribution of moisture across its surfaces. The outer area of the polymer composite first reaches high level of moisture absorption that promotes fungal growth and degradation (Wang *et al.,* 2011). WPCs with fibre content as high as 50% of its composition experiences higher moisture absorption (Cui *et al.,* 2011).

In addition the swelling and shrinking of wood-fibre particles upon absorption and desorption of water in a moist environment impacts stress on the WPCs. This stress leads to micro cracks and particle pull-out along the interfacial points of the polymer composite (Segerholm 2012).

Adhikary *et al*. (2010) reported that the use of acetylated Acacia magnum as reinforcement help to minimize moisture intake and swelling in WPCs. This will also help to reduce micro-organism and fungi growth (Segerholm, 2012). This phenomenon can be retarded by coating or plating the surface of the finished composite product with a water and UV radiation resistant material.

2.11 Manufacturing Methods/Processing Techniques

Composites that are wood- based in formulation are often made into a beam or panel structured geometry. The production of simple linear and complication shaped WPCs beginning from their molten preparation state can be carried out using extrusion processes and injection moulding. Polymer composite production first involve the blending or mixing together of the various components (polymer matrix and reinforcement) before it moulded, trimmed and cured into an expected end product. The mixing or compounding process facilitates homogeneity of the various components together. This can be done by ensuring adequate and even dispersion of the wood fillers across the molten polymer matrix space. This is however critical for polymer composites with high filler content formulation. In this case, proper wetting, encapsulation as well as the dispersion of the reinforcement particles enhances good stress transfer within the composite space. On the contrary, an uneven dispersion due to agglomeration of fibre particles and poor compounding process may ultimately lead to weak mechanical properties. To achieve better component interaction within the polymer composite, the compounded mixture is pelletized by extrusion before being re-melted and cured in a mould of a given dimension (Schirp and Stender, 2009).

2.11.1 Extrusion method

Extruder is one of the common processing technological equipment used in polymer composite production. This equipment has the capacity of compounding and heating up the component mix into a blended paste, which is then extruded as pellet. All the component materials are fed into a hopper that is metered to avoid clogging. Depending on the configuration, a single or twin screw mixes and move the materials forward through the length of the heated barrel to form an homogeneous mixture. At the end of the length of the barrel lies the die, which expresses out the blended pellets having a profile that is based on the configuration and diameter of the die. These blended pellets can be purchase by other manufacturer and processed into finished polymer composite products using injection moulding. Some extended linear panels, planks and poles are products of extruded WPCs (Schirp and Stender, 2009).

2.11.2 Injection moulding

Injection moulding technology as applied to polymer composite production, is applicable in the design and fabrication of a variety of complex shaped products according to the desire of the designer. Nevertheless, injection moulding is not often used in WPCs production even though their initial stage of material mixing or compounding is similar. The basic difference between the extruder and injection moulding is that, the compounded material is injected or emptied into a mould. Upon cooling, the mixed material in the mould is then ejected to allow another piece of polymer composite to be formed. While for an extruder, the compounded material is pushed into a die to form pellets (Schirp and Stender, 2009).

2.11.3 Wet processes for sheet formation

Wet processes are often deployed in the fabrication of WPC sheets used for shelving and door application in the automotive industry. In the wet process of WPC production, a slurry mixture of the component materials with chemical additive is prepared in water followed by hot pressing into a sheet. The board that houses the sheet is held together by a plastic scrim to put it in place. Extruders can also be used for this purpose (Pritchard, 2004).

2.12 Experimental Design

Before going to the laboratory to perform a set of experiment, it is imperative to develop a statistical Design of Experiment (DOE) in order to be able to optimize the process, minimize loss of material or reagents and also study the trend of experimental outcome. DOE is an efficient experiment planning technique that establishes the relationship between output and input variables of an experiment. These input variables are subject to manipulation to observe their corresponding effect (output). The output data obtained are analysed by studying its cause-and effect mechanism to draw-up a valid inference for the experiment (Ojewumi, 2016). In this case, mixture design of experiment was employed in this work.

2.12.1 Mixture design of experiments

Mixture Design of Experiment (MDE) is an offshoot of surface response methodology which investigates the cordiality between input and response variables. This is aimed at knowing the optimum parameters that characterize a particular experimental process through regression analysis of the participating data. Central Composite Design (CCD) and factorial design are also subclass of RSM.

The proportion of each component that makes up the mixture determines the expected final mixture response, and not the quantity of the mixture. One outstanding attribute of the mixture design experiment is based on the fact that component proportion (q) summation must equal unity (1). This establishes a relation between the independent input variables x_i, with components x_1, x_2 through to x_q as expressed in Equation 2.2 and 2.3.

$$\sum_{i=1}^{q} x_i = x_1 + x_2 + \cdots x_q = 1 \qquad (2.2)$$

$$x_i \geq 0, \quad i = 1,2 \dots \dots ., q \qquad (2.3)$$

The experimental space under MDE having q components is known as simplex. This is usually a figure with q-1 dimensions having q vertices in order to form a coordinated mixture system based on proportion. Figure 2.1 presents a three (3) component coordinate simplex mixture system (Myers *et al.*, 2009).

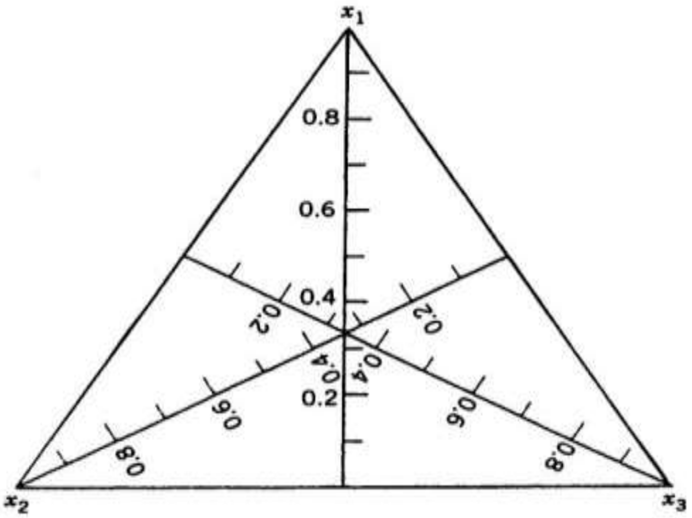


Figure 2.1: Simplex Coordinate System for a Three-component Mixture (Myers *et al.*, 2009)

A representation of the response surface of a given simplex space or region using polynomial equation can be properly captured by putting together lattice points that are evenly spread. A designed simplex lattice (q,m) is of articulated points with q components mixture, where the response surface takes into account a polynomial with m^{th} degree.

Cornell (2002) further observed that various challenges of mixture design exist, of which the summation of lower and upper limits of some component proportions is one of such. However, pseudo- simplex and constrained mixture design are strategies of addressing such challenges, where various techniques of model development and data analysis are employed.

2.12.2 Process-mixture experimental design

One of the challenges that influence the outcome of responses or output variables in design experiment of component mixture is process variable. This challenge can be resolved by adopting the strategy of process-mixture design. This however is a combination of component mixture and factorial process design variable. The application of this design concept is deployed in product formulation such as pharmaceutical, cleansing agents and food. Limited application is found in polymer composite production such as in the study of the mechanical properties of nanocomposite made from polymer-layered silicate (Mittal, 2008).

Process-mixture experimental design can also be employ to determine fibre size effect, fibre loading, fibre concentration treatment, fibre treatment duration, temperature, mixing time and a lot of other process variables on several properties of natural fibre hybrid polymer composite. Mixture-design of experiment employs the use of component ration as input variables, while Process-mixture design of experiment takes into account the combine effect of mixture and process variables in a strategic and dynamic way. This will help to explain how both process variables and component ration variables can determine the properties of a composite (Mittal., 2008). The effect of the optimisation process from the mixture-process design influences the model development, as well as the product outcome of the hybrid polymer composite for roofing purpose.

2.13 Roofing Materials

These are selective component building materials with specific properties used as outer covering on the top of a building or structure in order to provide shield from the effect of the elements of weather, such as rain and sun (cedarbureau.org).

Some popular roofing materials in use are;

i. Metal
ii. Slate
iii. Asphalt
iv. Wood
v. Tile
vi. Plastic

2.13.1 Metal

Metallic galvanized aluminium, Zinc, Copper, stainless steel and some other metals are deployed in roofing. Among all these, coated or galvanized Zinc is commonly in use in this part of the world. Most metal roofs are light weighted. Metal roofing panels are of varying length and prices relative to the metal type. On the other hand, corrosion is a major challenge in metal roofing and the rate corrosion is governed by the metal type and the thickness of the galvanized layer (Haddock, 2017).

2.13.2 Slate roof

These are roofing materials in use centuries ago in places like great Britain. Roofing slate are flat granite stone quarried from natural sedimentary rocks. The composition of slate roof is known to have high mica content of up to about 40%. The advantages of slate roof include its rating as a class A fire proof material. Its durability is second to none, as it can last for more than a century or more, having high water and heat resistance capacity (Kolle,1994).

2.13.3 Asphalt roofing shingles

Asphalt roofing shingles is made from a woven mat covered with numerous strata of asphalt. The topmost stratum of roofing shingle is engrained with tiny granules of minerals in order to shield the roofing shingle from the damaging effect of ultraviolet rays from sunlight. The mat-core is made from organic or fibre glass. Also some of the advantages of asphalt roofing shingle is its ease of installation, durability and affordability (www.cedarbureau.org).

2.13.4 Wood

Wood shingles and wood shakes are two main roofing materials made from wood. Shingles are produced when wood are sawn into long smooth constant shaped roofing materials. While wood shakes are produced by splitting wood into tapered shapes with rough surfaces. The cost and installation of wood shingles and shakes is relatively on the high side.

Categorically, woods are not classified under class A fire proof roofing materials, due to its ease of combustion and low fire resistance. As such fire retardant chemicals are used in treating them before they are used as roofing materials. Nonetheless, roofs made from wood have one of the best aesthetic appearances under display, in the building industry. They still take up new attractive grey-like appearance when expose to weather after a long time (Kolle, 1994).

2.13.5 Tile

Tiles are made from cement, clay and concrete. Roof tile falls under the class A rating as a fire resistant material. Though, its installation is time consuming and tasking (www.cedarbureau.org).

2.13.6 Plastic polymer sheets

Thermoplastics and polymer resins are finding acceptability and application in the building industry. The section of roofing in building is not an exception in this case. This is because of some attractive properties possessed by plastic polymer, which include water resistance. Some plastic roofing sheets presently in the market space are: polycarbonate skylight roofing sheet and polyurethane roofing sheet (polymerdatabase.com).

2.14 Requirement/Necessary Properties of a Good Roofing Material

Shelter is a critical need of life. Roofing however, is a necessary component that completes the structure of a building, of which the process of raising a building to completion is incomplete without the roofing component. There are various types of roofing sheet materials in the market, but all are expected to meet certain requirement according to international standard before they can be classified and used for roofing purpose (cedarbureau.org). Observation and studies over time according to AS-2049-2002 have shown that some of the key requirements of a good roofing sheet material are: resistance to moisture absorption, fire retardant capacity, good mechanical strength such as hardness, resistance to weathering effect, resistance to chemical attack and acoustic insulation (www.cedarbureau.org).

2.14.1 Strength/hardness

According to AS-2049-2002, roofing tiles are expected to pass an approved flexural strength in-line with (AS-4046-2002) to qualify as a roofing material. This is to ensure that the roofing tile can withstand some acceptable level of stress (load) during installation and maintenance. To be more specific according to standard, the minimum flexural strength of a roof tile should not be less than 3.325 N/mm of a given width of tile under exposure (www.cedarbureau.org).

2.14.2 Resistance to solar radiation effect

Amongst all the components of a building, roof is that component that is more exposed to the elements of weather than any other part, leading to degradation. Some of these elements of weather include rain and solar radiation from the sun. The colour and lustre of roofing materials tend to fade at a relative rate with time under such exposure. Similarly, dust, dirt and pollutants settle on these roofs, thereby obscuring its aesthetic beauty in dry season. Also, lichen and moss tend to grow on these roofs when there is a support structure of dust and dirt. As a way of combating and slowing the rate of roof degradation, materials that are more resistant to the adverse effect of natural weathering are incorporated into the formulation of these roofing sheets. In some cases, these retarding agents are used to gloss or form a coating film with reasonable thickness on the surface of the roofing sheet. Generally, materials made of alkaline substances shows very little discoloration over time under solar radiative effect (www.cedarbureau.org).

2.14.3 Water absorption and permeability resistance

The ability for roofing tile to resist water absorption is one of the requirements of a good roofing material. According to American standard of testing material (ASTM C373-2018), water absorption capacity for nonporous roofing tile is between 0.1 -0.5%, while porous roofing tile is between 9 -15% (www.theconstructor.org). Similarly, using a testing standard of AS 4046 -2002 for water absorption, roofing tiles are expected to comply with AS 2049-2002, and AS 4046 -2002 for permeability. General purpose tiles should have a water absorption capacity of not more than 10% (www.cedarbureau.org).

2.14.4 Heat and fire resistance

The ability of a roofing material to resist heat and fire is a critical requirement of a roofing tile or sheet to function. The use of Differential Scanning Calorimeter (DSC) is one of the instruments that can be used to investigate the oxidation, thermal behaviour and the fire resistance of polymer composites. Two different test methods can be used to determine this analysis (www.linseis.com).

Oxidation induction time (OIT) test: This is the time interval between the onset of the oxidation process and the decomposition of the polymer material. In this case, the atmosphere in the isothermal segment chamber is changed to oxygen.

Oxidation onset temperature (OOT) test: This is the onset temperature at which a polymer material begins to decompose when expose to oxidation process by heat or fire. This temperature is noted and recorded by the DSC machine. A constant heating rate is adopted in this case (www.linseis.com).

2.15 Weathering of Polymer Composite

Physical and scientific observations have shown that all existing materials such as polymer composite, when exposed to the environment are adversely affected by natural weathering. This ultimately leads to material degradation. Though, the rate of degradation differs. Aside natural weathering accelerated method of weathering under controlled condition can be simulated to initiate the process of weathering also on polymer and polymer composite (Rudi *et al*., 2019). Natural weathering test method is adopted for use in this work.

2.15.1 Natural and accelerated weathering test

Natural weathering is a degradation process experienced by exposed material such as polymer composite initiated by nature (environmental factors) such as rain, sunlight, humidity, freeze thaw, heat and photo-oxidation processes over a given period of time. The prediction of the lifespan of material such as polymer composite can be very cumbersome and time consuming. As such, immediate result cannot be obtained and relied upon. This is because natural degradation or the aging composite of polymer takes place over a cumulative extended period of time (Taylor *et al*., 2016). This is an indication that urgent and immediate analysis of the degradative effect of natural weathering of polymer composite may not be easily attainable or practicable.

In order to make up for this shortcoming, researchers have designed and adopted an artificial UV accelerated weatherometer for use. This is a simulated laboratory equipment that mimics outdoor natural weathering conditions. This gives researchers the opportunity to obtain results on natural degradation over a short period of time in comparison to natural weathering processes. However, there are reservations that accelerated or artificial weathering results may not absolutely reflect the outcome of a corresponding outdoor weathering degradation (Taylor *et al*., 2016). In order to reconcile this variation, Badji *et al.* (2018) proposed a correlation factor refer to as acceleration factor. This expresses a ratio between accelerated/ artificial weathering duration and natural weathering duration. This is to assist in capturing and translating the same effect of degradation for different materials.

For example, the degradation effect of pure polypropylene exposed to natural weathering over a period of one year is equivalent to 250 h accelerated weathering exposure. While the degradation effect of 750 h accelerated weathering on polypropylene composite is equivalent to one year natural weathering exposure (Mihai, 2020). Similarly, Azwa *et al.* (2013) reported that 400 - 2000 h accelerated weathering is equivalent to a minimum of 2 years natural weathering exposure. Furthermore, Friedrich (2018) carried out a comparative degradation review on wood polymer composite. This analysis reveals the fact that, the effect of natural weathering is 7.4 times the artificial accelerated weathering exposure.

In all of these, it is important to note that the equivalent of artificial weathering is not fix or constant universally, due to the following reasons - location of exposure, exposure conditions or factors, angle of inclination of exposure, the inherent property of the material under exposure and exposure protocol and standard.

2.15.2 Degradation and effect of weather on polymer composites

According to Rudi *et al*. (2019), in tropical countries or regions like Nigeria, the durability and performance of polymer composites are severely reduced and adversely affected. Harsh weather condition is responsible for this occurrence. Generally, plastic and polymer composites are susceptible to colour change in physical appearance, alteration in chemical and mechanical properties, loss in weight and degree of crystallinity, as well as embrittlement and chalking resulting from mechanical degradation (Bolaji and Mosobalaje, 2008; Rudi *et al.*, 2019). It is worthy to note that different materials including polymer composite respond and manifest varying degree of degradation on account of natural weathering. This variation in responses is occasioned by the differences in the reinforcing fibre/filler and polymer matrix that forms the composite. The degree and type of exposure is also a key factor. Highly crystalline polymer zones are characterized by chain scission resulting from polymer degradation, leading to cracks and embrittlement. Studies have shown that photo bleaching and discolouration are more pronounced in polymer composite with high lignin content. However, the addition of antioxidant mineral additives such as calcium carbonate and talc, have the potential of minimizing the occurrence of colour fading. Similarly, ultra violet (UV) stabilizers like titanium oxide, Hindered Amine Light stabilizers (HALs) and zinc oxide are incorporated into polymer composite to minimize the formation of radicals, strengthen its durability and preserve its aesthetic appearance over an extended period of weathering (Muasher and Sain 2006, Rudi *et al.*, 2019). The degradation of polymer composite can be initiated by artificial accelerated weathering or natural weathering. The former simulates the real natural weathering process. The UV degradation process of polymer composite reinforced with natural fibre is presented in Figure 2.2.

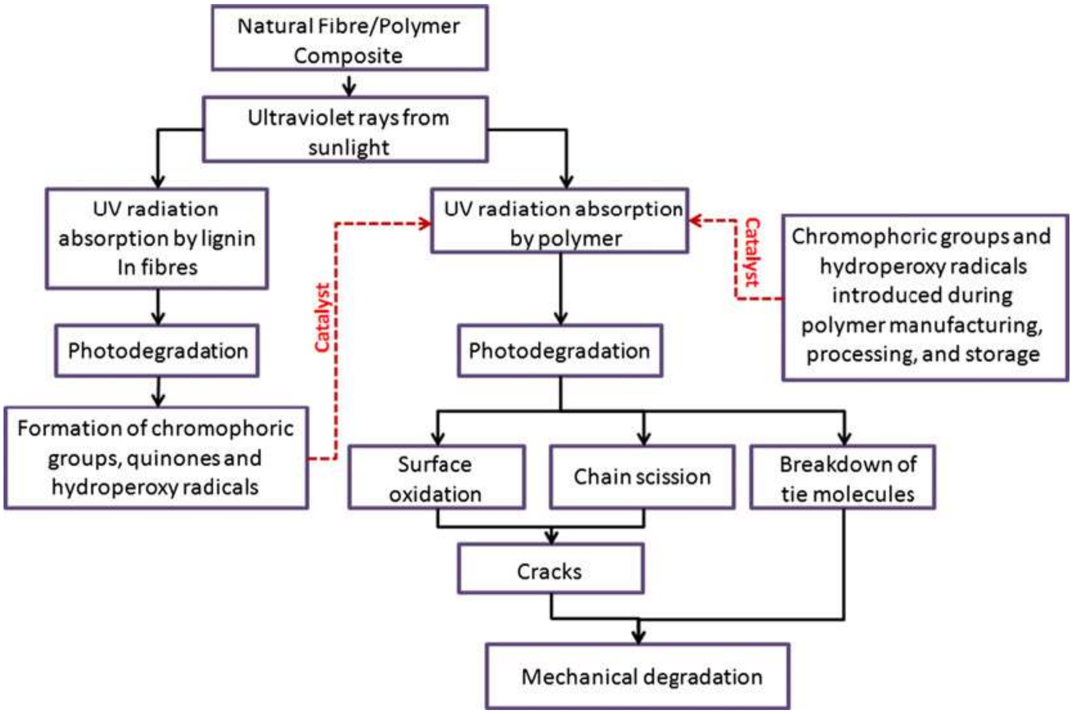


Figure 2.2: UV Degradation of Natural fibre/Polymer Composite and its components (Azwa *et al*., 2013).

2.15.3 Mechanism of plastic polymer degradation

The mechanism of the degradation of plastic polymer when exposed to weathering conditions goes through three basic stages: initiation, propagation and termination as shown in Equation 2.4 – 2.12. Equation 2.4 reveals the abstraction of hydrogen at initiation stage. Equation 2.5 presents the free radical reaction at propagation stage. Equation 2.6 presents the peroxyl radical reaction at propagation stage. Equation 2.7 reveals the splitting of hydro peroxide at propagation stage. Equation 2.8 and 2.9 present reaction of radicals, while Equation 2.10 – 2.12 present the termination stage of the plastic polymer degradation process.

$$R - H \rightarrow R^* + H^* \tag{2.4}$$

$$R^* + O_2 \rightarrow ROO^* \tag{2.5}$$

$$ROO^* + RH \rightarrow R^* + ROOH \tag{2.6}$$

$$ROOH \ \rightarrow RO^* + OH^* \tag{2.7}$$

$$RO^* + RH \rightarrow R^* + ROH \tag{2.8}$$

$$OH^* + RH \rightarrow R^* + H_2O \tag{2.9}$$

$$R^* + R^* \rightarrow R - R \tag{2.10}$$

$$2ROO^* \rightarrow ROOR + O_2 \tag{2.11}$$

$$R^* + ROO^* \rightarrow ROOR \tag{2.12}$$

2.15.4 Carbonyl index (CI) parameter

The formation of carbonyl functional group is one of the ways in which the effect and extent of degradation in plastic polymer can be detected and monitored. The identity of this functional group is found within the wavenumber of 1900- 1600cm^{-1} in the FTIR spectrum. The parameter that measures the extent of the formation of these carbonyl groups due to photo-oxidation is known as carbonyl index (CI). This index is accounted for by calculating the ratio of absorbance peak of a carbonyl group to a reference stable absorbance peak such as alkane – C-H.

$$Carbonyl\ Index = \frac{Absorbance\ peak\ of\ the\ carbonyl\ group(C{=}O)}{Absorbance\ peak\ of\ a\ stable\ reference\ peak(C{-}H)} \qquad (2.13)$$

A high carbonyl index value is a reflection of a high degree of thermal-oxidative degradation. Another method of analysis of carbonyl index is the specific area under band (SAUB) of the respective absorbance peaks of the FTIR spectrum (Kelly, 2018). The former method is used in this work.

2.16 Review of Other Related Works

Narongrit *et al*. (2003) investigated the effect of the content of wood sawdust on the properties of polyvinyl chloride (PVC)/sawdust composites. The rheological, mechanical and thermal degradation properties of PVC/sawdust composite were investigated. The research gap shows that only one fibre (sawdust) was used for the reinforcement of the polymer matrix (PVC). Also, the sawdust was not chemically treated.

Bolaji and Mosobalaje (2008) reported the development of a roofing material from virgin polyethylene reinforced with synthetic mineral additives (NH_4Cl and carbon black). The authors in this work recorded a maximum tensile strength of 6.24 MPa from the polymer composite produced. An artificial weathering environment was simulated through the use of a 500W halogen lamp, to physically observe the extent of degradation. The polymer composite produced was not subjected to natural weathering, and the rheological property of the polymer composite was also not investigated.

Samotu (2010) investigated the suitability of reinforcing pure water sachet (low density polyethylene) with carbonised palm kernel shell (CPKS) and iron filing to produce polymer composite for automobile bumper. The maximum impact energy (0.18 J/cm^2) and density (0.702 g/cm^3) was obtained with 5% CPKS and 5% iron filing reinforcement, while the maximum ultimate tensile strength is 8.24 N/mm^2. This value for tensile strength decreases with the reinforcing fillers. The car bumper was not subjected to thermal, water absorption and natural weathering test. Similarly, the CPKS fibre was not chemically treated.

Adama and Jimoh (2011) investigated the production and classification of ash from locust bean pod husk as a Pozzolan. Based on the properties obtained, LBPA was classified as a pozzolan (additive) for use in weak soil for road construction. Only particle size distribution and chemical composition analysis of the LBPA was carried out. The locust bean pod fibre was not chemically treated also.

Aghazadeh *et al.* (2011) researched on the effect of temperature and particle weight fraction on mechanical and micro‒mechanical properties of sand‒polyethylene terephthalate (PET) composite. Particulate composite was produced from recycled PET and silica particles. Design of experiment was not carried out. The PET composite produced was not tailored toward any specific application.

Aguwa and Okafor, (2012) carried out preliminary investigation into the use of locust bean pod (LBP) as Binder for production of laterite blocks for building. LBP extract solution was used as the only binder in the laterite block production. The compressive strength of laterite blocks produced with LBP extract increases with concentration. An increase of

78.57% in compressive strength was recorded with the addition of LBP extract. Though, the LBP fibre was not treated.

Atuanya *et al.* (2014) reported the physico-mechanical properties of polymer composite produced from used low density polyethylene (LDPE), reinforced with bean pod husk ash particulate. The physico-mechanical property of the reinforced polymer composites was investigated. Though, the beans pod husk was not chemically treated before use. The polymer composite produced was not tailored toward a specific application.

Ndububa and Uloko (2015) researched into the use of locust bean pod husk ash (LBPHA) as a pozzolanic material in concrete. Concrete was produced using LBPHA as a component partly representing cement in the concrete mix. The locust bean pod was not chemically treated. Only the compressive strength as well as the water absorption capacity of the LBPHA in the concrete was determined.

Bed (2015) reported the preparation and characterisation of wood plastic composite using used (LDPE/HDPE) Plastic and Sawdust. Wood plastic composite was produced from hard and soft wood with LDPE/HDPE polymers. The wood fibres were only treated with 5% NaOH concentration, and the application of the composite was not investigated.

Omoyeni *et al.* (2016) investigated the use of maize husk as reinforcement in used low density polyethylene (LDPE) waste material for composite board production. The compressive property of the maize husk/recycled LDPE composites was investigated & produced by compressive moulding method using Taguchi design. The maize husk was not chemically treated before use and its rheological properties were not investigated.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The materials used for this research are: *Eucalyptus globulus* sawdust, locust bean pod husk, clay and used low density polyethylene (empty water sachet). All the chemicals that were used are of analytical grade. The equipment used to carry out this research are listed in Table 3.1.

Table 3.1: List of Equipment Used

S/No	Equipment	Uses	Sources
1	Scanning Electron Microscopy (SEM)	To determine surface morphology of fibres/ filler.	AUST
2	Fourier Transform Infrared spectroscopy (FTIR)	To determine functional group and covalent bond in composite.	SHEDA
3	Compression moulding machine	To mould and cure polymer composite.	NILEST,
4	Differential scanning Calorimeter (DSC)	To determine the thermal stability of the composite.	STEP-B, KATPOLY
5	Lab Sieves & Mechanical Shakers	To separate fibre particle into micro sizes.	FUT
6	X- Ray Diffraction	To determine the crystallinity index.	NARICT
7	Universal Tensile Machine	To determine the mechanical properties of a composite.	AUST
8	Two rolling mill	For mixing compounding of fibre and polymer matrix	NILEST
9	Nano indenter	To determine hardness value of composite.	AUST

3.2 Processing and Preparation of the Fillers and Polymer Raw Materials

The processing and preparation of the reinforcing fillers (sawdust fibre, locust bean pod husk and clay) and the used low density polyethylene matrix for the hybrid composite is presented below:

3.2.1 Sample collection and preparation of sawdust

Sawdust from *Eucalyptus globulus* (EG) wood was collected from the saw mill in Birnin-Gwari forest in Kaduna State. Size reduction of the EG sawdust particles was carried out in a mill. It was then sieved and sun dried. Fine particle sizes ranging from 60 -100 mesh (250-150µm) was selected. It was further dried in an oven at a temperature of 80^{o}C for 24 h to further reduce the moisture content until constant weight was achieved. This was stored for further processing (chemical treatment) (Muhammad *et al*., 2011).

3.2.2 Chemical treatment of sawdust and carbonisation

The prepared EG sawdust particles were dried in an oven for 24 h at 105^{o}C to achieve a constant weight. A 100 g weight of sawdust each was taken and treated with sodium hydroxide based on the experimental design input factors. The treated sawdust was washed with enough distilled water until the pH of the solution attains neutrality to modify the sawdust particles in order to enhance better bonding and interaction with the polymer matrix. Thirteen (13) runs were carried out for the sawdust treatment. The 12th run was observed to have the highest optimum response of cellulose content. This was then carbonised in a furnace at 500^{o}C for two hours, to form char and ash particles. This was stored and used as one of the reinforcing fillers for the hybrid composite production (Muhammad *et al*., 2011).

3.2.3 Design of experiments

Central composite design (CCD) was used to design the chemical treatment process using NaOH. The design experiment showing the interaction between the input or independent factors which determines the responses (chemical composition) of the EG sawdust fibre and locust bean pod husk fibre is shown in Table 3.2.

Table 3.2: Experimental Design Using Central Composite Design

Input Factors	**-∝**	**-1**	**0**	**+1**	**+∝**
Treatment Concentration (%)	0.88	1.5	3	4.5	5.12
Contact Time (hours)	0.59	1	2	3	3.41

Thirteen (13) runs are generated and used based on the design of experiment for the alkaline treatment process of the *Eucalyptus globulus* sawdust (EGS) and locust bean pod husk (LBPH) as shown in Table 3.3.

Table 3.3: Experimental Design for the Alkaline Treatment Process for EGS and LBPH

STD	Run	Block	Input Factors	
		Block	Treatment Concentration of EGS and LBPH (%)	Contact Time (h)
8	1	Block 1	3	3.41
10	2	Block 1	3	2
6	3	Block 1	5.12	2
11	4	Block 1	3	2
1	5	Block 1	1.5	1
4	6	Block 1	4.5	3
2	7	Block 1	4.5	1
12	8	Block 1	3	2
13	9	Block 1	3	2
5	10	Block 1	0.88	2
3	11	Block 1	1.5	3
7	12	Block 1	3	0.59
9	13	Block 1	3	2

3.2.4 Sample collection and preparation of locust bean pod

Locust bean pod husk (LBPH) fibre was collected from the heap waste of farmers involved in the processing of locust bean condiment called *dawadawa* in Bosso, Minna, Niger State.

The husk were cleaned, dried in the sun and reduced into a particle size range of 60 -100 mesh (250-150µm) (Muhammad *et al*., 2011).

3.2.5 Chemical treatment of locust bean pod and carbonisation

The locust bean pod husk (LBPH) fibre was chemically treated using NaOH according to the experimental design presented in Table 3.3. Thirteen (13) runs were also carried out in all for the alkaline treatment of the locust bean pod husk fibre. The 3rd run was observed to have the highest optimum response of cellulose content. This was then carbonised in a furnace at 500^{o}C for 2 h to form carbonised ash particles (Atuanya *et al*., 2011). This was stored and used as one of the reinforcing filler for the hybrid polymer composite production.

3.2.6 Chemical composition of the natural fibres (EGS and LBPH)

Sequential extraction method of biomass analysis according to Sridevi *et al*. (2015) was used to determine the chemical composition (cellulose, hemicellulose, lignin, extractives and ash content) of the reinforcing fibres used. The procedure for the analysis is as follows:

The water soluble extractives were determined by heating 1 g each of the sawdust and locust bean pod husk respectively in 100 ml of water at 100^{o}C for two hours. The residue was washed repeatedly with water and acetone until a neutral pH is attained. It was later dried at 60^{o}C for 24 h in an oven. While the determination of ethanol soluble extractives was carried out the same way but ethanol was applied instead of water.

The lignin was extracted by heating the residue at 100°C in the presence of 2 ml of 10% acetic acid, 30 ml water and 0.6 g of sodium hypochlorite. After 1 h, another 0.6 g of hypochlorite and 2 ml of the acetic acid solution were added for further 1 h treatment. The residue was washed repeatedly with hot water, acetone and ether. It was dried at 60°C for 24 h.

The hemicelluloses were determined by mixing the residue with 24% KOH for 2 hours at room temperature. The residue was repeatedly washed with water, acetic acid, acetone and ether. It was finally dried at 60°C in an oven. The final residue was the cellulose content of the biomass used. The ash content was determined by heating 1 g of the biomass in a muffle furnace at 650°C for 3 hours. It was left to cool for 24 hours and the residue was weighed as the ash content.

3.2.7 Sample collection and preparation of clay

The clay sample used was collected from a clay deposit in Kutigi, Niger State. The clay material was crushed, cleaned and purified to remove organic particles. The clay sample was later reduced into fine particle size of 75µm, after which it was heated in an oven at a temperature of 80^{o}C for 24 h to achieve constant weight. This prepared clay sample was then calcined in a furnace at 500^{o}C for 2 h. The calcined clay was stored and used as additive filler for the hybrid polymer composite production (Olowokere *et al*., 2012).

3.2.8 Sample collection and preparation of used low density polyethylene

Post-consumer low density polyethylene (LDPE) popularly known as (pure water sachet) was obtained from pure water vendor in Bosso, Niger State, Nigeria. The used LDPE popularly called pure water sachets were cleaned, washed and dried in the sun to remove residual dirt. It was then shredded into smaller pieces using a pulverizing machine. This was kept for further use as the polymer matrix to be used for the production of hybrid polymer composite (Bed, 2015).

3.3 Processing Techniques of Polymer Composite

In this case, the processing of the hybrid polymer composite involves two stages, namely:

a) Preparation and processing of the reinforcing materials and polymer matrix – sawdust and locust bean pod husk and clay, as explained in this methodology.

b) Compounding and moulding of the prepared fillers samples and the recycled LDPE matrix in a two rolling mill and compression moulding machine to produce the hybrid polymer composite (Bed, 2015).

3.3.1 Compounding and moulding of hybrid polymer composite

During compounding, the low density polyethylene (used water sachet) was heated until it melt and begin to flow at 160^{o}C using a two rolling mill. The EG sawdust ash, locust bean pod LBPH ash, and clay were then thoroughly mixed together to obtain a homogeneous mixture with the melted LDPE matrix in the two rolling mill. The compounded homogeneous mixture is transferred into a rectangular mould and then placed in a compression moulding machine, where it is compressed and cured into a hybrid polymer composite (HPC) tile. Similarly, two compounded samples of used and virgin polyethylene matrices were also produced to serve as control samples for the HPC (Hietala, 2013).

3.3.2 Process-mixture experimental design

Process-mixture experimental design, which is a sub class of Response surface methodology (RSM) design of experiment, was used to determine the relationship and interaction amongst the independent variables known as controlling factors. This ultimately influences the production process of the hybrid polymer composite, through which the output or responses of the experimental process were measured and characterized (Ojewumi, 2016). In this research, the combined effect of both process variables and mixture variables (component proportion variables) was used to develop an optimized model that influences the product properties and quality of the hybrid polymer composite produced for roofing tiles. The process-mixture experimental design formulation for the hybrid polymer composite production is shown in Table 3.4.

Table 3.4a: Process–Mixture Design Experimental Formulation for Hybrid Polymer Composite

S/NO	**Four (4) Components Mixture**				**Two (2) Factors**	
S/NO	**EGSA wt%**	**LBPA wt%**	**CL wt%**	**PE wt%**	**T °C**	**MT min**
1	5.000	40.000	15.000	40.000	150	15.00
2	5.000	40.000	2.000	53.000	160	12.50
3	16.875	20.875	10.375	51.875	150	15.00
4	30.000	3.000	2.000	65.000	150	15.00
5	30.000	3.000	2.000	65.000	150	10.00
6	5.000	3.000	2.000	90.000	160	15.00
7	46.000	3.000	11.000	40.000	155	12.50
8	18.000	40.000	2.000	40.000	160	10.00
9	30.000	3.000	2.000	65.000	160	12.50
10	30.000	3.000	2.000	65.000	155	12.50
11	5.000	35.000	20.000	40.000	155	10.00
12	5.000	24.200	11.800	59.000	150	12.50
13	30.000	3.000	2.000	65.000	160	15.00
14	18.000	40.000	2.000	40.000	150	15.00
15	55.000	3.000	2.000	40.000	150	15.00
16	5.000	40.000	2.000	53.000	155	10.00
17	5.000	3.000	20.000	72.000	160	12.50
18	37.000	3.000	20.000	40.000	160	15.00
19	5.000	3.000	20.000	72.000	160	10.00
20	55.000	3.000	2.000	40.000	150	10.00
21	46.000	3.000	11.000	40.000	150	15.00
22	55.000	3.000	2.000	40.000	150	10.00

Table 3.4b: Continuation

23	5.000	3.000	20.000	72.000	150	10.00
24	5.000	24.200	11.800	59.000	150	10.00
25	18.000	40.000	2.000	40.000	160	10.00
26	30.000	3.000	2.000	65.000	160	12.50
27	37.000	3.000	20.000	40.000	150	12.50
28	30.000	3.000	2.000	65.000	155	15.00
29	5.000	3.000	20.000	72.000	150	15.00
30	55.000	3.000	2.000	40.000	160	15.00
31	11.500	40.000	8.500	40.000	150	10.00
32	16.875	20.875	10.375	51.875	155	15.00
33	5.000	3.000	20.000	72.000	155	15.00
34	37.000	3.000	20.000	40.000	150	10.00
35	36.500	21.500	2.000	40.000	160	12.50
36	5.000	3.000	2.000	90.000	150	12.50
37	5.000	40.000	2.000	53.000	150	15.00
38	5.000	37.500	17.500	40.000	150	13.75
39	5.000	3.000	2.000	90.000	160	10.00
40	5.000	35.000	20.000	40.000	150	10.00
41	5.000	40.000	2.000	53.000	150	10.00
42	30.000	3.000	2.000	65.000	160	10.00
43	11.500	40.000	8.500	40.000	150	12.50
44	5.000	3.000	2.000	90.000	150	15.00
45	5.000	35.000	20.000	40.000	150	10.00
46	5.000	21.500	2.000	71.500	150	12.50
47	5.000	35.000	20.000	40.000	160	15.00
48	5.000	40.000	15.000	40.000	155	15.00
49	36.500	21.500	2.000	40.000	150	10.00
50	5.000	3.000	20.000	72.000	160	10.00

Table 3.4c: Continuation

51	5.000	40.000	2.000	53.000	155	10.00
52	55.000	3.000	2.000	40.000	155	12.50
53	5.000	35.000	20.000	40.000	150	15.00
54	30.000	3.000	2.000	65.000	160	12.50
55	5.000	40.000	15.000	40.000	155	10.00
56	18.000	40.000	2.000	40.000	160	15.00
57	16.875	20.875	10.375	51.875	160	10.00
58	37.000	3.000	20.000	40.000	160	10.00
59	5.000	3.000	2.000	90.000	160	10.00
60	5.000	3.000	11.000	81.000	150	15.00
61	5.000	3.000	2.000	90.000	150	10.00
62	16.875	20.875	10.375	51.875	160	10.00
63	5.000	35.000	20.000	40.000	150	12.50
64	55.000	3.000	2.000	40.000	155	10.00
65	37.000	3.000	20.000	40.000	155	15.00
66	5.000	40.000	15.000	40.000	150	10.00
67	30.000	3.000	2.000	65.000	160	10.00
68	5.000	40.000	2.000	53.000	155	15.00
69	37.000	3.000	20.000	40.000	150	10.00
70	30.000	3.000	2.000	65.000	160	15.00

Where **EGSA** = *Eucalyptus globulus* Sawdust Ash, **LBPA** =Locust Bean Pod Ash, **CL** = Clay, **PE** = Polyethylene, **T** = Temperature, **MT**= Mixing Time.

The process–mixture components/factor determines the response quality of the hybrid polymer composite.

3.3.3 Procedure for the production process of hybrid polymer composite

The hybrid polymer composite (HPC) was produced using two roll mill machine and automatic compression moulding machine. The two roll mill machine was operated to work and compound both the low density polyethylene matrix and reinforcing fillers at an optimum temperature of 160^{o}C with an average speed of 75 rpm. The two rollers in the mill rotated at anticlockwise direction to each other.

40 wt% of low density polyethylene was loaded on the two roll milling machine to melt and flow at 160^{o}C. After which 5wt% of sawdust ash, 40 wt% of locust bean pod ash and 15 wt% of Kutigi clay were mixed and compounded homogeneously for a period of 6.5 minutes on the machine. The hot melted compounded chewing-gum-like plasticized composite was transferred into a mould of dimension (100x165x3mm), and then placed inside an automatic compression moulding machine for it be pressed and cured in to a rectangular shaped composite for 6 minutes at 160^{o}C. The cured composite sample in the mould was allowed to cool before it was removed from the mould.

The same production procedure was observed and maintained for 70 runs, all through the remaining composite production process, according to the process-mixture experimental design formulation in Table 3.4. The summary of the HPC production process flow chart is shown in Figure 3.1.

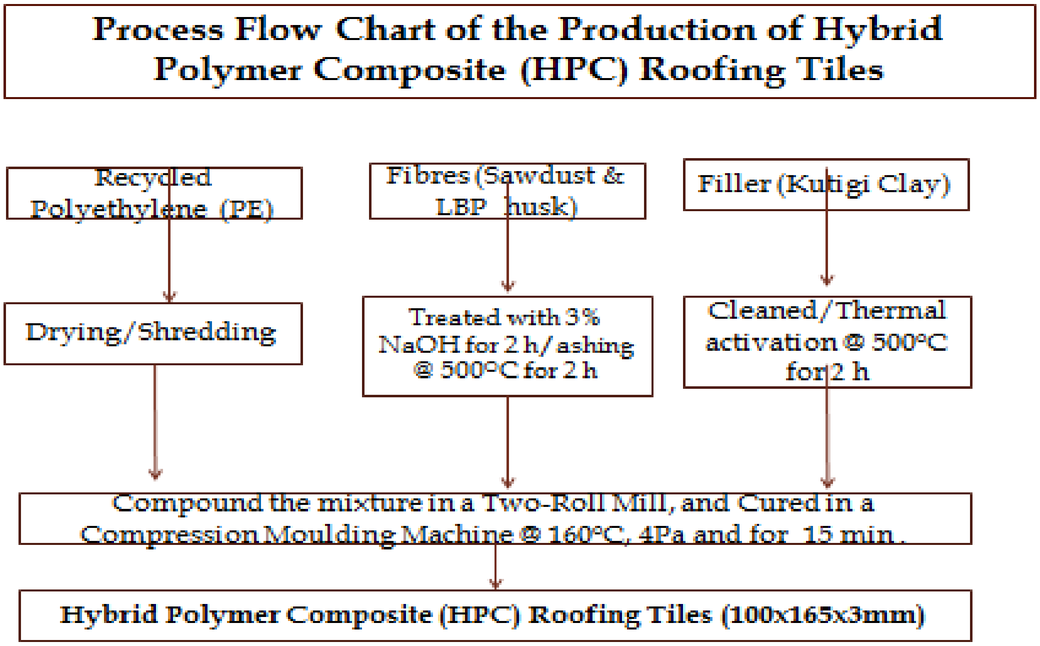


Figure 3.1: Production Process Flow Chart of the Hybrid Polymer Composite

3.4 Micro Structural Analysis

The following techniques were used to determine and analyse the micro structural properties of the reinforcing materials and the polymer matrix. Similarly, the hybrid polymer composite produced was also analysed.

3.4.1 Determination of the functional groups present in samples

The observations and changes in the functional group present in the raw, treated reinforcing materials and hybrid polymer composite was determined and captured by Fourier Transform Infrared (FTIR) spectroscopy machine of model NICOLET 155 thermo scientific Nicolet corporation, madison USA. The FTIR spectra of the samples were analyzed in the range of 4000 cm^{-1} to 500 cm^{-1}.

3.4.2 Determination of the morphology of samples

SEM- EDX (Phenom ProX Generation 5) machine was used to show the morphology or surface chemistry of the untreated, treated reinforcing fibre-ash, clay filler and hybrid polymer composite, alongside the corresponding elemental composition of the fibre-ash. This has help to further reveal the interfacial adhesion between the fillers and the polymer matrices.

3.4.3 Weathering test for the hybrid polymer composite as a roofing material

A natural weathering process performance evaluation test was carried out to ascertain the ability of the hybrid polymer composite to withstand harsh weather conditions such as ultra violet radiation, heat and rainfall and humidity.

The optimum hybrid polymer composite (HPC) sample, recycled polyethylene matrix, virgin polyethylene matrix and polycarbonate commercial sample were affixed unto a flat board and placed on the roof top of a building. This was done to expose all the sample materials to the effects natural weathering (sun, rain, wind, heat, humidity and ultra-violet ray) for a period of one year. Using FTIR analysis, the functional groups of these materials were determined before and after the natural weathering process. This is to ascertain the carbonyl index (CI). Similarly, the mechanical properties (flexural strength and hardness) were also determined to evaluate the extent of degradation (Kelly, 2018).

3.4.4 Thermal stability test

Differential Scanning Calorimeter (DSC) machine with model number 1-800-METTLER TOLEDO was used to determine the thermal and oxidative stability of the hybrid polymer composites**,** in order to determine the enthalpy change (ΔH), glass transition temperature

T_g, melting temperature T_m, degree of crystallization X_c, heat capacity (ΔCp) and oxidation onset temperature (OOT) of the HPC.

3.5 Mechanical Test

The following tests were carried out to ascertain the physico-mechanical properties of the raw and treated fabricated composite as a suitable material for roofing in building. The physico-mechanical test include: flexural strength, tensile strength, elongation and hardness.

3.5.1 Tensile strength test

The tensile test was carried out following American Society of Testing and Materials - ASTM D 638-01 (2002). Instron universal tensile testing machine was used with a maximum load of 5 kN, and each test was performed at a crosshead speed of 10 mm/min. Bluehill 3 software was used to run, collate and display the data. For each test, three replicate samples were tested, and the average value reported.

3.5.2 Flexural strength test

The flexural strength test was conducted using the three points bending test, following American Society of Testing and Materials - ASTM D 256 (2000). Instron universal testing machine was used at a maximum load of 0.5 kN and crosshead speed of 10 mm/min. Bluehill 3 software was used to run, collate and display the data. For each test, three replicate samples were tested, and the average value reported.

3.5.3 Hardness test

The hardness of the hybrid polymer composite samples are determined using a nanoindenter machine according to ASTM D785-98 (2002). For each test, three replicate samples were also tested and the average value reported.

3.6. Water Absorption Capacity Test

The Water Absorption Capacity (WAC) of the hybrid polymer composite in terms of change in mass was determined. The polymer composite samples were dried at 40°C until a constant weight is reached and recorded as (W_1), prior to immersion in a water bath for 72 hours. After this duration, the samples were removed and wiped properly with a towel, before it was reweighed as (W_2). Three replicate samples for each sample was used to obtain the average value. The Water absorption capacity was calculated using Equation 3.1.

$$\text{Water absorption \%} = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (3.1)$$

Where w_2 is the specimen weight after soaking and w_1 is the weight of sample before soaking (Muhammad *et al.*, 2011).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Characterisation of the Reinforcing Fibres, Filler and Used Low Density Polyethylene

Characterisation provides both the microscopic and macroscopic properties of a material. The chemical compositions of *Eucalyptus globulus* sawdust (EGS) and locust bean pod husk (LBPH) for the untreated samples are presented in Table 4.1.

Table 4.1: Chemical Composition of Untreated *Eucalyptus globulus* Sawdust (EGS) and Locust Bean Pod Husk (LBPH)

Sample	Cellulose %	Hemi-cellulose %	Lignin %	Extractive %	Ash %
Untreated EGS	41.3	23.2	31.4	3.4	0.7
Untreated LBPH	59.3	20.2	10.2	9.1	1.2

4.1.1 Untreated *Eucalyptus globulus* sawdust (EGS) and locust bean pod husk (LBPH)

The chemical composition of these materials, are made up of cellulose, hemicellulose, lignin, extractives (wax and oils) and ash. The cellulose content (41.3%) of the untreated EGS is the highest among other components and the lowest is ash with 0.7%. Similarly, the cellulose content (59.3%) of the raw LBPH fibre is the highest among other components, with the ash having the lowest content of 1.2%. Though, the cellulose content of untreated LBPH is comparably higher than that of EGS. This is because in most cases, fruit fibres have higher cellulose content than wood fibres (Khairiah and Khairul, 2006). This result is similar to that obtained by Pereira *et al.* (2013) on several species of EGS wood for charcoal yield, and for untreated sugar palm fibre by Hyas *et al*. (2017). The results of the treated EGS and LBPH are presented in Tables 4.2 and 4.3.

Table 4.2: Chemical Composition of Treated *Eucalyptus globulus* Sawdust at different Treatment Concentration and Contact Time

Std Run	**Factor 1**	**Factor 2**	**Responses**				
	NaOH Treatment Concentration (%)	**Contact Time (h)**	**Cellulose %**	**Hemi-cellulose %**	**Lignin %**	**Extractives %**	**Ash %**
1	1.50	1.00	45.2	22.2	29.1	3.2	0.3
2	4.50	1.00	67.1	11.1	19.6	2.1	0.1
3	1.50	3.00	47.3	20.1	30.1	2.3	0.2
4	4.50	3.00	73.1	8.1	16.1	2.4	0.3
5	0.88	2.00	44.1	21.2	31.2	3.1	0.4
6	5.12	2.00	73.8	9.1	14.3	2.3	0.5
7	3.00	0.59	48.4	19.9	28.7	2.9	0.1
8	3.00	3.41	55.2	16.8	24.3	3.1	0.6
9	3.00	2.00	74.2	9.4	14.1	1.9	0.4
10	3.00	2.00	74.0	9.6	14.2	1.8	0.4
11	3.00	2.00	74.1	9.5	14.0	2.1	0.3
12	3.00	2.00	74.6	9.3	14.1	1.8	0.2
13	3.00	2.00	74.4	9.5	14.2	1.6	0.3

Table 4.3: Chemical Composition of Treated Locust Bean Pod Husk at Different Treatment Concentration and Contact Time

Std Run	**Factor 1**	**Factor 2**	**Responses**				
	Treatment concentration (%)	**Contact Time (h)**	**Cellulose %**	**Hemi-cellulose %**	**Lignin %**	**Extractives %**	**Ash %**
1	1.50	1.00	74.20	9.00	7.00	8.80	1.00
2	4.50	1.00	55.70	15.50	20.10	8.20	0.50
3	1.50	3.00	80.00	6.10	5.00	8.00	0.90
4	4.50	3.00	53.80	14.40	23.50	7.70	0.60
5	0.88	2.00	60.20	13.00	23.10	2.60	1.10
6	5.12	2.00	51.20	18.00	25.20	5.10	0.50
7	3.00	0.59	67.40	10.70	9.60	11.50	0.80
8	3.00	3.41	61.10	12.30	22.10	3.40	1.10
9	3.00	2.00	60.1	16.1	13.1	9.5	1.2
10	3.00	2.00	60.0	16.1	13.2	9.6	1.1
11	3.00	2.00	59.9	16.2	13.5	9.4	1.0
12	3.00	2.00	60.2	16.0	13.0	9.6	1.2
13	3.00	2.00	60.0	16.0	13.3	9.7	1.0

4.2 Alkaline Treatment of *Eucalyptus globulus* Sawdust (EGS) and Locust Bean Pod Husk (LBPH)

The alkaline (NaOH) treatment of *Eucalyptus glubulus* sawdust presented some physical changes in the aspect of colour, and texture. Upon alkalisation (mercerisation), the fairly pink appearance of the raw sawdust changed to orange, while the natural fibre texture became coarse and rough in handling. This is similar to the observation of Lee *et al.* (2009).

The chemical composition of the treated EG sawdust as shown in Table 4.2 also comprise cellulose, hemicellulose, lignin, extractives and ash. On analysis, the alkaline treatment of the EG sawdust at different concentrations and contact time according to the experimental design in Table 3.3, reveal that the cellulose content increases with increase in alkaline concentration and contact time. While the hemicellulose, lignin, ash and extractive components were found to decrease with increasing alkaline concentration. However, the highest cellulose content obtained for EGS was 74.6% at experimental design conditions of 3% concentration for 2 hours. The observed increase in the cellulose content is probably due to the fact that some of the hemicellulose have been exposed, broken down, and then converted into cellulose due to its amorphous nature and branch-character, as a result of the mercerisation process. The same observation was also made by Amie *et al*. (2013) and Valadez-Gonzalez (1999). Similarly, other non-cellulose components (lignin, extractives and ash) have continued to decrease in percentage composition with increase in NaOH concentration as shown in Table 4.2. This is an indication that these components progressively dissolve in the alkaline solution, and are washed off. This is also observed by Jie and Fumei (2011). It can also be deduced from Table 4.2 that a longer treatment time beyond 2 h, and treatment concentration beyond 3% base on the experimental design, recorded reduced cellulose content and a deteriorating effect on the EGS fibre.

Observation on Table 4.3 for LBPH alkaline treatment shows that as the treatment concentration and contact time continue to increase from 0.87% to 1.5% and 1 – 2 h, the cellulose content increases, while other components like hemicellulose, lignin extractives and ash content continues to decrease. Hyas *et al*. (2017) recorded a similar observation with the exception of the ash content for sugar treated palm fibre. However, beyond 1.5%, the cellulose content begins to decrease progressively at 3, 4.5 and 5.12% NaOH concentration. In this case, the highest cellulose content obtained for LBPH was 80% at experimental design conditions of 1.5% alkaline treatment concentration and contact time of 3 hours. It is evident that excessive alkaline treatment beyond 1.5% has adverse effect on LBPH fibre. This is an indication that LBPH fibre requires moderate treatment concentration to achieve high cellulose content. In this case, LBPH fibre treatment concentration has a stronger effect on the fibre content than contact time.

Comparing the chemical composition of treated EGS and LBPH fibres, it is clear that the LBPH has higher cellulose content for both raw and treated fibre. This is an indication that sources of fibres from fruit husk are higher in cellulose content than in bast fibres such as wood sawdust (Khairiah and Khairul, 2006).

In general, modification of natural fibres such as EGS and LBPH through mercerisation (alkalisation) process, help to minimize their moisture absorption affinity, which is a threat to the durability and mechanical properties of polymer composites. This alkaline modification is achieved by breaking the hydrogen bonds existing between cellulose and other natural fibre components such as hemicellulose and lignin. Also, free hydroxyl groups in the natural fibres intending to bond with water molecules are eliminated (Dittenber and GangaRao, 2012). The EGS fibre with the optimum response based on the experimental design conditions was further subjected to FTIR analysis. This was then carbonised into ash at 500°C for two hours. The FTIR Spectra for raw (untreated) and treated EGS are presented in Figure 4.1 and 4.2 respectively.

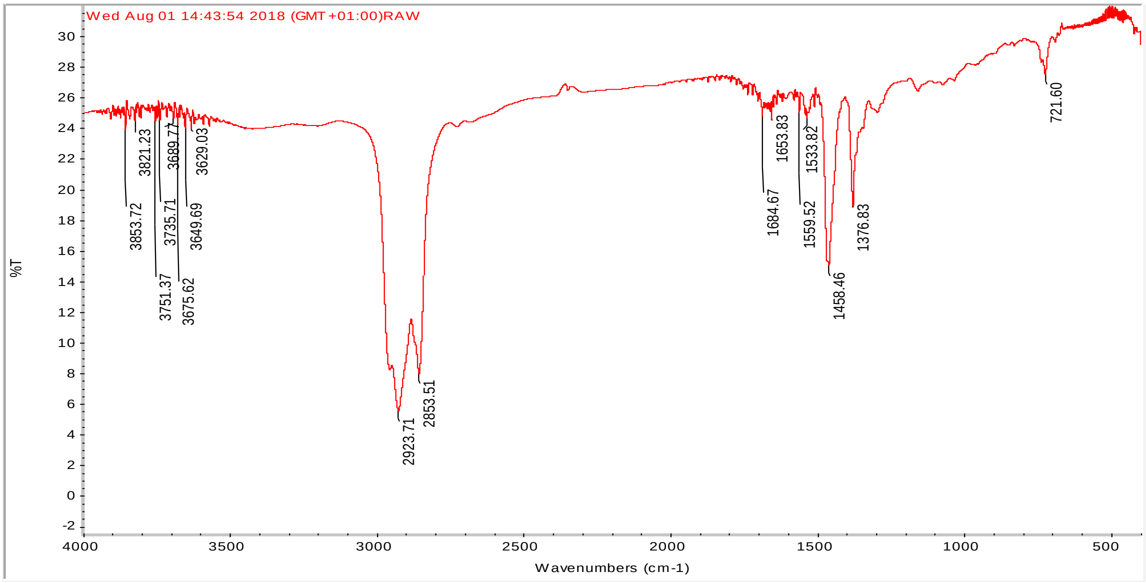


Figure 4.1: FTIR Analysis for Raw (Untreated) *Eucalyptus globulus* Sawdust

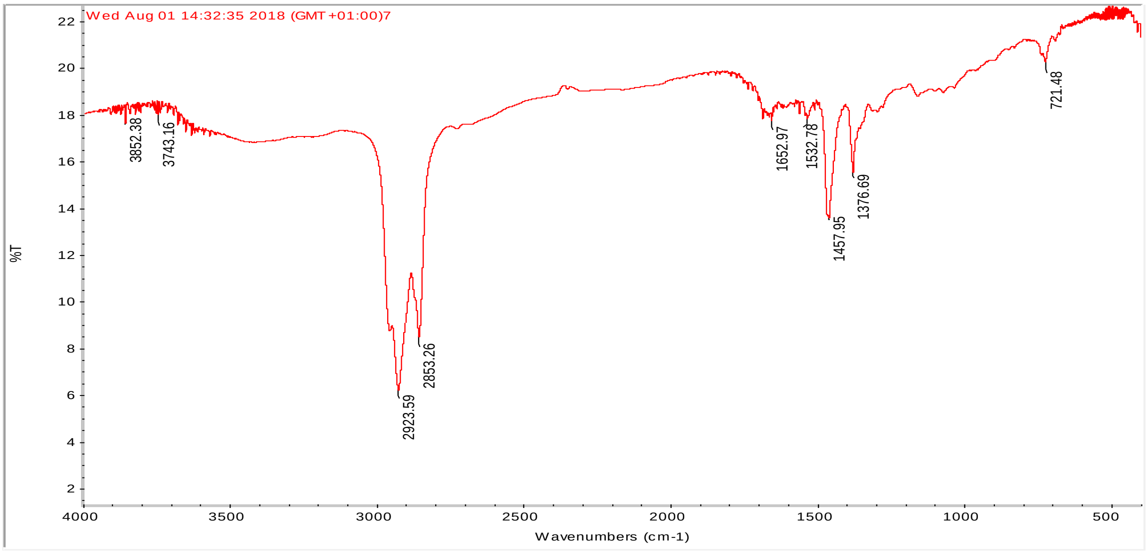


Figure 4.2: FTIR Analysis for Treated *Eucalyptus globulus* Sawdust at 3% NaOH for 2 h

4.2.1 FTIR for raw and treated EG sawdust

Figure 4.1 presents the FTIR information of raw *Eucalyptus globulus* sawdust (EGS). The absorbance region is within the fingerprint skeletal vibration region to single bond stretch region (500 cm^{-1} - 4000cm^{-1}). Three major chemical constituents namely cellulose, hemicellulose and lignin were observed from the raw EGS result based on their designated spectra. Beginning from the single bond stretch, 8 hydroxyl (OH) group peaks in the range of 3853.72 –3629.03cm^{-1} were observed. This functional group is evident in most natural fibres having cellulose and hemicellulose as part of their chemical compositions. This report is similar to (Alemdar and Sain 2008; Sheltami *et al.,* 2012; Jabar 2017 and Hyas *et al.,* 2017). The presence of these OH groups proves the hydrophilic nature of cellulose and hemicellulose in raw EGS. These OH groups are held together by hydrogen bond. This hydrophilic character can actually pose a challenge for raw EGS fibres to be used as a suitable and compactible reinforcing material with hydrophobic polymer resin in composite application. In addition, alkane C-H peaks were observed at 2923.71 and 2853.51 cm^{-1}. This is also an indicative presence of hydrocarbons in raw EGS as reported by Khalil *et al.* (2001). Further observations reveal that C=C double bond stretch groups and variable C=C aromatic rings are present indicating the presence of aromatic attribute of lignin component as observed at (1684.67 – 1653.83 cm^{-1}) and (1559.52 – 1533.82 cm^{-1}) respectively. Also aliphatic chloro compounds C–Cl stretch peaks is seen at a wavelength of 721.60 cm^{-1}.

It is important for raw fibres to be subjected to chemical treatment for it to be suitable for paper and composite application. The FTIR information on Figure 4.2 for the optimum treated EGS at a treatment concentration of 3% NaOH for 2 h shows a reduction in the number of OH groups compared to the raw EGS around 3800 – 3600 cm^-1. These hydroxyl groups that were removed are linked to the branched character of hemicellulose as well as the breakage of the hydrogen bonds situated between the cellulose-hemicellulose components. Similarly, there is also an elimination of some of the insoluble lignin components around 1600 -1500 cm^-1. This depicts clearly the positive effect of the mercerisation treatment process, which has help to reduce the hydrophilic property of the treated EGS fibre, for better adhesion with the polymer matrix.

4.2.2 Carbonisation of *Eucalyptus glubulus* Sawdust (EGS) and Locust Bean Pod Husk (LBPH)

The fibres (EGS and LBPH) at optimum alkaline treatment conditions were carbonised at 500^{o}C for 2 h. These were used as fillers for reinforcing recycled polyethylene matrix for hybrid composite production. Fibre ash was also produced from the raw EGS and LBPH to serve as control when analysing the effect of the alkaline treatment on the composite production.

A starting mass of 100g of raw EGS, raw LBPH, treated EG and treated LBPH fibre were carbonised separately. The mass of the carbonised sample that was produced from the treated EGS fibre was 26.58% less than the quantity obtained from raw EGS of equal starting mass. This reduction in mass was also observed with the LBPH fibre after carbonisation. This is because treated fibres generally have lesser density, diameter and moisture content compared to their raw fibres. This is also confirmed by Hyas *et al.* (2017). Also, most of the higher weight molecular components like lignin have been washed off and removed from the treated EGS and LBPH fibre as earlier observed during the alkaline treatment process.

4.3 Characterisation of the Raw and Treated Carbonised EGS Fibre

The micro structural properties comprising the elemental composition, morphology and functional groups of the raw and treated carbonised EGS fibres were analysed respectively using SEM–EDX and FTIR. Table 4.4 presents the elemental composition of the EGS ash.

Table 4.4: Elemental Composition for Untreated and Treated Carbonised Eucalyptus Globulus Sawdust Ash

Elemental Composition for Untreated Carbonised EGS			Elemental Composition for Treated Carbonised EGS		
Element Symbol	**Element Name**	**Untreated Weight Conc. (%)**	**Element Symbol**	**Element Name**	**Treated Weight Conc. (%)**
C	Carbon	87.68	Na	Sodium	57.59
Ca	Calcium	3.17	Ca	Calcium	10.16
I	Iodine	2.55	Zn	Zinc	8.61
Sn	Tin	1.75	Al	Aluminium	5.55
Zn	Zinc	1.69	V	Vanadium	3.94
Ag	Silver	0.87	Cr	Chromium	3.45
Al	Aluminium	0.53	Mn	Manganese	3.31
Na	Sodium	0.52	Mg	Magnesium	2.98
Mg	Magnesium	0.37	Si	Silicon	2.48
Si	Silicon	0.35	Ti	Titanium	1.94
S	Sulphur	0.26			
P	Phosphorus	0.26			

4.3.1 Elemental Composition for untreated and treated Carbonised EGS

The percentage (%) elemental composition of carbonised raw (untreated) EGS in Table 4.4 is expressed in a decreasing order - Carbon (C) >Calcium (Ca) > Iodine (I) > Tin (Sn) > Zinc (Zn) >Silver (Ag) > Aluminium (Al)>Sodium (Na) >Magnesium (Mg) > Silicon (Si) >Phosphorus(P). Carbon has the highest composition of 87.68%, while sulphur and phosphorus are the least with 0.26%. The result obtained here is different from the report of Naik *et al*. (2002), Udoeyo and Dashibil (2002) and Udoeyo *et al*. (2006). The high carbon content may be an indication of improper carbonisation of the raw fibre (Bhaskar, 2016). The elemental composition and concentration of wood ash is dependent on the wood type/specie, growth conditions, hydrodynamic of the furnace and combustion temperature (Chowdhury *et al*., 2014).

For the alkaline treated carbonised EGS, the elemental composition in a decreasing order shows that sodium is having 57.59%, while titanium recorded 1.94%. More number of elements was recorded in the raw carbonised EGS than the treated sample. C, I, Sn, S and P which were present in the raw EGS were found to be absent in the treated EGS. Leaching of these elements during alkaline treatment is responsible for the disappearance of these elements. Moreover, element like Tin is poisonous to health. Upon alkaline treatment of the raw EGS with NaOH, it was also observed that elements like Ca, Zn, Al, Na, Mg, and Si increase in their % weight compositions. This increase is due to the quantitative purification of these crude elements, which are now exposed by the alkalisation process. Consequently, the oxide components of Al_2O_3 and MgO in the treated ash will help to increase the fire resistance property of the hybrid polymer composite. Similarly, ZnO is also known to have a strong resistive effect to weathering (Layth *et al.,* 2015; Rudi *et al.,* 2019). Furthermore it was also observed that new transitional elements such as Vanadium, Chromium, Titanium and Manganese emerged in the treated EGS ash. These elements that are brought to the fore, must have been crude and unrefined elements buried and covered by the impurities or non-cellulosic components present in the raw EGS, prior to the alkaline treatment process. Also, chemical transformation and reaction of the mercerisation process may also be responsible. The oxides of these transitional elements such as titanium oxide are known to be good ultra-violet ray absorbers. The SEM image for carbonised raw (untreated) EGS is presented in Figure 4.5.

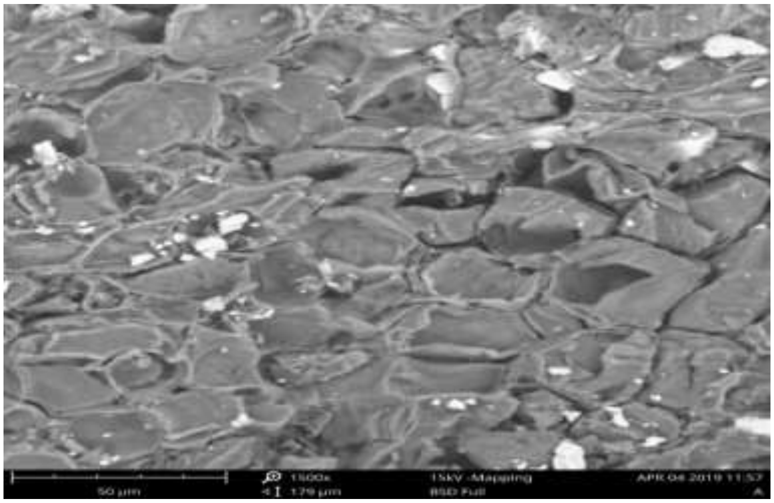


Figure 4.5: SEM Image for Carbonised Raw (Untreated) EGS

The morphology of the untreated EGS ash in Figure 4.5 is characterized by large patterns of regular shaped carbonised particles. Some few impurities were observed in form of white patches. A cursory look at the image shows that the particles sizes are larger in this case compared to the treated carbonised EGS particles in Figure 4.6. This is because the lignin content which offers rigidity and thermal stability to wood fibre is still relatively high in the untreated EGS fibre (Hyas *et al.*, 2017).

Chemical treatment of natural fibre in most cases, initiates a transformation in the morphology of the fibre. The SEM image for carbonised treated EGS is presented in Figure 4.6.

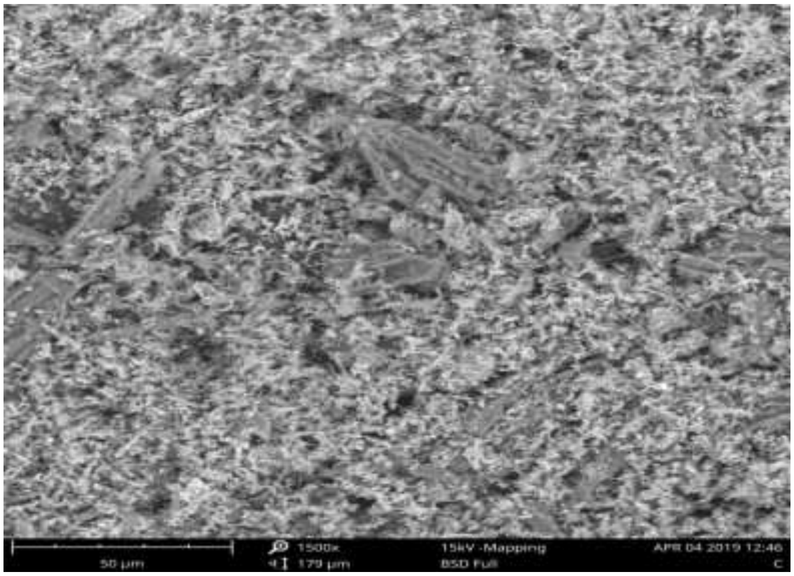


Figure 4.6: SEM Analysis for Carbonised Treated *Eucalyptus globulus* Sawdust

The SEM analysis of the treated EGS ash is characterized by smaller fine needled-like particles compared to the untreated EGS ash. This is because the treated EGS is less stable under heat during carbonisation as a result of the drastic reduction in its lignin content which was washed off during the alkaline treatment process. Hyas *et al.*, (2017) observed that treated fibres experiences decrease in diameter, density and moisture content after alkalisation. This will also lead to reduction in particle sizes after carbonisation at 500°C.

The behaviour of a natural fibre is largely dependent on the functional groups it possesses. The FTIR Spectrum for raw (untreated) EGS ash is presented in Figure 4.7a.

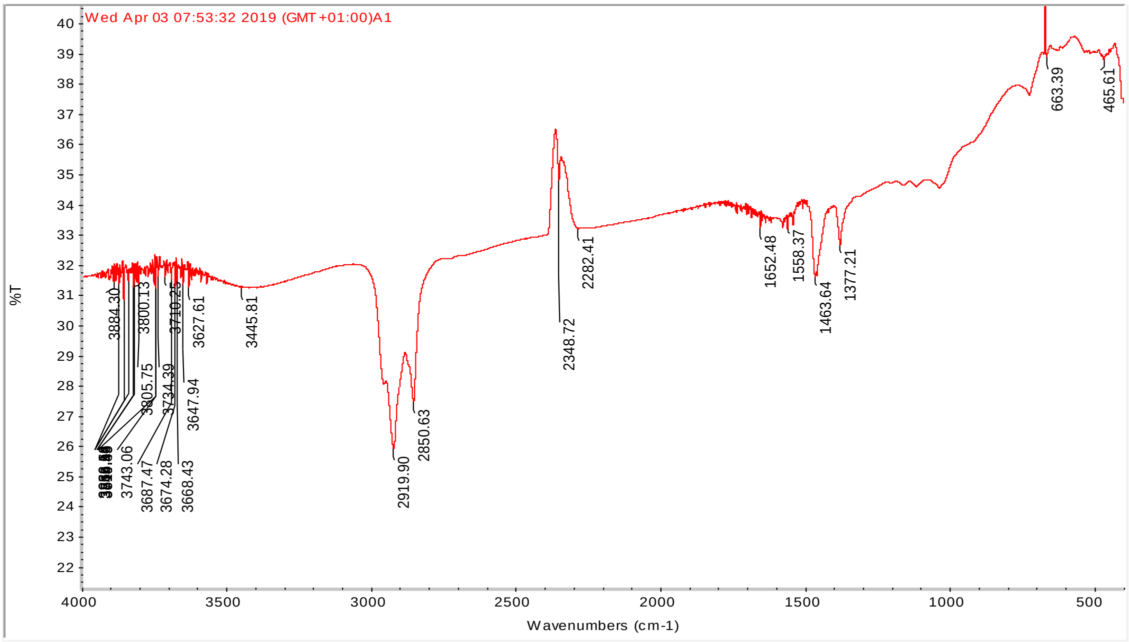


Figure 4.7a: FTIR Spectrum for Raw EGS Ash

The untreated carbonised EGS has higher amount of OH groups peaks ranging from 3878.58 – 3445.81 cm^{-1}. There are alkane C-H peaks at 2919.90 and 2850.63 cm^{-1}. All of these are in comparison to the raw EGS fibre. Two nitrile $C\equiv N$ groups were also observed in the EGS ash at 2348.72 and 2282.41 cm^{-1}. This is absent in the raw EGS fibre. The presence of C=C aromatic ring of lignin at 1652.48 and 1558.37 were detected in the carbonised EGS. These are indications of the high thermal stability of lignin at 500^{o}C compared to the thermal stability of other components (cellulose and hemicellulose) of the EGS fibre. This is similar to the observation by Hyas (2017) on sugar palm fibre. Ishak *et al*. (2012) assert the fact that the thermal degradation of lignin extends to as high as 900^{o}C.

Mercerisation of natural fibre in most cases, initiates a variation in the functional group of the fibre. The FTIR Spectrum for treated carbonised EGS is presented in Figure 4.7b.

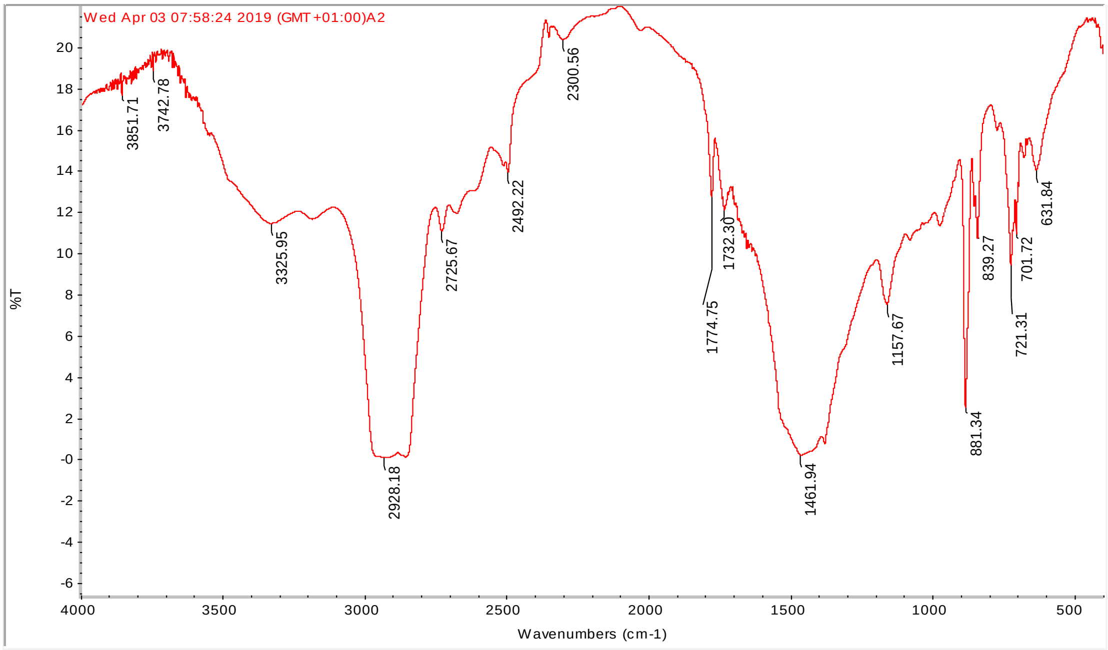


Figure 4.7b: FTIR Spectra for Treated Eucalyptus Globulus Sawdust Ash

Figure 4.7b shows that there is a drastic reduction in the number of OH peaks present in the carbonised treated EGS. This is an indication that the multiple OH group peaks that characterized the hemicellulose and cellulose have been broken down and washed off during the alkaline treatment process. The leaching of these OH groups which was initiated by the alkalisation process was further promoted during the carbonisation process. This is a sign that hemicellulose is less stable under heat as reported by Ishak *et al.* (2012) and Hyas (2017). There is an emergence of amine-N-H group peak at 3325.95 cm^{-1}. This N-H character confers an adsorbent property on the carbonised treated EGS. This same observation is reported by Alhassan *et al.* (2017), on activated carbon from sugarcane bagasse. Broad C-H and C=C aromatic ring were recorded at 2928.18 and 1461.94 respectively against the sharp peaks noticed from untreated carbonised EGS.

4.4 Characterisation of the Raw and Treated Locust Bean Pod Husk Ash (LBPHA)

The micro structural properties comprising the elemental composition, morphology and functional groups of the raw and treated carbonised LBPH fibres were analysed respectively, using SEM –EDX and FTIR. Table 4.5 presents the elemental composition of the LBPH ash.

Table 4.5: Elemental Composition for Untreated and Treated LBPH Ash

Elemental Composition for Untreated Carbonised LBPH			**Elemental Composition for Treated Carbonised LBPH**		
Element Symbol	**Element Name**	**Untreated Weight Conc. (%)**	**Element Symbol**	**Element Name**	**Treated Conc. (%)**
C	Carbon	46.58	C	Carbon	33.51
K	Potassium	21.51	Ca	Calcium	28.27
N	Nitrogen	17.11	Na	Sodium	25.86
Ca	Calcium	8.34	K	Potassium	5.25
Mg	Magnesium	3.27	Mg	Magnesium	2.82
Si	Silicon	1.56	Cd	Cadmium	2.79
Na	Sodium	0.91	Ti	Titanium	1.49
Al	Aluminium	0.73			

4.4.1 Elemental composition of raw and treated carbonised LBPH

The untreated carbonised LBPH fibre in Table 4.5 shows that carbon has the highest weight composition of 46.58% with aluminium (0.73%) as the least. Elemental analysis in Table 4.5 shows that N, Si and Al were leached from the raw LBPH during the alkaline treatment and carbonisation process leading to their absence in the treated carbonised LBPH. Titanium and cadmium which were initially hidden was exposed due to the mercerisation process of raw LBPH. The reason is similar to that earlier mentioned in elemental composition of EGS. In this case, titanium oxide serves as a good ultra violet radiation stabilizer for the hybrid polymer composite (HPC) in order for it to withstand harsh weather conditions as a roofing tile. Similarly, the oxide composition of magnesium has the attribute of good thermal stability needed by the HPC.

Furthermore, the percentage weight composition of carbon and potassium in the treated carbonised LBPH were found to reduce drastically by 28.06% and 75.59% respectively compared to their compositions in the raw carbonised LBPH. This is due to the partial leaching of these elements by mercerisation. On the other hand, a sharp increase in percentage weight concentration was observed in the treated carbonised LBPH for calcium and sodium from 8.34% to 28.27% and 0.91% to 25.86% respectively compared to the raw LBPH. The justification for this sharp and high increase is the fact that, quantitative crude contents of these elements have been actively and clearly exposed by the alkaline treatment process.

In most cases, the carbonisation of a natural fibre affects its morphology. The SEM image for Raw Carbonised LBPH is presented in Figure 4.8a.

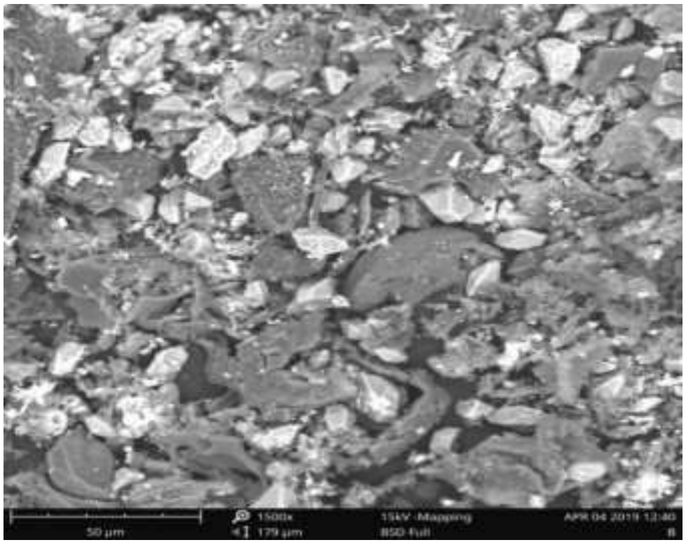


Figure 4.8a: SEM Image for Raw (untreated) Carbonised LBPH

The morphology of the untreated carbonised LBPH in Figure 4.8a is characterized with irregular particle shaped pattern with more impurities in form of white patches compared to the untreated carbonised EGS. However, these impurities can be reduced to the barest minimum through the alkalisation treatment process.

Chemical treatment of natural fibre in most cases, initiates a transformation in the morphology of the fibre. The SEM image for treated Carbonised LBPH is presented in Figure 4.8b.

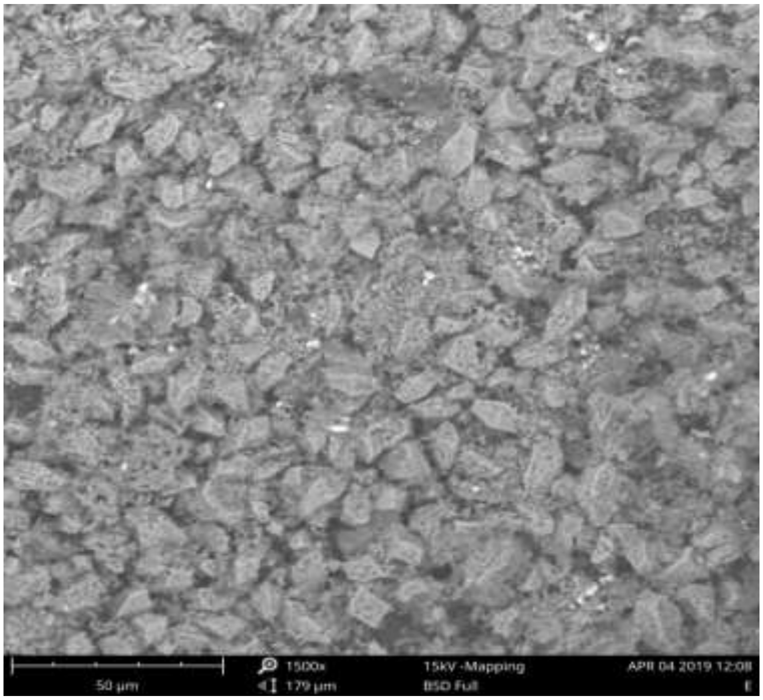


Figure 4.8b: SEM Analysis for Treated Carbonised LBPH

The morphology of the treated carbonised LBPH in this case is characterized by a regular particle shaped pattern with almost no visible sign of white patches of impurities. This is in comparison with the morphology of the raw carbonised LBPH fibre in Figure 4.8a. The absence of these impurities may have been initiated by the mercerisation and carbonisation process.

Functional group is the character base of a material. The FTIR spectra for untreated and treated carbonised LBPH are presented in Figure 4.9 and Figure 4.10 respectively.

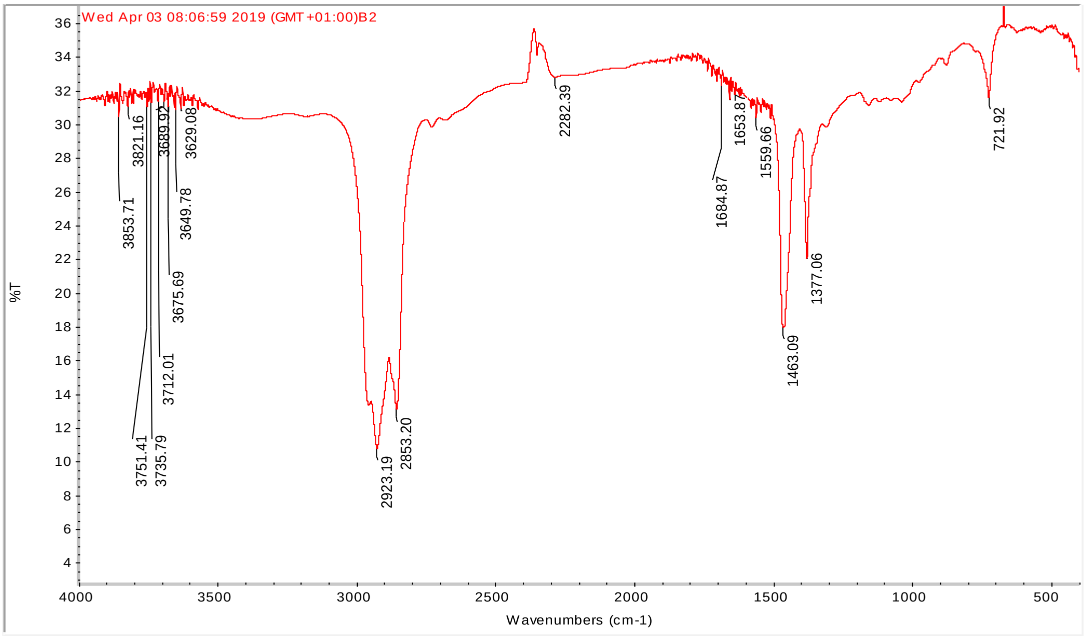


Figure 4.9 FTIR Spectrum for Untreated Carbonised LBPH

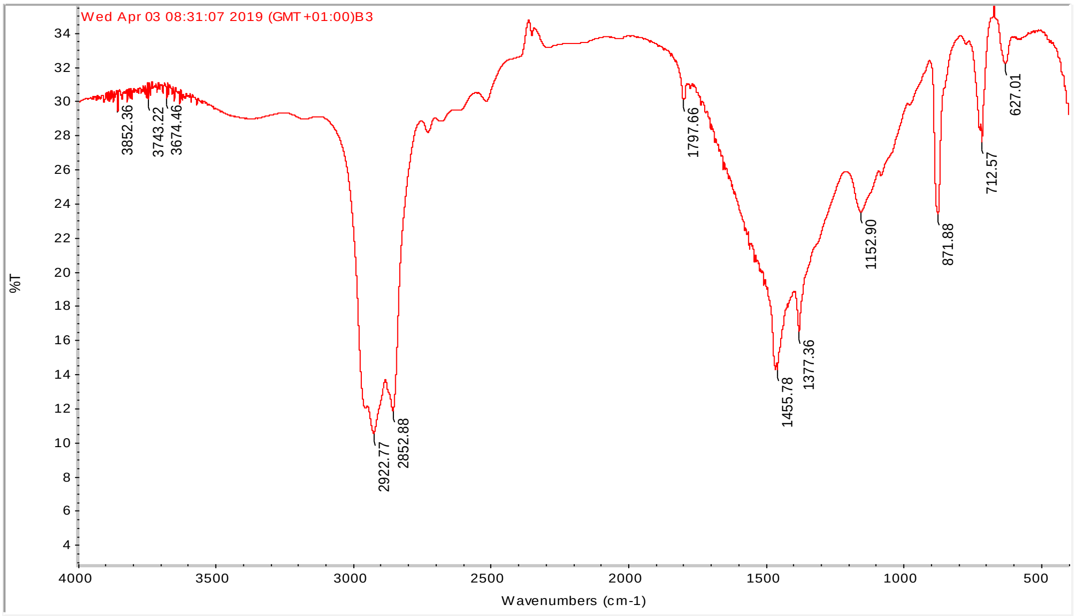


Figure 4.10 FTIR Spectrum for Treated Carbonised LBPH

Similar to previous observations from carbonised EGS, the untreated carbonised LBPH in Figure 4.9 has a relatively high amount of OH peaks ranging from 3853.71- 3629.08 cm^{-1}. C-H peaks are observed at 2923.19 and 2853.20 cm^{-1}, while nitrile peaks are observed at 2348.72 and 2282.41 cm^{-1}. The aromatic ring peaks were seen at 1652.48-1377.21 cm^{-1}. All these peaks are reflection of the presence of cellulose, hemicellulose and lignin in their carbonised form. The treated carbonised LBPH in Figure 4.10 have similar functional group properties like that of the treated carbonised EGS. Figure 4.10 also show a drastic reduction in the number and amount of OH peaks present in the carbonised treated LBPH. This is an indication that the multiple OH group peaks that characterized the hemicellulose and cellulose have been broken down and washed off during the alkaline treatment process. The leaching of these OH groups which was initiated by the alkalisation process was further promoted during the carbonisation process. This is a sign that hemicellulose is less stable under heat as reported by Ishak *et al.* (2012) and Hyas (2017).

4.5 Characterisation of Kutigi Clay

The micro structural properties comprising the elemental composition, morphology and functional groups of the raw and calcined Kutigi clay were analysed respectively, using SEM –EDX and FTIR. Table 4.6 present the elemental compositions of the Kutigi clay.

Table 4.6: Elemental Composition for Raw Kutigi Clay and Calcined Kutigi Clay

Elemental Composition for Raw Kutigi Clay			Elemental Composition for Calcined Kutigi Clay		
Element Symbol	**Element Name**	**Raw Weight Conc. (%)**	**Element Symbol**	**Element Name**	**Calcined Conc. (%)**
Si	Silicon	60.37	Si	Silicon	48.14
Al	Aluminium	27.44	Al	Aluminium	38.77
Sr	Strontium	5.13	C	Carbon	11.98
Fe	Iron	3.41	O	Oxygen	1.1
Cd	Cadmium	2.23			
Ti	Titanium	0.81			
Na	Sodium	0.62			

4.5.1 Elemental composition of Kutigi clay

The use of clay as a filler for this hybrid polymer composite is to impact good strength through hardness, as well as serve as a flame retardant. Preliminary investigation by Akhirevbulu *et al.* (2010) on the occurrence and physicochemical properties of Kutigi clay reveals that it is a kaolinite white and non-plastic residual (primary) clay, based on origin. Its non-plastic nature is a reflection of its low swelling-shrinking ratio. This is further confirmed by the elemental composition analysis on Table 4.6. The result reveals that silicon and Aluminium are present in appreciable amount while strontium, iron and cadmium are present in moderate quantity; but titanium and sodium are present in trace amount. Further analysis on this clay reveal that it has a pozolanic property since the sum total of Si, + Al+ Fe is ≥ to 70%. This is similar to the report by Adama and Jimoh (2011).

Result obtained from the calcined clay at 500^{o}C as shown on Table 4.6 presents a slight relative reduction in the silica content, while an increase is observed in the alumina content. This observation is in contrast to Hui *et al.* (2009). This contrast is due to the difference in the material composition as well as the thermal treatment process used. Some elements such as iron, strontium, sodium and cadmium which were present in trace amount, in the raw Kutigi kaolin clay, were not present in the kaolin clay sample after calcination. This is one of the effects of calcination due to volatilization of unstable components. The SEM image for raw Kutigi clay and calcined Kutigi clay are presented in Figure 4.11 and 4.12 respectively.

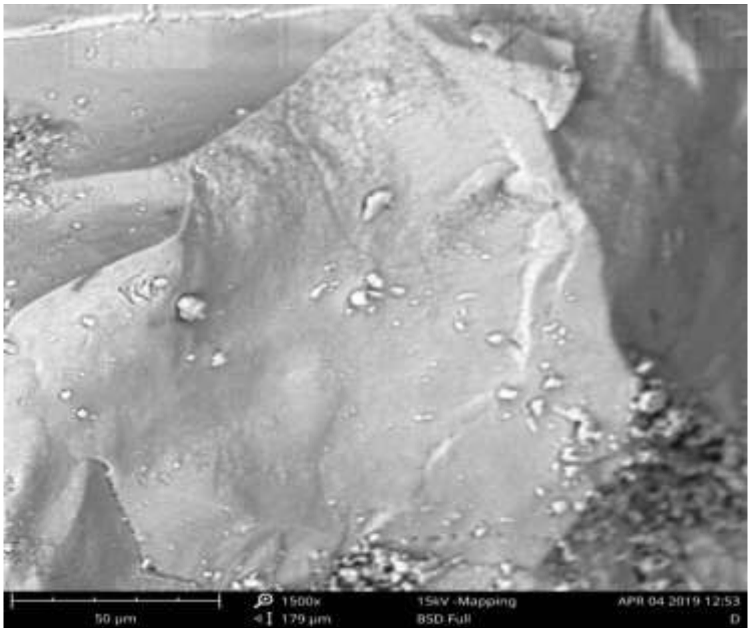


Figure 4.11: SEM Image for Raw Kutigi Clay

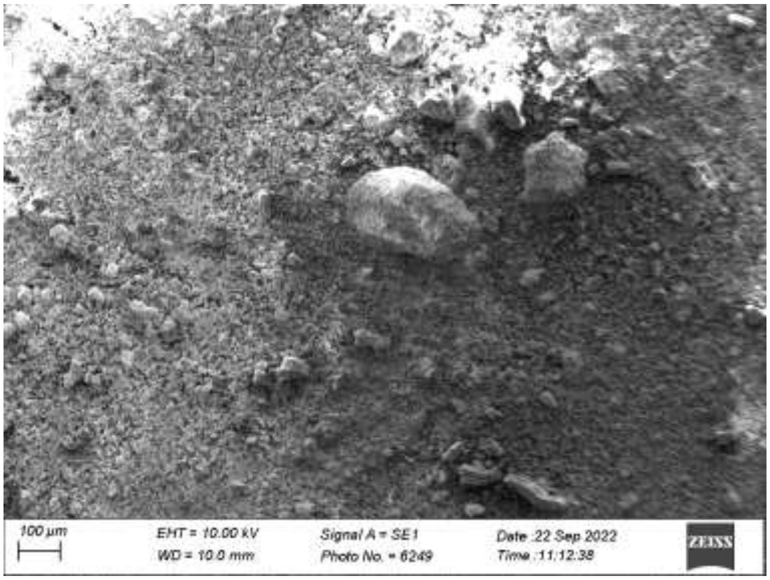


Figure 4.12: SEM Image for Calcined Kutigi Clay

The SEM image of the raw kaolin clay in Figure 4.11 presents a white appearance and smooth plane surface with some few defects and impurities on the clay surface. Upon calcination as shown on Figure 4.12, the physical appearance of the kaolin clay changed to an off-white orange colour dehydroxylated powdery material. This structural transformation caused by the calcination process changed the raw Kutigi clay sample into metakaolin, having a specific gravity of 2.59 and bulk density of 0.36 g/cm^3. The attributes of this metakaolin clay caused by calcination is confirmed by the properties in Table 4.6 for calcined Kutigi clay.

Calcination at the right temperature initiates transformation in clay. The FTIR Spectra for raw and calcined Kutigi clay is presented in Figure 4.13a and 4.13b respectively.

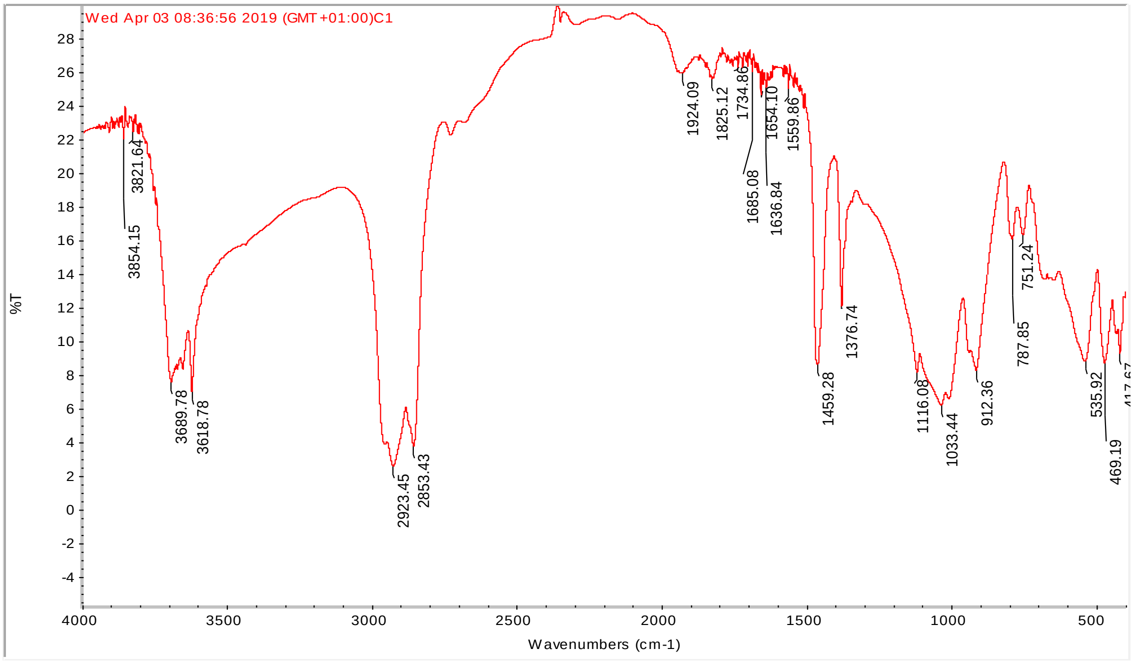


Figure 4.13a: FTIR Spectrum for Raw Kutigi Clay

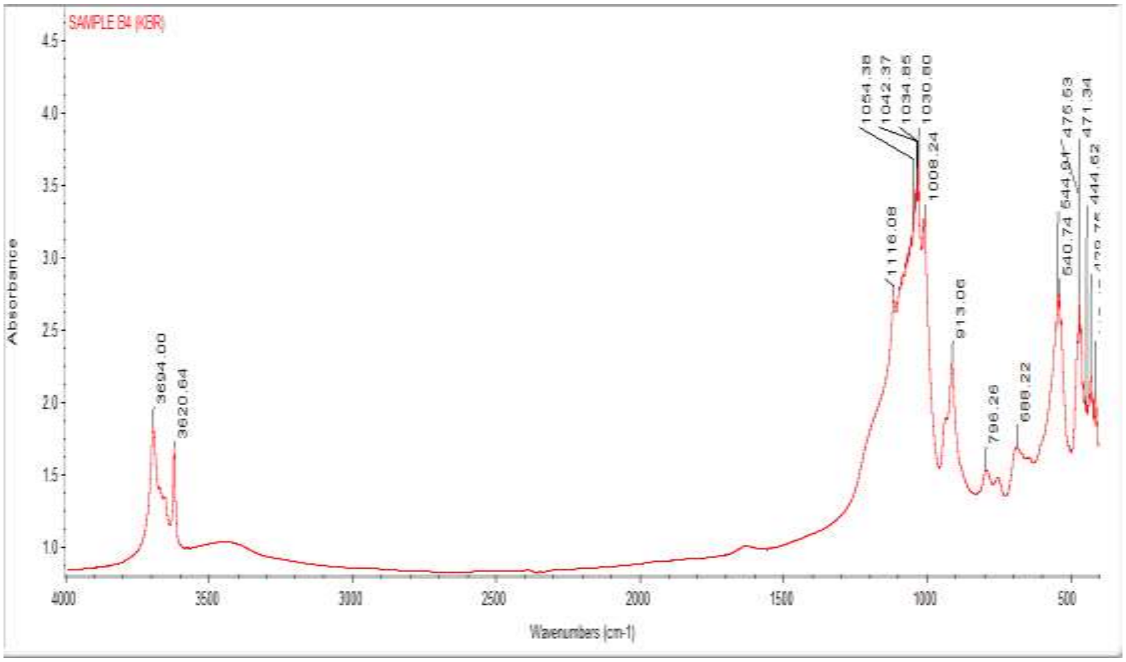


Figure 4.13b: FTIR Spectrum for Calcined Kutigi Clay

Figure 4.13a shows the presence of quartz mineral which is a property of kaolin clay, depicted by asymmetric and symmetric stretch vibrations of Si-O at 469.19 and 787.85cm^{-1} respectively. The peak at 535.92 cm^{-1} indicates the presence of Al-O-Si bend of feldspar and Si-O-Al deformation. The peaks at 751.24 cm^{-1} signifies Al-O-Si stretching in a kaolinite clay. The peak at 912.36 cm^{-1} represent Al-OH deformation band in kaolin. The band at 1033.44 – 1116.08 cm^{-1} represent Si-O stretch, normal to the planes. There exist C-H anti-asymmetric and symmetric stretch of organic materials present in the clay at 2853.43 and 2923 cm^{-1}. The peaks at 3618.78 to 3689.78 cm^{-1} represent the inner stretching surface of OH group. All these observations is further confirmed by the EDX analysis result and also by Bhaskar *et al*. (2016).

Furthermore, the FTIR spectrum in Figure 4.13b is presented and expressed in terms of absorbance which is an inverted presentation of transmittance. Observations from the spectrum show an absence of the C-H anti-asymmetric and symmetric stretch of organic materials which were initially present in the raw Kutigi clay. This absence may be as a result of the leaching of volatile organic materials initiated by the heat of calcination on the clay. The peaks at 3854.15 cm^{-1} and 3821.64 cm^{-1}in the raw clay are absent in the calcined clay. Peaks within 1900 – 1600cm^{-}1 are absent. These are some of the effects of calcination process.

4.6 Characterisation of the Used Low Density Polyethylene (LDPE)

Post-consumer pure water sachet is made from low density polyethylene. There is need to determine its functional group. The FTIR spectrum for used polyethelene (PE) is presented in Figure 4.14.

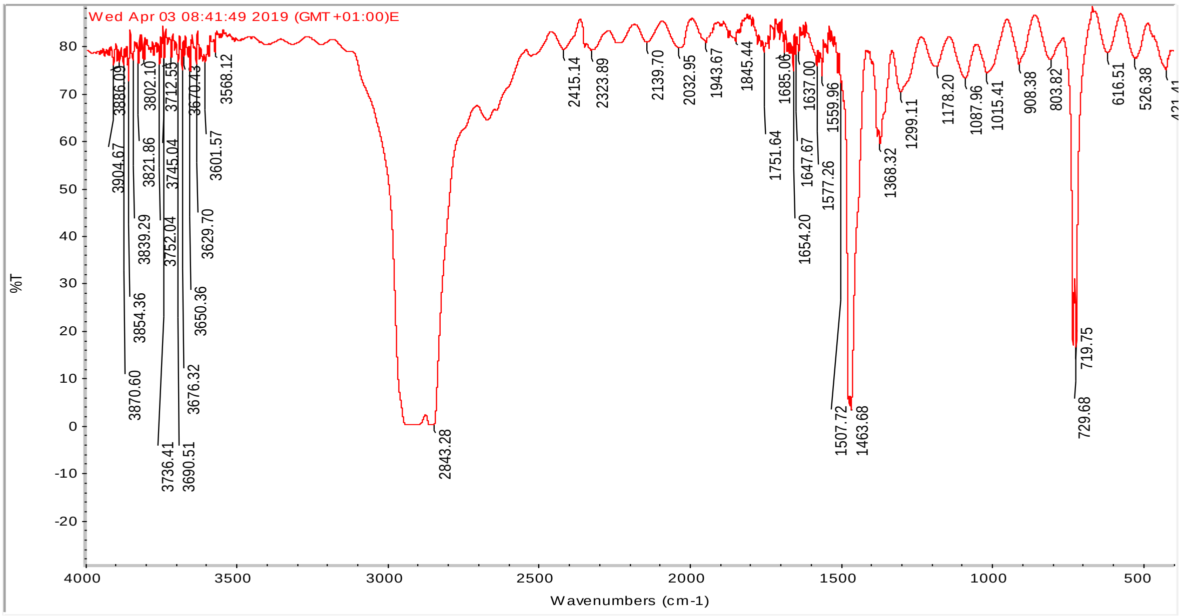


Figure 4.14: FTIR Spectrum for Used Low Density Polyethelene (LDPE)

The FTIR result for used polyethylene (PE) on Figure 4.14 reveal a strong broad C-H peak at 2843.28 cm^{-1}. There are clusters of phenolic functional groups ranging from 3904.67 – 3568.12 cm^{-1}. These phenolic compounds represent the antioxidant and additive that are added during processing of PE in order to enhance stabilization and anti-blocking (minimization of the adhesion of adjacent polymer film). C-Cl peak is observed at 729.68cm^{-1} and other halide groups (C-X). There are also alkene peaks at 1654.20 – 1637 cm^{-1}. These peaks are features of polyethylene compound. Variable alkene C=C double bond aromatic ring stretch also appeared at 1577.26 – 1507.72 cm^{-1}.

4.7 Statistical Evaluation and Modelling of the Treatment Process of EGS and LBPH Fibre

The statistical analysis of variance (ANOVA), measure of central tendencies, model equation and optimum parameters of the EGS and LBPH fibre treatment process for cellulose response is presented in this section. The ANOVA for EGS is presented in Table 4.7.

Table 4.7.: ANOVA for EGS Cellulose Response Surface Quadratic Model

source	Sum of Squares	df	Mean square	F value	p- value prob>F	
Model	1538.89	5	307.78	6.77	0.0131	significant
A- treat conc	493.01	1	493.01	10.84	0.0133	
B-contact time	248.83	1	248.83	5.47	0.0519	
AB	132.25	1	132.25	2.91	0.1319	
A^2	193.48	1	193.48	4.25	0.0781	
B^2	544.70	1	544.70	11.97	0.0105	
Residual	318.41	7	45.49			
Lack of fit	318.18	3	106.06	1828.63	<0.0001	significant
Pure error	0.23	4	0.058			
Cor.Total	1857.31	12				

In Table 4.7, the model F- value of 6.77 signifies a model that is significant. There is 1.31% possibility that a “model F-value” of this magnitude could probably occur as a result of noise. Values of “prob >F” that are less than 0.05 indicate a significance in their model terms. In this case, A and B^2 are significant model terms since the values of their “prob>F” is less than 0.05 as shown in Table 4.7. While model terms with values greater than 0.1 is a reflection of non-significant terms. In this case also, the model term AB which is 0.1319 is not a significant model term in relation to “prob>F”.

The lack of fit F-value is significant. This actually influences the fitness of a model.

The model summary of the statistical analysis of EGS cellulose response is presented in Table 4.8.

Table 4.8: Model Summary for EGS Cellulose Response

Std. Deviation	Mean	C.V (%)	PRESS	R-squared	Adj. R-squared	Pred. R-squared	Adeq. precision
6.74	65.57	10.29	2262.99	0.8286	0.7061	0.2184	7.389

The information in Table 4.8 captures the “Adeq precision” which measures the signal to noise ratio. The ratio in this case is 7.389, indicating an adequate signal, since it is greater than 4. As such, the design space can be easily navigated by the model. The coefficient of determination (R^2) is 0.8286 which is an indication that only 82.86% of the variability in the experimental data can be interpreted by the model.

The final model equation that describes the EGS treatment process in terms of coded factors is expressed in Equation 4.1.

Given that A = Treatment Concentration and B = Contact Time

Then $\text{Cellulose} = 74.26 + 7.85A + 5.58B - 5.75AB - 5.27A^2 - 8.85B^2$ (4.1)

From the residual model equation in Equation 4.1 for EGS cellulose response, each of the input factors has positive main effect on the property outcome of the cellulose yield. Nevertheless, treatment concentration (A) had a greater impact on the cellulose yield by value compared to contact time. Equation 4.1 is valid within the range of 1.5 to 4.5% treatment concentration and contact time of 1 to 3 h. The predicted optimum cellulose response contour plot and the overlay plot for EGS is presented in Figure 4.15 and 4.16 respectively.

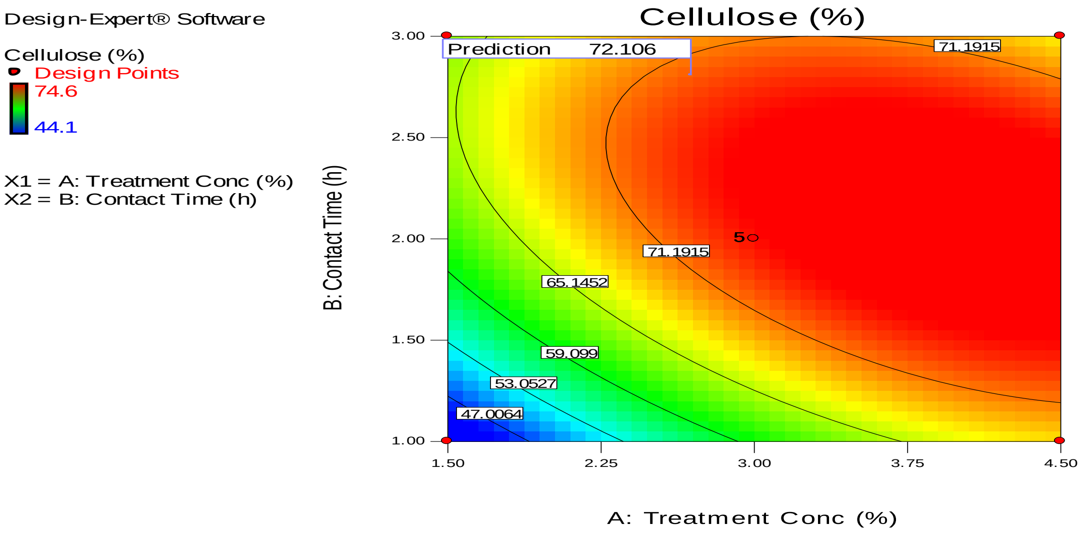


Figure 4.15: Predicted Optimum Cellulose Response Contour Plot for EGS

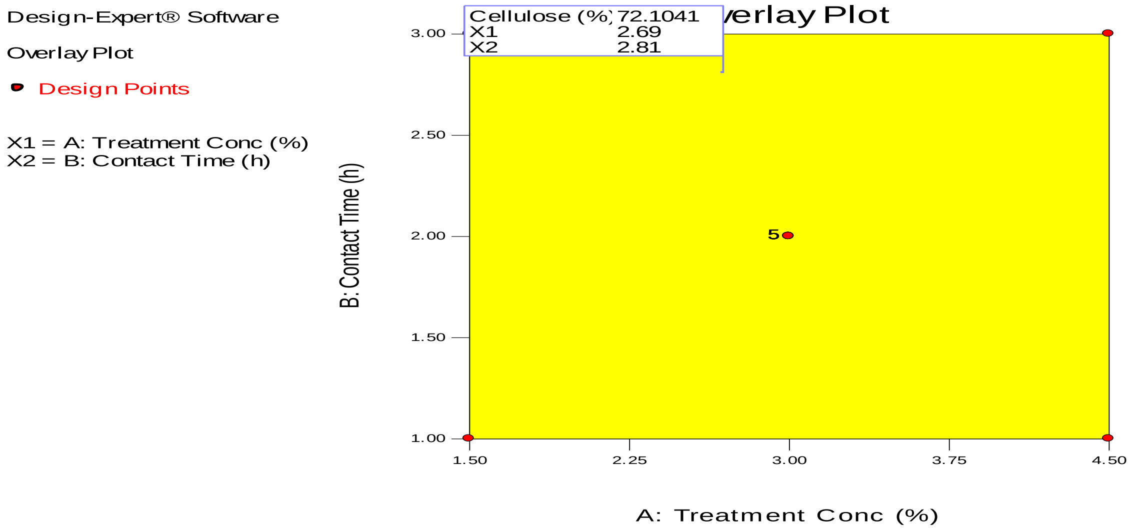


Figure 4.16: Overlay Plot for Cellulose Response for EGS

Figure 4.15 and 4.16 present the optimum treatment conditions that gives the predicted optimum composition of cellulose in the chemical composition of the EGS. The predicted optimum alkaline treatment concentration is 2.69% at a contact time of 2.81 h, to give a predicted cellulose composition of 72.1041%. An experimental confirmation of this predicted treatment condition recorded 71.20% cellulose content.

The statistical analysis of variance (ANOVA) for LBPH cellulose response is presented in Table 4.9.

Table 4.9: ANOVA for LBPH Cellulose Response Surface Quadratic Model

source	Sum of Squares	df	Mean square	F value	p- value prob>F	
Model	415.38	2	207.69	6.23	0.0175	significant
A- treat conc	412.25	1	412.25	12.38	0.0056	
B-contact time	3.14	1	3.14	0.094	0.7652	
Residual	333.12	10	33.31			
Lack of fit	333.07	6	55.51	4270.17	<0.0001	significant
Pure error	0.052	4	0.013			
Cor.Total	748.51	12				

In Table 4.9, the model F- value of 6.23 signifies that the model is significant. There is only a 1.75% chance that a "model F-value" of this magnitude could probably occur as a result of noise. Values of "prob >F" that are less than 0.05 indicate a significance in their model terms. In this case, treatment concentration (A) is a significant model term since the "prob>F" value is less than 0.05 as shown in Table 4.9. While model terms with values greater than 0.1 depicts a non-significance. In this case, B which is 0.7652 is not a significant model term in relation to "prob>F". The lack of fit F-value of 4270.17 is significant. This actually influences the fitness of a model.

The model summary of the statistical analysis of LBPH cellulose response is presented in Table 4.10.

Table 4.10: Model Summary for LBPH Cellulose Response

Std. Deviation	Mean	C.V (%)	PRESS	R-squared	Adj. R-squared	Pred. R-squared	Adeq. precision
5.77	61.83	9.33	718.69	0.7549	0.6659	0.0398	7.323

The information on Table 4.10 shows that the "Pred R-Squared" of 0.0398 is farther away from the "Adj R-Squared" of 0.6659, which is not expected. A large block effect may be responsible. Some things to consider are response tranformation, model reduction and outliers. "Adeq Precision" takes account of the signal to noise ratio. A ratio exceeding 4 is acceptable. The ratio of 7.323 in this case, portrays an adequate signal. The design space can be navigated using the model.

The final model equation that describes the LBPH treatment process in terms of coded factors is expressed in Equation 4.2.

Given that A = Treatment Concentration and B = Contact Time

Then $\text{Cellulose} = +61.83 - 7.18A - 0.63B$ (4.2)

Equation 4.2 is valid within the range of 1.5 to 4.5% treatment concentration and contact time of 1 to 3 h. The predicted optimum cellulose response contour plot and the overlay plot for LBPH is presented in Figure 4.17 and 4.18 respectively.

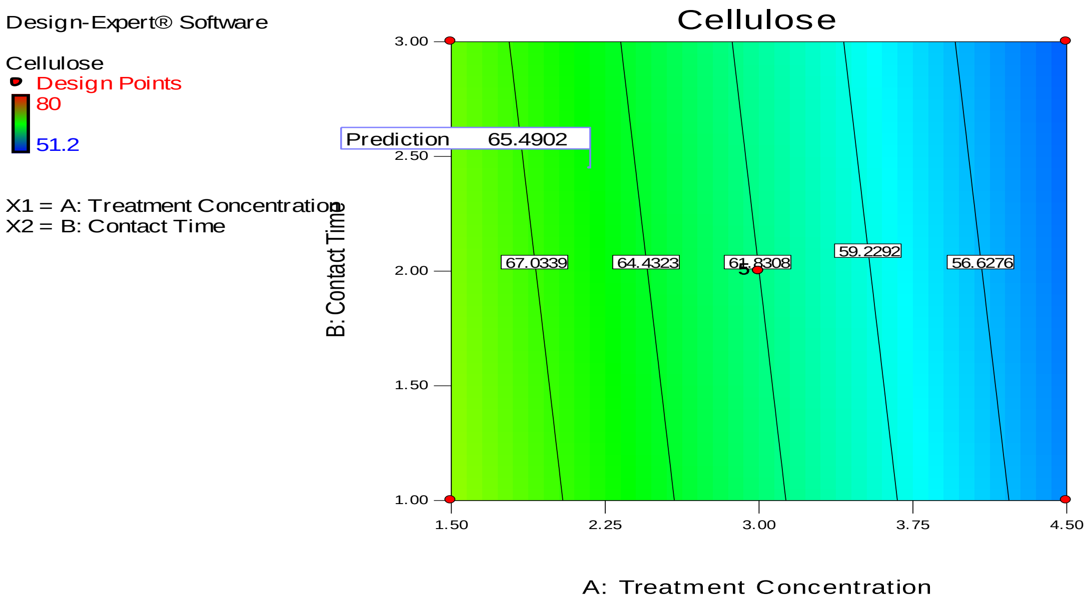


Figure 4.17: Predicted Optimum Cellulose Response Contour Plot for LBPH

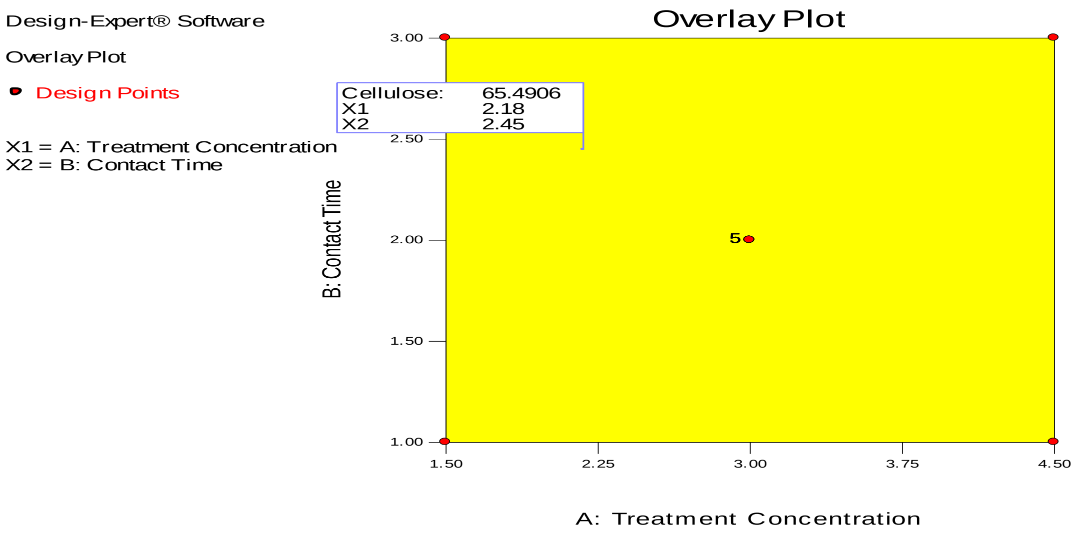


Figure 4.18: Overlay Plot for Cellulose Response for LBPH

Figure 4.17 and 4.18 present the optimum treatment conditions that give the optimum composition of cellulose and other non-cellulosic chemical composition of the LBPH. The predicted optimum alkaline treatment concentration is 2.18% at a contact time of 2.45 h, to give a cellulose composition of 65.4906%.

4.8 Characterisation of the Developed Hybrid Polymer Composites (HPC)

Characterisation of the developed hybrid polymer composite (HPC) presents the mechanical and micro structural properties of the HPC, coupled with the statistical analysis of the HPC production process. Similarly, the thermal properties and the water absorption capacity (WAC) of the HPC were also presented in this section. Furthermore, the degradation of the HPC which accounts for the performance evaluation, when exposed to natural weathering was also discussed in this section.

4.8.1 Mechanical properties of the hybrid polymer composites

Used low density polyethylene (LDPE) matrix was selected and used for this work. The recycled LDPE matrix was reinforced with EGS ash, LBPH ash and clay to produce the HPC with appreciable mechanical properties as shown in Table 4.11.

Table 4.11 shows the mechanical properties of the hybrid polymer composite in terms of flexural strength, tensile strength and hardness, of which the HPC$_{ί}$ (ί =1-70) represent different composite formulation property responses.

Table 4.11a: Mechanical Properties of the HPC

Experimental runs	**Flexural strength (MPa)**	**Tensile strength (MPa)**	**Hardness (MPa)**
HPC1	17.62	8.98	30.65
HPC2	**19.23**	**10.94**	17.59
HPC3	13.71	9.57	14.97
HPC4	13.21	9.50	31.83
HPC5	13.21	9.50	31.83
HPC6	12.93	9.26	14.19
HPC7	14.25	6.81	**35.27**
HPC8	16.00	7.29	15.80
HPC9	13.21	9.50	31.83
HPC10	13.21	9.50	31.83
HPC11	14.50	9.33	19.00
HPC12	13.47	10.03	29.13
HPC13	13.21	9.5	31.83
HPC14	16.10	7.18	15.90
HPC15	16.20	7.22	15.80
HPC16	19.22	10.25	17.59
HPC17	11.57	9.96	23.73
HPC18	14.69	9.34	19.51
HPC19	11.57	9.96	23.73
HPC20	16.00	7.21	15.70
HPC21	14.25	6.81	35.27
HPC22	16.10	7.25	15.80
HPC23	11.57	9.96	23.73
HPC24	13.47	10.03	29.13
HPC25	16.20	7.28	15.90
HPC26	13.21	9.50	31.83
HPC27	14.69	9.34	19.51
HPC28	13.21	9.50	31.83
HPC29	11.57	9.96	23.73
HPC30	16.00	7.25	15.70
HPC31	12.50	7.52	32.1
HPC32	13.71	9.57	14.97
HPC33	11.57	9.96	23.73
HPC34	14.69	9.34	19.51
HPC35	16.1	7.26	15.8
HPC36	12.93	9.26	14.19
HPC37	19.21	10.25	17.59
HPC38	10.78	10.01	18.73
HPC39	12.93	9.26	14.19
HPC40	14.6	9.32	19.1

Table 4.11b: Continuation

HPC41	19.22	10.25	17.59
HPC42	13.21	9.50	31.83
HPC43	12.6	7.51	32.2
HPC44	12.93	9.26	14.19
HPC45	14.67	9.33	19.2
HPC46	11.41	8.27	11.35
HPC47	14.5	9.32	19.20
HPC48	17.60	8.98	30.65
HPC49	16.20	7.19	15.7
HPC50	11.57	9.96	23.73
HPC51	19.23	10.25	17.59
HPC52	16.00	7.21	15.9
HPC53	14.68	9.33	19.30
HPC54	13.21	9.50	31.83
HPC55	17.62	8.98	30.65
HPC56	16.1	7.25	15.70
HPC57	13.71	9.57	14.97
HPC58	14.69	9.34	19.51
HPC59	12.93	9.26	14.19
HPC60	14.11	9.79	23.44
HPC61	12.93	9.26	14.19
HPC62	13.71	9.57	14.97
HPC63	14.50	9.32	19.40
HPC64	16.20	7.24	15.80
HPC65	14.69	9.34	19.51
HPC66	17.61	8.98	30.65
HPC67	13.21	9.50	31.83
HPC68	19.22	10.25	17.59
HPC69	14.69	9.34	19.51
HPC70	13.21	9.50	31.83

Table 4.11 presents the result of the mechanical properties (flexural strength, tensile strength and hardness) of the hybrid polymer composite (HPCs) produced according to the process-mixture design of experiment in Table 3.4. There are 70 runs in all. The result of the flexural strength, tensile strength and hardness property of the HPCs produced are within the range of 11.41−19.23MPa, 7.18−10.94 MPa and 14.19−35.27 MPa respectively. These values are higher than the recycled polyethylene and virgin polyethylene matrices. HPC 46 recorded the lowest value and HPC 2 and 51 recorded the highest value for

flexural strength. A general observation from Table 4.11 shows that clay content formulations above 11 wt% favours the hardness of the HPCs, while used polyethylene content above 50 wt% favour the flexural and tensile strength of the HPCs. The optimum mechanical property with the highest values for flexural, tensile and hardness are extracted from Table 4.11 and presented in Table 4.12–Table 4.14.

4.8.1.1 *Flexural strength property for optimum HPC*

The HCP with the optimum highest flexural strength is recorded in Table 4.12 alongside the flexural properties of the compounded recycled polyethylene (rPE) and compounded virgin polyethylene (PE) as control samples to monitor the effect of the reinforcement in the HPC.

Table 4.12: Flexural Strength property for Optimum HPC

Property	**Hybrid Polymer Composite (HPC2)**	**Recycled Polyethylene Matrix**	**Virgin Polyethylene Matrix**
Flexural Strength **(**MPa)	19.23	10.1	5.89

The flexural strength of a material is the maximum bending or transverse stress (load) a material can withstand before yielding or breaking permanently. All the hybrid composites reinforced with sawdust ash (SDA), locust bean pod ash (LBPA) and clay recorded higher flexural strength than the recycled and virgin polyethylene (PE) matrix without reinforcement. This is in agreement with Muhammad *et al.* (2011), Rezaur *et al.* (2010), Lou *et al. (*2007) and Joseph *et al.* (2002). This is an indication that the reinforcing fillers have a positive effect on the flexural strength of the hybrid polymer composite (HPC).

To be more specific, the component mixture with the formulation of 5% SDA, 40% LBPA, 2% clay and 53% rPE, processed at 160^{o}C in experimental HPC2 was found to give the highest flexural strength of 19.23MPa, compared to all other HPC. This is because the various component formulations in experimental HPC2 are present in an optimum and appropriate amount within the HPC2, thereby allowing effective load transfer along the HPC, when subjected to transverse stress. It was further observed that component mixture formulations with relatively high clay content just like in run 17 and 38, recorded low flexural strength within the range of 10 - 11MPa. The non-plastic nature of Kutigi clay as reported by Akhirevbulu *et al*. (2010) does not support effective load transfer in this HPC.

4.8.1.2 *Tensile strength property for optimum HPC*

.The HPC with the optimum highest tensile strength is recorded in Table 4.13 with the tensile properties of compounded recycled polyethylene (rPE) and compounded virgin polyethylene (PE) as control samples to monitor the effect of the reinforcement in the HPC.

Table 4.13: Tensile Strength Property for Optimum HPC

Property	**Hybrid Polymer Composite (HPC2)**	**Recycled Polyethylene Matrix**	**Virgin Polyethylene Matrix**
Tensile Strength **(**MPa)	10.94	10.48	7.53

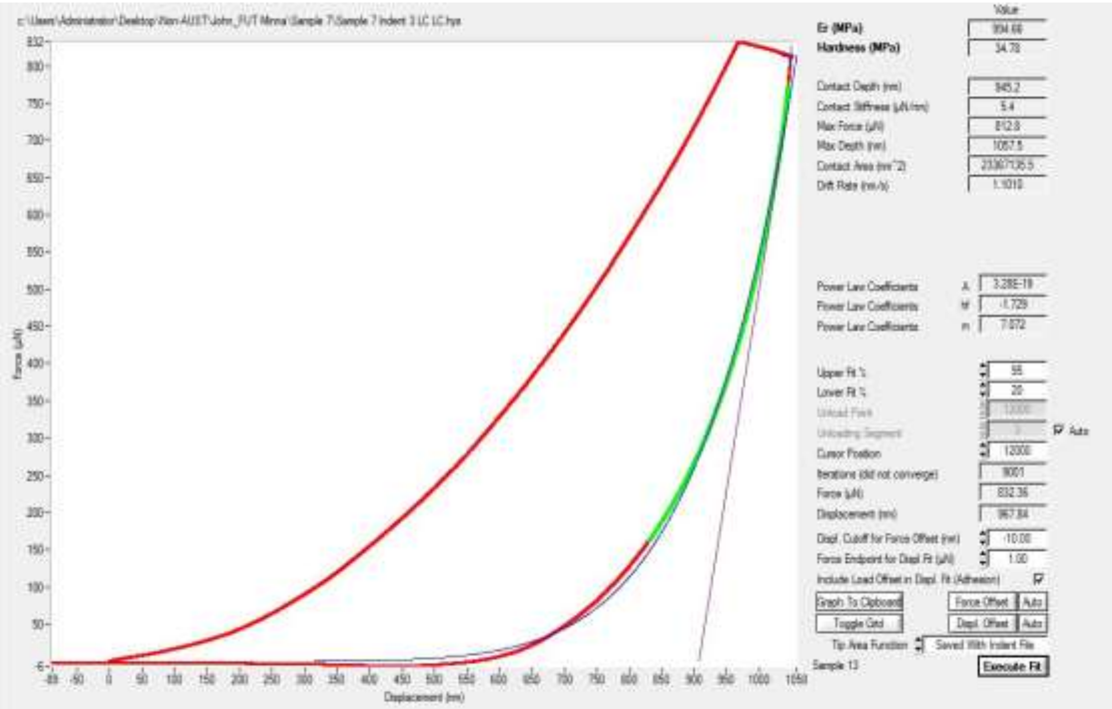
Tensile strength is the maximum stress a plastic polymer material can withstand while being stretched (pulled) before yielding or breaking. HPC2 from all the HPCs recorded the highest tensile strength value of 10.94 MPa as shown on Table 4.13. This value is greater than the minimum acceptable tensile strength (3MPa) for concrete based roofing tile as reported by Bolaji and Mosobalaje (2008). Furthermore, this value is 4.2% higher than that of the recycled polymer control matrix and 31.2% higher than the virgin polyethylene control matrix. Observations from the HPC component mixture formulation in most cases, shows a decrease in tensile strength, with increase in ash and clay content, thereby decreasing the plasticity of some of the HPCs. This is also in agreement with Rezaur *et al.* (2010); Atuanya *et al.* (2011) and Muhammad *et al.* (2011). It is obvious that the reinforcing fillers have minimal plasticity effect on the tensile strength of the hybrid polymer composite (HPC). Similarly, the non-plastic nature of Kutigi clay as reported by Akhirevbulu *et al*. (2010) also have minimal effective load transfer, as observed for flexural strength.

4.8.1.3 *Hardness property for optimum HPC*

The HPC with the optimum highest hardness value is recorded in Table 4.14 alongside the flexural properties of recycled polyethylene (rPE) and virgin polyethylene (vPE) as control samples to monitor the effect of the reinforcement in the HPC.

Table 4.14: Hardness Property for Optimum HPC

Property	**Hybrid Polymer Composite**	**Recycled Polyethylene Matrix**	**Virgin Polyethylene Matrix**
Hardness (MPa)	35.27	10.17	6.73



c:\Users\Administrator\Desktop\Nan AUST\John_FUT Minna\Sample 7\Sample 7 Indent 3 LC LC.hys

Er (MPa) 934.66
Hardness (MPa) 34.78

Contact Depth (nm) 945.2
Contact Stiffness (µN/nm) 5.4
Max Force (µN) 812.8
Max Depth (nm) 1057.5
Contact Area (nm^2) 23367136.5
Drift Rate (nm/s) 1.1010

Power Law Coefficients A 3.28E-19
Power Law Coefficients hf -1.729
Power Law Coefficients m 7.072

Upper Fit % 55
Lower Fit % 20
Unload Peak 12000
Unloading Segment 3 ☑ Auto
Cursor Position 12000
Iterations (did not converge) 9001
Force (µN) 832.36
Displacement (nm) 967.84
Displ. Cutoff for Force Offset (nm) -10.00
Force Endpoint for Displ. Fit (µN) 1.00
Include Load Offset in Displ. Fit (Adhesion) ☑
Tip Area Function Saved With Indent File
Sample 13

Figure 4.19: Load Versus Displacement Curve of the Nanoindenter Probe

The Hardness property of the HPC was analysed using a nano-indenter. The hardness values for all the HPC are greater than the recycled and virgin control matrices. This shows that the reinforcement of the recycled matrix using sawdust ash, locust bean pod ash and kutigi clay has a positive effect. It should be noted that HPC7 which has an appreciable flexural strength of 14.83MPa and tensile strength of 6.81MPa turned out to be the HPC with the best hardness property of 35.27MPa, from a component mixture of 46wt% SDA, 3wt% LBPA, 11wt% clay and 40% rPE, processed at 155^{o}C. The pozolanic property of Kutigi clay giving rise to cementitious effect is highly responsible for the increase in hardness recorded, though, below and above 11wt% clay component formulation, lesser values of hardness were recorded. This assertion is further confirmed by the EDX analysis of the HPC having high Silicon and Alumimium content. Chike *et al*. (2014) also observed a similar trend when maize cob ash was used as reinforcement in recycled low density polyethylene.

4.8.2 Micro structural properties of the hybrid polymer composite

The SEM, scanning probe microscopy (SPM) and EDX, elemental composition of the optimum hybrid polymer composite (HPC2) based on mechanical property were analysed. Similarly, two compounded samples of used and virgin polyethylene matrices were also produced to serve as control samples for the HPC. Figure 4.20 - 4.23 are the SEM, optical image, SPM, and EDX of the optimum hybrid polymer composite (HPC2).

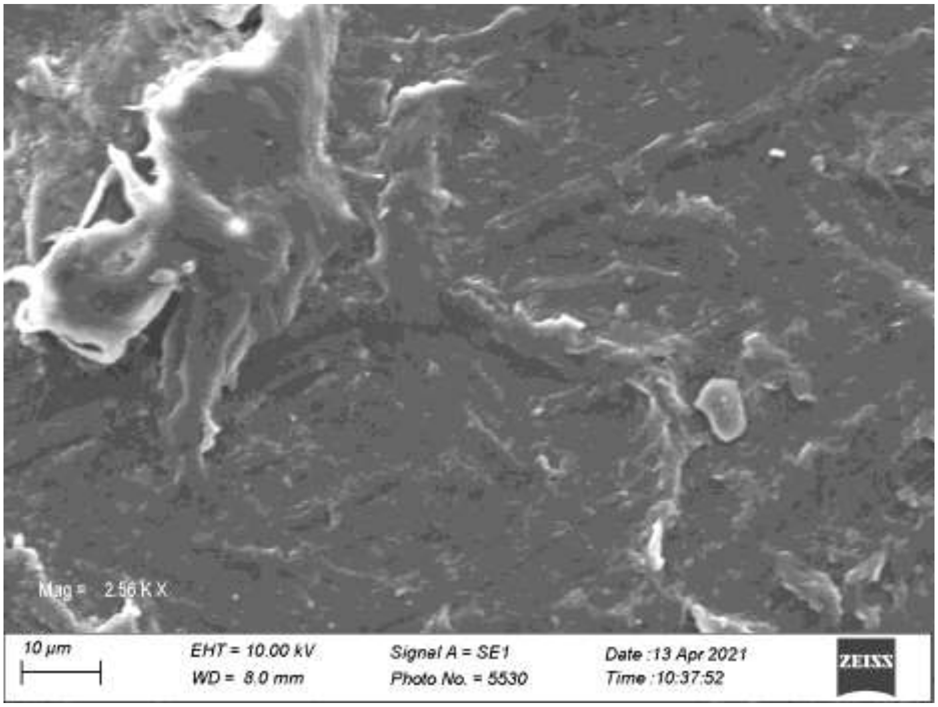


Figure 4.20: SEM for Optimum Hybrid Polymer Composite (HPC2)

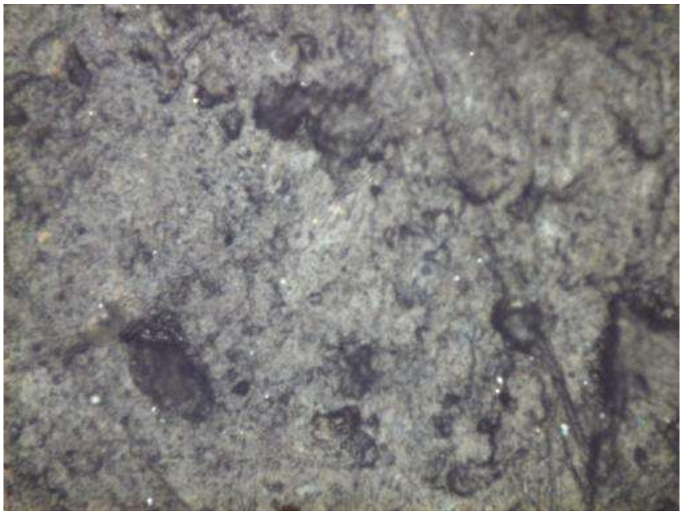


Figure 4.21: Optical Image of the HPC

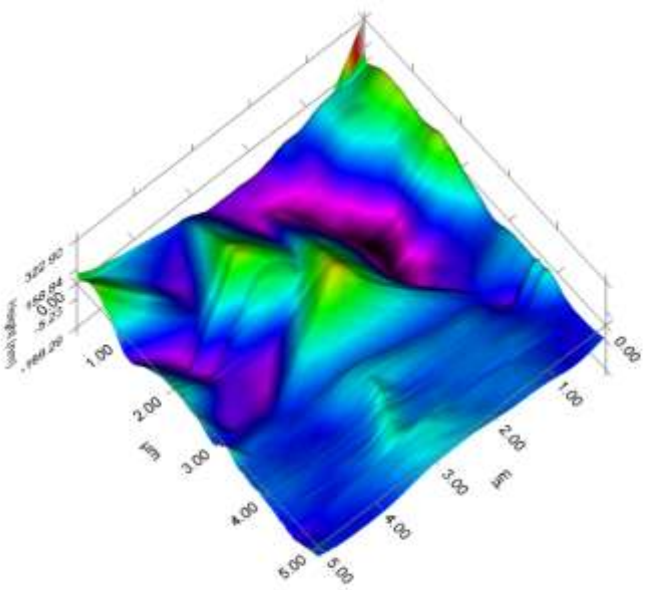
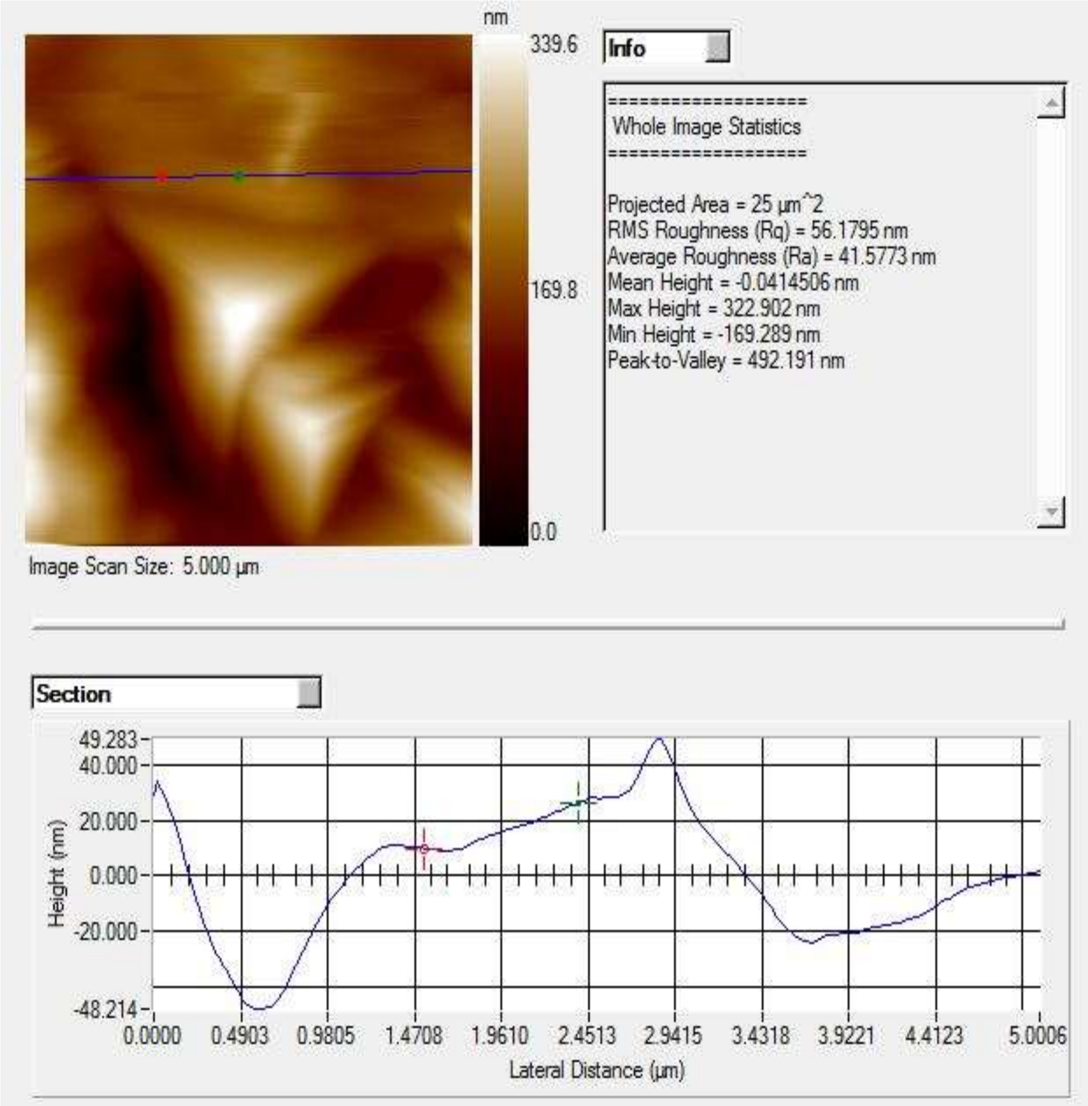


Figure 4.22a: Scanning Probe Microscopy (SPM) Image of the HPC



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===================
 Whole Image Statistics
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Projected Area = 25 µm^2
RMS Roughness (Rq) = 56.1795 nm
Average Roughness (Ra) = 41.5773 nm
Mean Height = -0.0414506 nm
Max Height = 322.902 nm
Min Height = -169.289 nm
Peak-to-Valley = 492.191 nm
```

Figure 4.22b: Scanning Probe Microscopy (SPM) Image of the HPC

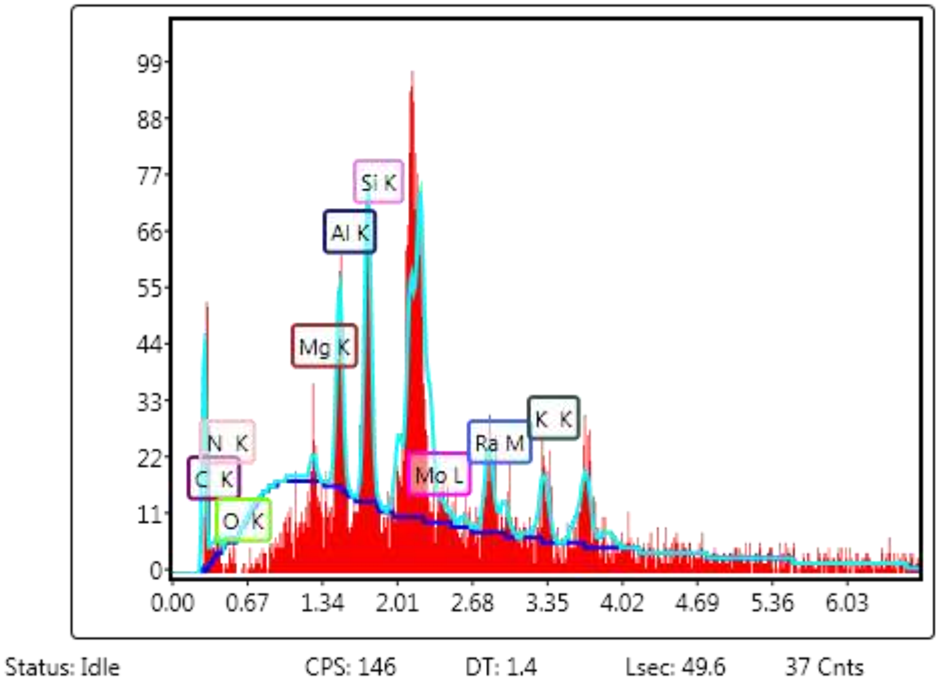

Figure 4.23: EDX of the HPC

Figure 4.20, 4.21, 4.22a, 4.22b and 4.23 presents the SEM, optical image, SPM and EDX of the hybrid polymer composite. The HPC SEM and optical image shows a reasonable high level of dispersion of the fillers (ash and clay) within the HPC space, with a minimal level of patches and agglomeration of filler in some few areas, as seen in its optical image. The information from the SPM image statistic of the HPC as captured by the probe indenter shows a projected area of 25µm^2, average surface roughness of 41.57nm, maxim height of 322.90 nm and a peak-to-valley value of 492.19nm. The presence and increase in the content of Silicon, Aluminium, magnesium and carbon from the HPC EDX result, in comparison to the recycled and virgin PE, is a clear refection of the effect of the reinforcing agents (fibre ash and clay). Molybdenum, which is a component of the industrial ink used as an imprint on the water sachet (low density polyethylene) is also detected. The cumulative effect of these components has impacted hardness, fire resistance property and ultra violet stabilizing effect on the HPC. Figure 4.24a and 4.24b presents the SEM- EDX image of the recycled polyethylene (PE) matrix.

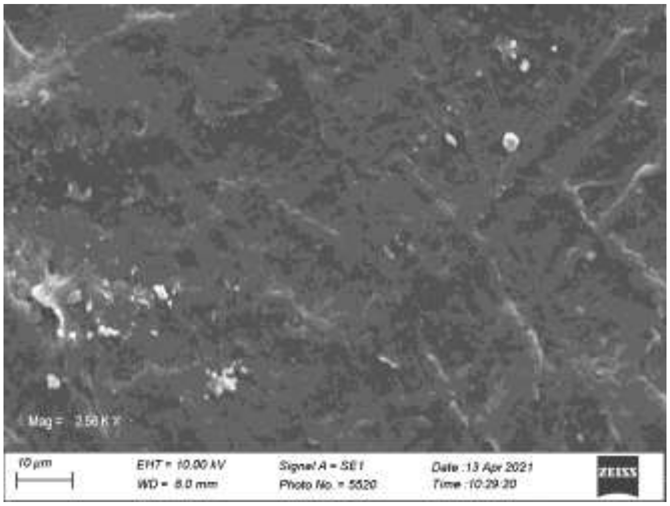

Figure 4.24a: SEM for Recycled Compounded PE Matrix

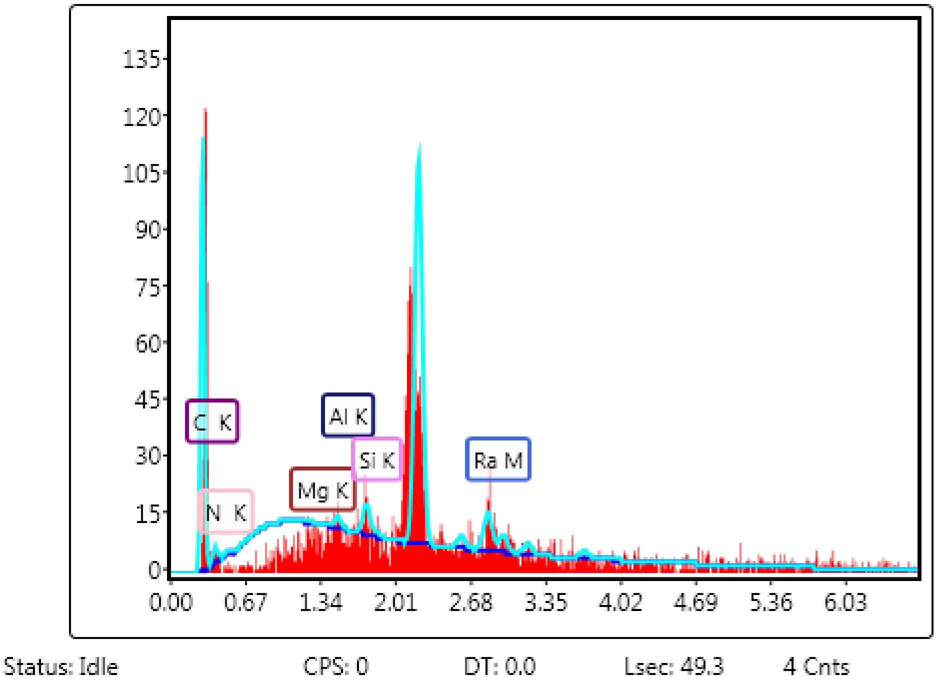

Figure 4.24b: EDX for Recycled Compounded PE Matrix

Figure 4.24a and 4.24b present the SEM image and EDX of the recycled compounded PE matrix. The morphology shows a dark surface background, which became more pronounced due to the ink label on the recycled pure sachet. Some few white spots were also observed on the SEM image. These patches may be impurities, foreign to the recycled PE matrix stock. The EDX analysis shows a high carbon content. This is expected because polyethylene is majorly characterized by carbon and hydrogen. The SEM-EDX image of the virgin PE is presented in Figure 4.25a and 4.25b.

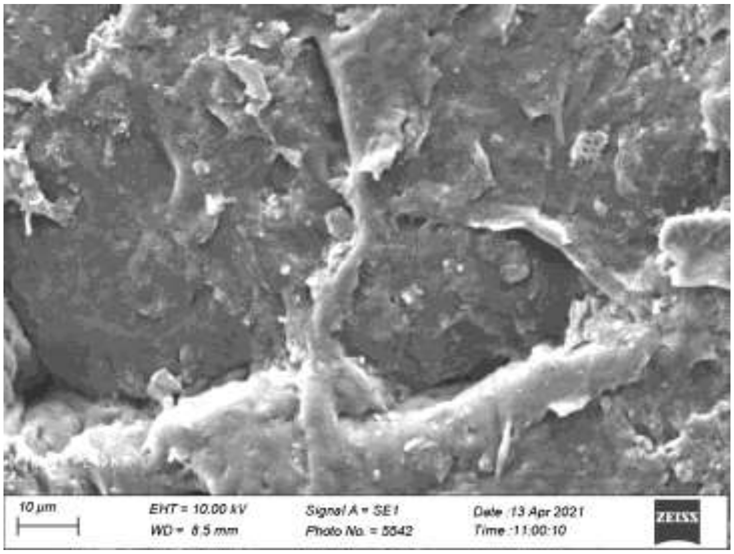

Figure 4.25a: SEM for Virgin Compounded PE Matrix

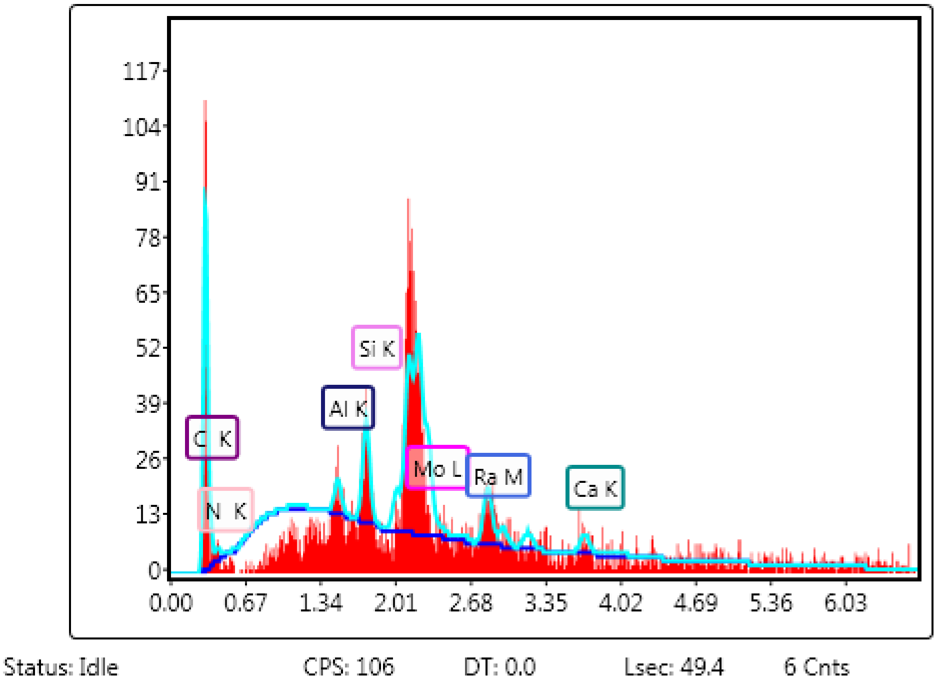

Figure 4.25b: EDX for Virgin Compounded PE Matrix

Figure 4.25a and 4.25b present the SEM image and EDX of the virgin compounded PE matrix. The image is characterized with inconsistency in its surface morphology. This may be signs of partial and non-uniform distribution of the melted polymer molecules within the matrix space. This phenomenon is supported by void caused by air bubbles during processing of the virgin PE pellet due to absence of filler. Similarly, a high carbon content is also observed from the EDX result, this signifies that hydrocarbon is the base stock of the virgin polyethylene.

4.8.3 Statistical evaluation and modelling of the hybrid polymer composite Production

The statistical analysis presents the ANOVA, model equation and the model graph optimum parameter of the HPC production process in relation to its mechanical properties of flexural strength, tensile strength and hardness. Table 4.15 shows the ANOVA for the flexural strength response of the HPC.

Table 4.15: ANOVA for Flexural Strength Response Surface Quadratic Model

Source	**Sum of Squares**	**df**	**Mean square**	**F value**	**p- value prob>F**	
Model	232.33	9	25.81	16.61	<0.0001	significant
Linear Mixture	166.44	3	55.48	35.70	<0.0001	
AB	27.39	1	27.39	17.62	<0.0001	
AC	1.41	1	1.41	0.91	0.3445	
AD	10.69	1	10.69	6.88	0.0110	
BC	6.43	1	6.43	4.14	0.00463	
CD	1.88	1	1.88	1.21	0.2756	
Residual	93.25	60	1.55			
Lack of fit	93.25	55	1.70			
Pure error	0.000	5	0.000			
Cor.Total	325.58	69				

The flexural strength response is a quadratic model expression. This shows the interaction of the reinforcing components that determines the flexural strength of the HPC. The model Equation for Flexural Strength is presented in Equation 4.3.

A= SAWDUST ASH (SDA)

B= LOCUST BEAN POD ASH (LBPA)

C= CLAY

D= RECYCLED POLYETHYLENE (PE)

$$\text{FLEXURAL STRENGTH}=16.32A+20.98B+19.49C+12.85D-16.62AB-12.79AC-5.31AD-25.75BC-2.16BD-14.85CD \tag{4.3}$$

Table 4.15 shows that the F-value test model from the ANOVA of the flexural strength response analysis is significant having a value of 16.61. This indicate that a strong interaction exist amongst the reinforcing materials (SDA, LBPA, Clay) with the polymer matrix (recycled polyethylene).

In addition, the P-value of <0.0001 which is less than 0.05 is an indication of its significance where the reinforcing or interacting materials have contributed in enhancing the flexural strength of the HPC. Each P-value on the analysis of variance for the reinforcing interacting materials show the degree of their impact on the flexural strength. However, the interaction of AB (0.0001), AD (0.0110), and BC (0.0463) among others had greater impact, while AC (0.3445) and CD (0.2756) had no significant impact on the flexural strength of the HPC.

The low residual value of the ANOVA of the flexural strength is a strong measure of the quality of a regression analysis result. The lower the value, the better. The 0.000 value observed as pure error is an indicative that the predictions in the model are correct on an average.

From the residual model equation for flexural strength, each of the reinforcing material has positive main effect on the property outcome of the HPC. Among all the reinforcing components, locust bean pod ash and clay had greater impact on the flexural strength base on their values. Though, the interaction of sawdust-recycled polyethylene (AD) also play a pivotal role in the flexural strength property compared to other interacting terms. Table 4.16 shows the ANOVA of the tensile strength response of the HPC.

Table 4.16: ANOVA for Tensile Strength Response Surface Quadratic Model

Source	**Sum of Squares**	**df**	**Mean square**	**F value**	**p- value prob>F**	
Model	64.88	9	7.21	39.91	<0.0001	significant
Linear Mixture	37.61	3	12.54	69.40	<0.0001	
AB	0.90	1	0.90	4.96	0.0297	
AC	0.87	1	0.87	4.83	0.0318	
AD	12.06	1	12.06	66.75	<0.0001	
BC	1.51	1	1.51	8.35	0.0054	
CD	1.19	1	1.19	6..61	0.0126	
Residual	10.84	60	0.18			
Lack of fit	10.84	55	0.20			
Pure error	0.000	5	0.000			
Cor.Total	75.72	69				

The model Equation for Tensile Strength is presented in Equation 4.4.

A= SAWDUST ASH (SDA)

B= LOCUST BEAN POD ASH (LBPA)

C= CLAY

D= RECYCLED POLYETHYLENE (PE)

TENSILE STRENGTH = 7.10A+8.5B+19.28C+9.15D-3.01AB-10.06AC+5.64AD-12.47BC+6.62BD-11.83CD (4.4)

Table 4.16 shows that the F-value test model from the ANOVA of the tensile strength response analysis is significant having a value of 39.91. This indicate that a strong interaction exist amongst the reinforcing materials (SDA, LBPA, Clay) with the polymer matrix (recycled polyethylene).

In addition, the P-value of <0.0001 which is less than 0.05 is also an indication of its significance where the reinforcing or interacting materials have contributed in enhancing the tensile strength of the HPC. Each P-value on the analysis of variance for the reinforced interacting materials shows the degree of their impact on the tensile strength. It should be noted that the interaction of all the linear mixture components in terms of AB (0.0297), AC (0.0318), AD (0.0001), BC (0.0054) and CD (0.0126) had good positive impact.

The low residual value of the ANOVA tensile strength is a strong measure of the quality of a regression analysis result. The 0.000 value observed as pure error is an indicative that the prediction in the model is correct on an average.

From the residual model equation for tensile strength, each of the reinforcing material has positive main effect on the property outcome of the HPC. Among all the main reinforcing components, clay had greater impact on the tensile strength base on its value. Though, the interaction of sawdust-recycled polyethylene (AD) and BD also played a pivotal role in the tensile strength property compared to other interacting terms. Table 4.17 shows the ANOVA of the hardness property response of the HPC.

Table 4.17: ANOVA for Hardness Response Surface Quadratic Model

Source	Sum of Squares	df	Mean square	F value	p- value prob>F	
Model	3323	59	56.33	7.75	0.0007	significant
Linear	99.37	3	33.12	4.56	0.0293	
Mixture						
AB	65.00	1	65.00	8.94	0.0136	
AC	253..23	1	253.23	34.84	0.0002	
AD	160.69	1	160.69	22.11	0.0008	
AE	0.25	1	0.25	0.034	0.8578	
AF	1.45	1	1.45	0.200	0.6648	
BC	260.73	1	260.73	35.87	0.0001	
BD	40.26	1	40.26	5.54	0.0404	
BE	0.35	1	0.35	0.048	0.8303	
CD	251.09	1	251.09	34.54	0.0002	
ABE	0.53	1	0.53	0.073	0.7932	
BE^2	76.36	1	76.36	10.51	0.0089	
BDF^2	110.35	1	110.35	15.18	0.003	
Residual	72.69	10	7.27			
Lack of fit	72.69	5	14.54			
Pure error	0.000	5	0.000			
Cor.Total	3396.33	69				

The model equation for Hardness property is presented in Equation 4.5.

A= SAWDUST ASH (SDA)

B= LOCUST BEAN POD ASH (LBPA)

C= CLAY

D= RECYCLED POLYETHYLENE (PE)

E= PROCESSING TEMPERATURE

F= MIXING TIME

$$\text{HARDNESS}=17.95A+ 0.16B- 349.99C +11.97D +97.88AB +599.04AC +67.47AD$$
$$+0.24AE +0.58AF + 607.33BC +75.62BD +75.62BD +0.68BE +602.08CD \qquad (4.5)$$

Table 4.17 shows that the F-value test model from the ANOVA of the hardness property response analysis is significant having a value of 7.75. This indicate that a strong interaction exist amongst the reinforcing materials (SDA, LBPA, Clay) with the polymer matrix (recycled polyethylene).

In addition, the P-value of 0.0007 which is less than 0.05 is also an indication of its significance where the reinforcing or interacting materials have contributed in enhancing the hardness property of the HPC. Each P-value on the analysis of variance for the reinforcing interacting materials shows the degree of their impact on the hardness property. It should be that the interaction of all the linear mixture components in terms of AB (0.0136), AC (0.0002), AD (0.0008), BC (0.0001), BD (0.0404), CD (0.0002), BE^2 (0.0089) and BDF^2 (0.003) had appreciable positive impact. While, AE (0.8578), AF (0.6648), BE (0.8303) and ABE (0.7932) has no significant impact on the hardness property of HPC. The 0.000 value observed as pure error on Table 4.17 is an indicative that the prediction in the model is correct on an average.

4.8.3.1 *Predicted optimum model graph plots*

In order to validate the optimum experimental result obtained during analysis for the HPC, predicted optimum results are also generated using the design expert software. Figure 4.26 show the predicted optimum model graph plot of the flexural strength of the hybrid polymer composite.

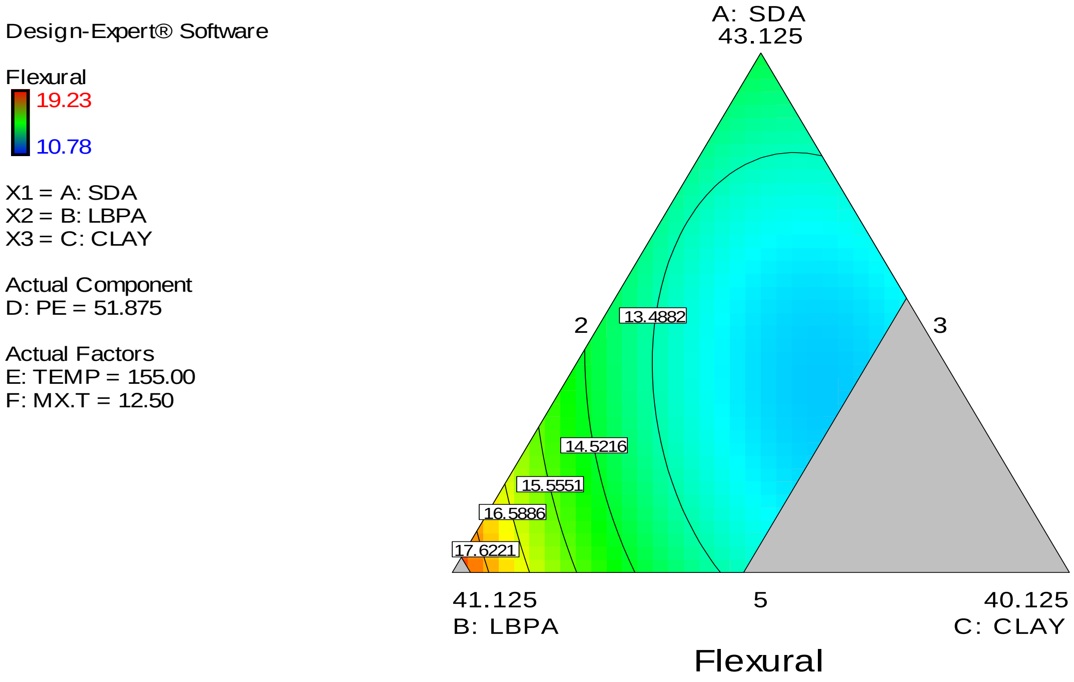

Figure 4.26: Predicted Model Graph for Flexural Strength

Similarly, validation of the actual optimum tensile strength of the HPC is investigated by comparing it with the predicted value generated using the design expert software. Figure 4.27 show the predicted optimum model graph plot of the tensile strength of the hybrid polymer composite.

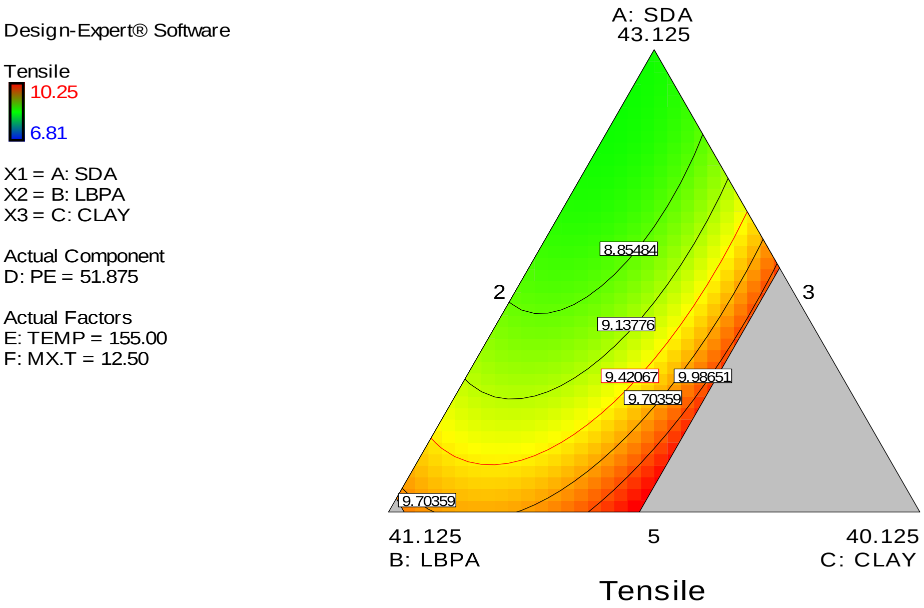

Figure 4.27: Predicted Model Graph for Tensile Strength

Similarly, validation of the actual optimum hardness property of the HPC is investigated by comparing it with the predicted value generated using the design expert software. Figure 4.28 show the predicted optimum model graph plot of the hardness of the hybrid polymer composite.

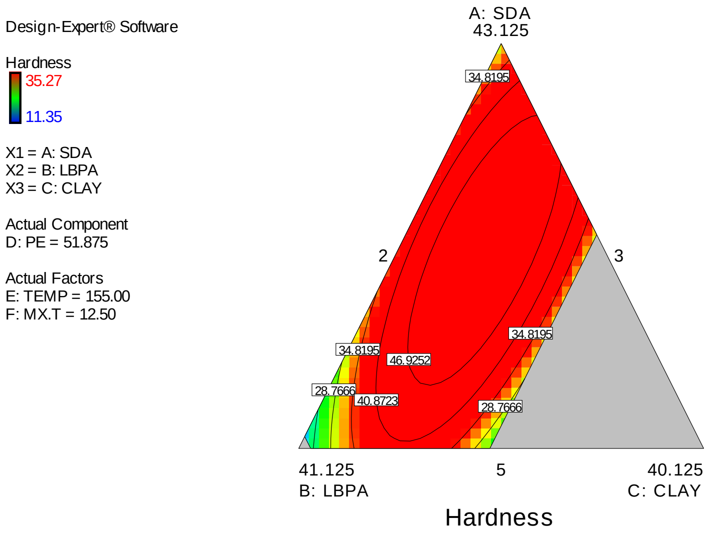

Figure 4.28: Predicted Model Graph for Hardness

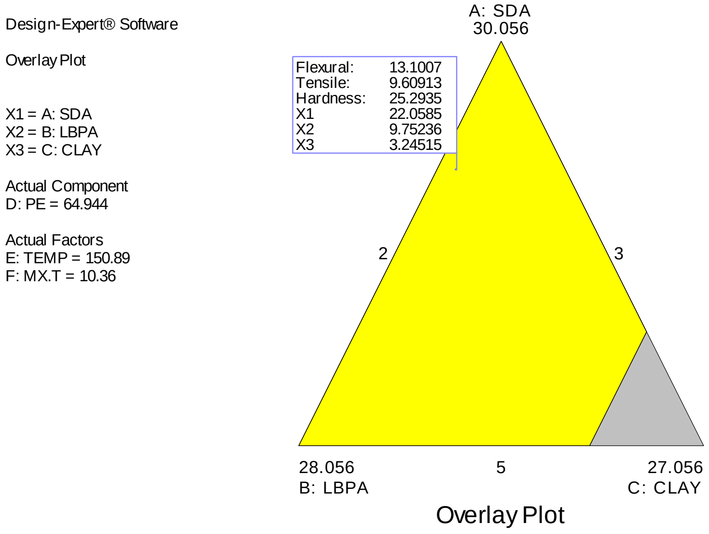

Figure 4.29: Predicted Optimisation Graphical Parameter

4.8.3.2 *Optimisation parameter and response*

In optimisation, the best out of a set of alternative solutions is chosen as a trade-off to others. The optimisation graph shows the feasible optimal response value. Within the design space, the regions containing coloured contour plots that meets the optimisation criteria condition are captured as seen in Figure 4.26 − 4.28. However, the presence of the small grey portion within the graph design space is an indicative that the portions or area do not meet up the optimisation response criteria. For the purpose of verification, hybrid polymer composite was produced using the predicted optimum formulation parameter. The mechanical property values obtained are 8.34MPa, 9.83MPa and 29.41MPa for flexural, tensile and hardness property respectively. These values obtained were close to the predicted values but lower than the actual optimum experimental values as shown in Table 4.18.

4.18: Summarized Optimisation Parameters of the HPC Production Process

Optimum Result from Experimental Analysis	**Predicted Optimum Parameter from Design Expert**
Flexural strength 19.23 MPa	Flexural strength 13.10 MPa
Tensile strength 10.94 MPa	Tensile strength 9.61 MPa
Hardness 35.27 MPa	Hardness 25.29 MPa
Formulation composition	Formulation composition
Sawdust ash (X1) 5%	Sawdust ash (X1) 22.06%
Locust bean pod ash (X2) 40%	Locust bean pod ash (X2) 9.75%
Clay (X3) 2%	Clay (X3) 3.25%
Recycled polyethylene (X4) 53%	Recycled polyethylene (X4) 64.94%
Melting temperature 160^{o}C	Melting temperature 150.89^{o}C
Mixing Time 12.5 Minutes	Mixing Time 10.36 Minutes

4.8.4 Thermal Properties of the Hybrid Polymer Composite (HPC)

Polymer Differential scanning calorimeter (DSC) machine was used to determine the thermal and oxidative stability of the hybrid polymer composites**,** in order to determine the enthalpy change (ΔH), glass transition temperature T_g, melting temperature T_m, degree of crystallization X_c and heat capacity (ΔCp) of the HPC as shown in Figure 4.30 and Table 4.19.

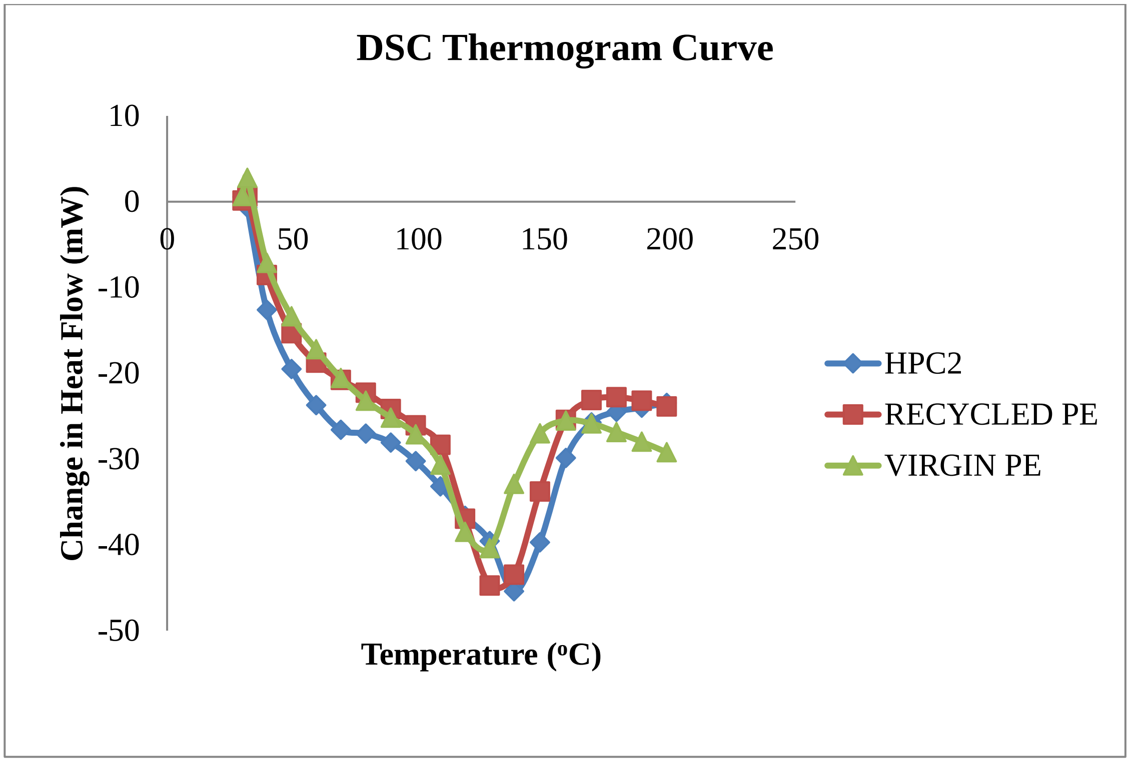

Figure 4.30: DSC Thermo gram Curve of the Hybrid Polymer Composite

Figure 4.30 show the change in heat flow of the polymer composite with temperature. Based on the mechanical property result, thermal analysis was carried out on the best optimum hybrid polymer composites, alongside the non-reinforced recycled and virgin matrices, which acts as control for this work, using differential scanning calorimeter (DSC) machine. All the thermal processes in this analysis are endothermic in nature since their glass transition temperatures T_g and melting temperatures T_m are initiated by absorption of heat, bearing in mind that polyolefin are semi-crystals (partly amorphous and crystal). It is important to also note that the thermo-gram curves in Figure 4.30 shows a negative change in heat flow with increase in temperature. This is because the heat flow to the experimental samples during the thermal analysis is lower than that received by the instrument reference material (Indium metal).

Table 4.19: Thermal Properties of Hybrid Polymer Composite from DSC

Thermal Properties	**HPC2**	**Recycled LDPE**	**Virgin LDPE**
Enthalpy Change (ΔH), J/g	148.68	196.63	163.40
Melting Temperature (T_m), °C	138.39	129.13	124.69
Transition Temperature (T_g), °C	63	37.78	36.32
Degree of Crystallization X_c, %	96.28	67.80	56.34
Heat capacity (ΔCp), J/gK	1.64	2.74	1.20
Oxidation Onset Temp. (OOT) (°C)	59.61	27.22	14.17

4.8.4.1 *Enthalpy change (∆H)*

Enthalpy is the heat content that accompanies a system (either heat gain or loss). The heat flow or change in enthalpy (∆H) value into the best optimum hybrid polymer composite is 148.68J/g. This enthalpy value is less than the values of the non-reinforced recycled and virgin polyethylene matrices as shown on Table 4.19. It is important to note that the recycling of low density polyethylene by heat, transforms it to crossed-linked polymers with stronger covalent bonds. This observation is responsible for the low enthalpy value of the HPCs caused by the strong covalent bond initiated by polymer crosslinking. The effect of cycles of heat of extrusion on recycled polyethylene initiates and strengthens the formation of crosslinking bonds within the polymer chain. This is similar to the report of Hietala (2013). Furthermore, the incorporation of fibre ashes and the Kutigi clay as fillers is also instrumental in improving the heat resistance and fire retarding property of the hybrid polymer composite being produced. This is a necessary property of any roofing material because when there is a high heat build-up in a system or material, it can easily result into flame. This trend is also observed by Huda and Mishra (2008) for polypropylene composite, while a counter result was observed in Salmah *et. al.* (2011).

4.8.4.2 *Melting temperature (T_m)*

Melting temperature (T_m) is the temperature at which a solid crystal material changes into liquid. The melting temperature (T_m) of the choicest hybrid polymer composites (HPC2) base on mechanical properties is 138.39°C. This temperature value is higher than the unreinforced recycled and virgin polymer matrices, used as control in this work. This observed trend is due to the positive effect of the reinforcing fillers containing magnesium, aluminium and silicon in the hybrid polymer composite. This increase in melting temperature observation is also supported by Salmah *et. al.* (2011).

Another reason is due to the crosslinking and gelation effect of the polymer chain arising from extended number of extrusion heating cycles during recycling. The nucleating effect of the inorganic salts of magnesium, aluminium and silicon, which is known to promote crystallinity has also contributed in increasing the melting point of the hybrid polymer composite, as observed by George (2016). In this case, the hybrid polymer composite has higher degree of crystallinity, when compared with the virgin and recycled matrices devoid of filler reinforcement. This high melting temperature value is higher than that of Bogoeva-Gaceva (2007). This property of high temperature resistance is a necessary requirement for a material to be used as a good roofing material.

4.8.4.3 *Glass transition temperature (T_g)*

The glass transition temperature (T_g) is the temperature at which the amorphous portion of a material will become soft or more rubber-like as it response to heat application. The glass transition temperature (T_g) of the hybrid polymer composites are higher than the recycled and virgin control composites. The non-plastic nature of Kutigi clay and amorphous property of the fibre ash as reinforcement in the hybrid polymer composite is responsible for this observation. Generally, glass transition temperature (T_g) is inversely proportional to plasticity as reported by George (2004).

4.8.4.4 *Degree of crystallization (Xc) and heat capacity (∆Cp)*

The degree of crystallization of the HPC is higher than that of the recycled and virgin control matrices This is because in this case, the fillers or reinforcing agents (ash and clay) yielded a speedy nucleating effect of crystal formation, thereby promoting the migration and diffusion of the recycled polyethylene molecular chains to the surface of the growing polymer crystal in the hybrid composite. Usually, nucleating agents which are organic insoluble particulate are added to polymers with the aim of increasing their crystallinity, and reducing the cycle time of transiting molten polymer into solids. In most cases, the melting point of nucleating agents is higher than that of polymer matrix (George 2016). This increase in degree of crystallization within a polymer composite due to kernel shell filler is also observed by Salmah *et. al.* (2011). Nevertheless, the degree of crystallinity (Xc) of the unreinforced recycled LDPE matrix is higher than the virgin LDPE control matrix. Obviously, the phenomenon of Gelation caused by cycles of thermal stress due to recycling may be responsible for this observation.

Furthermore, it is clear from Table 4.19 that the heat capacity of the recycled LDPE matrix is higher than that of the hybrid polymer composites as well as the pure virgin LDPE control. This phenomenon is caused by an uninterrupted network of increased crosslinking bonds, distributed across the recycled polymer matrix, occasioned by cycles of thermal extrusion.

4.8.4.5 *Oxidation onset temperature (OOT)*

This is the onset temperature at which a polymer material begins to decompose when exposed to oxidation process by heat or fire at a constant heating rate by the DSC machine. In this case, the HPC recorded a high OOT of 59.61^{o}C compared to the recycled and virgin matrices. This is because of the stabilizing effect of the reinforcing filler of clay and ash within the HPC. In the case of any fire incident, a polymer material with high OOT will offer a stiffer resistance to the attack of fire compared to those with lower OOT in value.

4.8.5 Water absorption capacity

Table 4.20 shows the varying degree of water absorption capacity (WAC) of the hybrid polymer composites according to the experimental design. These values were calculated using Equation 3.1.

Table 4.20a: Water Absorption Capacity (WAC)

HPC Experimental Runs	Water Absorption Capacity %
HPC1	1.04
HPC2	0.62
HPC3	1.16
HPC4	0.56
HPC5	0.57
HPC6	0.5
HPC7	1.65
HPC8	0.71
HPC9	0.56
HPC10	0.57
HPC11	1.60
HPC12	0.8
HPC13	0.56
HPC14	0.72
HPC15	0.71
HPC16	0.62
HPC17	0.51
HPC18	1.63
HPC19	0.51
HPC20	0.72
HPC21	1.65
HPC22	0.72
HPC23	0.51
HPC24	0.8
HPC25	0.71
HPC26	0.57
HPC27	1.63
HPC28	0.56
HPC29	0.51
HPC30	0.72
HPC31	1.30
HPC32	1.16
HPC33	0.51
HPC34	1.63
HPC35	0.71

Table 4.20b: Continuation

HPC36	0.5
HPC37	0.62
HPC38	0.86
HPC39	0.5
HPC40	1.60
HPC41	0.62
HPC42	0.56
HPC43	1.31
HPC44	0.5
HPC45	1.59
HPC46	1.14
HPC47	1.60
HPC48	1.04
HPC49	0.72
HPC50	0.51
HPC51	0.62
HPC52	0.71
HPC53	1.59
HPC54	0.57
HPC55	1.04
HPC56	0.72
HPC57	1.16
HPC58	1.63
HPC59	0.5
HPC60	1.23
HPC61	0.5
HPC62	1.16
HPC63	1.60
HPC64	0.71
HPC65	1.63
HPC66	1.04
HPC67	0.56
HPC68	0.62
HPC69	1.63
HPC70	0.56

Water absorption capacity (WAC) test was carried out for 72 h on the produced hybrid polymer composite as well as the recycled polyethylene and virgin polyethylene which serve as the reference (control) samples. Results show that most experimental formulations with 50% and above recycled polyethylene content, recorded lowest water absorption capacity. This is because of the low reinforcing filler content in these samples as well as the increasing level of covalent bond promoted by the crosslinking of the polymer molecules, present within the recycled polymeric chain of the polymer composite. HPC6, HPC36, HPC39, HPC44, HPC59 and HPC61 with experimental design formulation of 5% EGSA, 3% LBPA, 2% clay and 90% rPE recorded the lowest water absorption capacity of 0.50%. This value is within the acceptable WAC limit proposed for nonporous roofing tile by ASTM C373 -2018. Similarly, the value is 20 times lower than the permissible standard value for water absorption capacity in general purpose roofing tiles (AS-4046-2002 and ASTM C373 -2018). In this case, the lower the value – the better.

On the other hand, it was observed that experimental formulation with relative high clay, EGSA content, and relatively low rPE content recorded the highest level of water absorption capacity of 1.65%. To be more specific, experimental design formulation runs for HPC7 and HPC21 (46% EGSA, 3% LBPA, 11% clay and 40% rPE) recorded this highest level of water absorption capacity. The relative high clay and ash content may be responsible. Though, this value is still lower compared to that obtained in some other literatures. This however, is because of the non-plastic nature of Kutigi kaolinite clay used in this work, which has less swelling–shrinking ratio upon water absorption in order to retain the dimensional stability of the HPC. Other polymer composite literature like Chike *et al*. (2014) has similar result with regards to water absorption capacity. Table 4.21 shows the water absorption capacity of the optimum HPC and the control matrices samples.

Table 4.21: Water Absorption Capacity for Optimum HPC and Control Samples

Property	**Hybrid Polymer Composite (HPC2)**	**Recycled Polyethylene Matrix**	**Virgin Polyethylene Matrix**
Water Absorption Capacity (%)	0.50	0.38	0.10

The water absorption capacity (WAC) of the recycled PE and virgin PE were also analysed in comparison with that of the optimum HPC. Despite the low WAC of the optimum HPC which is 0.5%, this value is higher than that of the recycled and virgin PE matrix. Reasons being that both the recycled and virgin PE matrices are highly hydrophobic in nature with no filler reinforcement in them. Furthermore, these water tight surfaces are further promoted by the processing heat during production, which leaves almost no void on the polymer surface that can permit absorption of free water molecules.

4.9 Degradation of the Hybrid Polymer Composite (HPC) by Natural Weathering

This section present the Fourier transform infrared (FTIR) spectra of the freshly produced HPC, the FTIR spectra of the degraded HPC due to natural weathering, the carbonyl index parameter and the predictable life span of the HPC in comparison to others.

4.9.1 Before exposure to natural weathering

Figure 4.31 presents the Fourier transform infrared (FTIR) of the optimum HPC (2), recycled LDPE matrix (7), virgin LDPE matrix (Dd) and Polycarbonate commercial Market Sample (F) that were freshly produced.

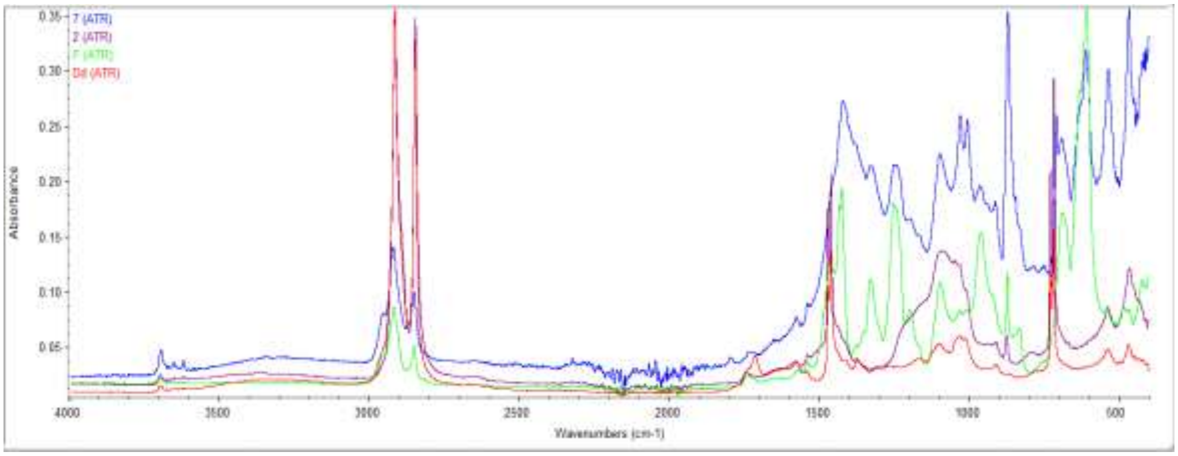

Figure 4.31: Figure: FTIR Spectra of the HPC (2), Recycled Polyethylene (7), Virgin PE (Dd) and Polycarbonate Market Sample (F)

The optimum HPC, recycled compounded matrix and virgin compounded matrix that were freshly produced were subjected to FTIR analysis. Result shows the characteristic of polyethylene –CH- functional group for HPC, recycled polyethylene matrix and virgin polyethylene matrix at 2914.94cm^{-1} and 2847.36cm^{-1}. Similarly, there are methylene (-CH$_2$-) peaks at 1462 and 1590. For the HPC, peaks of 718.91- 729.79cm^{-1} and 537.68cm^{-1} were also observed, depicting the presence of Al-O-Si stretching of the Kutigi kaolinite clay as reinforcement within the HPC. Furthermore, there is an evident disappearance of –OH- groups in the HPC FTIR spectra. This is a clear indicative effect of the heat accompanying the compounding process of the HPC production at 160^{o}C. This has also help to further eliminate any residual free and bound water molecules present in the fillers (carbonised ash and clay) used as reinforcement in the HPC. This will help to reduce the ease of HPC degradation when exposed to water, rain and humidity during its service life.

4.9.2 After exposure to natural weathering

Figure 4.32 presents the (FTIR) of the weathered optimum HPC (Aa), recycled compounded matrix (BK), virgin compounded matrix (Cc) and polycarbonate market sample (Dd) after exposure for one whole year, comprising the rainy and dry season. These samples were exposed to natural weathering in Lugbe, Abuja, Federal capital territory of Nigeria. The climatic condition for this location shows the following: average maximum temperature (34.58^{o}C), annual rainfall (806mm), average humidity (55.75%), average sunshine (8.5 h), average pressure (1010.83mbar) and ultra-violet (UV) index (7) (www.weather – atlas.com).

The observation of the effect of natural weathering on these samples after exposure is presented in Section 4.9.3 as carbonyl index effect, in relation to the degree of manifestation of carbonyl functional groups, caused by photo-oxidation degradation in the samples.

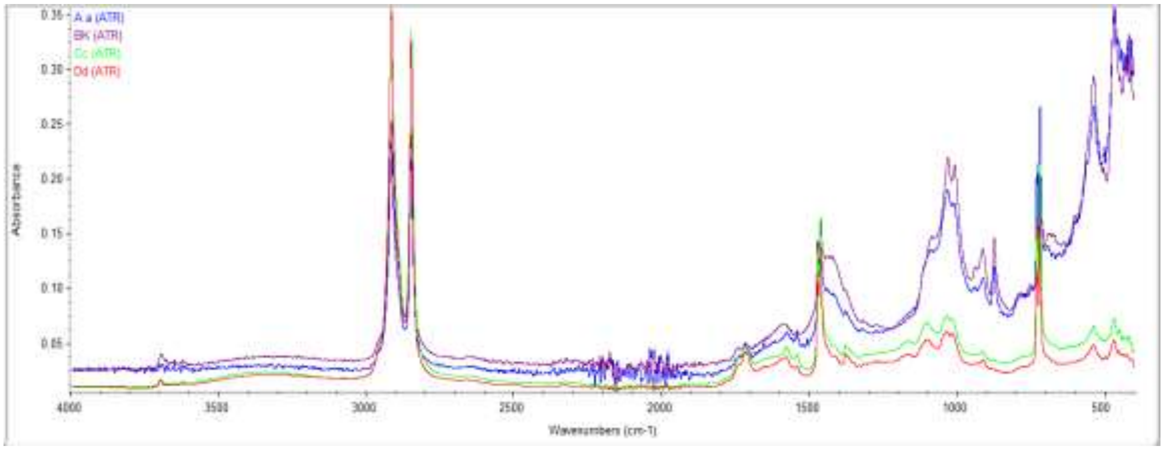

Figure 4.32: FTIR Spectra of the Weathered HPC (Aa), Recycled polyethylene Matrix (BK), Virgin PE (Cc) and Polycarbonate Market Sample (Dd)

Table 4.22 presents the FTIR peaks extracted from the set of spectra displayed in Figure 4.31 and Figure 4.32 for freshly prepared polymer composite samples as well as the weathered polymer composite samples after exposure to natural weathering.

Table 4.22: FTIR Peaks for Fresh Polymer Composite and Weathered Polymer Composite

Fxn. Grp.	**Before Weathering**				**After Weathering**			
	FTIR peaks for Fresh Polymer Composite (cm^{-1})				FTIR peaks for Weathered Polymer Composite (cm^{-1})			
	HPC	RPE	VPE	PC	HPC	RPE	VPE	PC
C-H	2914.94 - 2847.36	2914.83 - 2847.52	2915.14 - 2847.52	2917.20 - 2849.91	2914.77 - 2847.08	2914.65 - 2847.02	2914.92 - 2847.31	2917.41 - 2849.63
C=O	−	−	−	−	1979.81	1713.89	1714.77	1981.27
C≡C	−	−	−	−	2237.24 - 2147.97	−	−	2323.26 - 2034.43
C=O Ring	1590.15 - 1462.22	1472.06 - 1462.42	1462.79	1425.63	1577.10 - 1462.09	1577.26 - 1462.34	1578.39 - 1462.71	1425.54
C-F	1032.17	1031.53	1032.39	1099.31	1032.69	1033.92	1032.70	1094.53
C-Cl	718.91	729.90 - 719.03	729.59 - 719.18		729.66	729.76 - 718.97	729.61 - 719.22	−
CO3 -	−	−	−	874.16	−	−	−	873.96

Table 4.22 shows a clear comparison of the FTIR peaks extracted from Figure 4.31 and Figure 4.32. The columns of the freshly prepared samples before exposure are the extracted peaks from Figure 4.31, while the columns of the weathered samples after exposure to natural weathering are the extracted peaks from Figure 4.32. It should be noted that one clear distinction between these two set of FTIR peaks is the fact that, the weathered samples are basically characterized by the formation of carbonyl groups ranging from 1713.89 − 1981.27cm^{-1}. These observations are absent in all the freshly prepared samples.

Photo-oxidation leading to the formation of radicals is responsible for this phenomenon. This has caused the exposed polymer composite samples to degrade with varying degree of carbonyl index value, based on the level of environmental exposure and resistance of the composite to ultra violet effect. Furthermore, both the freshly prepared composites and weathered composites are associated with the following functional groups: C-H (2914.94cm^{-1} - 2847.36cm^{-1}), C-Cl (718.91cm^{-1}), C-F (1032.17cm^{-1}) and the aromatics (1590.15cm^{-1} – 1462.22cm^{-1}).

Figure 4.33 and Figure 4.34 presents the optical image and the scanning probe microscopy (SPM) image of the weathered HPC.

Figure 4.33: Optical Image of the Weathered HPC

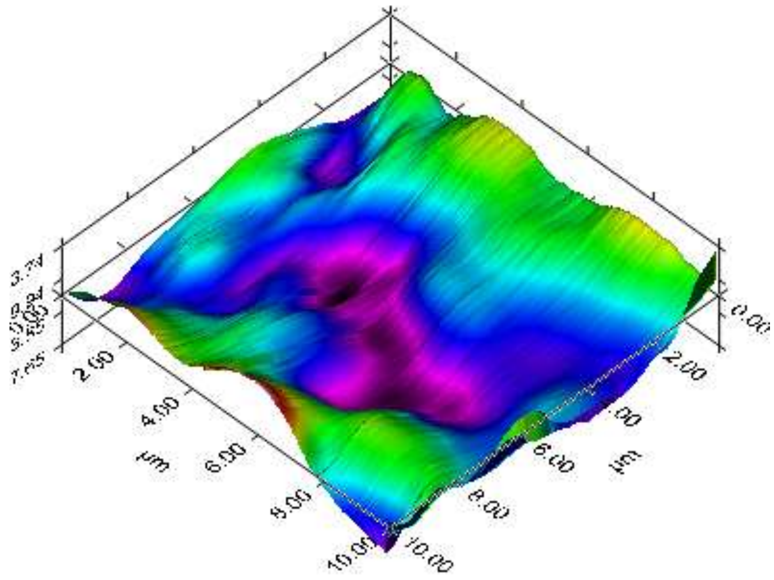

Figure 4.34: Scanning Probe Microscopy (SPM) Image of the Weathered HPC

Figure 4.33 shows the optical image of a reasonable high level of dispersion of the fillers (ash and clay) still present within the weathered HPC space, with a minimal level of patches and agglomeration of filler in some few areas due to weathering. This effect of weathering such as fading and colour change on the HPC sample is minimal compared to the control samples. Figure 4.34 shows the SPM atomic resolution of the surface imaging of the weathered HPC with high image magnification, where the friction and height of the surface of a given sample at nanoscale is determine through the use of a nano-indenter probe.

4.9.3 Carbonyl index

This is a measure of the extent of photo-oxidation or degradation of plastic polymer such as polyethylene, when exposed to weathering effects. Carbonyl index is accounted for by calculating the ratio of absorbance peak of a carbonyl group to a reference stable absorbance peak such as alkane – C-H, as expressed in Equation 2.4.

The above information from Fourier Transform Infrared (FTIR) analysis was used to determine the carbonyl index initiated, by the formation of carbonyl groups due to degradation caused by the combined effects of natural weathering - ultra violet ray, rain, humidity and heat. The carbonyl index of the HPC produced in comparison with 3 other polymer roofing tiles is presented in Table 4.23.

Table 4.23: Carbonyl Index Value of HPC, Recycled PE, Virgin PE and Polycarbonate Market Sample

Parameter	HPC	Recycled PE	Virgin PE	Polycarbonate Market Sample
Carbonyl Index	0.12	0.14	0.46	0.30

Degradation of the physical, mechanical and chemical properties of materials such as polymer composite is an adverse effect of natural weathering. Some of the observable physical degradation effects of natural weathering from the HPC are relative faded surface appearance, embrittlement and loss of weight due to chalking. Furthermore, a decrease in the mechanical properties of the HPCs was also observed for the hardness and flexural strength properties as captured in Table 4.24 and Table 4.25.

It is pertinent to note that, physical and mechanical degradation of polymer composites is a function of change or alteration in its chemical properties (functional groups). The extent of degradation in plastic polymer materials initiated by the formation of carbonyl functional group is accounted for, as carbonyl index (CI) as recorded in Table 4.22 – which is a measure of the chemical photo oxidation of polyolefin. In this case, the carbonyl index value of the HPC is 0.12. This low value is an indicative effect of its strong resistance to photo oxidation degradation when compared to other samples as shown in Table 4.23. The low carbonyl index value is predicated on the stabilizing effect of the reinforcing fillers (carbonised fibres and clay), thereby slowing down and inhibiting the formation of hydro peroxide and peroxide radicals, which is responsible for photo oxidation, leading to degradation of polymer composite. Kenichi *et al.* (2016) reported an increasing trend in carbonyl index values, with increase in outdoor exposure time and low irradiance, for accelerated weathering test using xenon arc lamp. However, Ljerka *et al*. (2014) opined that the resistance and stability of reinforced wood flour-high density polyethylene is dependent on the degree of wood filler dispersion within the composite, as well as the composition of the stabilizing filler.

4.9.4 Service life prediction based on degradation of mechanical properties

Based on the service life of roofing tiles, a comparison of the hardness and flexural strength of the optimum HPC sample, recycled PE matrix, virgin PE matrix and the polycarbonate market sample are presented in Table 4.24 and Table 4.25 before and after weather exposure. For the purpose of workability of roofing tile and sheets, the property of hardness and flexural strength are critical mechanical property of interest.

Table 4.24: Hardness Property Before and After Exposure

Degradation	**HPC Hardness (MPa)**	**Recycled PE Hardness (MPa)**	**Virgin PE Hardness (MPa)**	**Market Sample Hardness (MPa)**
Before exposure	35.27	10.17	6.73	107.6
After exposure	28.6	6.49	2.7	55.8
% Degradation	18.91%	36.2%	59.8%	48.1%

Table 4.25: Flexural Property Before and After Exposure

Degradation	HPC Flexural Strength (MPa)	Recycled PE Flexural Strength (MPa)	Virgin PE Flexural Strength (MPa)	Market Sample Flexural Strength (MPa)
Before exposure	19.23	10.1	5.89	25.91
After exposure	17.27	7.5	3.03	14.19
% Degradation	10.19%	25.7%	48.55%	45.2%

When building materials such as polymer composite tiles or sheet are exposed to natural or artificial weather condition, it experiences degradation or reduction in its mechanical properties (hardness and flexural strength). Table 4.24 shows that the hardness property of the HPC is greater than the recycled and virgin PE matrix, but is less than the polycarbonate sample sold in the market. Upon exposing all of these samples to natural weathering for a period of one year, a drastic degradation rate of 48.1% in the hardness property of the polycarbonate market sample was observed, despite its initial high value before exposure.

On the other hand, the percentage hardness degradation rate of the HPC under the same condition is 18.91%, which is the lowest of all as shown in Table 4.24. A similar observation is seen with the flexural strength properties of the samples under review as shown in Table 4.24. It can be deduced from this result that the rate of formation of hydro peroxide radicals and photo oxidation in the polycarbonate market sample is so high compared to the HPC and the compounded recycled PE matrix. All of these observations are further confirmed by the carbonyl index result earlier discussed in Table 4.23, which is a measure for determining the extent of degradation in plastic polymer. This will automatically translate in to a shorter service life span for the polycarbonate market sample in comparison to the HPC. As observed by Ljerka *et al.* (2014), the resistance and stability of reinforced polymer composite is dependent on the polymer matrix, degree of filler or additive dispersion within the composite, as well as the composition and concentration of the stabilizing fillers.

Furthermore, virgin PE matrix recorded the lowest result for all, as an indicative of its weak mechanical properties. The following reasons may be responsible: absence of fillers during compounding for easy workability, absence of strong crosslinking bond which is obtainable in recycled PE matrix and possible creation of void within the compounded virgin PE, which would have been filled by the reinforcing fillers. All of these stated observations rendered virgin PE vulnerable to degradation caused by weathering effects such as photo-oxidation. In addition, this same observation is further collaborated by its high carbonyl index value of 0.46 compared to others.

4.9.5 Cost analysis

For a new product to compete favourably with other existing established alternatives in the market space, there is need to carryout cost analysis in terms of production cost of the hybrid polymer composite, to determine its profitability when commercialized. The cost comparison analysis is shown in Table 4.26.

Cost of raw materials = ₦500

Cost of chemical treatment – 5,000/70 = ₦72 per tile

Cost of processing = ₦700 per tile

Mould =30,000/70 = ₦429

Logistics= 1000/70 = ₦15

Table 4.26: Cost Comparison of Commercial Roofing Materials with the HPC

Types of Roofing Sheet	**Dimension**	**Actual Cost**	**Cost Comparison per 1.44 m^2**
Galvanized Zinc sheet	1.8m x 0.8m x 0.6mm	₦ 1,200 per sheet	₦ 1,200
Aluminium sheet	1.22m x 2.44m x 1.5mm	₦ 4,800 per meter	₦ 2,323
Stone-coated Aluminum sheet	1.34m x 0.42m x 0.4mm	₦ 3,200 per meter	₦ 8,192
Polycarbonate twin-walled sheet	6m x 2.1m x 4mm	₦ 65,000 per sheet	₦10,500
Polycarbonate skylight	1.8m x 0.8m x 0.6mm	₦ 2,000 per sheet	₦2,000
HPC (**This Work)**	0.165m x0.1m x 3mm	**₦ 1,716 per tile**	**₦ 1,716**

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In a bid to convert waste to wealth and promote local content, low cost high performance hybrid polymer composite (HPC) for roofing tile was produced using two roll mill and compression moulding machine from polymeric and agricultural wastes, with clay as additive. Recycled LDPE popularly known as pure water sachet was reinforced with carbonised natural fibre produced from *Eucalyptus globulus* sawdust and locust bean pod husk with clay.

The chemical composition of the raw natural fibres shows that it is composed of cellulose, hemicellulose, lignin, ash and extractives (oil and wax). The mercerisation or alkaline treatment process of the LBPH fibre recorded a higher optimum cellulose yield of 80% at 1.5% NaOH for 3 h. This is in comparison with the EGS fibre, having a yield of 74.6%. at 3% NaOH for 2 h.

The chemical treatment of the natural fibres of EG and LBPH and carbonisation at 500 ^{o}C for two hours had a positive modifying effect on the elemental and oxide composition of the natural fibre-ash. There were exposure and improvement in the alumina, silica, magnesium and titanium content of the carbonised fibres. All of these components placed a prominent role in imparting thermal, fire and ultra violet (UV) retarding effect on the HPC. The calcination of the kaolin clay also imparted a high degree of hardness property on the HPC.

Statistical evaluation and modelling of the effect of the process variables indicate that the models of the mercerisation process and HPC production process are significant. Sodium hydroxide concentration variable has a more positive significant effect than the contact time, during the mercerisation of the natural fibres. Similarly, there exists an appreciable degree of strong interaction amongst the reinforcing components within the HPC mix, leading to good mechanical property and good resistance to fire and ultra violet (UV) effect of the HPC.

The Hybrid polymer composite produced from recycled polyethylene matrix have an improved and better mechanical properties than virgin polyethylene due to stronger covalent bond initiated by the cross-linking effect of double thermal mechanical extrusion processes.

The mechanical property of HPC2 with the formulation (5wt% EGSA, 40wt% LBPA, 2wt% clay and 53wt% PE) recorded the highest optimum flexural strength of 19.23MPa and tensile strength of 10.25MPa, while HPC7 recorded a maximum hardness value recorded was 35.27MPa. The thermal property DSC analysis further shows that HPC2 has a high resistance to heat and flame due to its high glass transition temperature (63^{o}C), melting temperature (138.39^{o}C) and enthalpy of 148.68J/g. The water absorption capacity of the HPC is as low as 0.5%, which is 20 times lower than the acceptable standard value for general roofing tiles, according to (ASTMC373-2018).

After one year of exposure of the HPC roofing tile to natural weathering, the rate of degradation of the mechanical property in terms of hardness and flexural was found to be the lowest when compared to the recycled polyethylene, virgin polyethylene and polycarbonate commercial sample. This observation for the HPC roofing tile is further confirmed by its low carbonyl index parameter of 0.12, as a reflection of its promising reliable service life span.

5.2 Recommendations

i. The use of Compactibilisers and hardener such as Maleic anhydride (MA) and poly[methylene (polyphenyl isocyanate)] (PMPPIC) towards strengthening the mechanical properties of Recycled polyvinyl chloride (PVC) composites should be researched into. This is because post-PVC has poor interfacial bonding with natural fibre.
ii. Research should be geared towards the design and advancement of 3-D print customized textile composite materials, for the purpose of precision in dimension, and ease of design.
iii. Research should be geared towards producing smart hybrid polymer composite that vacillate and respond positively, to anticipated change in environmental factors and stimuli, for performance and cost effectiveness.
iv. Research should be directed towards the use of artificial intelligence (AI) to promote advance homogeneous dispersion of reinforcement in polymer matrices, to enhance better interaction of the various component formulations.
v. Research should be explored into the production of smart roofing panel materials that are capable of adjusting to weather temperature variation through absorption and reflection of heat.
vi. The application of Digimat software should be researched to predict the behaviour of composite materials in structural design when subjected to load and aging.
vii. Comparative analysis of the effect of the differences in geographical location on the extent of degradation of the lifecycle of plastic polymers in Nigeria, should be researched into.

viii. Analysis of the effect and extent of Freeze degradation on polymer composite, should be researched into.

ix. Analysis of the effect, and extent of soil compost degradation on polymer composite, should be researched into.

x. Design and fabrication of a multipurpose polymeric waste recycling machine for composite production should be researched into.

5.3 Contribution to Knowledge

This research work was able to convert waste to wealth by producing a durable low-cost hybrid polymer composite (HPC) roofing tile, with a dimension of 100x165x3 mm, at a cost of ₦ 1,716 per tile, from polymeric waste and agricultural waste. This was produced from an optimised treated component mixture formulation of 53 wt% used low density polyethylene (pure water sachet) matrix, reinforced with 5 wt% *Eucalyptus globulus* sawdust fibre ash, 40wt% locust bean pod husk fibre ash and 2wt% kaolinite clay. The mechanical property (flexural strength, tensile strength and hardness) of the HPC is 19.23 MPa, 10.25 MPa and 35.27 MPa respectively. Similarly, the thermal/fire resistant property of the HPC reveal a melting temperature (T_m) of 138.39 ^oC, glass transition temperature (T_g) of 63 ^oC, oxidation onset temperature (OOT) of 59.61 ^oC, and a very low water absorption capacity of 0.5%. A low carbonyl index of 0.12 was observed over a period of one year, in relation to its resistance to the natural weathering effects of sunlight, rainfall, humidity and ultra violet ray. All of these results show that the HPC produced in this work is suitable for roofing purpose due to its good mechanical property and appreciable resistance to thermal, water and natural weathering effects.

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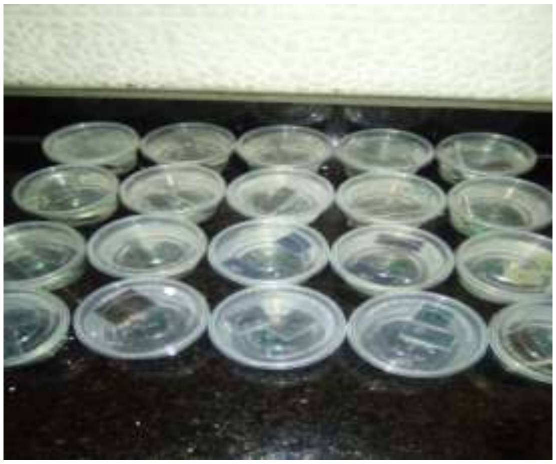
APPENDICES

Appendix I

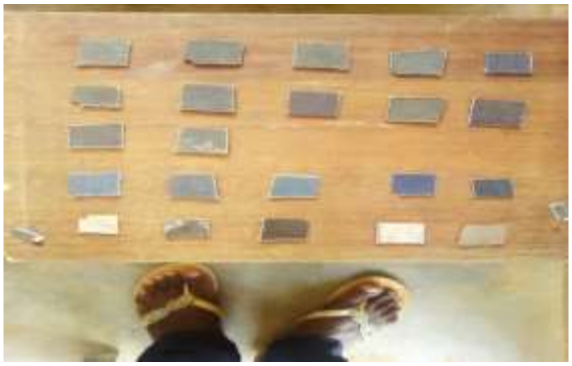
RAW AND CARBONISED MATERIALS FOR HYBRID POLYMER COMPOSITE PRODUCTION

 LOW DENSITY POLYETHYLENE (WATER SACHET)	 RAW EG SAWDUST
 LOCUST BEAN POD HUSK (LBPH)	 RAW KUTIGI KAOLIN CLAY
 RAW CARBONISED EG SAWDUST	 CARBONISED TREATED EG SAWDUST ASH
 TREATED CARBONISED LBPH	 CALCINED KUTIGI KAOLIN CLAY

APPENDIX II: PROCESSING AND ANALYSIS OF MATERIALS BY EQUIPMENT

 COMPOUNDING OF FILLERS AND POLYETHYLENE IN A TWO ROLLING MILL MACHAINE	 PROCESSED HPC
 MOULD FOR COMPRESSION	 COMPRESSION MOULDING MACHINE
 SAMPLE UNDER TENSION FOR TENSILE TEST	 WATER ABSORPTION CAPACITY TEST SET-UP

APPENDIX III: SAMPLES OF HYBRID POLYMER COMPOSITES

 FLAT HPC TILE	 FLAT VIRGIN PE TILE
 CORROGATED HPC	 CORROGATED REINFORCED HPC
 HPC TILES WITH DIFFERENT FORMULATIONS	 EXPOSED HPC TILES TO NATURAL WEATHERING