DEVELOPMENT AND CHARACTERIZATION OF POLY(LACTIC ACID)(PLA)/ GUINEACORN (*SORGHUM BICOLOR*) HUSKS PARTICULATE (GHP) COMPOSITES

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BY

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AHMADU BELLO UNIVERSITY, ZARIA,

NIGERIA.

OCTOBER, 2015.

DECLARATION

I declare that the work in this Thesis entitled "Development and characterization of Poly(Lactic Acid)(PLA)/Guineacorn(*sorghum bicolor*)husks particulate (GHP) Composites" has been carried out by me in the Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria, Nigeria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this Dissertation was previously presented for another degree or diploma at this or any other Institution.

_____ _____

Umar SHEHU Date

CERTIFICATION

This Thesis entitled "DEVELOPMENT AND CHARACTERIZATION OF POLY(LACTIC ACID)(PLA)/GUINEACORN(*SORGHUM BICOLOR*) HUSKS PARTICULATE (GHP) COMPOSITES**"** by Umar SHEHUmeets the regulations governing the award of the degree of Doctor of Philosophy in Metallurgical & Materials Engineering of the Ahmadu Bello University, Zaria, Nigeria and is approved for its contribution to knowledge and literary presentation.

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Abstract

The development and characterization of poly(lactic acid)(PLA)/guineacorn (*Sorghum bicolor*) husks particulates (GHP) composites as biodegradable or green composites was investigated to serve as an alternative to the conventional polymers which are non-degradable and are used for short term periods before discarding. The GHP was treated with Sodium hydroxide (NaOH) solution, 3- Aminopropyltriethoxysilane (3-APS) and a combination of both treatments but the PLA was blended with Biomax Strong 100 and Polyethylene glycol (PEG) as impact modifiers. Four formulations of the composites were produced by firstly melt mixing using extrusion and pelletizing before injection moulding. The GHP was characterized by density measurement, thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM). The composites produced were characterized by density measurements and mechanical testing such as tensile, impact, hardness and flexural tests. Others include water absorption test on all the composite formulations to study its effect on the mechanical properties. Soil burial test was used to evaluate the degradation of the composites.Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) were used for PLABM/GHP composites. Scanning Electron Microscopy (SEM) was used to studythe morphology of the composites, surfaces of water absorbed and soil buried specimens. The density of GHP lied between 1.45 and 1.46 g/cm^3, the TGA showed that GHP had 3-step degradation at 30-100^{o}C, 240-340^{o}C and above 340^{o}C while that of PLABM/GHP showed a one-step degradation and exhibited a maximum degradation temperature of 350^{o}C. The ash contents at 600^{o}C showed an increase with increase in GHP content.The density results of PLAP, PLABM, PLPG and PP and their composites lied between 1.26-1.40 g/cm^3,1.28-1.36 g/cm^3, 1.29-1.40 g/cm^3 and 0.96-1.12 g/cm^3 respectively. The results of theirtensile strength and elongation at break showed a general

decrease with increase in GHP content. The unreinforced matrices exhibited higher tensile strengths with maximum of 57.13MPa, and minimum of 25.88MPa as compared with various composites having a maximum of 45.48MPa and minimum of 16.63MPa. The results of the tensile modulus on the other hand showed a general increase as the GHP content was increased. The tensile modulus for the unreinforced matrices had a maximum of 2294.12MPa for PLAP and a minimum of 733MPa for PP. The morphological study of the tensile fractured surfaces revealed brittle failure for PLA matrices but ductile failure for PP matrix composites. The water absorption test showed a general increase in water absorption as GHP was increased from 0 to 40%. The maximum water absorption for the composites at 40% GHP were 11.36%, 12.46%, 21.12% and 6.8% for PLAP, PLABM, PLPG and PP composites respectively while the unreinforced matrices absorbed water to the tune of 0.53%, 0.92%, 1.93% and 0.3% for PLAP, PLABM, PLPG and PP respectively. The degradation test showed increase with GHP content. The weight losses for the unreinforced matrices were 0.36%, 0.20%, 0.46% and 0.08% for PLAP, PLABM, PLPG and PP respectively while at 40% GHP content for the ALKSIL treated composites, the weight losses were 5.05%, 24.16%, 14.83% and 1.65% for PLAP, PLABM, PLPG and PP composites respectively. The surface morphologies after soil burial revealed significant erosion and deep holes in most of the specimens due to the actions of microorganisms in the soil. From the DSC results, the glass transition temperature (Tg) of PLABM was 60^{o}C and melting temperature (Tm) was 150^{o}C. The storage modulus results showed a general increase with GHP content. The composites produced were light in weight, biodegradable and can be used for products intended for short-term use or indoor applications.

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Abbreviations

3-APS	3-Aminopropyltriethoxysilane
AA	Acrylic acid
ALK	Alkali treatment
ALKSIL	Alkali and Silane treatment
ASTM	American Society for Testing and Materials
BF	Bamboo fibre; Bamboo flour, Bagasse fibre
BM	Biomax strong 100
BP	Bamboo powder; Bagasse particles; Bagasse powder
CEN	European committee for standardization (French: comité Européen de Normalisation)
CG	Coffee ground
CPE	Chlorinated Polyethylene
CSP	Coconut shell particulates
DDGS	Distillers dried grains with solubles
DM	Maximum degradation
DMA	Dynamic mechanical analyser
DMTA	Dynamic mechanical thermal analyser
DSC	Differential scanning Calorimetry
DTG	Derivative thermogravimetric
EB	Electron beam; Elongation at break
EPO	Epoxidized palm oil

FTIR	Fourier transform infra-red spectroscopy
GHP	Guineacorn husks particulates
GPa	Giga Pascal
HDPE	High density Polyethylene
ISO	International standard organization
KF	Kenaf fibre
KFRC	Kenaf fibre reinforced composites
KN	Kilonewton
LDI	Lysine diisoscyanate
LDPE	Low density Polyethylene
MA	Maleic anhydride
MAPP	Maleic anhydride Polypropylene
MDI	Methylene diphenyl diisoscyante
MEKP	Methyl ethyl ketone peroxide
MFB	Medium length bamboo fibre
MMT	Montmorillonite
MPa	Mega Pascal
Mw	Molecular weight
NaOH	Sodium hydroxide
OPA	Oil palm ash
OPF	Oil palm fibre
PALF	Pineapple leaf fibre

PBAT	Poly(butylene adipate-co-terephthalate)
PBS	poly(butylene succinate)
PBSA	Poly(butylene succinate-co-Adipate)
PC	Polycarbonate
PCL	Polycaprolactone
PE	Polyethylene
PEG	Polyethylene glycol
PE-g-MA	Polyethylene-grafted maleic anhydride
PEO	Polyethylene oxide
PET	Polyethylene terephthalate
PF	Phenol formaldehyde
PGA	Polyglycolic acid
PHA	Polyhydroxyalkanoate
PHB	poly(3-hydroxybutyrate)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PKS	Palm kernel shell
PLA	Poly(lactic acid)
PLABM	Poly(lactic acid) blended with Biomax strong 100
PLAP	Pure Poly(lactic acid)
PLPG	Poly(lactic acid) blended with Polyethylene glycol
PMC	Polymer matrix composite
PP	Polypropylene

p-PLA	Plasticized Poly(lactic acid)
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl chloride
RH	Rice husk
RHA	Rice husk ash
RHDPE	Recycled high density polyethylene
RHF	Rice husk filler
rpm	Revolution per minute
RPP	Recycled polypropylene
SBP	Sugar beet pulp
SCB	Sugarcane bagasse
SEM	Scanning Electron Microscopy
SF	Soy flour
SIL	Silane treatment
SLS	Sodium laulryl sulfate
SP	Soy protein
SPC	Soy protein concentrate
SPI	Soy protein isolate
Tc	Crystallinity temperature
Tg	Glass transition temperature
TGA	Thermogravimetric analysis

Tm	Melting temperature
TPS	Thermoplastic starch
TPU	Thermoplastic polyurethane
UNTRD	Untreated
UP	Unsaturated polyester
UV	Ultra violet
VHDPE	Virgin high density polyethylene
WF	Wood fibre; Wood flour
XPS	X-ray photoelectron spectroscopy

Symbols

%	Percentage
CO_2	Carbon IV Oxide
E’	Storage Modulus
E”	Loss Modulus
g/cm^3	Gram per cubic centimeter
H_2O	Water
J/m	Joule per meter
^oC	Degree celcius
Tanδ	Loss factor
wt%	weight percent
Xc	Crystallinity

CHAPTER ONE

1.0 GENERAL INTRODUCTION

Synthetic polymeric materials have been extensively used globally because of their excellent chemical, physical and mechanical properties. Therefore, they have various forms and serve in many roles which make it almost impossible to imagine just one day without them (Gouda *et al.*, 2012; Obasi, 2012). Their versatility is the reason for their use in a wide range of applications such as packaging, structural (building materials), transportation, electrical components, biomedical and consumer products. Themultiuse of plastics is due to their unique capability to be manufactured to meet very specific functional needs for consumers as well as being cheap, not susceptible to loss of strength when wet and they improve product protection. (Lee, 2007; Pilla *et al.*, 2007).

Plastics are prevalent in almost every human activity. However, their expansion in use has become a source for concern due to their negative impact on the environment especially where they are used for a short period of time before discarding (Lee, 2007; Gouda *et al.*, 2012).

Plastics waste, especially plastics packaging that float or litter the oceans, rivers, seas and lakes are a major threat for birds, fish and other animals in those habitats (Lee, 2007; Pilla *et al.*, 2007). Worldwide, about one half of all discarded plastics come from packaging and out of this, almost a-third of them come from single-used-packaging that are discarded soon after use (Lee, 2007).

Production and expenses of plastic materials grow an average of 9% each year and production has grown from 1.5 million tons in 1950 to 245 million tons in 2008 (Gouda *et al.,* 2012). With the increase in global population, approximately 140 million tonnes of synthetic polymers are produced worldwide every year to meet growing demands (Premraj and Doble, 2005; Rudeekit *et al.,* 2008; Leja and Lewandowicz, 2010; Nampoothiri *et al.,* 2010). Since most plastics take a longtime to decay in nature due to their resistance against action of microorganisms and other environmental factors, disposing them after use is a big problem. Recycling and reusing are the processes to reduce the environmental pollution caused by postconsumer plastic materials (Gouda *et al.,* 2012) but this strategy of reuse has limitations because recycled plastics do not possess the same properties as their virgin counterparts and cannot be used in similar applications as their properties are known to deteriorate when recycling (Pilla *et al.,* 2007). Furthermore, the conventional plastics are obtained from petroleum resources which are considered to be finite and are decreasing every year leading to pressure to conserve these resources (Pilla *et al.,* 2007, Pilla *et al.,* 2008; Yu *et al.,* 2010; Liu *et al.,*2012; Srubar-III*et al.,*2012). Studies had shown that waste wood in the form of wood flour (WF), fibres or pulp is suitable as filler for polyolefin matrix composites.

The lack of degradability of conventional plastics and the closing of landfill sites as well as growing water and land pollution problems have led to growing concerns about plastics which makes it necessary to find a solution and prevent accumulation of thousands of tonnes of solid wastes every year. Awareness of the waste problem and its impact on the environment has awakened keen interest in the area of degradable polymers leading to increasing demands to develop materials with little or no burden on the environment (Shah *et al.,* 2008; Gouda *et al.,*

2012). Biodegradable polymers development offer a possible solution to waste-disposal problems associated with traditional petroleum-derived plastics (Mohanty *et al.,* 2000). These materials are designed to degrade under environmental conditions or in municipal and industrial biological waste treatment facilities (Gouda *et al.,* 2012). Other environmental benefits of biodegradable plastics include less greenhouse emissions, renewability of the base materials, sustainable, biocompatible, reduction of dependency on the depleting fossil fuels, they are CO_2 neutral and their degradation products are non-toxic to the environment (Pilla *et al.,* 2007; Pilla *et al.,* 2008; Yu *et al.,* 2010; Wang *et al.,* 2011).

There are numerous biodegradable polymers (Van deVelde and Kiekens, 2002) which mainly include aliphatic polyesters such as: Poly (Caprolactone) (PCL), Poly (Butylene Succinate) (PBS), Poly (Butylene Succinate-co-adipate) (PBSA) (Jiang and Zhang, 2011), Poly (lactic acid) (PLA) (Rudeekit *et al.,* 2008) and other aliphatic co-polyesters and aliphatic-aromatic co-polyesters such as poly (butylene adipate-co-terephthalate) (PBAT) (Jiang and Zhang, 2011). The most popular and important biodegradable polymers are poly(lactic acid) (PLA), poly(caprolactone) (PCL), polyethylene oxide (PEO), poly(3-hydroxybutyrate) (PHB), poly(butylene adipate terephthalate) (PBAT) and polyglycolic acid (PGA) (Baek *et al.,* 2013).

One of the most interesting bio-based polymers is poly (lactic acid) (PLA), an aliphatic polyester which is made from plants and is readily biodegradable which was developed to serve as an alternative to conventional polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) (Pilla *et al.,* 2007; Pilla *et al.,* 2008; Carrasco *et al.,* 2010; Wang *et al.,* 2011). It is the only thermoplastic polymer based on natural resources which can be produced with a capacity of over 140,000 tonnes per year (Bax and

Müssig, 2008; Lim *et al.,* 2008; Ranjan *et al.,* 2013; Senawi *et al.,* 2013) . In general, PLA is synthesized by ring-opening polymerization of lactide and lactic acid monomers, which are obtained from the fermentation of sugar beet, corn, sugar cane, potato etc. (Ljungberg *et al.,* 2003; Pilla *et al.,* 2007; Pilla *et al.,* 2008;Yu *et al.,*2010;Anuar *et al.,* 2012a;Liu *et al.,* 2012). PLA, in addition to being biodegradable, has some notable properties which are comparable to those of the conventional polymers and can substitute them in many ways, such as in packaging, barriers for sanitary products and diapers, planting, disposable cups and plates and others (Fortunati *et al.,* 2010; Wang *et al.,* 2011; Liu *et al.,* 2012). Also, PLA has high modulus, reasonable strength, good heat sealability, clarity, low emission of greenhouse gases and low amount of energy used for its production, biocompatibility etc (Pilla *et al.,* 2007; Pilla *et al.,* 2008; Yu *et al.,* 2010). However, it has some limitations such as high cost compared to the costs of conventional thermoplastics and brittleness which lower its widespread applicability and competitiveness (Pilla *et al.,* 2007; Lim *et al.,* 2008; Pilla *et al.,* 2008).

The stiffness and brittle nature of PLA can be overcome by use of plasticizers to improve its elongation and impact properties (Ljungberg *et al.,* 2003; Oksman *et al.,* 2003; Ren *et al.,* 2006). A number of low molecular weight compounds have been employed as plasticizers which serve as impact modifiers for PLA, for example, glycerol, Biomax strong (MatTaib *et al.,* 2012), Triactine, Tributyl citrate(Ljungberg *et al.,* 2003; Ren *et al.,* 2006), poly (ethylene glycol) (PEG) (Pluta *et al.,* 2006; Mat Taib *et al.,* 2010), citrate esters, partial fatty acid ester, ethylene oxide (Sawalha *et al.,* 2010). Essentially, the plasticizers were used to lower the glass transition temperature (Tg), increase ductility and improve the processibility of PLA (Rasal *et al.,* 2010).

In order to tailor the cost of materials and engineer the materials properties, development of bio-composites offered a convenient approach (Pilla *et al.,* 2007). As a result of growing environmental awareness, agro-fillers which are basically lignocellulosic materials have been used as reinforcing fillers in thermoplastic composite materials (Yang *et al.,* 2004).These natural fillers are especially being sought because they are inexpensive, are able to minimize the environmental pollution. They also have a high impact upon economics for thermoplastics while a general improvement in certain properties is also achieved (Yang *et al.,* 2004; Tserki *et al.,* 2005). The main advantage of lignocellulosic materials as compared to mineral fillers is their environmental friendliness (Tserki *et al.,* 2005). The use of these materials is expected to reduce waste deposit volume while undergoing degradation in a landfill and would be a possible sustainable solution to the uncertainty of the world's petroleum supply (Tserki *et al.,* 2005; Pilla *et al.,* 2007; Fakhrul and Islam, 2013). The benefits offered by lignocellulosic materials such as wood flour, rice husk flour, wheat straw, bagasse, kenaf, sisal etc. include making the final product light (Husseinsyah and Zakaria, 2011), decreasing the wear of the machinery used, low cost, biodegradability (Obasi, 2012) and absence of residues or toxic byproducts (Yang *et al.,* 2004). They are also abundant, renewable and generally of low density (Tserki *et al.,* 2006a).

However, the main disadvantage encountered during the incorporation of natural lignocellulosic materials into polymers is the lack of good interfacial adhesion between the two components which results in poor properties of the final material (Ragunathan *et al.,* 2012; MohamadRasidi *et al.,* 2014). It has been observed that lignocellulosic fillers in composite materials do not disperse easily in thermoplastic polymer such as polyolefin and biodegradable polymer as it tends to agglomerate during the compounding process. The low compatibility and poor adhesion

between filler and polymer lead to the low mechanical and thermal properties of the bio-composites (Kim *et al.,* 2007).The polar hydroxyl groups on the surface of the lignocellulosic materials have difficulty in forming a well bonded interface with a non-polar matrix, as the hydrogen bonds tend to prevent the wetting of the filler surfaces thus leading to poor mechanical properties and high water absorption (Tserki *et al.,* 2005; Tserki *et al.,* 2006a; Tserki *et al.,* 2006b; Gelfuso *et al.,* 2011; Reddy *et al.,* 2013; Nedjma *et al.,* 2014). Interfacial interactions can be improved by different kinds of physical (corona, plasma, laser, or ϒ-radiation) and chemical (esterification, silane treatment, sodium hydroxide) treatments (Halász and Csóka, 2012). These methods are usually based on the use of reagents which contain functional groups that are capable of being bonded to the hydroxyl groups of the lignocellulosic material, while maintaining good compatibility with the matrix. Interfacial compatibilization improves the stress transfer between the two components and leads to the improvement of mechanical and physical properties of the produced composites (Tserki *et al.,* 2005).

A careful study of our environment presents various forms of environmental pollutants (generally plastic wastes) which are scattered almost everywhere. Some of these items include 'packaged' water sachets, take-away packs, plastic (disposable) cups and spoons, empty plastic containers for water and soft drinks etc. These items have one thing in common which is; *use and discard immediately*. While efforts have been made to control these items in the environment especially by applying the 3Rs i.e. Recycle, Reuse and Remove, it has not been very effective. Example of Reuse can be seen where some of these containers for water and soft drinks are picked by the locals to package some local drinks such as 'Zobo' and 'Kunu' drinks for sale. The 'packaged' water sachets have been used as matrix for polymer composites by

incorporating agro-residues by some academics while other items are picked by locals to sell to some companies for recycling. However, these have not been very effective in removing these discarded items from the environment as not all can be recycled, reused or removed. As such, many find their way into nearby rivers or seas which poses a serious danger to the animals in those habitats. Others find their way into drainages which could eventually lead to flood as it could block water ways for free flow of rainwater. Similarly, some others find their way under the soil which could cause difficulties in the future especially when the area is to be developed. There is therefore, an urgent need to find a lasting solution to the problems posed by commodities that are used for a short period of time and discarded almost immediately after use.

Furthermore, agricultural crop residues such as Corn cob, Oil palm leaves, Palm kernel shell, Coconut coir and shell, Pineapple leaf, Banana leaves, Sugar cane bagasse, Rice husk, Guineacorn husk/stalks, wheat straw, Empty fruit bunch etc. are produced in billions of tonnes around the world. They can be obtained in abundance, low cost and are renewable sources of biomass. Among these large amount of residues, only a small quantity of the residues is applied as household fuel or fertilizer while another little portion is consumed by animals and the rest which is the major portion of the residues is either left to rot on the farmlands or burned in the field. As a result, it gives a negative effect on the environment due to the air pollution it would generate (Sahari and Sapuan,2011). The vital alternative to solve this problem is to use the agricultural residues as reinforcement in the development of polymer composites. A viable solution is to use the entire residues as natural fillers/fibres and combine them with polymer matrices derived from petroleum or renewable resources to produce a useful product for our daily applications (Sahari and Sapuan,2011).

1.1 Guineacorn (*Sorghum bicolor*)

Guineacorn is a cereal crop which is grown in different parts of the world such as the United States, India, Nigeria, Argentina, China, Ethiopia etc (FAO, 2013). Nigeria is the largest sorghum producer in West Africa, accounting for about 71% of the total regional sorghum output (FAO, 2013; Zalkuwi *et al.,* 2014). Nigeria's sorghum production also accounted for 35% of the African production in 2007 (Sorghum production, 2014; Iloh *et al.,* 2014). The country is the third largest world producer after the United States and India (Maikasuwa and Ala, 2013; USDA, 2014). However, 90% of sorghum produced by United States and India is used as animal feed, making Nigeria the world leading country for food grain sorghum production. In Nigeria, sorghum is the third cereal in terms of production after maize and millet (Maikasuwa and Ala, 2013; USDA, 2014) with more than 4.5 million tonnes harvested in 2010 representing 25% of the total cereal production (FAO, 2013). It is the primary food crop in virtually all the Northern part of the country (FAO, 2013, USDA, 2014).The residues, stems, husks associated with the crop is a source of feed to the animals.

The aim of this study therefore, is to produce a fully degradable composites (green or bio-composites) using a biopolymer, Poly (lactic acid) (PLA) as the matrix and an agricultural residue, Guineacorn husks particles as the reinforcement. This is intended to give an immediate solution to the environmental challenges facing us with respect to commodities that are used and discarded almost immediately.

1.2 Aim and Objectives

The aim of this study is to produce a biodegradable composite referred to as green composites or bio-composites based on Poly(lactic acid)(PLA) and Guineacorn husks particles (GHP) using the injection moulding method.

The specific objectives include:

- To study the effect of the variation of GHP loading (0 - 40%) in the PLA matrix
- To characterize the treated and untreated GHP through density measurement, thermogravimetric analysis and Scanning electron microscopy
- To study the effect of plasticizers such as Biomax strong and Polyethylene glycol (PEG) in the composites produced
- To study the effect of alkali treatment, silane treatment and a combination of alkali and silane treatment on the composites
- To characterize both the treated and untreated composites produced through:
- Mechanical tests: Tensile, Impact and 3-point bending test otherwise called flexural test
- Thermal stability tests using: Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA)
- Morphological studies using Scanning Electron Microscopy (SEM)
- To carry out water absorption test for all the composites produced
- To carry out a simple soil burial test to test for degradability using the weight loss method as criterion

- To produce Polypropylene (PP)/Guineacorn husks particles composites for the purpose of comparison.

1.3 Background

Conventional or commodity polymers such as Polypropylene (PP), Polyethylene (PE), Polyvinyl chloride (PVC) etc. made from petroleum resources have brought considerable benefits to human life. However, they persist for many years after disposal thereby raising concern on the negative impact on the environment and also on fossil resources which are known to be finite. These polymers seem inappropriate for applications involving plastics that have short life span in terms of usage i.e. those plastics that are used once and then disposed. Furthermore, plastics are soiled with food and other biological substances which makes recycling difficult or expensive. On the basis of these, researches to alleviate pollution and litter problems have focused on developing bio-based composites consisting of biopolymers and agricultural residues. These products are expected to reduce our dependency on the depleting fossil fuels and decrease CO_2 released into the atmosphere. Since biopolymers and agricultural residues are degradable, their use as a substitute for their non-degradable counter parts as fillers can be beneficial to the environment. Therefore, the use of these products will go a long way in tackling the problems associated with the build-up of solid wastes in the environment especially from commodities which are used for a short period of time.

1.4 Justification

Thousands of tonnes of different crops are produced annually and most of their wastes do not have any utilization. Therefore, different agricultural wastes such as wheat husk, rice husk and their straws, hemp fibres, coir, coconut shell, date pits, palm kernel seeds etc. are now being used as reinforcement in polymer matrices for commercial purposes.

Nigeria is blessed with a good number of agricultural produce from which a great amount of wastes are generated annually. Guineacorn (*Sorghum bicolor*) is one of the major food crops of the world and millions of tonnes are produced annually. The production of this crop also generates millions of tonnes of byproducts annually and these byproducts are cheap and abundantly available but with limited use. Therefore, the possibility of finding use for Guineacorn (*Sorghum bicolor*) wastes i.e. husks in bio/green composite manufacturing will help in opening market for what was hitherto considered as waste and thrown away.

1.5 Scope of the Research

The scope of the research is as follows:

1. Treating the Guineacorn husks particulates (GHP) with sodium hydroxide (NaOH), 3-Aminopropyltriethoxysilane, and a combination of the two treatments.
2. Production of PLA/GHP composites with addition of Biomax strong 100 and Polyethylene glycol (PEG) as plasticizers
3. Production of PP/GHP composites

4. Characterizing the GHP by density measurements, thermal gravimetric analysis (TGA), and Scanning Electron Microscopy (SEM) for the treated and untreated particulates.
5. Characterizing the composites produced by:
    - ✓ Measurement of density for all the composites produced
    - ✓ Carrying out water absorption test for all the composites produced
    - ✓ Soil burial test for the composites produced
    - ✓ Mechanical tests : Tensile, Flexural, Impact and Hardness
    - ✓ Thermal stability test for only PLA/Biomax strong 100/GHP composites using : Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetric analysis (TGA)
6. Morphological studies using Scanning Electron Microscopy (SEM) for tensile fractured surfaces
7. Mechanical properties (Tensile, Flexural and Impact) after water absorption test
8. SEM analysis for surfaces of water absorbed and soil buried composites.

1.6 Contribution to Knowledge

1. The use of GHP as filler for composite production has been established.
2. Awareness on the use of cereal by-products (Agricultural wastes) as fillers for the production of polymer composites would lead to conservation of wood resources especially in countries where they are limited, particularly so in Nigeria where deforestation is a problem.
3. Exposing the possibility of producing a completely green composites (i.e 100% biodegradable) which is a composite based on biodegradable polymer and biodegradable fillers. This will preserve our environment from pollution of plastics and the likes.
4. Reduction of environmental pollution by creating an immediate solution to waste disposal problems since the composite produced has been established to be biodegradable.
5. The utilization of agricultural wastes i.e. Guineacorn husks as reinforcement in polymer matrix could bring economic benefits and reduce the environmental impacts of plastics.
6. Creating awareness on the use of different agricultural wastes as reinforcement in biodegradable polymer matrices as well as on the existence of biodegradable polymers.
7. Commodity plastics manufacturers would be encouraged to use biodegradable plastics for commodity products having understood the processability and properties established from this study.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Polymers

The unique and attractive properties of polymers have led to their emergence as the materials used for a wide range of applications (Yousif *et al.,* 2009).

There are a number of polymers available depending on the starting raw ingredients with several broad categories, each having numerous variations. The most common of these are polyesters, vinyl esters, epoxies, phenolics, polyimides, polyamides, polypropylene, polyether ether ketone (PEEK) and others (Jose *et al.*, 2012). The major advantages of polymers as matrixmaterials are low cost, easy processability, good chemical resistance and low specific gravity. Some of their disadvantages include low strength, low modulus and low operating temperatures which limit their use. Varieties of polymers for composites production are thermoplastic polymers, thermosetting polymers, elastomers as well as their blends (Jose *et al.,* 2012).

2.1.1Thermoplastics

Thermoplastics are polymers consisting of linear or branched chain molecules having strong intramolecular bonds but weak intermolecular bonds. They can be reshaped by application of heat and pressure and are either semicrystalline or amorphous in structure. Examples include Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Nylons, Polycarbonate (PC), Polyether ether ketone, Polysulfone, Polyphenylene sulfide, etc. (Jose *et al.,* 2012).

2.1.2 Thermosetting polymers

Thermosets are those polymers with cross-linked or network structures having covalent bonds with all molecules. They do not soften but decompose on heating because, once they are solidified by the cross-linking process, they cannot be reshaped. Common examples are epoxies, polyesters, phenolics, ureas, melamine, silicone and polyimides (Jose *et al.,* 2012).

2.1.3 Elastomers

An elastomer is a polymer with the property of viscoelasticity, generally having low Young's modulus and high yield strain compared with other materials. Each of the monomers that link to form the polymer is usually made of carbon, hydrogen, oxygen and silicon. Elastomers are amorphous polymers existing above their glass transition temperature (Tg), and their primary uses are for seals, adhesives and moulded flexible parts. Examples include natural rubber, synthetic polyisoprene, polybutadiene, chloroprene rubber, butyl rubber, ethylene propylene rubber, silicone rubber, fluoroelastomers, thermoplastic elastomers etc. (Jose *et al.,* 2012).

2.2 Biopolymers

The annual production of conventional (synthetic) polymers is estimated at 140 million tonnes. Since they are extremely stable, the production and the use of these materials increase the problem of waste disposal and their degradation cycles in the biosphere are limited (Premraj and Doble, 2005; Rudeekit *et al.*, 2008). Therefore, the rapid growth in the usage of plastic products, persistence of plastics in the environment, the shortage of landfill sites and entrapment by the

ingestion of packaging plastic by marine and land animals have raised efforts to look for better alternatives (Khalid *et al.,* 2008).

Furthermore, therising oil prices in the 1970s helped to stimulate early interest in biodegradable polymers and concerns over the shrinking availability of landfill sites are reviving interests in biodegradable materials today. First developed in the 1980s, biodegradable polymers as used in films, moulded articles, sheets e.t.c., constitute a market that is still developing (Mohanty *et al.,* 2000). Environmental and economic factors are now pushing the trend towards greater pursuit of bio-based polymers (such as polylactic acid (PLA), polyhydroxy butyrate (PHB), cellulosic plastics, soy-based plastic and starch plastic) and materials (Mohanty *et al.,* 2002 and 2004).Much attention has been paid to biodegradable polymers in recent years because of their wide range of applications in fields of biomedicine, packaging and agriculture(Tănase*et al.,* 2014). According to ISO, CEN definition, biodegradation is the degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of the exposed material and resulting in the production of carbon dioxide, water, mineral salts (mineralization) and new microbial cellular constituents (Iovino *et al.,* 2008). Degradable plastics are grouped by the American Society for Testing and Materials (ASTM D20.96) (Sriroth *et al.,* 2000) as:

a. Photodegradable plastics- a degradable plastic in which the degradation results from the action of natural daylight;
b. Oxidatively degradable plastics- a degradable plastic in which the degradation results from oxidation;

c. Hydrolytically degradable plastics- a degradable plastic in which the degradation results from hydrolysis; and
d. Biodegradable plastics- a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.

Accordingly, biodegradable polymeric materials are classified as natural or synthetic depending on their origin (Satyanarayana *et al.,* 2009). The classification of these polymers and their nomenclature is shown in Figure 2.1. The first group is agro-polymers (e.g. polysaccharides) obtained from biomass by fractionation. The second and third groups are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants (e.g. poly (hydroxyalkanoate) (PHA)) and by synthesis from monomers obtained from biomass (e.g. Poly (lactic acid) (PLA)). The fourth group is made up of polyesters synthesized by the petrochemical process (e.g. poly (caprolactone) (PCL)). A large number of these biopolymers are commercially available, they show a large range of properties and can compete with the traditional non-biodegradable polymers in different industrial fields (e.g. packaging) (John and Thomas, 2008).

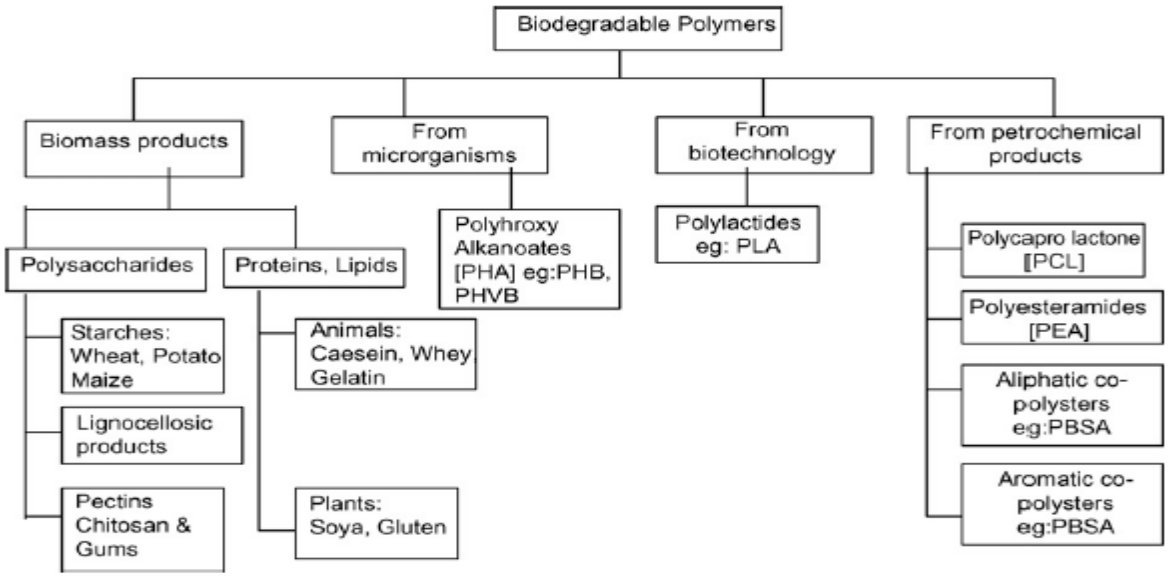


Figure 2.1: Classification of biopolymers(John and Thomas, 2008)

2.2.1 Naturally occurring Biodegradable Polymers

In the last century, the development of biopolymers was significantly hampered due to the advent of low-cost petrochemical polymers. It was only about two decades ago that intensive research on biopolymers was revived, primarily due to the issues of environmental pollution and the depletion of fossil oils. Modern technologies provide new insights of the synthesis, structures and properties of the biopolymers. These new findings have enabled developments of biopolymers with novel processing characteristics and properties which can be used for a wide range of applications (Jiang and Zhang, 2011). Lignocellulosic materials appear to be suitable filler for high cost biodegradable matrices offering a way of reducing the cost of the end product. A few investigations have been made on the possibilities to use natural fibres as reinforcement with renewable biopolymers such as soy-oil based epoxy, starch, polycaprolactone (PCL),

polyhydroxybutyrate (PHB), modified cellulose, acetic acid, polylactic acid (PLA) and polyester amide for composite (Oksman *et al.,* 2003; Mohamad Haafiz*et al.*,2013).

*2.2.1.1Starch*Starch, which is produced in plants, is an inexpensive, abundant, biodegradable and renewable natural resource (Huang*et al.,* 2004; Dean *et al.,* 2007). It consists of a mixture of linear amylose (poly-a-1,4D-glucopyranoside) and branched amylopectin (poly-a-1,4D-glucopyranoside and a-1, 6-Dglucopyranoside) and exists in the form of discrete granules. Amylose has a molecular weight of several hundred thousand whereas that of amylopectin is in the order of tens of millions. Starch is not melt-able in its natural form and therefore cannot be processed as a thermoplastic. However, it can be thermoplasticized by disruption and plasticization of starch macromolecules using heat in the presence of water and plasticizers such as glycerol. The resultant starch is termed thermoplastic starch (TPS). The products made from TPS are water sensitive with poor physical and mechanical properties. The mechanical weaknesses of these materials for packaging application can be improved by incorporation of a synthetic polymer or an inorganic reinforcing material including Montmorillonite (MMT). Numerous studies exploring the use of TPS as a thermoplastic polymer have been conducted (Dean *et al.,* 2007; Majdzadeh-Ardakani *et al.,* 2010; Jiang and Zhang, 2011).

Huang *et al.*,(2004) produced glycerol-plasticized TPS/Montmorillonite composites and reported that the tensile strength, Young's modulus and breaking energy were greatly improved. Also, they reported that the water-resistant property of the composite was better than that of the matrix.

Cyras*et al.*, (2008) studied the properties of TPS/Montmorillonite Nano- composites and found that the thermal resistance of the Nano- composite was improved and there was a significant reduction in water absorption with the addition of the reinforcement. Dean *et al.,* (2007) prepared melt-extruded TPS/clay Nano-composites and reported that the most significant improvement in modulus was observed in the system containing higher levels of clay for both dry-blended and ultrasonically treated samples. They related the modulus obtained to the intrinsic properties of the components rather than dispersion and interfacial interaction in their conclusion. Figure 2.2 shows the chemical structure of starch.

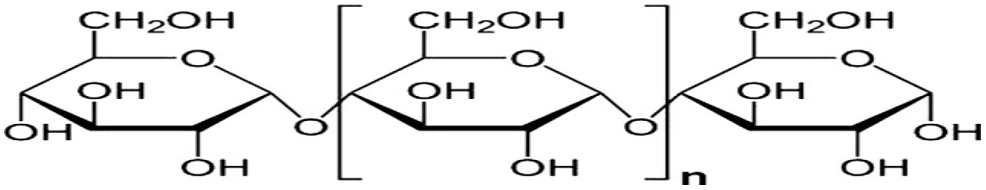


Figure 2.2: chemical structure of starch(Jiang and Zhang, 2011)

2.2.1.2 Soy Protein Plastic (SPP)

As a renewable plant-based polymer, soy protein (SP) has attracted intensive research interests in the non-food industrial applications (Zhang *et al.,* 2006). The major attractive features of soy protein-based plastics which has made them a viable source of raw material for the plastics industryincluderelative abundance, moderate costs, local and well-established production practices, as well as biodegradability and environmentally friendly. Furthermore, its use in biodegradable resins will reduce environmental wastes and add value to agricultural byproducts

(Zhang *et al.*, 2001; Graiver *et al.*, 2004). It is commercially available in three different grades from soybean processing plants: soy protein isolate (SPI) (about 90% protein content), soy protein concentrate (SPC) (65–72% protein content), and soy flour (SF) (about 54% protein) (John and Bhattacharya, 1999; Graiver *et al.*, 2004). A major disadvantage of soy protein–based plastics is their water sensitivity (Mungara *et al.*, 2002). Water sensitivity has been reduced by blending biopolymers with other polymers of hydrophobic nature such as polyesters. By producing blends of soy protein and some of these biodegradable polyesters, the cost of the product would be significantly reduced. In addition, using low-cost brands of soy protein such as SPC and SF, the final products could be cost competitive with petrochemical plastics (Mungara *et al.*, 2002).

2.2.2 Biodegradable Polymers Derived from Renewable Resources

Unlike the aforementioned natural polymers, some polymers can be produced from naturally occurring bio-sources. PLAs and PHAs are the two most important polymers within this category. They have received much attention in terms of research and are finding different applications due to their unique combinations of properties (Jiang and Zhang, 2011).

2.2.2.1 Poly(lactic acid) (PLA)

PLA is a biodegradable, semi-crystalline, linear aliphatic thermoplastic polyester that is manufactured from lactic acid produced by bacterial fermentation of renewable resources such as whey, corn, sugarcane, potato or molasses which is then polymerised to poly(lactic acid) either

by gradual polycondensation or by ring opening polymerisation as shown in Figure 2.3 (Ljungberg *et al.,* 2003; Graupner *et al.,* 2009; Jiang and Zhang, 2011; Hassan *et al.,* 2013). It is characterized by good bio-compatibility, non-toxic by-products, excellent transparency, high strength and modulus, biodegradability (Aydın *et al.,* 2011; Jiang and Zhang, 2011; Hassan *et al.,* 2013).

PLA can be conveniently processed similarly as polyolefins and other thermoplastics using existing polymer processing equipment and techniques such as injection-moulding, compression moulding, extrusion and thermoforming etc.It is suitable for biodegradable packaging such as bottles, food containers and wrappers due to itsclarity. It has also been used for food service ware, grocery and composting bags, mulch films, coatings for paper and cardboard, fibres for clothing, carpets, sheets and towels and wall coverings. Also, in biomedical applications, it is used for sutures, stents, prosthetic materials, pins, scaffolds, dialysis media and drug delivery devices (Aydın*et al.,* 2011; Kim *et al.,* 2012; Hassan *et al.,* 2013). PLA is completely compostable as it degrades primarily by hydrolysis through a two-stage process. First, random chain scission of the ester groups of PLA reduces its molecular weight. The speed of chain scission depends on the pH value, temperature and moisture levels of the environment. Embrittlement of the polymer occurs with the reduction of its molecular weight. Second, low-molecular-weight PLA is metabolized by microorganisms yielding carbon dioxide, water and humus (Ljungberg *et al.,* 2003; Jiang and Zhang, 2011). Properties of PLA can be modified through the use of lignocellulosic fillers that reduce the cost of the material without restricting their biodegradability (Aydın*et al.,* 2011).

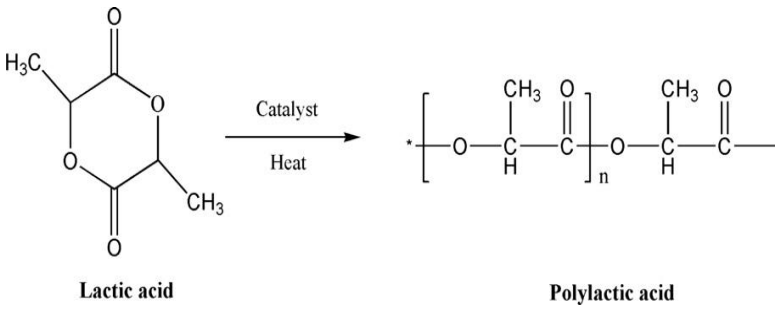
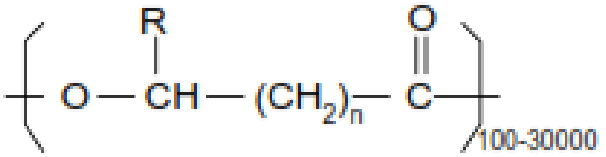


Figure 2.3: Synthesis and structure of PLA (Jiang and Zhang, 2011).

2.2.2.2 Polyhydroxyalkanoates (PHA)

PHAs are a family of aliphatic biodegradable polyesters with different side groups and different numbers of carbon atoms in the repeating units (Figure 2.4) which is synthesized via bacterial fermentation under nutrient-limited conditions in the presence of excess carbon source. PHAs are of interest because they (1) are biodegradable, (2) can be microbially synthesized using natural carbon sources, including sugar and methane, and (3) are highly crystalline and hydrophobic, demonstrating good mechanical properties similar to conventional polyolefin thermoplastics used in commercial wood plastic composites(Jiang and Zhang, 2011; Srubar- III *et al.*,2012). It has been discovered that extracellular PHAs are degraded bynumerous bacteria and some fungi and their breakdown products are metabolise to carbon dioxide and water. Thus, PHA products can be degraded completely and rapidly by composting (typically 3–9months) (Poirier, 1999). With their inherent biocompatibility and biodegradability, PHAs have found important applications in medical and pharmaceutical areas including wound management (e.g. sutures, skin substitutes, nerve cuffs,), vascular system (e.g. Heart valves, cardiovascular fabrics, and vascular grafts), orthopedics (e.g., scaffold, spinal cages, bone graft substitutes, and internal fixation devices), and

drug delivery systems (Bhatt *et al.*, 2008; Jiang and Zhang, 2011). Application of PHAs as commodities are limited due to their high cost and thus, attention is being focused on composite products where total product biodegradability can be attained for little extra cost. The major drawbacks of PHAs are its low melting temperature and crystallization rate. A common way to minimize these undesirable properties is to prepare its block and graft copolymers and blends with suitable well defined polymers. Polymer blending offers interesting possibility of preparing biodegradable materials with useful mechanical properties (Bhatt *et al.*, 2008).



n =1	R =	hydrogen	poly (-3-hydroxypropionate)
		methyl	poly (-3-hydroxybutyrate)
		ethyl	poly(3-horoxyvalerate)
		propyl	poly (-3-hydroxyhexanoate)
		pentyl	poly (-3-hydroxyoctanoate)
		nonyl	poly (-3-hydroxydodecanoate)
n = 2	R =	hydrogen	poly (-4-hydroxybutyrate)
n = 3	R =	hydrogen	poly (-5-hydroxyvalerate)

Figure 2.4: General structure of PHAs (Ojumu et al., 2004; Jiang and Zhang, 2011).

2.2.3 Biodegradable Polymers Derived from Petroleum

Petroleum-based biodegradable polyesters are synthesized by polycondensation reaction between aliphatic diacids and aliphatic diols or by ring-opening polymerization of lactones. Typical synthetic aliphatic polyesters include PCL, PBS, and their copolymers (Jiang and Zhang, 2011).

2.2.3.1 Polycaprolactone (PCL).

Polycaprolactone (PCL) is a biodegradable, biocompatible, semi-crystalline aliphatic polyester synthesized by ring-opening polymerization of caprolactone as shown in Figure 2.5. It is a polyester with a number of potential applications from agricultural usage to biomedical devices. Large-scale application of PCL has been limited due to their relatively high cost, as well as some intrinsic inferior properties. An effective and economic method in resolving this problem is by blending biodegradable polymers with other materials (natural or synthetic) (Zhao *et al.*, 2008). Therefore, PCL is often blended with polymers like Polypropylene (PP), Polycarbonate (PC), Polyethylene oxide (PEO) and starch to produce composites with desired properties (Tsuji and Suzuyoshi, 2002). PCL is completely degradable through enzyme activities (Jiang and Zhang, 2011).

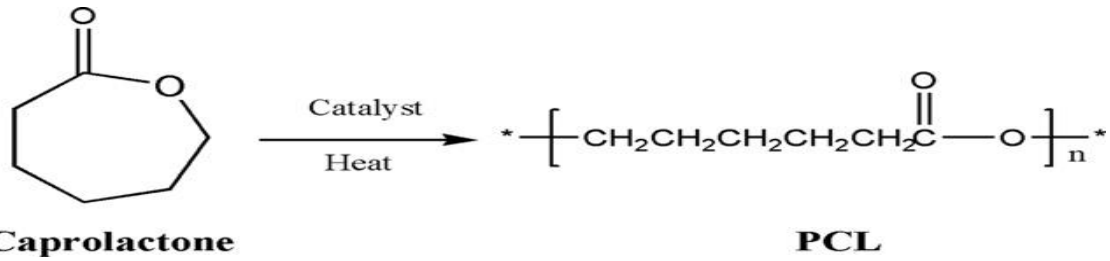


Figure 2.5: Synthesis and structure of PCL (Jiang and Zhang, 2011)

2.2.3.2 Poly(butylene succinate) (PBS).

Polybutylene succinate (PBS) is one of the aliphatic thermoplastic polyesters with a range of desirable properties including biodegradability, melt processability, and both thermal and

chemical resistance. It is synthesized through the polycondensation reaction of glycols such as 1,4-butanediol and aliphatic dicarboxylic acid such as succinic acid which is used as principal raw materials. Aliphatic polyesters can be naturally degraded into the natural environment by bacteria and fungi. In recent years, many attempts have focused on making PBS composites from cellulosic materials with low cost, renewability, biodegradability and nontoxicity (Kim *et al.*, 2005a; Shih *et al.*, 2006; Jiang and Zhang, 2011; Calabia *et al.*, 2013).

Furthermore, PBS is a white crystalline thermoplastic having a melting point which similar to that of low density Polyethylene (LDPE), tensile strength in the range of that of Polyethylene (PE) and Polypropylene (PP), stiffness in the range of that of LDPE and HDPE (Shih *et al.*, 2006). Therefore, different reinforcing fillers such as rice straw, wood flour, jute fibre, water bamboo husks etc have been used as reinforcements in PBS to enhance its properties and reduce its high cost (Calabia *et al.*, 2013).

2.3 Polymer Matrix Composites (PMCs)

Polymer matrix composites (PMCs) are among the best entrenched engineering composite materials. The three classes of polymers namely; thermoplastics, thermosets and rubbers are all employed as matrices (Jalham, 2003). The applications for both thermoplastic and thermoset based composites concern mainly automotive industry or domestic objects (Taj *et al.*, 2007).

PMCs are very popular due to their low cost and simple fabrication methods. Use of non-reinforced polymers as structural materials is limited by low level of their mechanical properties, namely strength, modulus and impact resistance. Reinforcement of polymers by strong fibrous

network permits fabrication of PMCs which is characterized by: a) High specific strength b) High specific stiffness c) High fracture resistance d) Good abrasion resistance e) Good impact resistance f) Good corrosion resistance g) Good fatigue resistance h) Low cost (Jose *et al.*, 2012)

In the last couple of years, there have been major developments in the design and fabrication of high strength materials, primarily due to the development of polymer composite materials (Husseinsyah and Zakaria, 2011). Synthetic polymer composite materials are currently widely used in many industrial areas to meet light-weight and high strength requirements. However, with the increasing amount of synthetic polymer materials present worldwide, environmental issues such as disposal treatment, waste disposal services and incineration pollution are becoming increasingly important (Suardana *et al.*, 2011).

Advanced polymer composites containing carbon and glass fibres have been utilized extensively in the aerospace, automotive and construction industries. Since the matrices and the fibre reinforcements in these advanced composites are based on mineral resources, their long term sustainability is problematic. While recycling may be a viable strategy, the complicated mixed morphology of composite materials makes them inherently difficult to recycle. In comparison, several bio-composites have been developed that offer certain environmental advantages at the end of their use cycle when composites are land filled or incinerated. Bio-composites therefore, are defined as composite materials that combine lignocellulosic materials such as sisal, jute, hemp, and kenaf with either biodegradable or non-biodegradable polymers (Lee *et al.*, 2009).

2.3.1 Bio/Green Composites

Growing global environmental and social concerns, the high rate of depletion of petroleum resources and new environmental regulations has forced the search for new composites and green materials that are compatible with the environment. In fact, renewable sources of polymeric materials reinforced with lignocellulosic fillers derived from annually renewable resources, offer an answer to maintaining sustainable development of economically and ecologically attractive materials with respect to ultimate disposability and raw materials use (Avella *et al.,* 2009). The main motivation for developing bio-composites is to create new materials that are completely environmentally compatible in terms of production, usage and removal. Since raw materials are entirely taken from biologically renewable resources, bio-composites are expected to be fully integrated into natural cycles (George *et al.,* 2001).

A number of literatures have defined bio-composites as those composites that are composed of lignocellulosic materials dispersed in polymeric matrices, i.e biodegradable polymers (poly(lactic acid) (PLA), polyhydroxyalkanoates (PHAs),soy plastic, starch plastic *etc.*) and/or non-biodegradable polymers i.e. thermoplastics like polypropylene (PP),polyvinyl chloride (PVC), High density polyethylene (HDPE), Low density polyethylene (LDPE), Chlorinated polyethylene (CPE), Normal polystyrene (PS), etc.; thermosets like epoxy, vinyl ester, Unsaturated polyester resins (as in fibreglass), Phenolic, Novolac and Polyamide etc (Mohanty *et al.,* 2001; Khanam *et al.,* 2007; Taj *et al.,* 2007; Dobircau *et al.,* 2009; Kumar *et al.,* 2010; Khanjanzadeh *et al.,* 2012)

Today, it seems very difficult to fabricate green composites with higher performance in terms of long time behaviour which is often in contradiction with the biodegradability performance

requirement. Thus, green composites have to be used effectively for many applications such as consumer products with short life cycles or products intended for one time or short time use before disposal. A number of bio-fillers have good intrinsic mechanical properties associated with low density, light-weight and non-toxic nature. Above all these advantages, they are low cost materials which are abundantly available in nature. The biodegradable nature of plant fibres can contribute to the formation of a healthy eco-system as well as the high performance that fulfils the economic interest of industries (Dobircau *et al.,* 2009).

Lee and Wang (2006) developed bio-composites with desirable interfacial properties from biodegradable polymers, PLA and PBS with bamboo fibre using lysine-di-isocyanate as a bio-based coupling agent. The bio-composite developed showed appreciably improved tensile properties and water resistance by adding coupling agent. Oksman *et al.,* (2003) investigated the use of flax fibre reinforced PLA composites using triacetin as plasticizer for PLA in order to improve the impact properties. Their results showed that mechanical properties of PLA and flax fibre composites were promising but addition of plasticizer did not show any positive effect on impact strength of composites. Tserki *et al.,* (2006b) studied biodegradable polymer matrix composites based on lignocellulosic waste flours (spruce, olive husk and paper flours) as reinforcement and polyester, bionolle 3020 was used as a matrix. The incorporation of the waste flours into the polymer matrix reduced the tensile strength and significantly increased its tensile modulus, water absorption and biodegradation rate. The use of bionolle-g-MA compatibilizer significantly improved the mechanical properties of the composite, especially their tensile strengths.

2.4 Lignocellulosic Materials

A number of lignocellulosic materials, such as jute, hemp, sisal, abaca etc. have been used as reinforcements for biodegradable bio-composites due to their good mechanical properties and low specific mass (Kumar *et al.*, 2010).

Lignocellulosic fillers/fibres, depending on their performance when incorporated in a plastic matrix can be classified as (1) Flours which can be considered as particulate fillers that enhance (increase) the tensile and flexural moduli of the composites while having little effect on the composite strengths. (2) Fibres which have higher aspect ratios and contribute to an increase in the moduli of the composite as well as its strength when suitable additives are employed to improve stress transfer between the matrix and the fibres (Rowell *et al.*, 1999).

2.4.1 Advantages and Disadvantages of Lignocellulosic fibres/fillers

The advantages of using lignocellulosic materials as fillers/reinforcements in plastics are numerous. They include low densities, high specific properties (such as high filling levels possibly resulting in high stiffness properties) and biodegradability. There are also wide materials availability (throughout the world), rural job generation, enhancement of nonfood agricultural/ farm-based economy, low energy consumption, low requirements on processing equipment, no abrasion during processing and lower costs. The main advantage of lignocellulosic materials upon mineral fillers is their environmental friendliness (Rowell *et al.*, 1999; Tserki *et al.*, 2005).

The limitationsencountered with the use of lignocellulosic materials is their low processing temperature due to the possibility of degradation and/or the possibility of volatile emissions that could affect composite properties. The processing temperatures are thus limited to about 200°C, although it is possible to use higher temperatures for short periods (Rowell *et al.*, 1999; Ewulonu and Igwe, 2011). Another drawback is the high moisture absorption of lignocellulosic materials. Moisture absorption can result in swelling of the fibre resulting in dimensional instability in the lignocellulosic filler composites. The absorption of moisture by the fillers is minimized in the composite due to encapsulation by the polymer and good filler-matrix bonding. Good adhesion decreases the rate and amount of water absorbed in the interphase region of the composite (Rowell *et al.*, 1999). Water absorption and specific gravity of lignocellulosic filler composites are important characteristics that determine end use applications of these materials. Good wetting of the filler by the matrix can decrease the rate and amount of water absorbed by the composite (Rowell *et al.*, 1999).

2.4.2 Surface Modification/Treatment of Lignocellulosic materials

The composite interface is the diffusion or reaction site in which the constituent phases are chemically and/or mechanically combined. Interfacial adhesion between filler and matrix plays a significantrole in characterizing the mechanical properties of composites. Poor adhesion across the phase boundary results in poor mechanical properties of the compositedue to relatively weak dispersion of force between the constituent phases (Kabir *et al.*, 2011).

Lignocellulosic materials consist mainly of cellulose; a natural polymer rich in hydroxyl groups. The other components which are made up of hemicelluloses, pectin and lignin are also molecules rich in hydroxyl, carboxyl and other functional groups which makes the materials significantly hydrophilic in nature while most polymer matrices are hydrophobic in nature. As a result, there is the problem of compatibility between the filler and the matrix leading to poor dispersion, weak interface and ultimately inferior quality composites. Appropriate methods such as (1) Physical methods and (2) Chemical methods are used to tackle compatibility problems in order to improve adhesion between the composite constituents. In both cases, however, the major goal is to improve the wettability of the constituents and promote adhesion by the induction of chemical bonding and/or the adjusting of surface energy (Zafeiropoulos, 2008).

2.4.2.1 Physical methods for surface modification

Physical treatments are used tomodify the structural and surface properties of fibres without the use of chemical agents. Some examples of physical treatments include corona, plasma, heat treatments, electric discharge method etc. (Joffe and Andersons, 2008; Kabir *et al.*, 2011). Physical treatments do not broadly modify the chemical composition of the fibres but enhance the interface generally by increasing the mechanical bonding between the fibre and the matrix. One of the most attractive features of physical treatments is the fact that they are `clean' since they do not involve the use of chemicals (Zafeiropoulos, 2008).

Corona treatment: Corona is defined as a luminous, appreciable discharge that occurs due to excessive localized electric field gradient on an object that causes the ionization and possible

electrical breakdown of the air adjacent to this point. Corona discharges are relatively low power electrical discharges that take place at or near atmospheric pressure. The corona is generated by strong electric fields associated with small diameter wires, needles or sharp edges on an electrode (Mukhopadhyay and Fangueiro, 2009). Gassan and Gutowski (2000) studied the effect of corona discharge and UV treatments on the properties of Epoxy/Jute composites; Ragoubi *et al.,* (2010) evaluated the impact of corona treatment on the mechanical properties of PP/Hemp composites while the effect of corona discharge on the mechanical and thermal properties of composites using miscanthus fibres and polylactic acid or polypropylene matrix was studied also by Ragoubi *et al.* (2012).

Electron Beam (EB): Electron beam irradiation are conducted to create a hydrophobic group, cause cross-linking and increase the interfacial surface area of fibres. The electron beam (EB) irradiation technique is being increasingly utilized to alter the surfaces of various materials, such as fibres, textiles and films. Cotton fabrics have been coated with pigment colours using EB to improve colour fastness, water absorption and crease resistance (El-Naggara *et al.,* 2005). Han *et al.,* (2006) irradiated natural fibres with EB to improve adhesion between the fibres and thermoplastics and reported that EB irradiation is effective in both impurity removal and functional group development on the surface of natural fibres for better bonding between natural fibre and polymer matrix.

2.4.2.2 Chemical Methods

Chemical modifications are usually applied to optimize the interface of fibres in that they may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix so as to induce the required properties in the polymer (Sreekala *et al.,* 2000; Li *et al.,* 2007; Singha and Thakur, 2009). Generally, chemical coupling agents are molecules possessing two functions; (1) they react with hydroxyl groups of cellulose and (2) they react with functional groups of the matrix. Quite a number of researchers have investigated the chemical modifications of lignocellulosic materials which is aimed at improving the adhesion with polymer matrices. The following are some of the chemical methods used for surface modification of natural fibres.

Alkali (NaOH) treatment (Mercerization): Alkali treatment disrupts the hydrogen bonding in the network structure of the lignocellulosic fibres thereby increasing surface roughness. This treatment removes a certain amount of lignin, pectin, wax and oils covering the external surface of the fibre cell wall, depolymerizes cellulose and exposes the short length crystallites (John and Anandjiwala, 2008; Karthikeyan and Balamurugan, 2012; Murali *et al.,* 2014). The equation of reaction is as follows (John and Anandjiwala, 2008)

$$\text{Fibre} - \text{OH} + \text{NaOH} \longrightarrow \text{Fibre} - \text{O} - \text{Na} + \text{H}_2\text{O} \qquad (1)$$

In mercerization treatment, fillers are immersed in NaOH solution for a given period of time, removed, washed and subsequently dried. Ray *et al.,* (2001) treated jute fibres with 5% aqueous NaOH solution for 2, 4, 6 and 8 hrs. at 30^{o}C and submitted that 4hrs treated fibre gave the best properties tested while Goud and Rao (2011) treated Roystonea-regia fibre with 5% NaOH

solution for 2h and recorded 8, 8.2 and 2.6% increase in tensile strength, tensile modulus and percent elongation at break respectively at 20% fibre content. In a similar report by Abdal-hay *et al.,* (2012), date palm fibres were treated with 6% NaOH solution to observe that artificial and natural impurities, oils, waxes, residual hemicelluloses and lignin were etched away which gave them a reason to believe that the fibre diameters were reduced to form finer micro-fibres which wasconfirmed in their SEM analysis. It is reported that alkali treatment has two effects on the fibre: (1) it increases surface roughness resulting in better mechanical interlocking; and (2) it increases the amount of cellulose exposed on the fibre surface, thus increasing the number of possible reaction sites (Murali *et al.,* 2014). Van de Weyenberg *et al.,* (2003) reported that alkali treatment gave up to a 30% increase in tensile properties (both strength and modulus) for flax fibre–epoxy composites and coincided with the removal of pectin. However, at a higher concentration of NaOH above a certain limit (5%), there is reduction in properties as reported by Mishra *et al.,* (2003). This is because high alkali concentration results in the excess delignification of natural fillers and consequently results in a weaker or damaged fibre.

Acetylation: Acetylation treatment involves a reaction introducing an acetyl functional group (CH_3COO -) into an organic compound. This involves the generation of acetic acid (CH_3COOH) as a by-product which must be removed from the lignocellulosic material before it is used. Chemical modification with acetic anhydride (CH_3-C (=O)-O-C (=O)-CH_3) replaces the polymer hydroxyl groups of the cell wall with acetyl groups making them to become hydrophobic. The reaction of acetic anhydride with fibre is written as: (Kumar *et al.,* 2011).

$$\text{Fibre} - OH + CH_3 - C(=O) - O - C(=O) - CH_3 \longrightarrow \text{Fibre} - OCOCH_3 + CH_3COOH \quad (2)$$

Mishra *et al.*, (2003) investigated the acetylation of sisal fibres. Dewaxed sisal fibre was immersed in 5 and 10% NaOH solution for 1 h at 30^{o}C; the alkali-treated fibre was soaked in glacial acetic acid for 1 h at 30^{o}C; it was decanted and soaked in acetic anhydride containing one drop of concentrated H_2SO_4 for 5 min. Nair *et al.*, (2001) treated raw sisal fibre in 18% NaOH solution, then in glacial acetic acid and finally in acetic anhydride containing two drops of concentrated H_2SO_4 for 1 h. The treated surface of sisal fibre reportedly became very rough and had a number of voids that provided better mechanical interlocking with the polystyrene (PS) matrix. Moreover, the thermal stability of treated fibre composites was found to be higher than that of untreated fibre composite because of better thermal stability of treated fibres and improved fibre–matrix interactions in treated fibre composites (Nair *et al.*, 2001). It was also reported that acetylated natural fibre-reinforced polyester composites exhibited higher bio-resistance and less tensile strength loss compared to composites with silane treated fibre in biological tests (Abdul Khalil and Ismail, 2001)

It was reported that acetylation treatment reduces moisture absorption of natural fibres. Reduction of about 50% of moisture uptake for acetylated jute fibres and of up to 65% for acetylated pine fibres has been reported in the literature. Acetylation has also been found to enhance the interface in flax/polypropylene composites (John and Anandjiwala, 2008).

Silane treatment:Silane with chemical formula $SiH_4$is a coupling agentwhich is capable of reducing the number of cellulose hydroxyl groups in the fibre– matrix interface. In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fibre, forming stable covalent bonds to the cell wall that are chemisorbed onto the fibre surface (Kumar *et al.*, 2011; Tajul Islam *et al.*, 2013). The chemical

composition of silane coupling agents (bifunctional siloxane molecules) allows forming a chemical link between the surface of the cellulose fibre and the polymer matrix through a siloxane bridge. This co-reactivity provides molecular continuity across the interface region of the composite. It also provides the hydrocarbon chains that restrain fibre swelling into the matrix. Natural fibres exhibit micropores on their surfaces and silane coupling agent act as a surface coating which penetrates into the pores and develop mechanically interlocked coating on their surface (Kabir *et al.*, 2011). The reaction schemes are given as follows (Kumar *et al.*, 2011):

$$CH_2CHSi(OC_2H_5)_3 \longrightarrow CH_2CHSi(OH)_3 + 3C_2H_5OH \quad (3)$$

$$CH_2CHSi(OH)_3 + H_2O + \text{fibre-OH} \longrightarrow CH_2CHSi(OH)_3O - \text{fibre} \quad (4)$$

Silane coupling agents have been found to be effective in modifying natural fibre–polymer matrix interface and increasing the interfacial strength. Three-aminopropyltrimethoxy silane with concentration of 1% in a solution of acetone and water (50/50 by volume) for 2 h was reportedly used to modify the flax surface (Van de Weyenberg *et al.*, 2003).

Silane solutions in a water and ethanol mixture (40-60) was used by Huda *et al.*, (2008a) and Singha and Thakur (2009) to treat kenaf fibres for PLA composites and Grewia optiva fibres for phenol- formaldehyde composites respectively. A study of the influence of different silane coupling agents on the properties of henequen fibre-reinforced polymer composites was carried out. The authors used FTIR and XPS to show that the reaction between silane and cellulose takes place only at temperatures above 70^{o}C (John and Ananjiwala, 2008).

Permanganate treatment:Permanganate is a compound that contains permanganate group MnO^{-}_{4}. Permanganate treatment leads to the formation of cellulose radical through MnO^{-}_{3} ion formation. The treatment is conducted by using potassium permanganate ($KMnO_4$) solution (in acetone) in different concentrations with soaking duration from 1 to 3 min after alkaline pre-treatment (Li *et al.,* 2007). Permanganate treatment was observed to reduce the hydrophilic tendency of fibres and thus, decrease in the water absorption of fibre-reinforced composite. The hydrophilic tendency of fibre decreased as the $KMnO_4$ concentrations increased. However, at higher $KMnO_4$ concentrations of 1%, degradation of cellulosic fibre occurred which resulted in the formation of polar groups between fibre and matrix (Li *et al.,* 2007).

Other chemical treatments:Other chemical modification of lignocellulosic materials include the use of Stearic acid $CH_3(CH_2)_{16}COOH$), maleated coupling agent, Benzoylation treatment etc. The Benzoylation treatment uses benzoyl chloride to reduce the hydrophilic tendency of the fillers and improve filler- matrix adhesion, thereby increasing the strength of the composite. During benzoylation treatment, alkali pretreatment is used to activate the hydroxyl groups of the filler. Then it is soaked in benzoyl chloride solution for 15mins. Afterwards, ethanol solution is used for 1hr to remove the benzoyl chloride that adhered to the filler surface followed by washing with water and oven drying (Kabir *et al.,* 2011).

2.5 previous work done

2.5.1 Agro-Flours/Fibres reinforced non-degradable/petroleum-based Polymers

The discussion on the petroleum-based polymers reinforced lignocellulosic materials would be limited to thermoplastic and thermoset polymers.

2.5.1.1 Agro-Flours/Fibres reinforced Thermoset Polymers.

Thermoset polymers are used as matrices for most structural composite materials. The main advantage of thermoset polymers is their low viscosity and can thus be introduced into fillers at low pressures. They are processed by simple processing techniques such as hand lay-up and spraying, compression, resin transfer, injection and pressure bag moulding operations. Examples of thermosetting polymers are epoxy resins and unsaturated polyesters (UP); phenolic resins (including phenol-formaldehydes); amino resins (e.g. melamine-formaldehydes and urea-formaldehydes) and polyurethane (Deepa *et al.,* 2011).

Polyester composites:Unsaturated polyesters arepopular thermoset polymers used as polymer matrix in composites for decades due to their versatility in properties and applications. They possess many advantages compared to other thermosetting polymers including room temperature cure capability, good mechanical properties and transparency. The curing of unsaturated polyester is due to a polymerization reaction that causes cross linking among individual linear polymer chains. No by-product is formed during the curing reaction; hence it can be moulded, cast and laminated at low pressures and temperatures (Aziz *et al.,* 2005). Extensive studies have

been reported on the incorporation of agro-flours/fibres in polyester matrix. Hardinnawirda and SitiRabiatull (2012) studied the effect of rice husks as fillers in unsaturated polyester resin as matrix with methyl ethyl ketone peroxide (MEKP) as catalyst. It was found that tensile strengths of the composites slightly decreased with increasing filler loading due to the poor interfacial bonding that existed between the hydrophilic filler and hydrophobic matrix. In the water absorption test, they observed that the water absorption increased with increase in filler loading due to the presence of voids in the natural filler polymer composites. In a similar study, Ahmad *et al.*, (2007) produced composites of unsaturated polyester with rice husk as filler using the simple hand lay-up technique. They observed a general decrease in tensile strength as the filler loading increases but the alkali treated particles had higher strengths than the untreated particles. The reason for the poor tensile strength, they explained, was that in particulate filled composites, discontinuities are created which generate weak structures due to poor stress-transfer at the filled-polymer interphases. However, with alkali treatment, there was an improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking which promoted more resin-filler interpenetration at the interface.

It was reported that alkali treatment improves the surface adhesive characteristics of fillers by removing the natural and artificial impurities such as lignin, wax and pectin, thereby producing rough surface topography. The alkali treatment also helps to improve the dispersion of filler in the matrix, leading to the reduction of the agglomeration of the filler (Ahmad *et al.*, 2007).

Husseinsyah and Zakaria, (2011) produced a composite of coconut shell and polyester using the hand lay-up technique. The filler size used was 304µm and the filler content was from 0-60% at 15% interval. The study showed that the tensile strength of the composite decreased with the

addition of 15% filler content and then started to increase afterwards while the elongation at break decreased as the filler content increased. The decrease in elongation at break was due to a decrease in deformability of rigid interface between the filler and the polyester matrix. Water absorption behaviour showed an initial sharp water absorption uptake followed by gradual increase until equilibrium water content was achieved. The reason being that coconut shell is a lignocellulosic material and possesses the tendency to absorb moisture from the environment. Their conclusion on the morphology of the fractured surface indicated that the filler- matrix interaction improved with an increase of the filler in the matrix.

The effect of NaOH and Sodium Laulryl Sulfate (SLS) treatments on banana/kenaf hybrid and woven hybrid composites using polyester as the matrix was investigated by Thiruchitrambalam *et al.,* (2009). They observed that tensile strength of SLS treated fibre was higher than that of NaOH treated fibre with about 13% and 10% for the non-woven and woven hybrid composites respectively. Similar trends were shown in the flexural and impact tests results. Different reports (Li *et al.*, 2007;John and Anandjiwala, 2008; kabir *et al.*, 2011; Kumar *et al.*, 2011) have shown that surface modification by chemical treatments of fibres such as alkali, silane, acetylation etc resulted in significant increase in tensile strengths and other properties of lignocellulosic materials since the chemical modifications are considered to optimize the interface of fibres. Also, chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the matrix thereby producing composites with better properties. As a result, the SLS treatment which does not have a wide publication in literatures compared to other chemical modifiers, gave a better result than the alkali treatment because, cleaner fibre surface was

obtained than with the alkali treatment thereby improving the adhesion between fibre and matrix which in turn, led to better mechanical properties than the alkali treated fibres.

Epoxy matrix:Epoxies are amongst the important classes of thermosetting polymers which are widely used as matrices for fibre-reinforced composite materials and as structural adhesives. They are amorphous, highly cross linked polymers which results in them possessing various desirable properties such as high tensile strength and modulus, ease in processing, good thermal and chemical resistance and dimensional stability. However, they exhibit low toughness and poor crack resistancewhich could be modified before they can be considered for many end-use applications (Bhaskar and Singh, 2013). The various agro-flours/fibres that have been used as reinforcements to this important matrix resin are outlined.

Sapuan *et al.*, (2003) investigated the tensile and flexural properties of coconut shell filler particles in epoxy matrix. They found at the end of their study that the tensile and flexural strengths of the composites increased as the filler content increased. There was a linear behaviour with sharp fracture in the tensile testing while there was slightly nonlinear behaviour prior to sharp fracture for the flexural test.

Masoodi and Pillai (2012) investigated the water absorption and swelling tests of jute fibres and two types of epoxy (traditional and bio-based) resins. Their results indicated a high swelling rate at the beginning of the wetting test but subsequently, the rate of swelling decreased asymptotically. Moreover, the bio-epoxy composites had higher water absorption and swelling measurements than the traditional epoxy resin. A reason they offered for that is possibly due to the use of cellulose and hydroxyl group in bio-epoxies. Furthermore, they submitted that addition

of more jute fibres to the composite parts led to higher rates of swelling and water absorption in all the composites. For the fibre percentage of 40%, the measured values of volume swellings were 19% and 24% for the epoxy and bio-epoxy matrices, respectively. The highest amount of water absorption values, which were measured for composites with 40% fibres, were 17.5% and 26% for the epoxy and bi-epoxy composites respectively.

An improvement in the mechanical properties of alkalised jute fibre reinforced epoxy composites was observed by Gassan and Bledzki (1999). By this process, shrinkage of the fibres during treatment had significant effects on fibre structure and, as a result, on the mechanical properties of the fibres. Regarding fibre-matrix adhesion, the rougher surface morphology after NaOH treatment did not lead to any improvement but the composite strength and stiffness generally increased.

Others:The few other thermoset resins used as matrices and few literatures thereof include phenolic resins (including phenol-formaldehydes (PF)); amino resins (e.g. melamine-formaldehydes and urea-formaldehydes) and polyurethane. Some of the works of their composites are outlined hereafter.

Sreekala *et al.*,(2000) investigated the use of surface modification of oil palm fibres as reinforcement in PF resin. The fibres were subjected to different chemical modifications such as mercerisation, acrylonitrile grafting, acrylation, latex coating, permanganate treatment, acetylation and peroxide treatment. They came to a conclusion that treatment of fibre changes the stress-strain characteristics, tensile strength, tensile modulus and elongation at break of the composites. The incorporation of the modified fibres resulted in composites having excellent

impact resistance. Upon morphological studies with SEM, the authors observed that significant changes occurred to the fibre surface upon modification due to different treatment methods.

Rozman *et al.,* (2003) used rice husk (RH) as reinforcement in polyurethane (PU) matrix for composite production. Flexural, tensile and impact tests were carried out to which the tested properties improved with the incorporation of rice husk. They also noted that the size of RH played significant role in the properties since the smaller size RH produces composites with higher strengths. Badri *et al.,* (2005) studied the mechanical properties of Polyurethane composites from oil palm resources (refined, bleached and deodorized palm kernel oil).

Raju *et al.,* (2012) used groundnut shell particles of size 600µm BS sieve to reinforce vinyl Ester resin.

2.5.1.2 Agro-Flours/Fibres Reinforced Thermoplastic Polymers.

Thermoplastic composites are composites that use a thermoplastic polymer as a matrix. A thermoplastic polymer is a long chain polymer withmedium to high molecular weight whichiseither amorphous in structure or semi-crystalline. They possess excellent properties such as toughness, resistance to chemical attack and recyclability. Methods such as extrusion and injection moulding are used for the processing of their composites. An advantage of thermoplastics is that they can be moulded non-isothermally, i.e., they can be rapidly heated and rapidly cooled without affecting their microstructures. In thermoplastics, most of the works reported so far deals with commodity polymers such as Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), and Poly (vinyl chloride) (PVC) (Deepa *et al.,* 2011). However, from

numerous literatures, it was found that works on Polyethylene (both high and low density) and Polypropylene were mostly reported.

Polyethylene matrix:Polyethylene (PE), a non-degradable polymer which is the first commodity plastic to be used for food packaging came into general use in the 1950s. Since then, it has achieved its leading position as a packaging material for a wide range of foods and beverages due to its relatively low cost, versatile properties and the ease of manufacture. The main end products of PE plastics used for food packaging are films, bottles and other containers made by thermoforming and blow moulding processes (Behjat *et al.,* 2009).

Some of the documented literatures on the use of lignocellulosic materials (agro-flour/fibres) as reinforcements in Polyethylene matrix are outlined hereafter.

Behjat *et al.,* (2009) used cellulose derived from kenaf plant to reinforce both high and low density Polyethylene (HDPE and LDPE) using polyethylene glycol (PEG) as a plasticizer and then tested for biodegradability using soil burial test for a period of 120 days. Their results indicated that the composites biodegradability increased with increasing cellulose content. The degradability of LDPE was highest with 5% PEG while that of HDPE was highest with 7% PEG.

Yao *et al.,* (2008) investigated the effect of fibre type and loading using virgin and recycled high-density polyethylene (VHDPE and RHDPE) as matrices. The fibres used were wood fibre and four rice straw components (i.e., rice husk, rice straw leaf, rice straw stem and whole rice straw). Their findings indicated that both VHDPE and RHDPE, rice straw fibre systems had comparable mechanical properties with those of wood composites. Increase in fibre loading led to increased moduli and decreased tensile and impact strengths. Composite panels with rice husk

had the smallest storage moduli, but their impact strengths were comparable or better than those of other straw fibres.

Ishidi *et al.,* (2011a) used alkali-treated palm kernel nut shell (300µm particle size) to form composites with HDPE as matrix. Their results indicated that fillers incorporated into the polymer matrix influenced the melting and crystallization temperatures of the composites. Another study of Ishidi *et al.*,(2011b) studied the physio-mechanical properties of HDPE/palm kernel nut shell composites.

Alsewailem and Binkhder (2010) prepared and characterized composites based on date pits and HDPE. The findings of that work indicated that addition of date pits reduced the tensile strength and izod impact strength of the resulting composites. They attributed the reduction in mechanical properties of the composite system to possibly a coarse morphology of the composite systems, especially in the absence of an appropriate coupling agent.

Herrera-Franco and Valadez-Gonza´lez (2004) studied the mechanical behaviour of high density polyethylene (HDPE) reinforced with continuous henequen fibres. The fibres were treated with 2% w/v NaOH solution and also with silane coupling agent. The henequen fibres were further impregnated with a 1.5% w/w HDPE/xylene solution. At the end of the study, they concluded that the mechanical properties, specifically, the tensile strength did not improve significantly when high silane concentrations were used to treat the fibre. Still on the use of HDPE matrix, Obasi (2012) carried out a study in which he reinforced HDPE with corncob flour to produce composites. Tensile test, water absorption study and soil burial test were carried out on the produced composites. He stated at the end of the study that tensile test decreased slightly but it

then improved on the addition of PE-g-MA as coupling agent. Also, they found out that the composites degraded increasingly as the filler loading increased both for the treated and untreated samples.

Rassiah *et al.,* (2012) studied the effect of sodium hydroxide on the water absorption and biodegradability of Low Density Polyethylene (LDPE)/sugarcane Bagasse (SCB) composites. At the end of their study, they suggested that sugarcane bagasse could be used as a biodegradable filler in polymeric matrices so as to minimize environmental pollution.

Polypropylene matrix:Polypropylene (PP) is one of the most extensively used plastics both in developed and developing countries. It provides advantages in regard to economy (price), ecology (recycling behavior) (Haque *et al.,* 2010), easy processability (Azuma *et al.,* 2009) and has been used as matrix in many kinds of composites (Qui *et al.,* 2006). In the last few decades, detailed investigations have been undertaken and reported on the use of PP as matrix for composites production with lignocellulosic materials as reinforcement.

Some of the documented works on the use of polypropylene as matrix reinforced with agro-flours/fibres to produce composites are outlined. First is the work of Bledzki *et al.,* (2010) who studied the potentials of grain by-products (wheat husk and rye husk) as reinforcements in polypropylene matrix. They investigated the thermal degradation characteristics, bulk density, water absorption and solubility index as well as the tensile and charpy impact tests. One of the conclusion of their study stated that wheat husk and rye husk were thermally stable at 235^{o}C and 210^{o}C respectively.

Suardana *et al.,* (2011) studied the effects of NaOH and silane coupling agent treatments on themechanical properties of hemp fibres and hemp/PP composites. Conclusively, they submitted that alkaline treatment decreased the density and tensile strength but increased the weight loss of hemp fibres while silane treatment decreased the density but increased the weight and tensile strength of hemp single fibre due to the silane coating on the fibre surface. The alkaline treatment of hemp fibre increased the tensile and flexural strengths of hemp/PP composites, indicating that interfacial bonding improved after alkaline treatment. As opposed to the NaOH treatment, the tensile and flexural strengths of the Silane-treated composites were nearly equal to those of the untreated hemp fibre/PP composites. Their findings suggested that the silane treatment of the hemp fibres did not affect the mechanical properties of the composites.

Ashori and Nourbakhsh (2010) studied the potentials of sunflower stalk, corn stalk and bagasse fibres as reinforcement for polypropylene as an alternative to wood fibres. They subsequently compared the effects of two grades (Eastman G-3003 and G-3216) of coupling agents on the mechanical properties of the composites produced. They concluded that the mechanical properties of the composites treated with both grades of coupling agents were superior to those of the untreated ones due to the stronger interfacial bonding between the fibre and the matrix polymer.

Abu-Sharkhand Hamid (2004) compounded date palm leaves with PP and UV stabilizers to form composite materials. They then studied the stability of the composites produced in natural weathering conditions of Saudi Arabia and in accelerated weathering conditions. They concluded that PP/date palm cellulose fibre composites were found to be much more stable than PP under the severe natural weathering conditions of Saudi Arabia and in accelerated weathering. In

addition, compatibilized samples were generally less stable than uncompatibilized ones as a result of the lower stability of the maleated polypropylene used.

Fuad *et al.,* (1995) studied the effect of applying titanate (LICA 38), zirconate (NZ 44) and silane (PROSIL 2020 and PROSIL 9234) coupling agents to rice husk ash (RHA) in polypropylene composites. The conclusion of the work showed that the four coupling agents used gave various changes to the mechanical properties of the composites produced. They also submitted that most of the RHA composites had better impact properties but lower tensile and flexural strengths. They suggested that suitable applications for the RHA composites would be in components demanding high stiffness, excellent dimension stability with reasonable tensile and impact properties.

Zabihzadeh *et al.,* (2011) used rapeseed stalks as fillers in polypropylene matrix to form composites. They concluded that increasing the filler content reduced the flexural strength of the composites significantly. However, the flexural modulus increased with increase in filler content.

The few documented reports on composites with other thermoplastic matrices include the works of Wirawan *et al.,* (2009) who made a review on the mechanical properties of natural fibre reinforced PVC composites; Threepopnatkul *et al.,* (2009) studied the properties of pineapple leaf fibre reinforced polycarbonate composites; El-Shekeil *et al.,* (2012)studied the influence of fibre content on mechanical (i.e. tensile, flexural, impact, hardness and abrasion resistance) and thermal (i.e. TGA) properties of kenaf bast fibre reinforced thermoplastic polyurethane (TPU) composites. Furthermore, Schlemmer *et al.,* (2009) studied the degradation of different polystyrene/thermoplastic starch blends buried in soil.

2.5.2 Agro- Flours/Fibres Reinforced Biodegradable Polymers (Green Composites)

The growing concern in environmental impact led to the evolution of plastics that degrade rapidly leading to a complete mineralization (Avella *et al.,* 2005). The non-degradability of plastics and the closing of landfill sites as well as the problems of growing water and land pollution have led to concern about plastics. The growing interest in environmental issues has led to increasing demands to develop materials which do not burden the environment significantly. Biodegradation is necessary for water-soluble or water-immiscible polymers because, eventually, they enter streams and these can neither be recycled nor incinerated (Shah *et al.,* 2008).

Furthermore, bio-based products obtained from renewable resources also maintain carbon dioxide neutrality as depicted in Figure 2.6. Environmentally-friendly bio-composites manufactured from plant-derived fibres and crop-derived plastics are novel materials which would be of great importance to the materials world as a solution to growing environmental threat and also as a solution to the uncertainty of petroleum supply. Biopolymers are also moving into stream use, and may soon be competing with commodity plastics, as a result of the sales growth of more than 20–30% per year (Mohanty *et al.,* 2002).

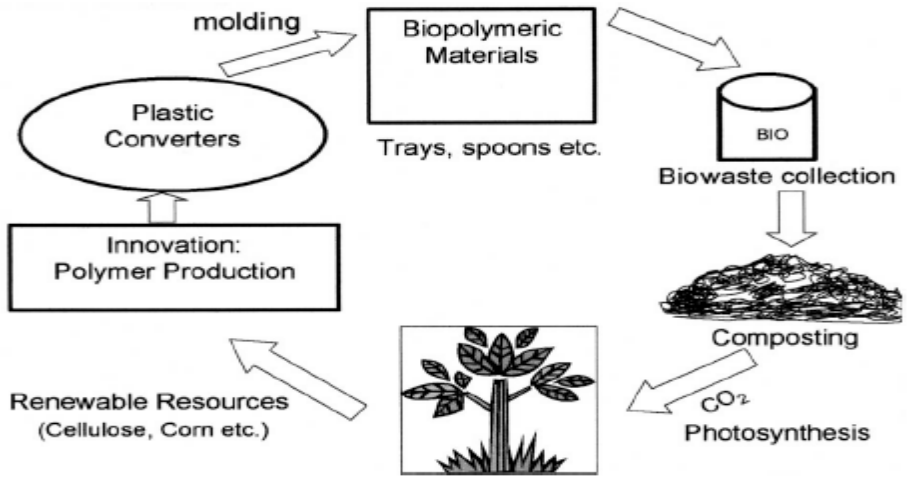


Figure 2.6: Carbondioxide sequestration(Mohanty et al., 2002).

The special challenges of these bio-composites are their eco attributes that make them environmentally friendly, completely degradable and sustainable (Avella *et al.,* 2009).

A number of reports have been documented on the possibilities of reinforcing biopolymers with agro-flours/fibres to produce what is known as green composites. They are known as green composites because they use agricultural-based polymers and biodegradable plant-based fillers. They can be used in non-durable applications (a few years), products intended for short-term use (a few times) or indoor applications (like wood or automotive parts) (Finkenstadt *et al.,* 2007ab).

2.5.2.1 Poly (butylene succinate) (PBS) Matrix

PBS is one of the most important biodegradable polyesters in use. It is synthesized by polycondensation between succinic acid and butanediol by esterification between the diacid and the diol and then polycondensation under high temperature to form high-molecular-weight PBS. Showa Highpolymer (Japan) synthesized and commercialized various aliphatic co- polyesters (PBS and PBSA) based on succinate, adipate, ethylene glycol and 1, 4-butanediol under the trade name "Bionolle." They exhibit melting temperatures >100^{o}C and thermal degradable temperatures >300^{o}C and other properties similar to LDPE, HDPE and PP. They are capable of being processed by injection moulding, extrusion and film blowing using conventional polymer processing equipment. Therefore, they are considered to be the potential alternatives to petrochemical polyolefins (Jiang and Zhang, 2011).

Ishiaku *et al.*,(2005) investigated the mechanical and morphological properties of short fibre reinforced jute/poly butylene succinate (PBS) biodegradable composites with a special emphasis on the effect of a dual gated mould in the fabrication of welded specimens. They observed that incorporation of jute fibre conferred drastic changes on the stress-strain properties of the matrix as the elongation at break dropped from 16% in the matrix to just 10% in the composite. Also, the tensile strength of the composite was lower than that of matrix but tensile modulus increased. Lee and Wang (2006) investigated the effects of lysine-based diisocyanate (LDI) coupling agent on the properties of bio-composites from poly (lactic acid) (PLA), poly (butylene succinate) (PBS) and bamboo fibre (BF). Tensile properties, water resistance and interfacial adhesion of both PLA/BF and PBS/BF composites were improved by the addition of LDI. The biodegradability of PBS/Jute composites by compost soil burial test was investigated by Liu *et*

al.,(2009). The order of higher weight loss due to biodegradability of the composite for the effect of fibre surface modification was PBS/untreated jute > PBS/alkali treated jute > PBS/coupling agent treated jute. The weight loss of PBS/10% jute composite after 180 days was 62.5%.

Similar investigations on the use of PBS as matrix was documented by Kim *et al.*,(2005ab) who reported the production of rice husk flour (RHF) and wood flour (WF) filled polybutylene succinate (PBS) bio-composites as alternatives to cellulosic material filled conventional plastic (polyolefins) composites. They compared the mechanical properties between conventional plastics and agro-flour–filled PBS bio-composites. They evaluated the biodegradability and mechanical properties of agro-flour–filled PBS bio-composites according to the content and filler particle size of agro-flour. As the agro-flour loading was increased, the tensile strength of the bio-composites decreased as a result of the weak interfacial bonding between filler and matrix polymer. The tensile strength of WF-filled PBS bio-composites was higher than that of RHF-filled PBS bio-composites as a result of the higher holocellulose and lignin contents of WF. The Izod impact strength of RHF-filled PBS bio-composites was lower than that of RHF-filled PP and HDPE composites because of the very brittle characteristics of PBS. As filler loading increased, the Izod impact strength of agro-flour– filled PBS bio-composites decreased because of the poor interfacial adhesion when impact occurred which allowed the cracks to easily propagate. Another study of Kim *et al.*,(2005b) investigated the thermal properties of agro-flour-filled (RHF and WF) polybutylene succinate (PBS) bio-composites. They analysed the thermal properties such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analyzer (DMTA) according to the agro-flour contents and mesh size. In the conclusion of their work, they submitted that the results they obtained indicated

that the degree of compatibility and interfacial adhesion were dependent on the mixing ratio of agro-flour in the PBS. The storage modulus (*E*') of the agro-flour-filled PBS systems was higher than that of neat PBS and increased with increasing agro-flour content, because of the increasing stiffness of the bio-composites. They further stated that larger filler particle size produced increased *E*' values for the bio-composites compared to smaller particle size.

2.5.2.2 Poly(Caprolactone) (PCL) Matrix

PCL is a degradable and semi-crystalline aliphatic polyester synthesized by ring-opening polymerization of caprolactone. It can be a waxy solid (Mw below several thousands) or a solid polymer (Mw above 20,000) and exhibits mechanical properties similar to PE possessing a tensile strength of 12-30MPa. It can be spun into fibres or blown films under 200^{o}C without thermal degradation. Its drawback, however, is its low melting point (~60^{o}C) which prohibits its applications at elevated temperatures. Therefore, PCL is often blended with other polymers such as PP, Polycarbonate (PC), Polyethylene oxide (PEO) and starch to produce composites with desired properties (Jiang and Zhang, 2011).

Teramoto *et al.*,(2004) investigated the biodegradation of aliphatic polyester composites such as poly(e-caprolactone) (PCL), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(butylene succinate) (PBS) and poly(lactic acid) (PLA) with 10 wt.% untreated or acetic anhydride-treated (AA-) abaca fibres by the soil-burial test. With the neat polyesters, the order of higher weight loss after the burial was PCL > PHBV > PBS > PLA. The presence of untreated

abaca or AA- treated abaca did not pronouncedly affect the weight loss because PCL itself has a relatively high rate of biodegradability.

Other reports on PCL studies include works of Zhao *et al.*,(2008) who investigated the biodegradation behaviour of Polycaprolactone/rice husk eco-composites in simulated soil medium; Calil *et al.*,(2007) who studied the enzymatic degradation of poly (e-caprolactone) and cellulose acetate blends by lipase and α-amylase. Wu (2003) investigated the physical properties and biodegradability of maleated-polycaprolactone/starch composites while Chang *et al.,* (2012) studied the influence of maleic anhydride treated kenaf dust filled Polycaprolactone/Thermoplastic Sago starch composites.

2.5.2.3 Polyhydroxyalkanoates (PHA) Matrix

PHAs are biodegradable polyesters that are synthesized and accumulated by bacteria as carbon and energy storage materials under limiting nutrients condition in the presence of excess carbon source. The polymers are stored in the cells as discrete granules with sizes between 0.2 and 0.5 μm. Molecular weight of PHAs, depending on the species of bacteria and their growth condition, is in the range of $2x10^5$ to $3x10^6$ Da. The homopolymer PHB is a highly crystalline thermoplastic with a melting temperature (Tm) of about 175^oC. PHAs are consumed by microorganisms as an energy source and therefore, are readily biodegradable in microbial active environments such as compost. PHAs are finding more applications in packaging, single-use and disposable items, house-wares, appliances, electrical and electronics, consumer durables, agriculture and soil stabilization, adhesives, paints, coatings etc. (Jiang and Zhang, 2011).

Some documented reports on the use of PHA and its composites include the report of Sahari and Sapuan (2011) who documented a review on natural fibre reinforced biodegradable polymer composites where they reported a work by Singh and Mohanty that developed 'green' composites using bamboo fibre and PHBV which is a family of PHA.

Furthermore, Bledzki and Jaszkiewicz (2010) studied the mechanical performance of bio-composites based on PLA and PHBV reinforced with natural fibres (man-made cellulose, jute and abaca fibres) and made comparative study to PP. Tensile and impact tests were used to investigate the mechanical performance. The tested bio-composites clearly showed better or comparable characteristic values than the natural fibre reinforced PP. They reported an increase in stiffness, a significant increase in strength (> 50%) and a noticeable improvement in notch impact strength.

2.5.2.4 Poly (lactic acid) (PLA) Matrix

PLA is a synthetic biodegradable polyester that is made by bacterial fermentation of carbohydrates such as corn, sugarcane, potatoes and other biomass. PLA can be synthesized by direct condensation polymerization, azeotropic dehydrative condensation or ring-opening polymerization of lactide. Direct condensation polymerization is the least expensive method because it can only produce low-molecular weight PLA owing to the fact that it is difficult to remove water completely from the reaction mixture. PLA is well known for its biocompatibility and biodegradability and being a thermoplastic polymer, it can be conveniently processed using the existing polymer processing equipment and techniques (Jiang and Zhang, 2011).

The various work that have been documented on PLA and its composites include works of Finkenstadt *et al.,* (2007a) whose investigation was based on the evaluation of Poly (lactic acid) and sugar beet pulp (SBP) green composites. The SBP was ground to a particle size of less than 300µm and was compounded with the PLA in a co-rotating twin-screw extruder after which it was injection moulded to various test sizes; thermal and mechanical properties were evaluated. The result for the thermal properties after extrusion and injection moulding indicated that the glass transition temperature (Tg) of PLA was 58^{o}C and the melting temperature (Tm) was 151^{o}C from 61^{o}C and 151^{o}C respectively. They explained that the lower Tg indicated that some degradation of PLA took place during thermo-mechanical processing. As for the mechanical properties, the Young's modulus of the composite increased from 1945MPa (pure PLA) to 2590MPa as SBP increased to 45% while the tensile strength decreased with increasing SBP content from 69.55MPa (pure PLA) to 29.55MPa for 45% SBP content.

Oksman *et al.,* (2003) investigated the use of flax fibre reinforced PLA composites using triacetin as plasticizer for PLA in order to improve the impact properties. Their results showed that mechanical properties of PLA and flax fibre composites were promising but addition of plasticizer did not show any positive effect on impact strength of composites.

The mechanical properties of injection moulded PLA/Cordenka® rayon fibres and flax fibre composites were tested and compared. The highest impact strength of 72kJ/m^2 and tensile strength of 58MPa were found for Cordenka® reinforced PLA at 30 wt% fibre content. The highest Young's modulus of 6.31 GPa was found for the composite made of PLA and flax. A poor adhesion between the matrix and the fibres was shown for both composites using SEM. The promising impact properties of the presented PLA/Cordenka® composites showed their potential

as an alternative to traditional composites (Bax andMu□ssig, 2008). The suitability of wood fibres (WF) as reinforcements in PLA based composites was investigated in comparison with WF reinforced polypropylene composites. It was observed from the results that 40 wt% of WF resulted in an improvement of about 200% of the flexural modulus of PLA comparable to that obtained for polypropylene composites reinforced with the same amount of WF. Also, flexural strength of WF/PLA composites improved from about 100 MPa for the neat PLA to about 115MPa for PLA based composites at 20-40 wt% of WF (Avella *et al.*, 2009).

Mat Taib *et al.*,(2008)investigated the tensile properties and water absorption behaviour of bio-composites produced with 10 wt% polyethylene glycol (PEG) plasticized- poly (lactic acid) (p-PLA) reinforced with kenaf fibres (KF). The composites which contained fibre loading up to 40 wt% were prepared by Haake internal mixer and then compression moulded. At the end of their study, they observed that the incorporation of KF into p-PLA increased both the tensile strength and tensile modulus of the resulted composites except the strain at break. Also, they stated that the reinforcing effect of KF was observed when the fibre content exceeded 10 wt%. Scanning electron microscopy (SEM) of the tensile fractured surfaces revealed a very good adhesion between KF and p-PLA matrix. Water absorption behaviour of p-PLA/KF composites were studied by immersion in distilled water at room temperature for 60 days. All composites as well as unfilled p-PLA were found to exhibit non-Fickian behaviour. The deviation from Fickian water uptake behaviour was attributed to the development of microcracks on the surface and inside the composites. In addition to microcracks that occurred along the fibre length, water absorption too caused fibre-matrix debonding. Both were revealed via SEM examination on the surfaces of p- PLA/KF composites. Results suggested that KBF is a potential reinforcement for

plasticized poly(lactic acid) composites but possible applications should avoid high humidity environment.

2.6 Mechanical properties of bio-composites

The introduction of natural fillers in polymer matrices have significant advantages compared to traditional fillers such as glass and carbon fibres which have been variously used in composites. Polymer based composites reinforced with natural filler have increased worldwide due to their advantages such as low cost, low density, renewable and biodegradable character, good mechanical and thermal properties and their environmental friendliness. Numerous researches have been conducted to take advantages of these wide range of natural fillers properties (Essabir *et al.,* 2013a).

The incorporation of natural fillers into polymer matrices causes substantial changes in the mechanical properties of the resulting composites. The mechanical properties of composites reinforced by particles generally depend on the dispersion /distribution state, interfacial adhesion between particles and matrices, morphology and particle loading of the fillers (Essabir *et al.,* 2013a).

There have been numerous reports on the studies of mechanical properties (Tensile, Flexural, Hardness, and Impact etc.) of bio-composites

Tensile test is a measure of the ability of a material to withstand forces that tend to pull it apart and to what extent the material stretches before fracture. It is a fundamental mechanical test

where a carefully prepared specimen is loaded in a controlled manner while measuring the applied load and the elongation of the specimen over some distance. A number of properties are obtained from the test which include tensile strength, modulus of elasticity, elongation at break etc. During the test, the specimen is positioned vertically in the grips of the testing machine and the grips are then tightened firmly to prevent any slippage with gauge length kept at a specified distance. The main product of a tensile test is a load against elongation curve which is then converted into a stress against strain curve (Mofokeng, 2010; Kumar *et al.*, 2014). One of the most used methods for the tensile test is the ASTMD638 method.According to the method, dumbbell shape (Type IV) specimen is needed for reinforced composite testing.

At start of the test, the specimen elongates thereby increasing the resistance of the specimen which is detected by a load cell. This load value is recorded until a rupture of the specimen occurs. Instrument software provided along with the equipment will calculate the tensile properties e.g. tensile strength, tensile modulus and elongation at break (Mokhtar *et al.*, 2007).

Flexural strength is the ability of a material to withstand bending forces applied perpendicular to its longitudinal axis. The flexural load is a combination of compressive and tensile stresses. As described in ASTM D790, three-point loading system applied on a supported beam was utilized (Mokhtar *et al.*, 2007).

Hardness is generally used to describe the resistance of a material to surface indentation, scratching or marring while impact test determines the ability of a material to withstand an impact load which depends on the material's toughness (Siregar *et al.*, 2010).

Investigation on the mechanical properties of rice husks fibre reinforced polyester composites by Surata *et al.,* (2014) showed that tensile strength and modulus as well as flexural strength and modulus increased with increase in fibre weight fraction. Also, the mechanical properties further improved with alkalization of the fibres due to better interfacial bonding between the fibre and the matrix.

Studies on the mechanical, thermal and morphological properties of Poly(lactic acid)/Epoxidized palm olein blendwas conducted by Silverajah *et al.,* (2012). They reported that the addition of 1% epoxidized palm oil (EPO) in PLA matrix was enough to increase the tensile strength and tensile modulus of the neat PLA because, above that amount, the strength and modulus decreased. A similar trend was observed in the results for flexural strength and modulus. The impact strength recorded an improvement of 10% over the neat polymer with same quantity of EPO.

The mechanical and thermal properties of PP/Almond shell particles bio-composites was studied by Essabir *et al.,* (2013b). Their results showed an improvement in mechanical properties from the use of almond shells particles in the PP matrix with and without maleic anhydride compatibilizer, corresponding to a gain in Young's modulus of 35% and 56.2% respectively at 30 wt.% almond shells particle content. In another study of Essabir *et al.,* (2013a), they reported a linear increase in Young's modulus of PP/Argan nut-shell particles bio-composites with an increase in particle content as compared to neat PP. However, there was a decrease in tensile strength with particle content and with particle size. They concluded that the mechanical properties of PP/Argan nut-shell particles bio-composites depended on particle size, degree of dispersion, interfacial adhesion and particle content.

Yussuf *et al.,* (2010) compared the properties of Polylactic acid/kenaf and Polylactic acid/rice husk composites and reported that all the composites produced had higher modulus than the pure PLA matrix. They observed that flexural modulus increased from 3.4 to 4.5GPa and from 3.4 to 4GPa by adding kenaf fibres and rice husk fibres respectively into PLA matrix. As for flexural strength, it however decreased from 110MPa to 90MPa and 85MPa by adding kenaf and rice husk fibres respectively. The impact strength also had similar behaviour with flexural strength as it decreased from 37J/m for pure PLA to 34J/m and 30J/m when reinforced with kenaf and rice husk fibres respectively.

Furthermore, Petinakis *et al.,* (2009) reported an almost independent case for tensile strength on addition of wood-flour to PLA matrix. They suggested that a weak adhesion existed between the wood-flour particles and the matrix. However, they recorded about 95% improvement in tensile modulus in the micro-composites relative to the neat PLA matrix as the particles content increased but there was reduction in elongation at break of the composites. The micro-composites further showed an increase in the impact strength with increase in wood-flour content reaching a maximum value at 20% w/w of the particles beyond which the impact strength was almost constant.

In the study of Structure–morphology–mechanical properties relationship of polypropylene/lignocellulosic composites by Părpărită *et al.,* (2014), impact strength was found to decrease in composites relative to the matrix PP because the lignocellulosic components probably reduced the mobility of the polymer chains and by extension, the ability to absorb energy during fracture propagation. The hardness values of the composites were found to be higher than that of the pure matrix probably due to the formation of a more rigid surface of the

composites relative to the pure matrix. A reduction in impact strength of PP/Wood-flour composites relative to pure PP was also reported by Nourbakhsh *et al.,* (2010). Their reason for such was that the presence of wood particles in PP matrix caused points of stress concentrations which then led to provide sites for crack initiation.

2.7 Thermal properties of bio-composites

Thermal analysis of polymers is an important study used for understanding the structure–property relation and mastering the technology for industrial production of different polymeric materials, especially fiber-reinforced composites. Moreover, it is a useful technique to determine the thermal stability of the materials, especially with the processing conditions in mind (Doan *et al.,* 2007; Luz *et al.,* 2008). It is a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program (Salama *et al.,* 2012).

The manufacturing temperature and variety of applications in industry of bio-composites are influenced by the thermal characteristics of the agro-flour and biodegradable polymer.

Therefore, in thermogravimetric analysis (TGA), the mass of a sample in a controlled atmosphere is recorded as a function of temperature or time as the temperature of the sample is increased. It is used to measure the moisture content, thermal breakdown and thermal stability of bio-composites. Differential scanning calorimetry (DSC) is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. A number of important physical changes in a

polymer may be measured by DSC. These include the glass transition temperature (Tg), the crystallization temperature (Tc), the melt temperature (Tm) and the degradation or decomposition temperature (TD). Dynamic mechanical analyzer (DMA) on the other handhas been widely used for investigating the structures and viscoelastic behaviours of bio-composites so as to determine their storage modulus (*E*'), loss modulus (*E*'') and loss factor (tan δ). The response of the bio-composites to this treatment can provide information on the stiffness of the bio-composites (Sandler *et al.,* 1998; Kim *et al.,* 2005b; Salama *et al.,* 2012).

Studies on the dynamic mechanical and thermal analysis of untreated and alkali – treated jute fibres reinforced Vinylester was carried out by Ray *et al.,* (2002). They observed, at the end of their study that storage modulus of the composites increased with fibre loading but decreased with increase in temperature.

In a similar study by Doan *et al.,* (2007), the thermal, hydrothermal and dynamic behaviour of Polypropylene/jute fibre composites was investigated. They also observed an increase in storage modulus with increase in fibre content and a decrease in storage modulus with an increase in temperature. They found out that there was a significant difference caused by molecular weight of polypropylene, content of Jute fibre and maleic anhydride modified polypropylene.

Mohanty *et al.,* (2006) investigated the mechanical and dynamic mechanical analysis of HDPE/jute fibre composites and concluded that an increase in storage modulus was observed with increase in fibre loading but the damping properties decreased as compared to the unreinforced matrix.

Yu *et al.,* (2010) investigated the effect of fibre surface-treatments on the thermal properties of poly(lactic acid)/ramie composites and reported that the storage modulus of PLA composites, after the DMA process, was higher than that of the neat matrix. Also, they observed that composites with surface treatment exhibited higher storage modulus than those for the untreated. Furthermore, the TGA results showed that the PLA degradation took place in a single stage and it occurred at 328^{o}C. They also reported that thermal degradation of treated composites increased relative to that of the untreated while that of the untreated showed lower degradation temperature as compared to the neat PLA matrix. The DSC results showed an increase in Tg of the composites relative to PLA matrix and crystallization peaks became smaller as untreated fibres were added into the matrix which then disappeared with addition of treated ramie fibre.

Essabir *et al.,* (2013b) observed in their TGA results, three degradation peaks for almond shell (AS) particles in their study. The peaks were observed at 285-320^{o}C, 320-430^{o}C and 432^{o}C representing thermal decomposition of hemicellulose, cellulose and lignin respectively. They concluded that the addition of particles to polymer matrices reduce the overall thermal stability of resulting composites. In another study (Yussuf *et al.,* 2010), TGA results showed that thermal stability of PLA reinforced with kenaf fibre and rice husk reduced relative to the pure matrix. They also observed three stages of decomposition of the natural fillers at 30-150^{o}C which is due to moisture evaporation, 230-360^{o}C which is due to degradation of cellulosic substances and above 360^{o}C which is due to degradation of non- cellulosic substances.

In a study that investigated the effect of low-concentration alkali solution pretreatment on the properties of Poly(lactic acid)/bamboo particles (BP) composites, Qian *et al.,* (2013) reported an increase in degree of crystallinity of the composite produced after alkali treatment of BP. They

observed degree of crystallinity of untreated PLA/BP composite to be 6.07% while that of treated PLA/BP composite at 3 hours was 14.35%. They concluded that BP had a heterogeneous nucleation effect during the crystallization of PLA.

2.8 Water absorption of bio-composites

All polymer composites absorb moisture in humid atmosphere and when immersed in water. The water uptake of polymer composites depend on the hydrophilic nature of the polymers and fillers (Alvarez and Vazquez, 2004; Dhakal *et al.*, 2007).

Lignocellulosic based composites absorb water and cause undesirable dimensional changes in the final product. It may also cause rapid debonding and loss of structural integrity of the material's mechanical properties (Tserki *et al.,* 2006a). Three different mechanisms have been proposed for moisture penetration into composites. The main process is diffusion of water molecules inside the microgaps between the polymer chains. The others are the capillary transport of water into the gaps and flaws created at the interface of filler and matrix and then the diffusion of water molecules into the microcracks formed in the matrix arising from the swelling of fillers (Razavi-Nouri *et al.,* 2006; Dhakal *et al.,* 2007). Generally, the moisture diffusion in a bio-composites depends on factors which include volume fraction of fillers, voids, viscosity of matrix, humidity and temperature (Dhakal *et al.,* 2007)

A number of researches have been conducted on the effects of moisture absorption on bio-composites. Sreekala and Thomas (2003) investigated the effect of surface modification on water sorption behaviour of oil palm fibres. Their investigation was carried out at different

temperatures of 30, 50, 70 and 90^{o}C. They observed at the end of their study that the diffusion mechanism for all the systems were non-Fickian and treatments reduced the water uptake at all temperatures. They reported also that mechanical performance of the fibres decreased on water sorption. Razavi-Nouri *et al.,* (2006) investigated the mechanical properties and water absorption behaviour of chopped rice husk filled polypropylene composites. They concluded that water absorption of the composites increased with an increase in filler loading. The effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites at 25 and 100 ^{o}C was studied by Dhakal *et al.,* (2007). They concluded that the moisture uptake increased with increase in fibre volume fraction and the tensile and flexural properties of the composites decreased with increase in moisture uptake. Other studies on water absorption include those of Alvarez *et al.,* (2003) who investigated the mechanical properties and water absorption behaviour of MaterBi-Y/Sisal fibre composites; Yang *et al.,* (2006) who studied water absorption behaviour and mechanical properties of lignocellulosic filler–polyolefin bio-composites.

2.9 Biodegradation of bio-composites

Biodegradation of a polymeric material is a chemical degradation obtained by the action of naturally occurring microorganisms such as bacteria and fungi through enzymatic action into metabolic products (e.g., H_2O, CO_2, CH_4, biomass etc.) of microorganisms. The actions of microorganisms on polymers are influenced by two different processes:1. Direct action: The deterioration of plastics which serve as a nutritive substance for the growth of the microorganisms 2. Indirect action: The influence of metabolic products of the microorganisms,

e.g., discoloration or further deterioration (Mohan and Srivastava, 2010). Reports have it that microorganism colonization occurs when materials are exposed to the biological environment like soil and water. The reason being that the material may be susceptible to secondary factors that result in an enhanced biological activity. All phases of polymer-reinforced lignocellulosics, including the fillers, resins, and the filler–resin interfaces are susceptible to some type of microbial degradation **(**Abdulkhalil *et al.,* 2010**).**

In recent years, biodegradable polymers and plastics have gained increasing attention because of growing recognition worldwide of the need to reduce global environmental pollution. These biodegradable materials can be completely degraded into natural ecosystems such as active sludge, natural soil, lake and marine. Bio-composites therefore, are composed of biodegradable polymers which serve as matrices and cellulosic materials which act as the reinforcing fillers. There are many studies concerning the use of bio-fibre and bio-flour as reinforcements in biodegradable polymer bio-composite systems. These reinforcing materials can be naturally degraded by microorganisms and play a significant role in degrading natural organic substances in the ecosystem **(**Kim *et al.,* 2006**).**

Kim *et al.,* (2006) conducted a natural and aerobic compost soil biodegradation studies for PBS/rice husk flour (RHF) for 80 days. They observed that tensile strength of pure PBS decreased slightly after 10 days of exposure. They further observed that as filler content was increased, the tensile strength and impact strength of PBS and its bio-composites decreased more rapidly with passing days. The study showed that addition of RHF enhanced biodegradability of PBS due to the increased polymer surface created after the consumption of RHF by microorganisms. Conclusively, they observed that the reduction in mechanical properties as well

as weight loss of the bio-composites in the natural soil were lower than those observed in the compost soil because of the high temperature and humidity in the chamber.

Schlemmer *et al.,* (2009) prepared blends of Polystyrene (PS) and thermoplastic starch (TPS) by solvent casting method using glycerol and buriti oil as plasticizers and then subjected them to soil burial test for six months. After the soil burial test, TGA results showed that blends ofPS/TPS with glycerol or buriti oil presented less stages of thermal degradation than the original ones. Furthermore, PS/TPS blends with buriti oil presented even less degradation stages than blends with glycerol but more degradability compared to those of glycerol.

Abdulkhalil *et al.,* (2010) carried out a study to evaluate the effect of biodegradation on the mechanical properties (tensile, flexural, and impact) and the mass loss of oil palm fibre (OPF) filled recycled PP (RPP) composites using soil burial tests for 12 months. They observed a general decrease in the mechanical properties with an increase in exposure time and the effects of biodegradation increased with burial period. The tensile strength, tensile modulus, elongation at break and toughness of the composites decreased by 38, 37, 40, and 47% respectively while the flexural strength and modulus decreased by 40% and 37% respectively. There was also a 47% reduction in impact strength relative to the values obtained before the test. Furthermore, the masses of the composites, PP and RPP also decreased with exposure time. They explained that it could be due to the increase in water uptake of the composites during burial which led to swelling thereby causing micro-cracking of the composites resulting in a decrease in the mechanical properties and mass loss. The highest mass loss, at 12.7% after 12 months was observed in the composite samples while the lowest mass loss at 9.2% was exhibited by the PP samples whereas RPP showed a 10.7% reduction in mass over the same period.

Obasi (2012) produced bio-composite of HDPE/ corncob flour and tested the biodegradability by soil burial for 9 weeks. The result showed that, water diffuses into the composite samples in the soil which leads to swelling thereby enhancing biodegradation.

Sapuan *et al.,* (2013) studied the effect of soil burial on the mechanical properties of thermoplastic polyurethane (TPU)/ kenaf fibre (KF) composites. They reported that tensile strength of the composite decreased but flexural strength and modulus did not show any significant change after 80 days of soil burial. Also, they submitted that weather, humidity, temperature and degradation process contributed in the reduction of tensile strength and that TPU as a matrix needed more time to degrade.

2.10 Biodegradable composites based on poly (lactic acid)

Green composites use agricultural-based polymers and biodegradable plant-based fillers. They can be used in non-durable applications (a few years), products intended for short-term use (a few times) or indoor applications (like wood or automotive parts). Poly(lactic acid) (PLA) is a hydrophobic polymer prepared from renewable agricultural-based feed stocks which are fermented to lactic acid and then polymerized (Finkenstadt *et al.,* 2007ab). It can be extruded and injection moulded and is biodegradable in soil, compost or water and the degradation products of PLA are non-toxic to the environment. The use of renewable and biodegradable fillers is desirable to provide cost-competitive polymer composites**(**Finkenstadt *et al.,* 2007ab; Mohamed *et al.,* 2009**).** At the same time, PLA is nearly CO_2 neutral and reduces dependency on oil for the production of composite materials (Van den Oever *et al.,* 2010).

PLA is a sustainable alternative to petrochemical-derived products since the lactides from which it is ultimately produced can be produced on a mass scale by the microbial fermentation of agricultural by-products mainly the carbohydrate rich substances (Andreopoulos, 2014).

In the last years, different lignocellulosic materials have been employed in order to modify the properties of PLA. Up to now, the most studied natural fibre reinforcements for PLA are kenaf (Huda *et al.*, 2008a; Ochi,2008; Anuar *et al.*, 2012b),flax (Bax and Müssig,2008; Kumar *et al.*, 2010),hemp (Islam *et al.*, 2010; Baghaei *et al.*, 2013) bamboo (Okubo *et al.*, 2009; Kang and Kim, 2011), jute and wood fibres (Huda *et al.*, 2006; Ma and Joo, 2011; Memon and Nakai, 2013; Gupta *et al.*, 2014). Huda *et al.*, (2008a)worked on kenaf fibre reinforced PLA laminated composites prepared by compression moulding using the film-stacking method. Their goal was to evaluate the mechanical and thermal properties of the composites as a function of modification of the kenaf fibre using alkali and silane treatments. They found that both silane and alkali-treated fibre reinforced composite offered superior mechanical properties compared to untreated fibre reinforced composite. The alkali- followed by silane-treated fibre reinforced composite also significantly improved mechanical properties. It was found that standard PLA resins are suitable for the manufacture of kenaf fibre reinforced laminated biocomposites with useful engineering properties. The effects of the alkali treated natural fibres on the mechanical properties of PLA/hemp fibres were studied by Hu and Lim (2007). They fabricated completely biodegradable composites of PLA reinforced with short hemp fibres by using the hot-press method. The results showed that the composite with 40% volume fraction of alkali treated fibre possessed the best mechanical properties. The tensile strength, elastic modulus and flexural strength of the composite with 40% treated fibre were 54.6 MPa, 8.5 GPa, and 112.7 MPa respectively, which

are much higher than those of neat PLA. The composites have lower densities, which were measured to be from 1.19gcm^{-3} to 1.25gcm^{-3}. Bamboo fibre (BF) reinforced PLA composites were prepared in order to improve the impact strength and heat resistance of PLA (Tokoro *et al.,* 2008). Three different types of BF (short fibre bundle, alkali-treated filament and steam exploded filament) were extracted from raw bamboo by either sodium hydroxide treatment or steam explosion in conjunction with mechanical processing. Composite samples were fabricated by injection moulding using PLA/BF pellets prepared by a twin-screw extruding machine. Among them, the highest bending strength was obtained when steam-exploded filaments were put into PLA matrix. Impact strength of PLA was not greatly improved by addition of short fibre bundles. In order to improve the impact strength of PLA/BF composites, PLA composite samples were alternatively fabricated by hot pressing using medium length bamboo fibre bundles (MFB) to avoid the decrease in fibre length at fabrication. Impact strength of PLA/MFB composite significantly increased, in which long fibre bundles were pulled out from the matrix.

The effects of surface treatment of pineapple leaf fibres (PALF) on the performance of the natural fibre-reinforced renewable composites was studied for laminated composites prepared by compression moulding using the film stacking method (Huda *et al.,* 2008b). The results have shown that mechanical properties of the PLA laminated composites were remarkably improved after chemical treatment. It was found that both silane- and alkali-treated fibre reinforced composites offered superior mechanical properties compared to untreated fibre reinforced composites. Differential scanning calorimetry (DSC) results suggested that surface treatment of PALF affects the crystallization properties of the PLA matrix. Other fillers that have been used as reinforcements in PLA matrix for biocomposites production include Corncob (Faludi *et*

*al.,*2013a), Phormium tenax (De-Rosa *et al.,* 2011), Coconut shell powder (Chun *et al.,* 2012), Wood flour (Liu *et al.,* 2013) etc.

2.11 Agro-wastes or lignocellulosic materials as reinforcing fillers

Development of composites using agro-wastes or lignocellulosic materials as reinforcing fillers with thermoplastic polymers as matrices has been the focus of attention (Yang *et al.,* 2007). By embedding natural reinforcing fillers into bio-polymeric matrices; new materials called bio-composites are created and are still being developed. Since both components are biodegradable, the component as the integral part is also expected to be biodegradable. The natural fillers which are lignocellulosic in nature are widely distributed in the biosphere in the form of trees (woods), plants and crops (Mohanty *et al.,* 2000). Many researchers have studied different agro-wastes or lignocellulosic materials as reinforcement in different polymer matrices among which include the works of Kumar & Anandjiwala (2010) whoprepared flax fibre reinforced PLA by solution casting cum compression moulding method and conducted several studies. They compared this method with injection moulded method of the same composite constituents and found that injection moulded composite specimens showed almost the same tensile strength and elongation at break when compared to composite prepared from solution casting cum compression moulding method. But injection moulded flax/PLA showed higher modulus than solution cast cum compression moulded. Ashori and Nourbakhsh (2010)investigated the use of sunflower stalk, corn stalk and bagasse fibre in Polypropylene matrix. They concluded that bagasse fibre gave the best mechanical properties in the treated and untreated conditions. Çöpü *et al.,* (2007) studied the possibility of using hazelnut husk for particle board production. Their findings

indicated that hazelnut husk is a valuable renewable natural resource for particle board production and could be utilized as a substitute for wood in board production. Choi *et al.,* (2006)studied the use of rice husks – plastic composite for building materials and they found out that the apparent density of rice-husk – plastic composite increased with increasing binder content and the flexural strength was encouraging.

Elsaid *et al.,* (2011) studied the mechanical properties of kenaf fibre reinforced concrete. They evaluated the basic characteristics of kenaf fibre reinforced concrete (KFRC). They established suitable mixtures for KFRC with contents of 1.2% and 2.4%. They concluded that in order to maintain the workability of KFRC, the use of a cement rich mixture and coarse aggregates with a maximum diameter of 9.5mm is required. Premalal *et al.*,(2002) studied the effect of RH loading in the PP matrix. In terms of mechanical properties, Young's Modulus and flexural modulus increased whereas yield strength and elongation at break decreased with increase in filler loading.

The incorporation of RH as reinforced filler in PP has also been reported by Yang *et al.*,(2004, 2007). Their study revealed that tensile strength, notched and unnotched izod impact strengths were lowered by the addition of RH. However, tensile modulus increased with increasing RH loading. They also studied the effect of compatibilizing agent on mechanical properties of rice husk filled polypropylene composite. The tensile strengths of composites decreased as the filler loading increased but significantly improved with maleated Polypropylene. Both notched and unnotched izod impact strengths were almost the same with the addition of compatibilizing agent.

In another research, Yang, *et al.*,(2006) studied rice husk flour and wood flour filled polyolefin bio-composites to determine their physical and mechanical properties as a function of filler loading and type of filler. Polyolefin (HDPE, LDPE and PP) were used as matrix polymers. Thickness swelling and water absorption of bio-composites slightly increased while mechanical properties decreased as filler loading increased but their values remained negligible as compared with those of the wood-based composites and solid woods. With increased filler loading, the poor interfacial bonding between the filler and the matrix polymers caused the tensile strength and izod impact strength of the composites to be reduced. The poor interfacial bonding resulted in an increase in the number of micro voids causing increased water absorption. The use of compatibilizing agents had a positive effect on these bio-composites. With the addition of the compatibilizing agent, the interfacial bonding between the filler and the matrix polymer was greatly improved resulting in improved dimensional stabilities and water absorption behaviours. Thus, making them suitable for use in damp places such as the interior of bathrooms, wood decks, food packaging, etc.

Choi *et al.*,(2006) developed a new recycling method for rice husks and waste expanded polystyrene by combining both wastes. Rice husk-plastic composites were prepared for apparent density, water absorption, expansion in thickness, and dry and wet flexural strengths. The apparent density of the composites increased with increasing binder content and filler-binder ratio. Their flexural strengths and wet flexural strengths reached maximum at a binder content of 30% and a filler-binder ratio of 1.0. Their water absorption and expansion in thickness decreased with increasing binder content and filler-binder ratio. Due to high flexural strength and water resistance, these composites were proposed to be used as building material.

Other studies that used agro-wastes as fillers in polymer matrices for composites production include those of Salmah *et al.,* (2012) who used coconut shell powder to reinforce polylactic acid for bio-composites; Shehu *et al.,* (2014) who used palm kernel shell (PKS) particulate as reinforcement in polyester matrix; Viet *et al.,* (2012) who studied kenaf powder filled recycled high density polyethylene/natural rubber bio-composites; Ueberschaer *et al.,* (2006) who investigated the micromechanical properties of injection-moulded starch–wood particle composites; wood flour filled PLA was studied by Febrianto *et al.,* (2006); pine needle reinforced Urea-formaldehyde was studied by Singha and Thakur (2009) etc.

2.12 Studies on sorghum and its wastes

Studies on the use of sorghum or its wastes as reinforcement in polymer matrices have not been widely reported in literatures. The few available literatures on the use of sorghum and its wastes include; Chukwu *et al.,* (2011) whodetermined some physical and chemical properties of two cultivated varieties of guinea corn (brown and white).Physical properties (pericarp, colour, kernel size, 1000- Kernel weight and moisture content) andchemical composition (oil, crude fibre, ash and protein content) were determined. Reddy & Yang (2007)used sorghum leaves and stems to produce natural cellulose fibres with properties suitable for composites, textiles and other high-value fibrous application. The leaf and stem fibres produced are multicellular and have similar cellulose contents. They also found out that the breaking tenacity and elongation of the fibres are similar to that of natural cellulose fibres such as kenaf and corn stalk fibres. Finally,Yakubu *et al.,* (2010)studied the Physico-mechanical effects of surface modified sorghum stalk powder on reinforced rubber. The surface treatments given were with groundnut

oil, alkaline and 3-chloro-2-hydroxyl propyl trimethyl-ammonium chloride. At the end, they observed that the impact tests demonstrated critical loading effects for all the different samples and the hardness index did not show much difference between the untreated and treated fillers but generally, there was improvement from the use of the tertiary ammonium salt of cellulosic filler as reinforcing material for natural rubber.

Based on the aforementioned literatures and to the best of my knowledge, there is no work that has been carried out on the use of Guineacorn husks as reinforcement in polymer matrix; whether biodegradable or non-biodegradable. Therefore, production of completely biodegradable composites was carried out in this study using Poly(lactic acid) (PLA), a biopolymer and Guineacorn husks particulate (GHP).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 materials

The materials used during the course of this research include Poly(lactic acid)(PLA) grade 3051D from Nature works (USA), Polypropylene (PP) (Titanpro) homopolymer grade 6431 from Malaysia, Guineacorn husks particles (GHP) from Zaria, Nigeria, 3-Aminopropyltriethoxysilane (3-APS) cat.44,014-0 Lot: 12100 from Sigma Aldrich, Germany, Sodium hydroxide (NaOH) BP pellets, Acetic acid (glacial) 100% AOS,ISO, methanol, Plastic containers, Laboratory trays, Hand gloves, Nose masks, Biomax strong 100 from Nature Works (USA), Polyethylene glycol (PEG 1000) 81190 from Sigma Aldrich, Germany , Desiccator, Silica gel.

3.2 Equipment

The equipment used in the course of the research are listed in Table 3.1

Table 3.1: List of equipment

S/No.	Equipment	Model	Model Number
1.	Laboratory sized mini-crusher	NA	NA
2.	Precision weighing balance (0.00001g)	precisa	NA
3.	Brabender Single Screw Extruder	837420	083002
4.	Granulator (Pelletizer)	881207	088051
5.	Injection Moulding Machine	BOY 22M	38345
6.	Binder Humidity Chamber	KBF240	05-91400
7.	Micromeritics Helium-gas pycnometer (Accupuc1330)	133/3401/00	3604
8.	Impact tester	Zwick	74864
9.	100KN Instron Universal testing machine	5982	5982R4262
10.	Zeiss Scanning Electron Microscope (SEM)	SUPRA	35VP
11.	Scanning Electron microscope	JOEL-JSM	5600 series
12.	Mitutoyo Universal Hardness testing machine	HR-521/521L	400211202
13	Mettle Toledo Differential Scanning Calorimetry	Star^{e}	NA
14.	Perkin Elmer Thermogravimetric Analysis	Pyris6	NA
15.	Mettle Toledo Dynamic Mechanical Analyser	DMA861^{e}	NA
16.	Shore D Hardness tester	TECLOCK	GS-702G

All the laboratory work/procedures were carried out using the facilities provided by the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Malaysia.

3.3 Methods

3.3.1 Preparation of Guineacorn(*Sorghum bicolor*) husks particulates (GHP)

The Guineacorn (*Sorghum bicolor*) stalk after the removal of the edible cereals were gathered from the local farmers in Zaria, Kaduna State, Nigeria after the harvest period (November-December) and the husks removed manually from the stalks. The husks were then washed thoroughly with water and detergent solution to remove all forms of dirt including stones, dried and subsequently ground in a mini crusher having a sieve of 0.5mm attached to its outlet. The particulates were then oven dried at 105^{o}C for 24 hours and then stored before embarking on further processes. To remove volatile materials, the particulates were soaked in hot water for 24hrs, washed and dried in air and subsequently oven dried at 105^{o}C for 24 hours. The particulates were designated as untreated (UNTRD). The untreated particulates were treated with sodium hydroxide (NaOH) solution, 3-Aminopropyltriethoxysilane (3-APS) coupling agent and a combination of both treatments. The untreated particulates were used as control in this study.

3.3.1.1 Alkali (ALK) treatment

The untreated (UNTRD) particulates were treated with 5% sodium hydroxide (NaOH) solution for 24hours at room temperature after which it was washed with distilled water until all the

NaOH was eliminated (Mishra *et al.*, 2003). A little quantity of acetic acid was added to help in the quick neutralization process. This was confirmed by using a pH meter which showed neutral state of 7.2. After washing, the particulates were kept in air for 2 days to dry before oven drying at 105^{o}C for 6 hours.

3.3.1.2 Silane (SIL) treatment

The untreated particulates were treated with 3% of 3-Aminopropyltriethoxysilane (3-APS)silane coupling agent. This was achieved by first hydrolysing the silane coupling agent in a methanol/water mixture in the ratio 50/50. The pH of the mixture was adjusted to 4.5 by adding a small quantity of acetic acid. The whole mixture was stirred before introducing the particulates into the mixture and left for 3hrs. The particulates were then removed, washed and kept in air for 2 days before oven drying at 105^{o}C for 6hours.

3.3.1.3 Combination of Alkali and Silane (ALKSIL) treatment

The untreated particulates were first treated with sodium hydroxide solution as described in section 3.3.1.1 followed by treatment with silane coupling agent as described in section 3.3.1.2.After the treatments, the particulates were placed in plastic bags, sealed and stored in a desiccator before further processing.

3.3.2 Compounding of composite materials

Four formulations consisting of 3 Poly(lactic acid)(PLA) and 1Polypropylene (PP) were prepared for compounding; two PLA formulations were blended with plasticizers,which included Biomax strong 100 (BM) and Polyethylene Glycol (PEG 1000) which were 5% and 10% by weight of PLA respectively while the last formulation was without a plasticizer. The Guineacorn husks particulates (GHP) (untreated and treated) were oven dried at 80^{o}C for 6hrs, the PLA were also dried at 55^{o}C for 4hrs while the PP was used directly without drying. The compositions of the samples are shown in Table 3.2.

The compounding was accomplished for all the formulations using a Brabender single screw extruder with the following temperature profiles from hopper to nozzle:

i. PLA/Biomax (PLABM)/GHP: 160^{o}C/ 175^{o}C/ 175^{o}C/ 165^{o}C; screw speed 40rpm
ii. PLA/GHP (PLAP) : 160^{o}C/ 175^{o}C/ 175^{o}C/ 165^{o}C; screw speed 40rpm
iii. PLA/PEG(PLPG)/GHP: 170^{o}C/180^{o}C/180^{o}C/175^{o}C; screw speed 60rpm
iv. PP/GHP : 180^{o}C/ 190^{o}C/ 190^{o}C/ 185^{o}C; screw speed 40rpm

The mixture of resin and particulates were introduced into the hopper of the extruder for compounding and subsequently extruded as long strands. The PLPG formulation was extruded at a screw speed of 60rpm because of the viscous nature of PEG 1000 and requires a higher speed for extrusion. The extrudates were collected in a water tank with continuous flow of water which served as a cooling medium. The extrudates were then pelletized using a Brabender granulator. PLA samples were dried in the oven at 55^{o}C before while the PP samples were dried at 60^{o}C before injection moulding.

3.3.3 Injection moulding

The pellets were introduced into a BOY 22M injection moulding machine to produce the various standard test samples of tensile, flexural and impact according to ASTM D638,790 and 256 respectively. The temperature profiles used for the different formulations were as follows:

i. PLA/Biomax(PLABM)/GHP: 145 ^{o}C /180 ^{o}C /180 ^{o}C /165 ^{o}C

ii. PLA/GHP (PLAP) : 145 ^{o}C /180 ^{o}C /180 ^{o}C /165 ^{o}C

iii. PLA/PEG(PLPG)/GHP: 185^{o}C/190^{o}C/190^{o}C/180^{o}C

iv. PP/GHP : 190^{o}C/ 200^{o}C/ 200^{o}C/ 180^{o}C

Injection speed of 45: 53: 29 mm/s, injection pressure was 50bar, back pressure was 5 bar, mould temperature was 30 ^{o}C and cooling time was 30 seconds. After moulding, all the test samples were conditioned in a Binder KBF240 Humidity chamber for 40hrs at 23 ^{o}C and 50% relative humidity prior to testing.

Table 3.2: Compositions of the investigated untreated and treated samples

S/No.	**PLAP/GHP**	**PLABM/GHP**	**PLPG/GHP**	**PP/GHP**
1.	100/0	100/0	100/0	100/0
2	90/10	90/10	90/10	90/10
3	80/20	80/20	80/20	80/20

4	70/30	70/30	70/30	70/30
5	60/40	60/40	60/40	60/40

3.4 Physical properties

3.4.1 Density measurement

The guineacorn husks particulates (GHP), PLAP/GHP, PLABM/GHP, PLPG/GHP and PP/GHP composites were subjected to density measurements using a Helium-gas pycnometer. Each of the sample was weighed and introduced into a $10cm^3$ capacity sample holder of the pycnometer which was then inserted into the machine and tightly covered. The measured weigh of each sample to be tested was recorded in the machine before pressing the start button on the machine. On starting the machine, a number of cycles involving purging and determination of volume of the samples was initiated. This was done for about 15minutes before the calculated densities were displayed on the screen of the machine. 3 values were given for each sample and the average values were recorded.

3.4.2 Water Absorption Test

Water absorption tests were carried out according to ASTM D 570 for all the composites produced.Before the immersion, the specimens were oven dried at 50^oC for 24hrs, cooled and weighed with a weighing balance to the nearest 0.0001g. The initial weights (W_1) of the samples after drying were recorded. Then, they were submerged in various containers with distilled water at room temperature for 24hours. At the end of this period, the specimens were removed, wiped with a dry clean cloth and immediately weighed to get the wet weight (W_t). The specimens were

weighed every day for two weeks then subsequently every day except Saturdays and Sundays for the next two weeks making a total of 30 days.

The percent increase in weight during immersion was calculated using the following equation:

$$\% \text{ water absorbed} = \frac{Wt - W1}{W1} \times 100 \quad (3.1)$$

Where W_t is the weight of the samples at time t of immersion and W_1 is the initial weight.

Tensile, flexural and impact samples were used for the test after which the various appropriate mechanical testing were carried out on the specimens.

3.4.3 Soil Burial Test

Biodegradation test was performed on all the produced composites using the simple soil burial test and weight loss method was used for evaluation. Before the burial, all the samples were properly dried in an oven at 50^{o}C for 24hrs and their initial weights (W_0) were recorded. The specimens were buried in the normal soil in the garden within the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Malaysia for a period of 3 months. After the completion of the test, the specimens were dug out and washed by using running water in order to remove the sand from the surface of the samples, and all specimens were dried in the oven at a temperature of 55^{o}C for 12hrs before recording their final weights (W_1). The weight losses of the buried samples were calculated and evaluated using the following(Yussuf *et al*., 2010):

Weight loss (%) = $\frac{w0-w1}{w0}$ x 100 (3.2)

Where W_0 and W_1 are weights of specimens before and after the burial test respectively.

3.5 Mechanical testing

3.5.1 Tensile test

According to ASTM (D638), dumbbell shape (Type IV) specimen is needed for reinforced composite testing. The testing was done in a standard laboratory atmosphere of 23°C ± 5°C and 50 ± 5 percent relative humidity. Each of the specimen (Figure 3.1) measuring 146.49 X 9.96 X 3.52mm was positioned vertically in the grips of the testing machine. The grips were tightened firmly to prevent any slippage with gauge length kept at 77mm. As the tensile test starts, the specimen elongates; the resistance of the specimen increases and is detected by a load cell. This load value was recorded until a rupture of the specimen occurred. Instrument software (Bluehill) provided along with the equipment was used to calculate the tensile properties such as Tensile strength, tensile modulus and elongation at break. The test was performed using a 100KN capacity Instron 5982 Universal Testing Machine at a crosshead speed of 2mm/min for PLA and its composites and 10mm/min for PP and its composites and a gauge length of 77mm. Three samples were tested for each composition and formulation and the average value for each was recorded. It was noticed that the unreinforced PP sample did not fracture after the maximum stress was reached.



Figure3.1: Dumbbell specimen for tensile test

3.5.2 Flexural test

3-point bending test otherwise called flexural test was performed on the specimens measuring 126.49 X 12.90 X 3.05mm according to ASTM D790 using Instron 5982 Universal Testing Machine at a crosshead speed of 5mm/min for PLA and its composites and 20mm/min for PP and its composites and a span length of 80mm. At the commencement of the test, the specimens were rested on the two supports of the bottom fixture, perpendicular to the loading nose. Then,

the upper anvil was manually adjusted just barely touching the composite bar by turning the knob attached to the machine. The test was subsequently run and automatically stopped at rupture or when there was a maximum deflection of the sample. It was noticed that most of the PP samples did not fracture like the PLA samples.

Three samples were tested for each composition and formulation and the average values were recorded. Flexural strength and flexural modulus were evaluated using the Bluehill software.



Figure 3.2: Flexural test specimen

3.5.3 Izod impact test

Unnotched Izod impact test was conducted on all the composite samples produced according to ASTM D256 with a Zwick impact testing machine. A 7.5J hammer was used for the samples.

The dimension of the samples was 63X12.9X3.05mm. Three samples were used for the impact test for all the composites produced and the average values were recorded.



Figure3.3: Impact test specimen

3.5.4 Hardness test

For the purpose of this study, Durometer hardness test was performed on PP and PP composites to measure the relative hardness of the materials. The method was based on the rate of penetration of a specified indenter forced into the material under specified condition and the sample was placed on a flat surface. The pressure foot of the instrument was pressed on the specimen, making sure it was parallel to the surface of the specimen. Each sample was subjected

to 10 Durometer hardness reading at different positions on the sample base. The average value for each sample was recorded in `accordance to ASTM D2240.

Furthermore, a Mitutoyo Universal Hardness testing machine was also used to test the hardness of the PLA and its composites. The surfaces of injection moulded specimens were smooth enough so there was no surface preparation before carrying out the test. The test type was Rockwell hardness with R scale (HRR), the indenter used was ¼ inch steel ball with minor and major loads of 10 and 60Kgf respectively. The samples were placed on the anvil and the load was applied by adjusting the knob of the machine down to effect a penetration on the specimen after which it was released from the surface of the specimen. The hardness values were read directly from the screen of the machine.

3.6 Thermal analyses

3.6.1 Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC 6 differential scanning calorimeter was the DSC instrument used to characterize the samples. The instrument was computercontrolled and the calculations were performed using Star^{e} software. All the analyses wereperformed under nitrogen flow (20 ml/min). The PLABM/GHP Composite samples were analysed from 25 to 200 ^{o}C at a rate of 10^{o}/min. The samples were heated, cooled, and reheated under the same conditions. Only the second heating scan was used to determine the melting enthalpies and temperatures. The %crystallinity (%Xc) of

PLABM and its composites was evaluated using the following equation:

$$\%Xc = \left(\frac{\Delta Hm}{\Delta H^{\circ}\left(1-\frac{\%wt\ filler}{100}\right)}\right) * 100 \qquad (3.3)$$

Where ΔHm is the melting enthalpy (from second heating scan), ΔH^0 is the melting enthalpy of a 100% crystalline PLA (93.0J/g) (Battegazzore *et al.*, 2014) and %wt filler is the filler weight percentage.

3.6.2 Dynamic mechanical analysis (DMA)

A Mettler Toledo DMA 861^e was used in determining the thermo-mechanical properties of all the PLABM/GHP Composite samples. Impact test samples were used for the analysis in dual cantilever mode and the parameters were as follows:

Frequency 1 Hz

Amplitude 20 µm

Temperature range -20 to 140 °C

Heating rate 5 °C/ min

Preloading force 1 N

Sample length 63mm

Sample width 12.90mm

Sample thickness 3.05mm

3.6.3 Thermogravimetric analysis (TGA)

The TGA analyses were carried out in a Perkin-Elmer Pyris 6 TGA thermogravimetric analyser. Nitrogen was used as the purge gas at the rate of 20 ml/ min. The samples (5-10 mg) were heated from 30 to 600 ºC at a rate of 10 ºC/ min. The instrument was computer controlled and the calculations performed on the curves were done using Pyris6 software.

3.7Scanning Electron Microscopy (SEM)

The tensile fractured surfaces of the PLA and PP and their composites were studied by using SUPRA^{TM} 35VP and JOEL-JSM 5600 series Scanning Electron Microscopes (SEM). The specimens were sputter coated with a thin layer of gold to avoid electrostatic charging during sample examination. And also the outer surface of the composted samples (soil buried samples for biodegradability test) and water absorbed samples were evaluated and assessed.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Filler Characterization

4.1.1 Density

The results for the density values of GHP (treated and untreated) are as shown in Figure 4.1.

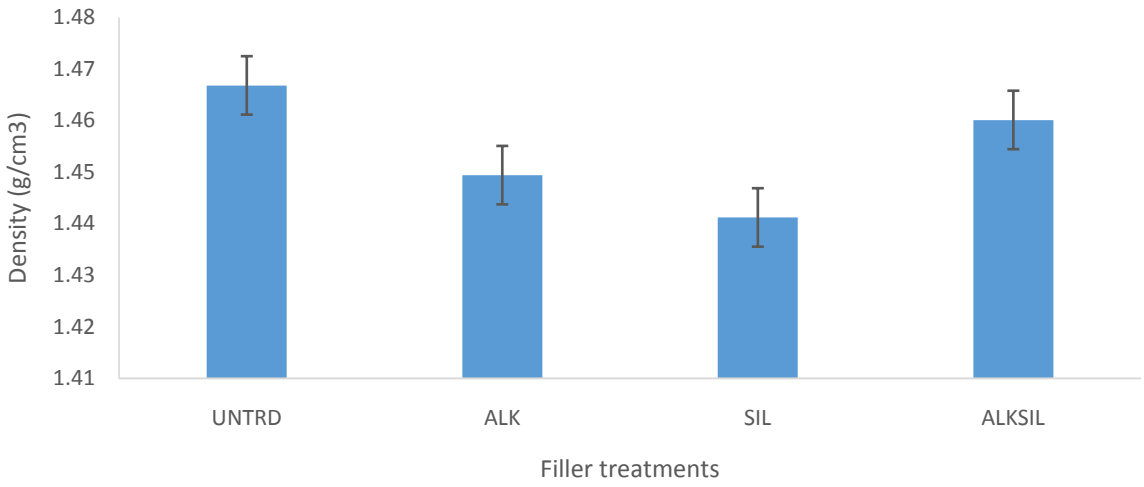


Figure 4.1: Density of Guineacorn Husks Particulates against various treatments

From Figure 4.1, it was observed that the UNTRD GHP had the highest density value of 1.47g/cm^3. The treated GHP on the other hand, had slightly lower density values of 1.46g/cm^3, 1.45g/cm^3 and 1.44g/cm^3 for ALKSIL, ALK and SIL treatments respectively. The reduction of density with surface treatments to the tune of 0.46%, 1.19% and 1.75% respectively are not so significant.

The density values obtained in this study which lied between 1.44 and 1.47g/cm^{3}were higher than those of some lignocellulosic fillers such as Rice husk flour (RHF) with a density value of 1.30 g/cm^3 (Rosa *et al*., 2009), 1.068 g/cm^3 for wood apple shell particulate (Ojha *et al*., 2014) but lower than other lignocellulosic fillers such ascoconut shell particulates with a density value of 1.60 g/cm^3 (Bhaskar and Singh, 2013; Ojha *et al*., 2014), 1.5- 1.6 g/cm^3 for cotton fibres , 1.5 g/cm^3 for abaca, flax and sisal fibres (Bledzki and Gassan, 1999; Bledzki and Jaszkiewicz, 2010; Gil-Castell *et al*., 2014) and 1.524 g/cm^3 for Date palm fibres (Abdal-hay *et al*., 2012).

The reduction of density values with surface treatment containing alkali could be attributed to the fact that alkali treatment removes surface impurities and makes the surface of fibre rough (Yu *et al*., 2010; Thao tran *et al*., 2014). The reduction of density with silane treatment could be attributed to the removal of waxes from the filler as reported by Thao tran *et al*., (2014). The reduction of density value with surface treatment has been reported by Suardana *et al*., (2011) who stated that the density value of untreated hemp fibre as 1.249 g/cm^3 but on treatment with NaOH and silane coupling agent, the density values reduced to 1.127 g/cm^3 and 1.150 g/cm^3 respectively.

4.1.2 Thermogravimetric Analysis (TGA)

The thermal analysis curves together with their derivative (DTG) curves which show the stages of decompositions and maximum decomposition temperatures are shown in Figures 4.2a and 4.2b and the TGA data are summarized in Table 4.1.

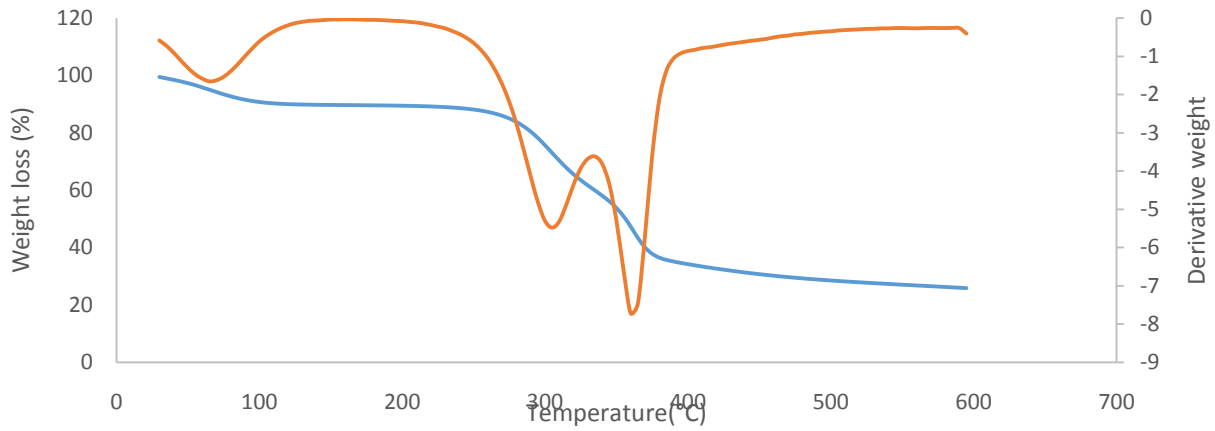


Figure 4.2a: Weight loss and derivative weight of UNTRD GHP against temperature

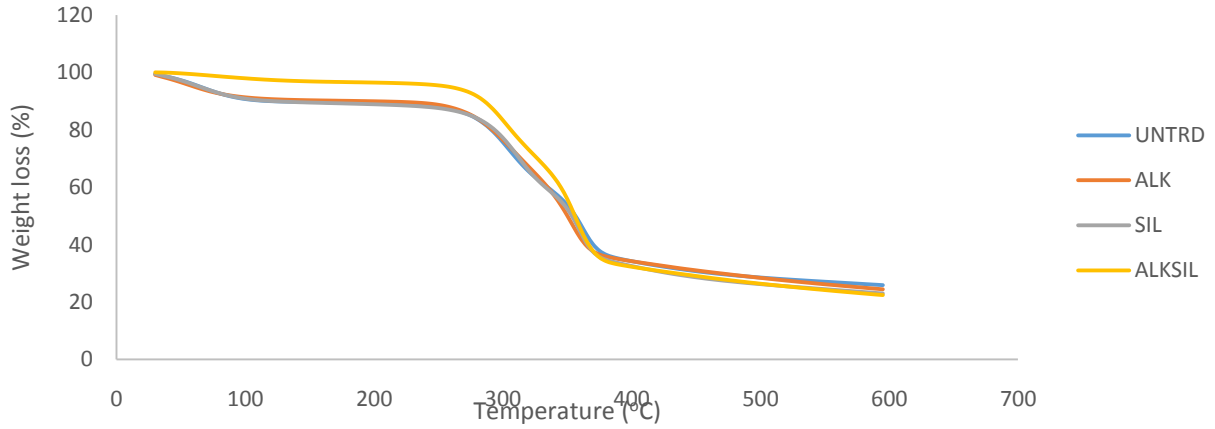


Figure 4.2b: Weight loss of treated and untreated GHP against temperature

Table 4.1: Summary of TGA data for GHP

GHP	Onset (°C)	Endset (°C)	Dmax (°C)	Residue (%)
UNTRD	250	380	360	25.82
ALK	250	375	355	24.37

SIL	265	370	360	22.93
ALKSIL	260	380	355	22.45

TGA is used in obtaining the thermal stability of fillers at their processing temperatures (Battegazzore *et al*., 2014). The TGA and DTG curves (Figure 4.2a) show that the GHP exhibited 3- step decomposition. This was also reported for other fillers such as Kenaf fibre and Rice husks (Yussuf *et al*., 2010), Cocoa pod husk (Chun *et al*., 2013ab) and Coffee ground and Bamboo flour (Baek *et al*., 2013).

The decomposition stages include:

i. $30^{o}C$ – $110^{o}C$ - due to the evaporation of moisture content in the filler (Norashikin and Ibrahim, 2009 ;Yussuf *et al*., 2010; Baek *et al*., 2013; Chun *et al*., 2013a; Essabir *et al*., 2013a)

ii. $240\ ^{o}C$ – $340\ ^{o}C$ – due to the decomposition of cellulosic substances such as cellulose and hemicellulose (Yussuf *et al*., 2010; Baek *et al*., 2013; Chun *et al*., 2013a).

iii. Above $340\ ^{o}C$ – due to the decomposition of non-cellulosic substances in the filler (Yussuf *et al*., 2010; Baek *et al*., 2013).

From the combined curves (Figure 4.2b), it was observed that the ALKSIL treated GHP exhibited the highest thermal stability while the others which include the UNTRD, ALK and SIL treated GHP overlapped.

The derivatives of the thermogravimetric curves (DTG) of treated and untreated GHP show the main decomposition temperatures of the GHP (dmax) presented in Table 4.1. It indicated that GHP, whether treated or untreated is stable up to 340 ^{o}C with a maximum rate of decomposition at 350^{o}C.

From Table 4.1, the onset decomposition temperature of UNTRD and ALK treated GHP was 250^{o}C while it was 265 ^{o}C for SIL treated GHP and 260 ^{o}C for ALKSIL treated GHP. Also, the maximum decomposition temperature for UNTRD and SIL treated GHP was 360 ^{o}C while that of ALK and ALKSIL treated GHP was 355^{o}C.

The residues or ash contents at 600 ^{o}C was highest for the UNTRD GHP with a value of 26% while the least residue was obtained for the ALKSIL treated GHP with a value of 22% . The reason for relative high residue for the UNTRD GHP and lower values for the treated GHP could be due to the presence of impurities with regards to the UNTRD that were probably removed with various surface treatments.

4.1.3 Morphological study of GHP

The SEM images for both the treated and untreated GHP fillers are shown in Plates I a-I d.

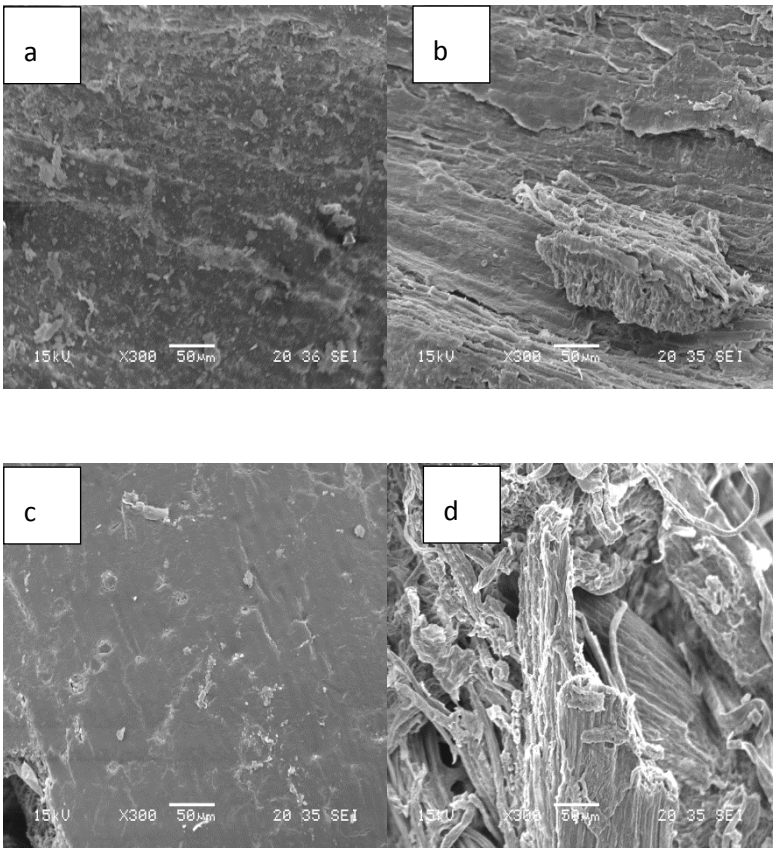


Plate I: SEM micrographs of treated and untreated GHP(a). UNTRD (b). ALK treated (c). SIL treated (d). ALKSIL treated

From Plate Ia which shows the SEM image for UNTRD GHP, it was observed that the filler exhibited some scaly substances that could be waxes which cover the surface of the filler. The scaly covering was said to be a membrane layer called pellicle (Suardana *et al*., 2011).

The SEM image for ALK treated GHP (Plate Ib) showed a rough and cleaner image as compared with the UNTRD. Treatment with alkali removes surface impurities such as lignin, pectin, hemicellulose, oils covering the external surface of the filler cell wall and makes the surface of fillers rougher (Kushwaha and Kumar, 2009; Yu *et al*., 2010; Suardana *et al*., 2011; Senawi *et*

al., 2013; Thao tran *et al*., 2014). The membrane that was observed in the UNTRD GHP was removed after alkali treatment.

The SIL treated GHP in Plate Ic looks a bit similar to that of UNTRD GHP but with little difference which could be as a result of removal of waxes from the surface of the GHP. As reported by Thao tran *et al*., (2014), silane treatment removes waxes from husks surfaces which does not really lead to very noticeable change of the GHP surface after SIL treatment.

Suardana *et al*., (2011) reported that SIL treatment resulted in the coating of natural filler surfaces as it was deposited on the filler surface which suggests the similarity between the UNTRD and SIL treated GHP.

Plate Id shows the SEM image of ALKSIL treated GHP. The image showed a clean, rough as well as a coated surface which resulted from the alkali treatment followed by silane treatment.

4.2 Composites Characterization

4.2.1 Physical properties

4.2.1.1 Density

Figures 4.3 to 4.6 and Tables A1 to A4 in appendix A are the density results for the various composites formulations produced.

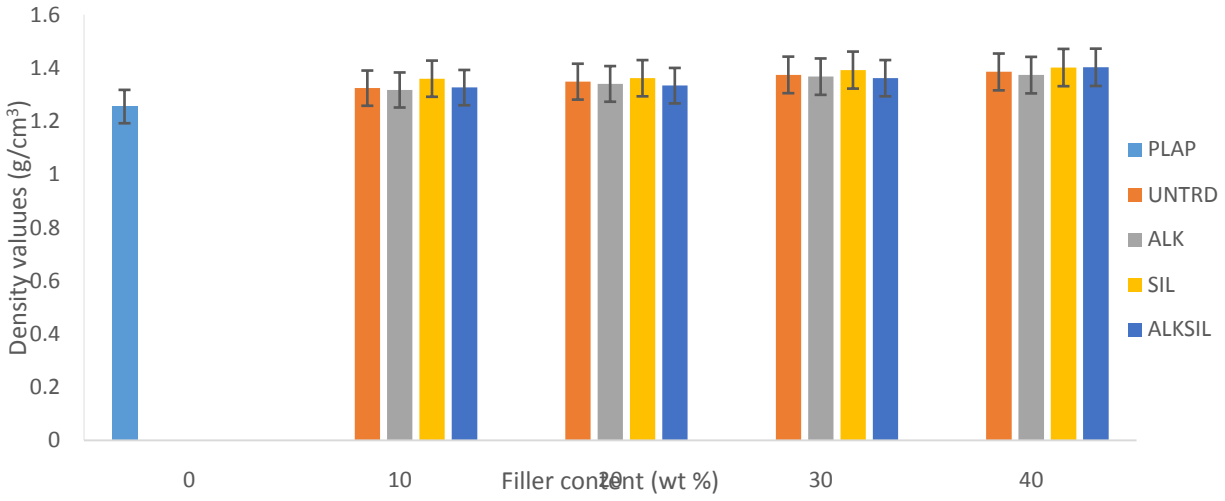


Figure 4.3: Density of PLAP/GHP against filler content for various treatments

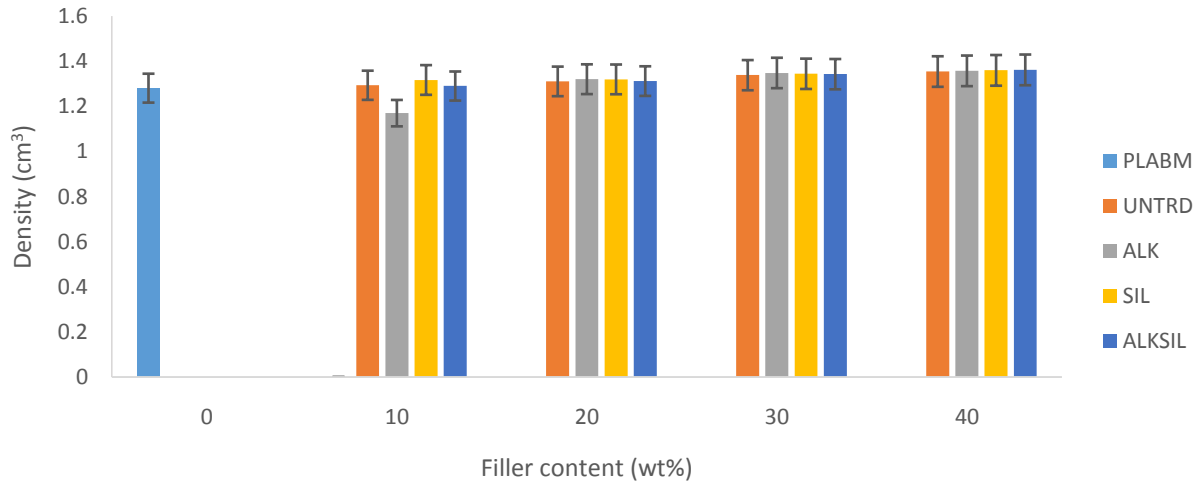


Figure 4.4: Density of PLABM/GHP against filler content for various treatments

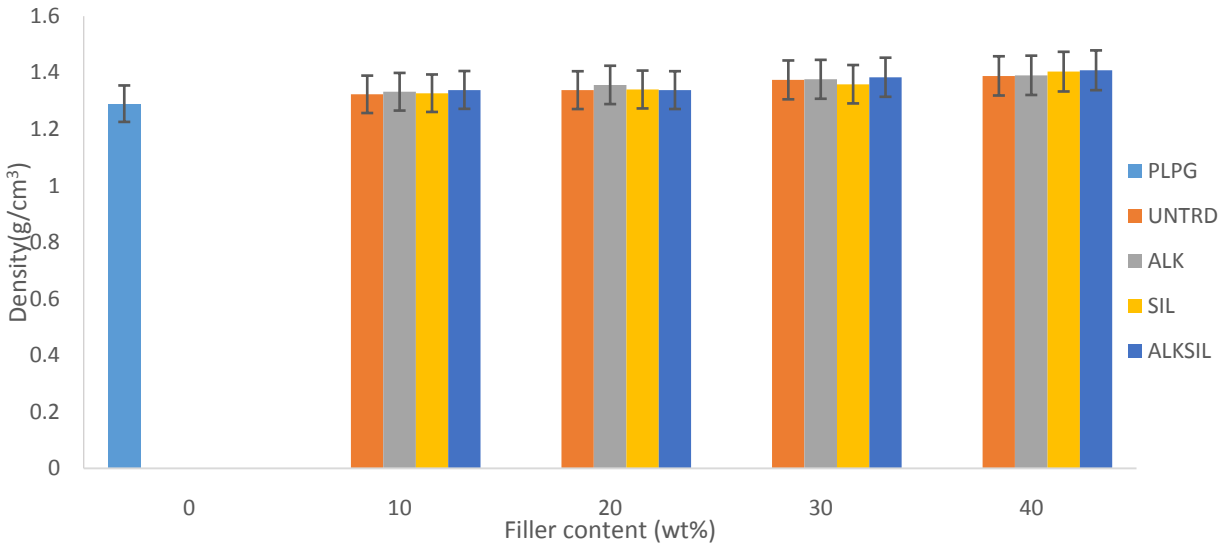


Figure 4.5 Density of PLPG/GHP against filler content for various treatments

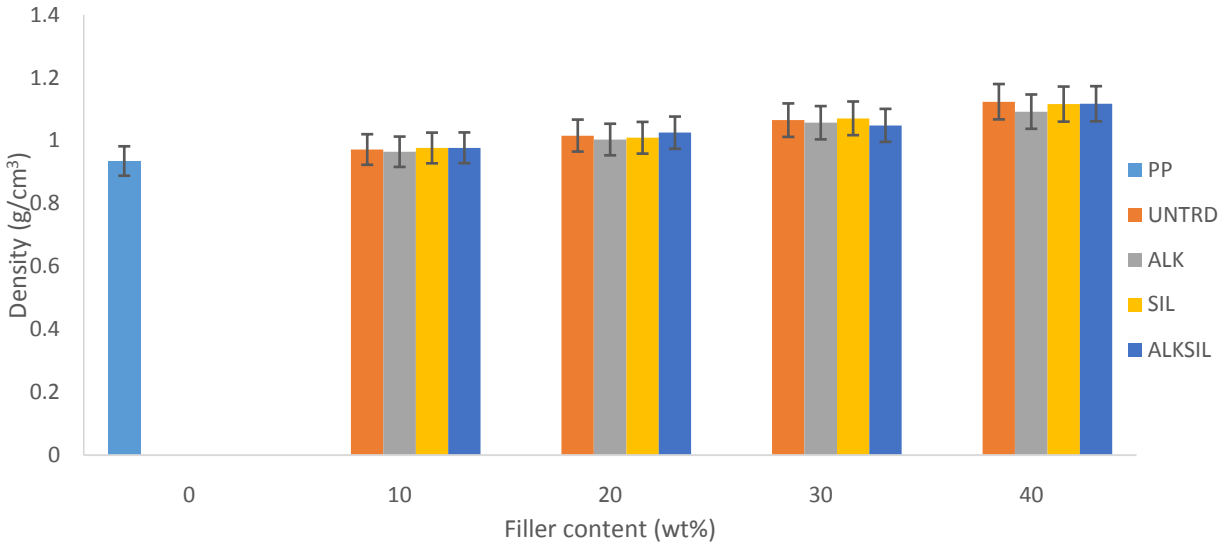


Figure 4.6: Density of PP/GHP against filler content for various treatments

The results showed that the density values for the various composites were higher than those of their various matrices. Also, the density values increased with filler loading. The increase in

density values of composites with filler contents over that of their various matrices was due to the higher density values for the fillers compared to that of the matrix (Pilla *et al*., 2008; Ojha *et al*., 2014).

The results for the density of PLAP/GHP composites in Figure 4.3 indicates that the density value for unreinforced PLAP was 1.29g/cm^3 and this increased with filler loading for both the treated and untreated composites. The higher density of composites over that of the matrix was expected since the filler had higher density than the matrix. It was also observed that for the same filler content, the density values for SIL treated composites were the highest while the least density values were exhibited by ALK treated composites.

The results for the density of PLABM/GHP composites,Figure 4.4shows that the matrix exhibits a density of 1.28g/cm^3 and this value increased with filler loading for all the composites.At 10% filler content, SIL treated composite had the highest density value of 1.32g/cm^3 while the ALK treated composite exhibited the least value of 1.17g/cm^3. At 40% filler content, ALKSIL treated composites had the highest density value of 1.36g/cm^3 while that of UNTRD composite had the least value of 1.35g/cm$^{3.}$

The density of PLPG matrix was 1.29g/ cm^3 and this increased with filler loading as presented in Figure 4.5. There were different density values recorded for different treatments at all filler loading but the ALKSIL treated composite at 40% filler content exhibited the highest density value of 1.41g/cm$^{3.}$ Other density values for the same filler content (40%) were 1.40g/cm^3, 1.39g/cm^3 and 1.39g/ cm^3 for SIL, ALK and UNTRD composites respectively.

The density values for PP and its composites lied within the range of 0.96 and 1.12g/ cm^3 Figure 4.6. The results indicated that the density values for PP and its composites were very much lower than those of the various PLA matrices and their various composites.

The density results in Figures 4.3 to 4.6 showed that the unreinforced matrices had density values of 1.29g/cm^3,1.28g/cm^3,1.29g/$cm^3$and 0.94g/cm^3 for PLAP, PLABM, PLPG and PP respectively. Within the PLA matrices, PLABM exhibited the least density value of 1.28g/cm^3 probably due to the influence of Biomax strong which is very light.

The reported density values for PLA from other studies were 1.24g/cm^3 (Lee *et al*., 2009; Faludi *et al*., 2013ab), 1.25g/ cm^3 (Huda *et al*., 2008b; Fortunati *et al*.,2010; De-Rosa *et al*., 2011) while the density value reported for PP matrix was 0.9g/cm^3 (Premalal *et al*., 2002; Essabir *et al*., 2013b), 0.91 g/cm^3 (Yang *et al*., 2006; Rosa *et al*., 2009), 0.905-0.917 g/cm^3 (Părpăriță *et al*., 2014) and 0.95g/cm^3 (Ashori and Nourbakhsh, 2010).

The density values obtained for PLA and its composites from this study showed that they lied within the range of 1.2 and 1.4 g/cm^3. Surface treatment led to slight increase in density values of the composites in some cases which may lead to higher compatibility between the filler and matrix thereby reducing the amount of voids in the end product. Fillers generally have low density which makes it possible to produce composite of low weights at low cost (Castellano *et al.*, 2004) and low weights are among the advantages of composites materials (Kim *et al*., 2007).

Essentially, the composites produced in this study were light weight which would be very useful in applications requiring low weight (Rosa *et al*., 2009).

4.2.2 Mechanical Properties

4.2.2.1 Tensile Strength

The results for the tensile strengths for all the formulations of composites are presented in Figures 4.7 to 4.10 and Tables B1 to B4 in Appendix B.

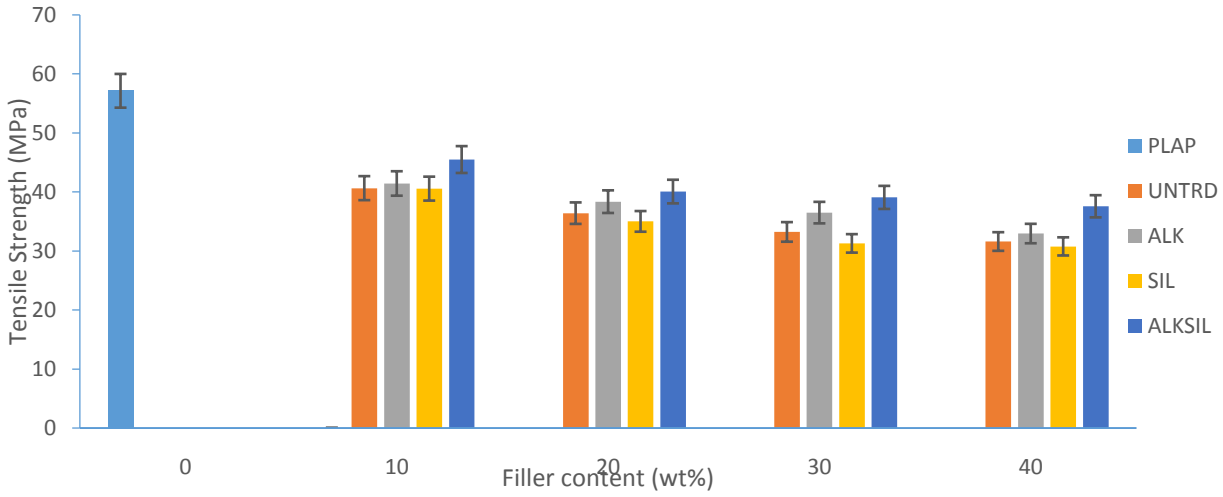


Figure 4.7: Tensile strength of PLAP/GHP Composites against filler content for various treatments

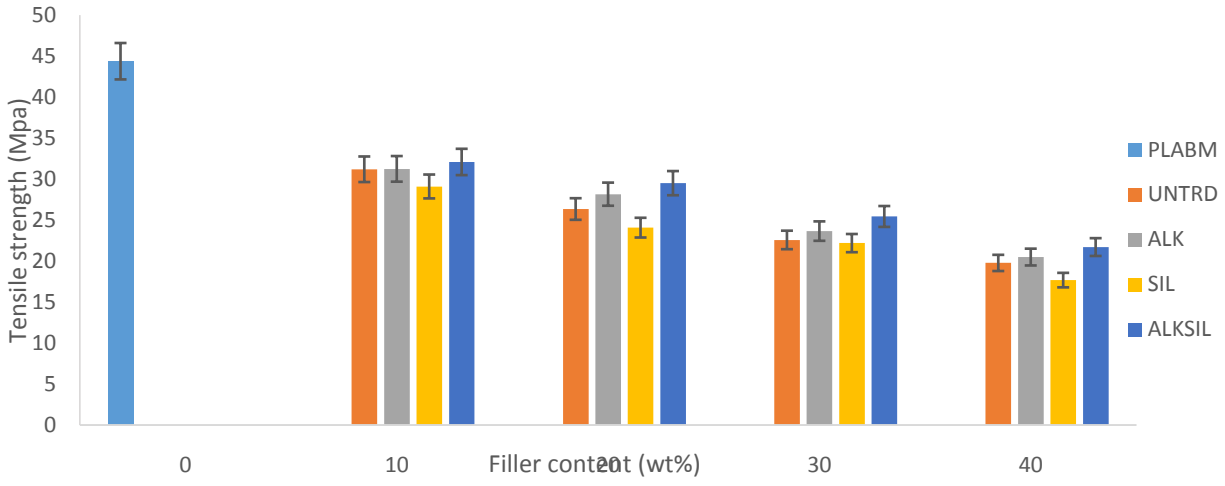


Figure 4.8: Tensile strength of PLABM/GHP Composites against filler content for various treatments

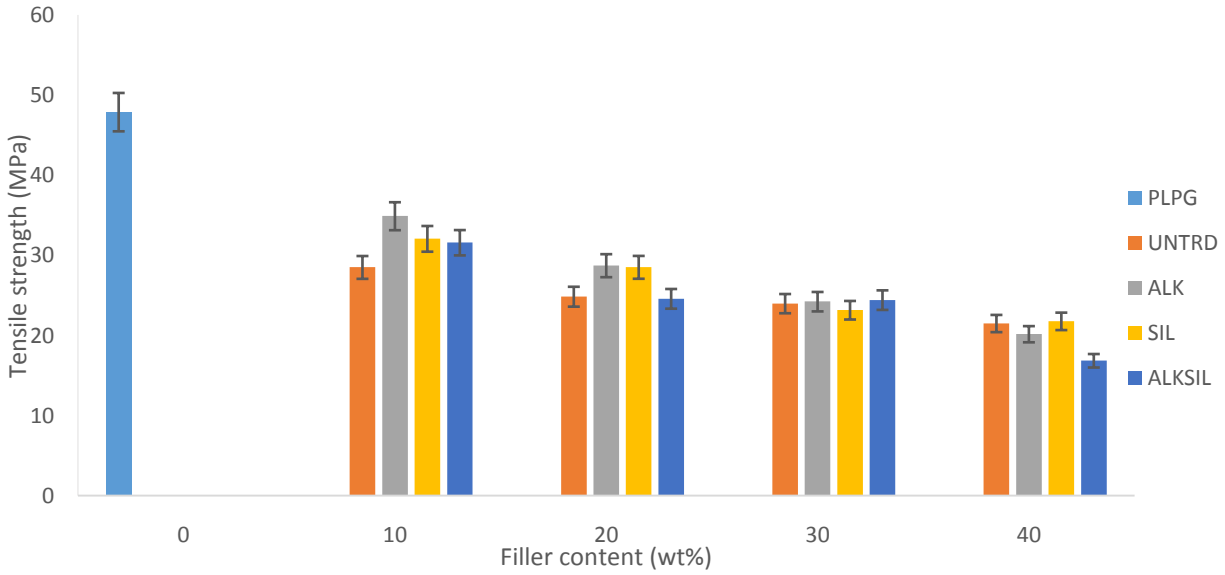


Figure 4.9: Tensile strength of PLPG/GHP Composites against filler content for various treatments

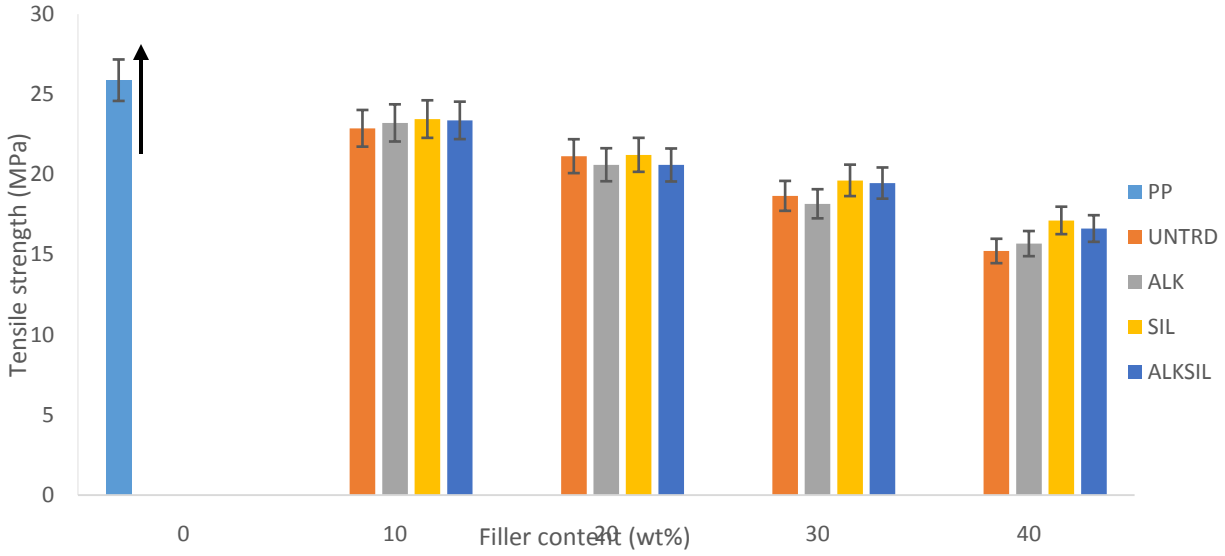


Figure 4.10: Tensile strength of PP/GHP Composites against filler content for various treatments

From the tensile strength results in Figures 4.7 to 4.10, a general decrease in tensile strengths with filler loading was observed for the treated and untreated composites. Also, the neat polymers (matrices) had higher tensile strengths than the reinforced composites. This observation is in agreement with those of other investigators such as those of (Finkenstadt *et al.*, 2007a) that reported a decrease in tensile strength in PLA/sugar beet pulp (SBP) composite from 69.5MPa for pure PLA to 29.55MPa for 45% SBP content. Also, Clarizio and Tatara (2012) reported a drop in tensile strength from 59.6MPa for pure PLA to 11.2MPa for reinforced bio-composite reinforced with distillers dried grains with solubles (DDGS). Others include studies of Rosa *et al*., (2009), Yang *et al*., (2007) and Finkenstadt *et al*., (2007b) that reported reduction in the tensile strengths of composites as compared to the matrices but they remained within acceptable limits (Imoisili *et al*.,2012; Yang *et al*., 2004 and 2006). As for the reinforced composites, the treated composites showed higher tensile strengths than the untreated ones in most cases.

Figure 4.7 shows results for tensile strength of PLAP/GHP composites. It was observed that the PLAP matrix with a tensile strength of 57.13MPa had a higher tensile strength than the reinforced treated or untreated composites. The tensile strengths of the reinforced composites at 10% and 40% filler contents were 40.64MPa and 31.59MPa, 41.43MPa and 32.95MPa, 40.56MPa and 30.77MPa and 45.48MPa and 37.57MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively. The observed trend was a progressive decrease in tensile strengths with filler loading for all the reinforced composites.

Another observation in the results was that, compared to the untreated composites, ALKSIL and ALK treated composites showed higher tensile strengths while the tensile strengths of the SIL treated composites gave the least values for all the filler contents investigated.

Figure 4.8 shows the tensile strength results for PLABM/GHP composites. The results were similar to those of Figure 4.7 but with lower values. The tensile strength of PLABM was 44.37MPa while different and lower values were obtained at different filler contents for the untreated and treated composites. At 10% filler content, the tensile strengths obtained were 31.20MPa, 31.24MPa, 29.10MPa and 32.09MPa while at 20% filler content, were 26.35MPa, 28.16MPa, 24.08MPa and 29.50MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively. At 40% filler content, the tensile strengths obtained were 19.78MPa, 20.49MPa, 17.68MPa and 21.71MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively. The lower tensile strength values obtained for PLABM and its composites as compared to those of PLAP and its composites could be attributed to the effect of Biomax strong which is light and probably of low tensile strength compared to PLA.

Figure 4.9 presents the tensile strength results of PLPG/GHP composites. The tensile strength of PLPG was 47.88MPa which is 16.2% lower than that of PLAP but 7.9% higher than PLABM.The results obtained here was a bit different from those of Figures 4.7 and 4.8 in that, the SIL treated composites showed higher tensile strengths than that of the untreated ones at 10 and 20% filler contents and it recorded the highest tensile strength at 40% filler content followed by UNTRD, ALK and ALKSIL treated composites with values of 21.78MPa, 21.50MPa, 20.17MPa and 16.86MPa respectively. The tensile strengths for ALK and SIL treated composites showed higher values at 10 and 20% filler contents as compared to those of the UNTRD and ALKSIL treated composites. The values obtained at 10% filler content were 34.90MPa, 32.07MPa, 31.59MPa and 28.50MPa for ALK,SIL,ALKSIL and UNTRD composites respectively while at 20% filler content, the values obtained were 28.72MPa, 28.52MPa, 24.85MPa and 24.58MPa for ALK, SIL, UNTRD and ALKSIL treated composites respectively.

The results for tensile strength of PP/GHP composites given in Figure 4.10 shows similar trend of decrease in tensile strengths with filler loading with the unreinforced PP having a tensile strength of 25.88MPa. The arrow indicates that the virgin PP did not fracture during the test but a value was assigned by the Instron machine at the termination of the test after excessive necking of the specimen. The tensile strength values of PP and its composites were lower than those of the various PLA matrices and their composites. The tensile strengths obtained at 10% filler content were 22.89MPa, 23.21MPa, 23.45MPa and 23.37MPa while the values obtained at 40% filler content were 15.23MPa, 15.68MPa, 17.13MPa and 16.63MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively.

Decrease in tensile strengths of lignocellulosic particle-filled composites is a general trend that has been variously reported by (Yang *et al*., 2004; Kim *et al*., 2005a; Tserki *et al*., 2006a; Ahmad *et al*., 2007; Kim *et al*., 2007; Yang *et al*., 2007; Rosa *et al*., 2009; Saini *et al*., 2010; Ewulonu and Igwe, 2011; Hussein *et al*., 2011; Kim *et al*., 2011; Chun *et al*., 2012; Salmah *et al*., 2012; Hardinnawirda and SitiRabiatull , 2012; Ibrahim *et al*., 2012; Imoisili *et al*., 2012, Baek *et al*., 2013; Chun *et al*., 2013a; Essabir *et al*., 2013a; Eze *et al*., 2013; Fakhrul *et al*., 2013 and Koutsomitopoulou *et al*., 2014). However, some other reports have shown increase in tensile strengths with filler loading (Onuegbu and Igwe, 2011; Ojha *et al*., 2014).

Tserki *et al*., (2006a); Ahmad *et al*., (2007); Rosa *et al*., (2009); Thamae *et al*., (2009); Ewulonu and Igwe (2011); Chun *et al*., (2012) and Viet *et al*., (2012) gave the reason for general decrease of tensile strength with filler loading for particle filled composites as probably due to the irregular shape exhibited by the fillers which may not be able to maximize the interfacial surface area and are rather poor in their ability to support the stress transfer from the matrix leading to weak bond between the flour and matrix which subsequently leads to reduction in tensile strength with filler loading. This is unlike the reinforcing fillers such as glass, carbon and Aramid fibres which confer improvement in mechanical properties of the resulting composites.

Ahmad *et al*., (2007); Hardinnawirda and SitiRabiatull (2012) and Părpăriță *et al*., (2014) believed that with increase in filler content, the interfacial area between the polymer and filler increase due to increase in microspaces creating discontinuities which results in the weakening of the interfacial bonding between the constituents leading to a decrease in tensile strength.

Another school of thought had it that the declining tensile strength for particle filled composites as presented by Yang *et al*., (2006); Ahmad *et al*., (2007); Rosa *et al*., (2009); Viet *et al*., 2012; Eze *et al*., (2013) is that agglomeration is one characteristic of fillers during composite production which could generate flaws that lead to creation of voids that become larger in size as filler contents increase.

Furthermore, with increase in filler content, a situation leading to more filler-to-filler interaction than filler-to-matrix interaction could arise and this could lead to generation of voids at filler-to-matrix interface and stress transfer to the filler become inefficient leading to low strength values; the weak bonding that resulted from the aforementioned could probably obstruct the stress propagation from matrix to filler and then cause the tensile strength to decrease with filler loading (Tserki *et al*., 2006a; Yang *et al*., 2007 ; Hardinnawirda and SitiRabiatull, 2012; Baek *et al*., 2013; Chun *et al*., 2013a; Eze *et al*., 2013; Mohamad Hafiz *et al*., 2013; Sujaritjun *et al*., 2013).

Conclusively, strength of particle-filled polymer composites depends on the interfacial adhesion between the matrix and filler which will facilitate the transfer of stress to the filler during deformation (Hussein *et al*., 2011). It was reported that the tensile strength of particle-filled composites is more sensitive to the matrix properties (Razavi-Nouri *et al*., 2006) but with increase in the filler content, the matrix content decreases which could probably lead to strength reduction (Ibrahim *et al*., 2012).

A number of reports have been presented on improvement of tensile strength of surface treated composites as compared to the untreated ones.

Ahmad *et al*., (2007) reported an improvement in tensile strength of alkali-treated composites as compared to the untreated composites. They reported that alkali treatment resulted in an improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking (Asumani *et al*., 2012; Senawi *et al*., 2013; Qian *et al*., 2013)hence, promoting resin-filler interpenetration at the interface. Furthermore, alkali treatment helps to improve the dispersion of fillers in the matrix thereby reducing filler agglomeration. In their study, tensile strength of Polyester/Rice husk flour (RHF) composites was 17MPa for alkali treated composites and 12MPa for untreated composites at 10% filler content as against 25MPa for the Polyester matrix (Ahmad *et al*., 2007).

Ewulonu and Igwe (2011) reported an improvement in tensile strength of composites on addition of maleic anhydride polyethylene (MAPE) compatibilizer over the untreated composites. Suardana*et al*., (2011) reported an increase in tensile strength of PP/hemp fibre composites with alkali treatment but a decrease was recorded with silane treatment as compared to the untreated composites. Gelfuso *et al*., (2011) on the other hand, reported that alkali treatment did not improve the tensile strength of PP/coconut coir fibre composites. Imoisili *et al*., (2012) reported an increase in tensile strength of their studied composite system on alkali and silane treatment with respect to the untreated composites while Rosa *et al*., (2009) reported that the addition of maleic anhydride PP (MAPP) to PP/RHF increased the tensile strength of the composites with respect to the untreated composites. However, Salmah *et al*., (2011) reported higher tensile strength of treated composites as compared to the untreated ones only at higher filler contents. They reported that 3- Aminopropyltriethoxysilane (3-APS) proved to be effective in enhancing the dispersion, adhesion and compatibility of PP/Chitosan composites.

Baek *et al*., (2013) produced PLA/Coffee ground (CG) and PLA/Bamboo flour (BF) composites at 30% filler content. They reported a tensile strength of 60.1MPa for pure PLA and 48MPa for PLA/BF composites and 45MPa for PLA/CG composites at 10% filler content. On treating the fillers with 4,4-Methylene diphenyl diisocyanate (MDI) coupling agent, they recorded improvements in the tensile strengths of both PLA/CG and PLA/BF composites as compared to the untreated ones.

Saini *et al*., (2010) produced a composite made of polyvinyl chloride (PVC) and bagasse powder (BP) and reported a decrease in tensile strength with increase in BP content. Alkali treatment of the BP did not show a marked improvement in the tensile strength of the resulting composites. Salmah *et al*., (2012) reported an increase in the tensile strength of acrylic acid treated coconut shell powder composite as compared to the untreated ones.

Tserki *et al*., (2006a) produced composites using Bionolle 3020 as matrix and three different fillers (spruce, olive husk and paper flour) as reinforcements. They reported improvements in the tensile strengths of the surface treated filler composites with respect to the untreated ones.

From the foregoing discussion, it is clear that not all treated composite systems resulted in improved tensile strengths. As the graphs in Figures 4.7 and 4.8 for PLAP/GHP and PLABM/GHP composites respectively depict, for all the filler contents, the tensile strengths of the composites containing SIL treated fillers exhibited the least values; they were even lower than those containing the untreated fillers while the highest tensile strengths were observed in the composites containing ALKSIL treated fillers followed by those of ALK treated fillers while the graphs of PLPG/GHP and PP/GHPcomposites in Figures 4.9 and 4.10 respectively depict

irregular behaviours of tensile strengths with or without surface treatments. Furthermore, ThaoTran *et al*., (2014) reported that NaOH treatment did not improve the tensile strength of PLA/RHF and PLA/Wheat husk (WH) composites in comparison with the untreated ones; infact, there was a 35-40% reduction in strength on treatment with NaOH. Their explanation was that loss in strength could be as a result of lower interfacial adhesion between PLA and alkali treated fillers. Gomes *et al*., (2007) also reported similar behaviour with alkali treatment. However, there was improvement in the tensile strength when the fillers were given combined treatment of alkali and silane treatment.

The surface treatments given to lignocellulosic materials are for the purpose of creating good dispersion of fillers in the polymer matrix. From this study, it appears that SIL treatment may not be an appropriate surface treatment for the filler under investigation. Apparently, these results appear to be in contrast with some other findings especially the case of the silane treated composites having lower tensile strengths than the untreated ones. Such studies include those of Agunsoye and Aigbodion (2013) who reported an increment in tensile strength of bagasse filled recycled polyethylene bio-composites which was due to the good distribution and dispersion of the bagasse particles in the matrix. Tserki *et al*., (2006b) reported that the substitution of hyrdrophilic hydroxyl groups of the lignocellulosic material with acetyl and propionyl groups rendered the lignocellulosic flour surface more hydrophobic and thus more compatible to hydrophobic polymeric matrix leading to a material with improved properties. Herrera-Franco and Valadez-Gonza´lez (2004) reported that tensile strengths of high density polyethylene (HDPE)/Henequen fibre composites treated with NaOH seems to be at par with those of the unreinforced composites but the strength increased significantly as the fibres were treated with

silane. Also, the strength further increased as the fibres were treated with a combination of alkali and silane indicating good chemical and mechanical interaction. Calabia *et al*., (2013) used three different silane treatments on cotton fibres which were then reinforced with Poly (Butylene Succinate) (PBS) and concluded that all three treatments had a higher tensile strength than the untreated fibre composites. Kang and Kim (2011) observed that composites of PLA and APS treated bamboo fibres gave better strengths than those containing untreated bamboo fibres.

From the foregoing discussion, it is clear that different systems are affected in different ways with respect to surface treatments given to fillers for composites production as some treatments on some fillers would result in improvement in tensile strengths, same treatments on other fillers or other systems would reduce the strengths as evident from the present study.

Based on the views expressed, it could be argued that different fillers or fibres and composites systems have suitable treatments which lead to improvement in tensile properties and do not make any meaningful contribution on the strengths of others. An interesting study to buttress this point was carried out by Sreekala *et al*., (2000) where they investigated the influence of fibre surface modifications on the mechanical performance of oil Palm fibre reinforced phenol formaldehyde composites. The fibres were subjected to different chemical modifications such as mercerization (alkali treatment), acrylonitrile grafting, acrylation, latex coating, permanganate treatment, acetylation, silane and peroxide treatments. At the end of the study, they observed that, of all the surface treatments done on the fibre only that of silane and acrylated treatments gave better tensile strengths than the untreated fibre composites.

4.2.2.2 Tensile Modulus

The tensile modulus results for all the composite formulations are shown Figures 4.11 to 4.14 and Tables B1 to B4 in Appendix B.

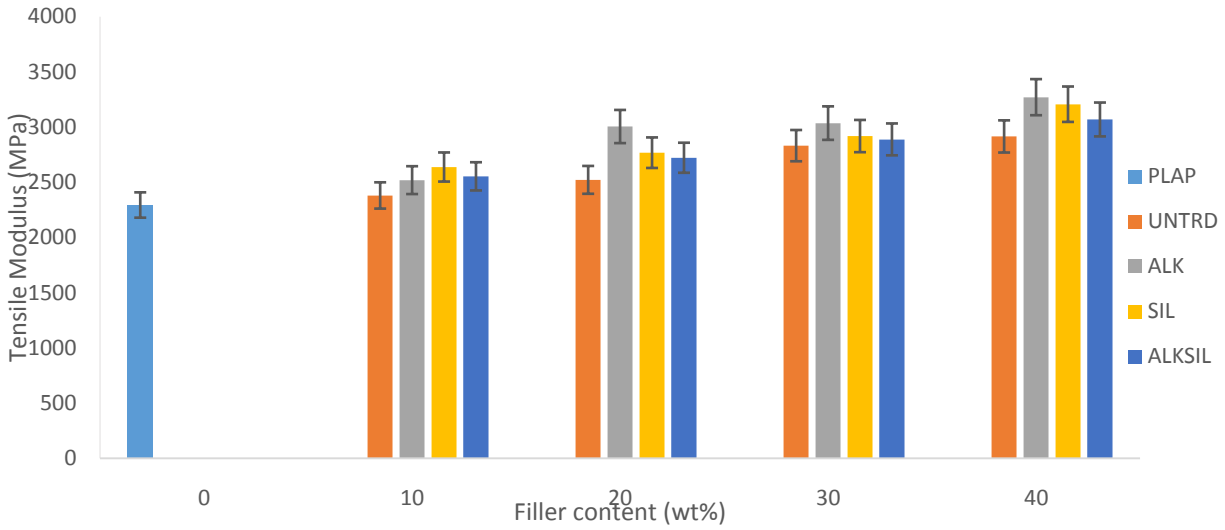


Figure 4.11: Tensile Modulus of PLAP/GHP Composites against filler content for various treatments

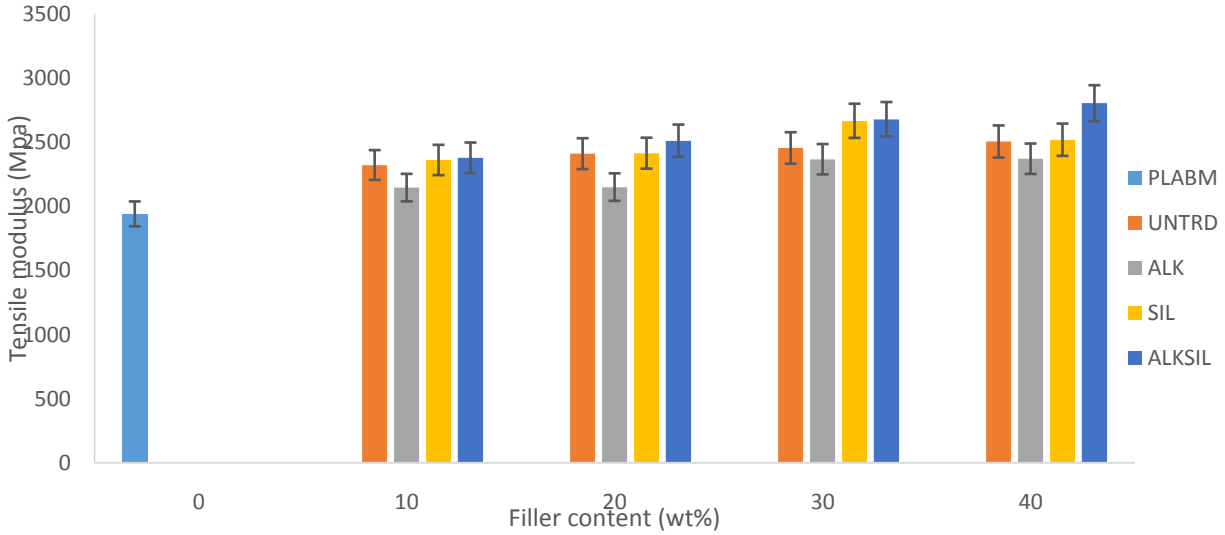


Figure 4.12: Tensile Modulus of PLABM/GHP Composites against filler content for various treatments

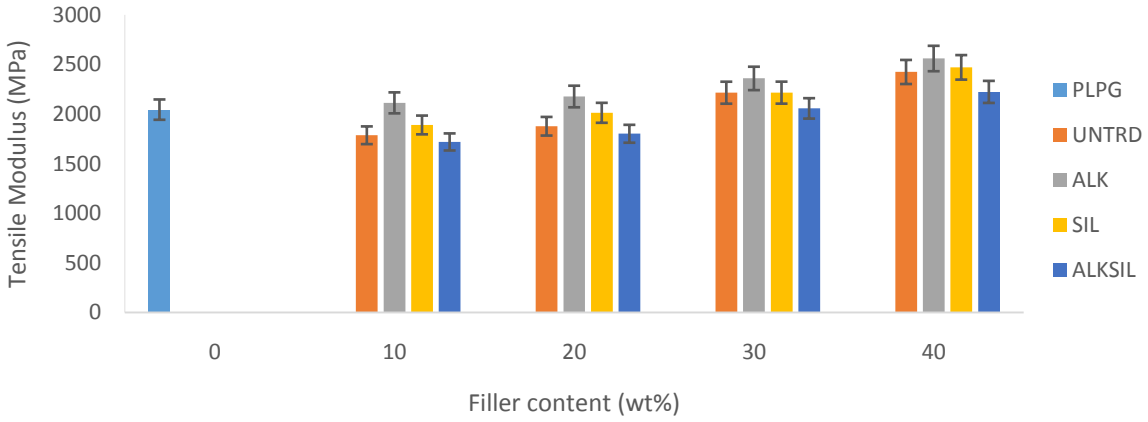


Figure 4.13: Tensile Modulus of PLPG/GHP Composites against filler content for various treatments

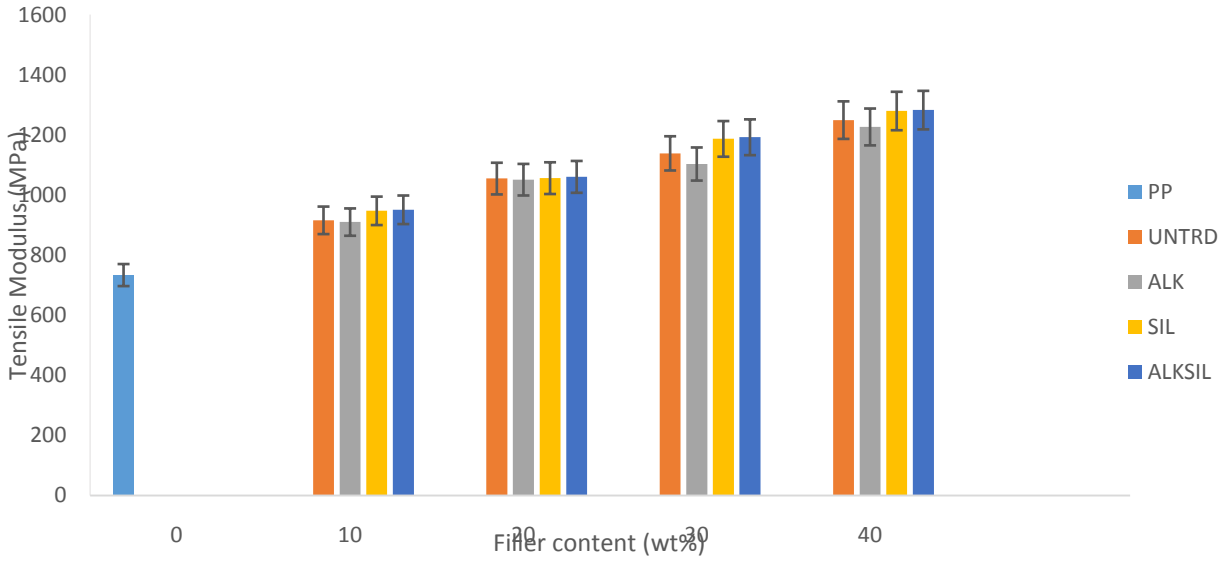


Figure 4.14: Tensile Modulus of PP/GHP Composites against filler content for various treatments

From the results, a general trend of increase in tensile modulus with GHP loading was observed. In almost all the cases, the tensile modulus of the composites with or without surface treatments were higher than those of the various unreinforced matrices with some exceptions observed in PLPG/GHP composites Figure 4.13 where the tensile moduli of some reinforced composites were lower than that of the unreinforced matrix.

The results obtained are in agreement with various other findings of (Yang *et al*., 2004; Huda *et al*., 2006; Tserki *et al*., 2006a; Lee *et al*., 2008; Pilla *et al*., 2008; Ashori and Nourbakhsh, 2010; Onuegbu and Igwe, 2011; Shumigin *et al*., 2011; Ibrahim *et al*., 2012; Imoisili *et al*., 2012; Fakhrul *et al*., 2013) that also documented increase in tensile modulus with filler loading.

The general increase in tensile modulus with filler loading is commonly attributed to the inherent rigidity of fillers which exhibit higher stiffness than the polymer matrices (Rosa *et al*., 2009; Salmah *et al*., 2012; Eze *et al*., 2013).

Furthermore, the increase in tensile modulus with filler loading could also be attributed to the restriction of polymer chain mobility by the rigid fillers which results in a stiffening effect in polymer/filler composites thereby increasing the rigidity of the composites (Mat Taib *et al*., 2010; Chun *et al*., 2012; Ibrahim *et al*., 2012).

Most of the results presented in this study are consistent with those of other studies which reported the increment in tensile modulus from the neat PLA to higher values for the reinforced untreated composites and even higher values when the fillers were given various treatments. Also, they reported increment in modulus as filler content increases due to the possibility of restricting the macromolecules mobility imposed by the presence of particles and as modulus is a

measure of a material's stiffness, increase in filler content makes the material become stiffer (Shumigin *et al*., 2011;Viet *et al*., 2012; Eze *et al*., 2013;MohamadHaafiz *et al*., 2013) On the contrary, Aydın *et al*., (2011) reported a decrease in tensile modulus of their composite system.

The tensile modulus results of Figure 4.11 shows a progressive increase with GHP loading. The tensile modulus of PLAP matrix with a value of 2294.15MPa was lower than those of the reinforced composites with or without surface treatments. The UNTRD composites had tensile moduli that ranged between 2380.54MPa at 10% filler content and 2915.20MPa at 40% filler content. The treated composites had tensile moduli that ranged between 2519.46MPa and 3270.69MPa for ALK treated composites, 2638.26MPa and 3206.92MPa for SIL treated composites and 2553.80MPa and 3068.86MPa for ALKSIL treated composites at 10% and 40% filler contents respectively.

The tensile modulus results unlike the tensile strengths results, for the treated composites were higher than those of the UNTRD composites and it was clear that SIL treatment improved the tensile modulus. The order of increase of tensile modulus at each filler content is as follows:

i. At 10% filler content, UNTRD < ALK < ALKSIL < SIL
ii. At 20% filler content, UNTRD < ALKSIL < SIL < ALK
iii. At 30% filler content, UNTRD < ALKSIL < SIL < ALK
iv. At 40% filler content, UNTRD < ALKSIL < SIL < ALK

This indicated that for all the filler contents, the tensile moduli for ALK treated composites were highest except at 10% filler content where the highest tensile modulus was recorded for SIL treated composites.

Figure 4.12 is the tensile modulus results for PLABM/GHP composites which shows that the tensile modulus of PLABM matrix was 1941.46MPa, a value which was lower than those of the reinforced composites with or without surface treatments. The results were similar to the tensile strengths results where the values obtained for the neat matrix and reinforced composites were lower than those of PLAP and its composites.

It was also observed from the results that the tensile moduli of ALK treated composites were lower than even the UNTRD composites while those of the ALKSIL treated ones recorded the highest values.

Figure 4.13 shows the tensile modulus results for PLPG/GHP composites. The tensile modulus of neat PLPG was 2045.44MPa; a value that was 5.36% higher than that of neat PLABM and 12.16% lower than that of neat PLAP. The results also showed a progressive increase in tensile modulus with GHP loading even though the values here were lower than those of PLAP/GHP and PLABM/GHP composites. The tensile modulus lied between 1787.02MPa and 2424.76MPa for UNTRD, 2113.61MPa and 2560.42MPa for ALK, 1890.94MPa and 2471.34MPa for SIL and then 1719.63MPa and 2223.95MPa for ALKSIL composites. The significant increment were obtained at higher filler loadings of 30% and 40% filler contents while at lower filler contents (10% and 20%), the tensile moduli were a bit lower than that of the neat matrix.

The ALK and SIL treated composites showed higher tensile moduli while ALSKIL treatment did not influence the tensile modulus as seen in the results because, for all the filler loading, the tensile modulus for UNTRD composites were higher than those of the ALKSIL treated composites.

The tensile modulus for neat PP was 733.44MPa and higher values were obtained for both the treated and untreated PP/GHP composites Figure 4.14.The values for tensile moduli for PP/GHP composites lied between 915.58MPa and 1249.03MPa, 909.75MPa and 1226.83MPa, 947.20MPa and 1279.39MPa and then 950.64MPa and 1282.37MPa at 10% and 40% GHP loading and for UNTRD, ALK treated, SIL treated and ALKSIL treated composites respectively. The values obtained for the tensile moduli of PP and its composites were all lower than those obtained for the various PLA matrices and their composites.

Furthermore, it was observed that ALK treatment did not improve the tensile modulus in comparison to the untreated composites. However, SIL and ALKSIL treatments improved the tensile modulus of PP composites as seen from the results in Figure 4.14.

From the results obtained, it could be inferred that increase in tensile modulus of composites with GHP loading is an indication that lignocellulosic fillers have the ability to impart greater stiffness to the matrix and since increase in filler content resulted in increase in tensile modulus, it means tensile modulus is dependent on the filler content rather than the matrix (Ahmad *et al*., 2007; Thamae *et al*., 2009). It was reported that higher filler contents in polymer matrices showed much higher density which resulted in stiffer composites (Pilla *et al*., 2008).

Chun *et al*., (2012) reported an increase in tensile modulus of PLA/coconut shell particulates (CSP) composite with increase in CSP content for both treated and untreated composites. They reported that maleic anhydride (MA) treated composites showed higher modulus than the untreated composites.

While some investigators such as (Chun *et al*., 2012; Imoisili *et al*., 2012; Salmah *et al*., 2012) reported improvement of tensile modulus with surface treatments over the untreated composites, some other investigators such as (Tserki *et al*., 2006a; Rosa *et al*., 2009) reported otherwise.

From the results of tensile modulus obtained in this study, it was observed that the tensile modulus of PLA and its composites were higher than those of PP and its composites. This is an observation that is contrary to what Bajpai *et al*., (2012) obtained in their study where they reported that tensile modulus of PLA and PP and their composites increased with filler loading with PP composites having higher values than PLA composites.

4.2.2.3 Elongation at Break (EB)

Figures 4.15 to 4.18 and Tables B1 to B4 (Appendix B) are the results for the elongation at break (EB) of all the composite formulations.

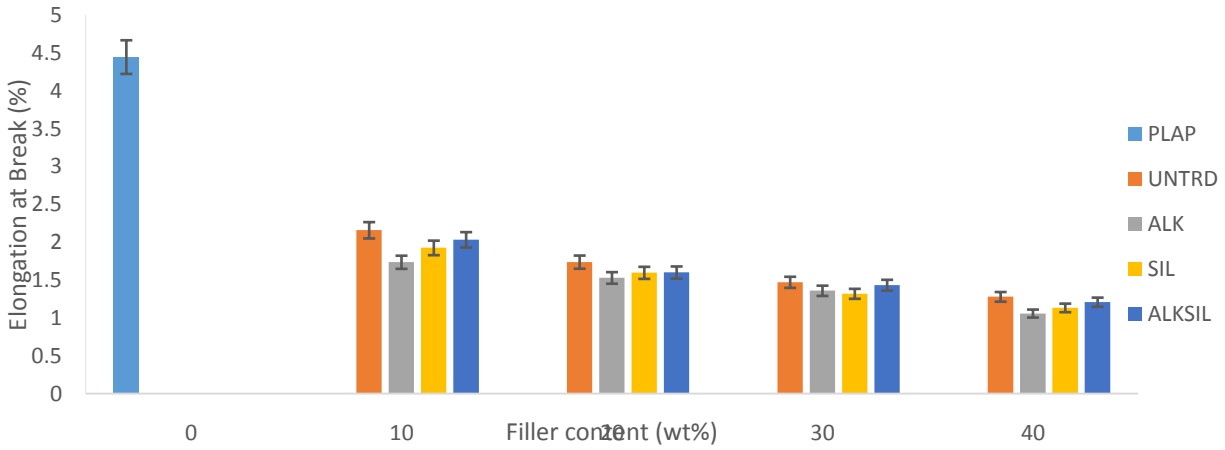


Figure 4.15: Elongation at Break of PLAP/GHP Composites against filler content for various treatments

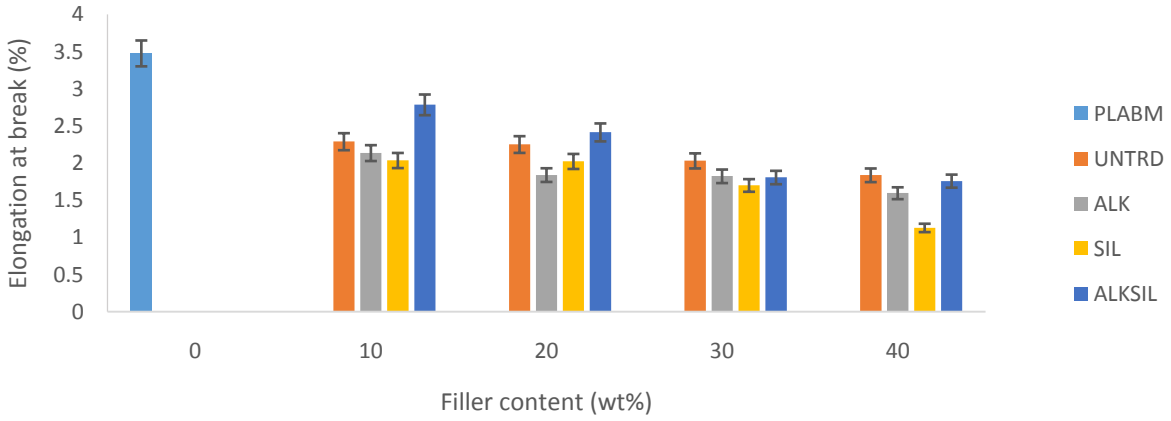


Figure 4.16: Elongation at Break of PLABM/GHP Composites against filler content for various treatments

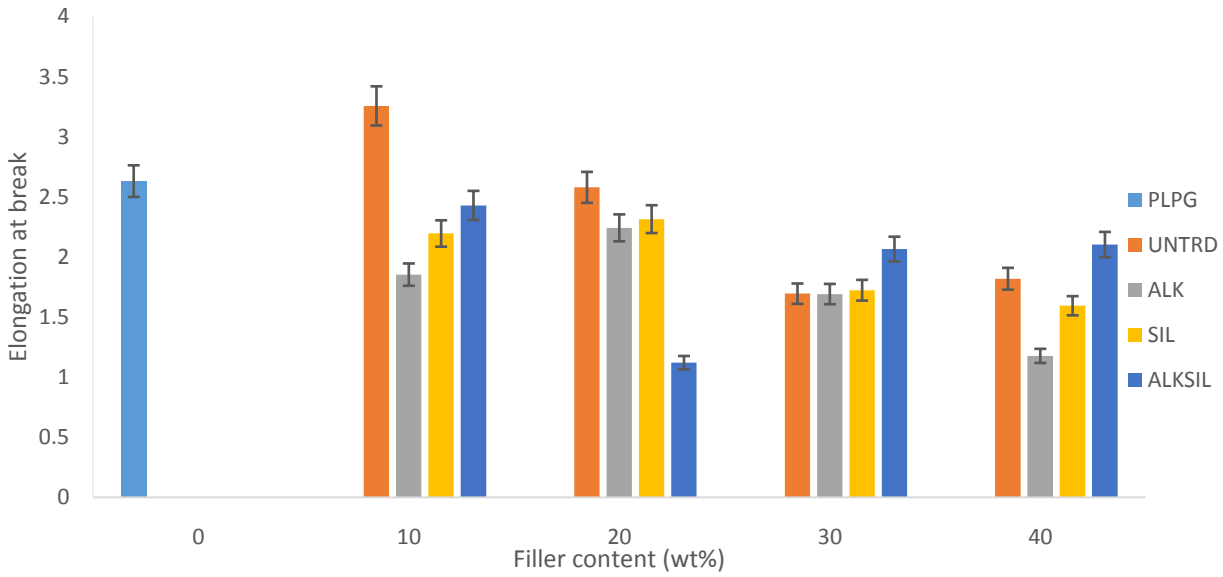


Figure 4.17: Elongation at Break of PLPG/GHP Composites against filler content for various treatments

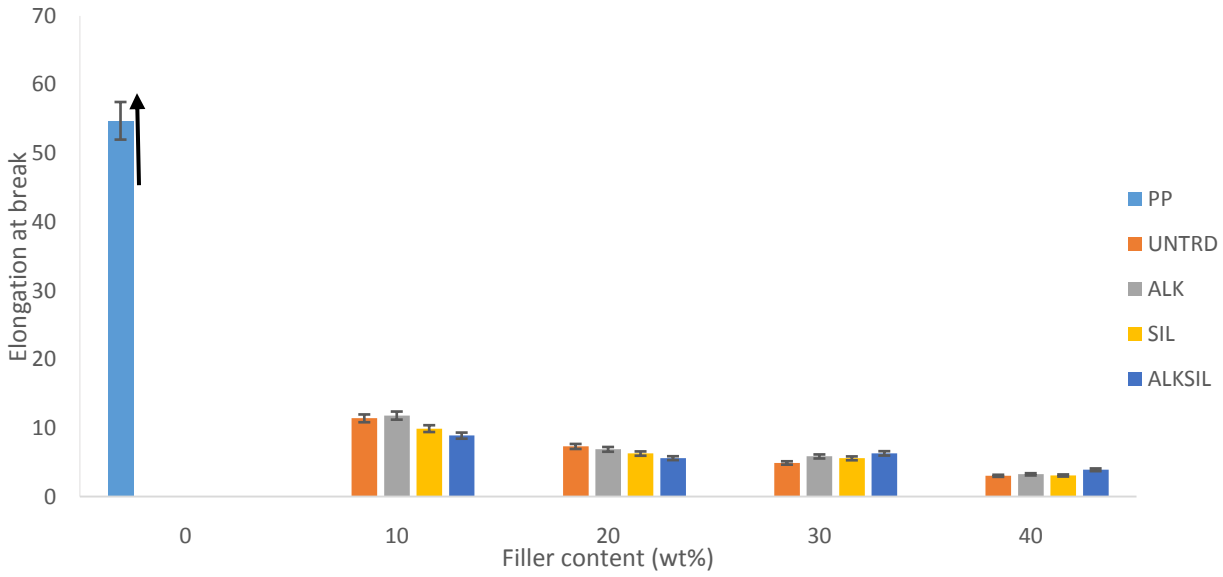


Figure 4.18: Elongation at Break of PP/GHP Composites against filler content for various treatments

The observations from the results indicated that all the unreinforced matrices had higher EB compared to their various composites with that of PP and its composites being the highest. The arrow indicates that virgin PP has much higher EB but due to the termination of the test, the machine assigned the recorded value which is probably much lower than the actual EB of virgin PP.

Figure 4.15 shows the EB results of PLAP/GHP composites. The EB for the matrix was 4.45% while lower values were obtained for its composites with or without surface treatments. The general observation on the EB was that they decreased with GHP loading. ALK and SIL treated composites exhibited lower EB than ALKSIL and UNTRD composites with those of UNTRD composites exhibiting the highest values.

The EB of PLABM/GHP composites with a value of 3.48% for PLABM matrix and various lower values for its composites are shown in Figure 4.16. The EB also decreased with GHP loading and similar to the PLAP/GHP composites, the ALKSIL and UNTRD composites showed higher EB values than those of ALK and SIL treated composites.

Figure 4.17 shows the EB results for PLPG/GHP composites with that of the matrix being 2.63%; a value that is lower than those of PLAP and PLABM. A defined trend was not observed for this system unlike those of Figures 4.15 and 4.16 earlier discussed. This could probably be due to the interaction of PEG at different treatments and different GHP loading. The EB at 10% GHP content was greater than that of the matrix. Generally, the UNTRD composites showed higher values than the treated ones.

The recorded EB for PP matrix was 54.72% and lower values were obtained for its composites as seen in Figure 4.18. It was noticed that the EB of PP and its composites were all higher than those of the various PLA matrices and their composites. This behaviour was envisaged as PP is a tougher polymer than PLA. A drastic reduction of EB on incorporation of GHP was observed and these further reduced with filler loading. The UNTRD composites showed a higher EB than the treated ones at 20% filler content while at 10% filler content, it was less than only the ALK treated composites.

The reduction in EB with filler loading have been variously reported (Ahmad *et al*., 2007; Ewulonu and Igwe, 2011; Onuegbu and Igwe, 2011; Salmah *et al*., 2011; Ibrahim *et al*., 2012; Salmah *et al*., 2012; Eze *et al*., 2013). The reduction could be attributed to the fact that fillers cause polymer matrices to lose their elastic properties due to stiffening effect which leads to restriction of polymer chain mobility. Also, with increase in filler content, the matrix reduces in quantity which consequently reduces the effect of the matrix as compared to that of the filler which then leads to an increase in modulus of composites but reduction of EB (Ahmad *et al*., 2007; Chun *et al*., 2012; Ibrahim *et al*., 2012; Eze *et al*., 2013).

Ibrahim *et al*., (2012) reported that incorporation of oil palm ash (OPA) in unsaturated polyester (UP) reduces its EB drastically which is as a result of reduction in the volume of the matrix.

Mat Taib *et al*., (2010) reported that addition of Kenaf fibre drastically decreased the EB of plasticized PLA. They attributed the behaviour to the stiffening effect of kenaf fibre which restricts the mobility of the PLA chains. The presence of PEG as a plasticizer however, did not

improve the EB of the composites as the values were similar to those of the unplasticized composites.

Chun *et al*., (2012) reported a decrease in the EB of treated and untreated PLA/ coconut shell particulate (CSP) composite with increase in CSP content. The addition of CSP reduced the chain mobility of PLA matrix and resulted in more rigid and brittle composites. Treated composites exhibited lower EB compared to the untreated composites.

Rosa *et al*., (2009) reported that incorporation of Rice husk flour (RHF) in PP matrix resulted in an abrupt drop in EB. The effect of coupling agent on EB was not evident.

Saini *et al*., (2010) reported that EB of PVC/bagasse powder (BP) composites decreased with incorporation of BP. This was probably due to restriction in polymer chain mobility. EB of PVC was 38% while that of 10% BP content was 5% and it was 3% at 40% BP content.

Salmah *et al*., (2012) reported the EB of PLA as 4% and on addition of 15% CSP, the EB was 2.2% and it was 1.4% when the CSP content was 60%. They observed that acrylic acid (AA) treatment did not show any improvement in EB over the untreated ones.

4.2.2.4 Flexural Strength

The flexural strength results for all the produced composites in Tables B1 to B4 in Appendix B and Figures 4.19 to 4.22 are presented as follows:

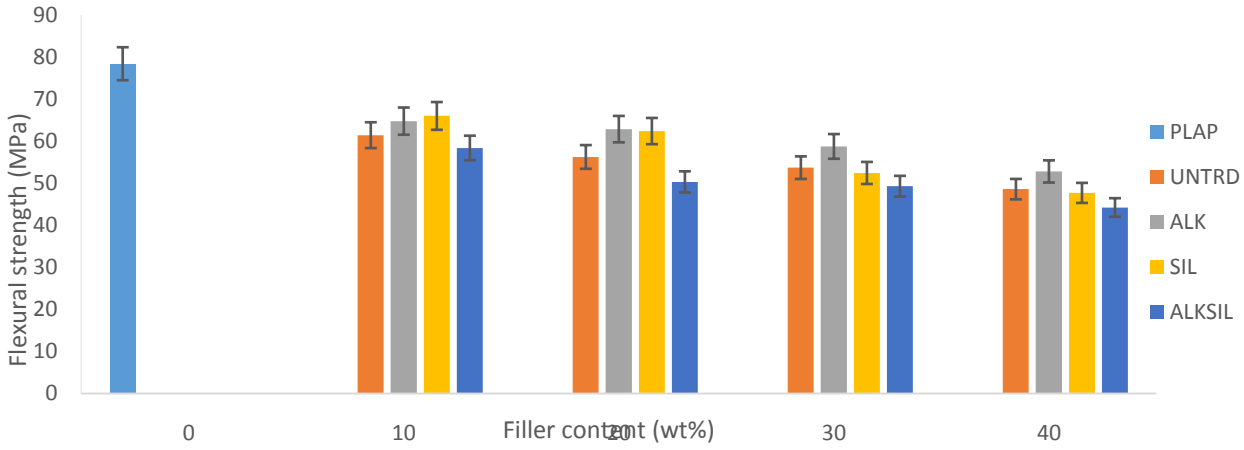


Figure 4.19: Flexural Strength of PLAP/GHP Composites against filler content for various treatments

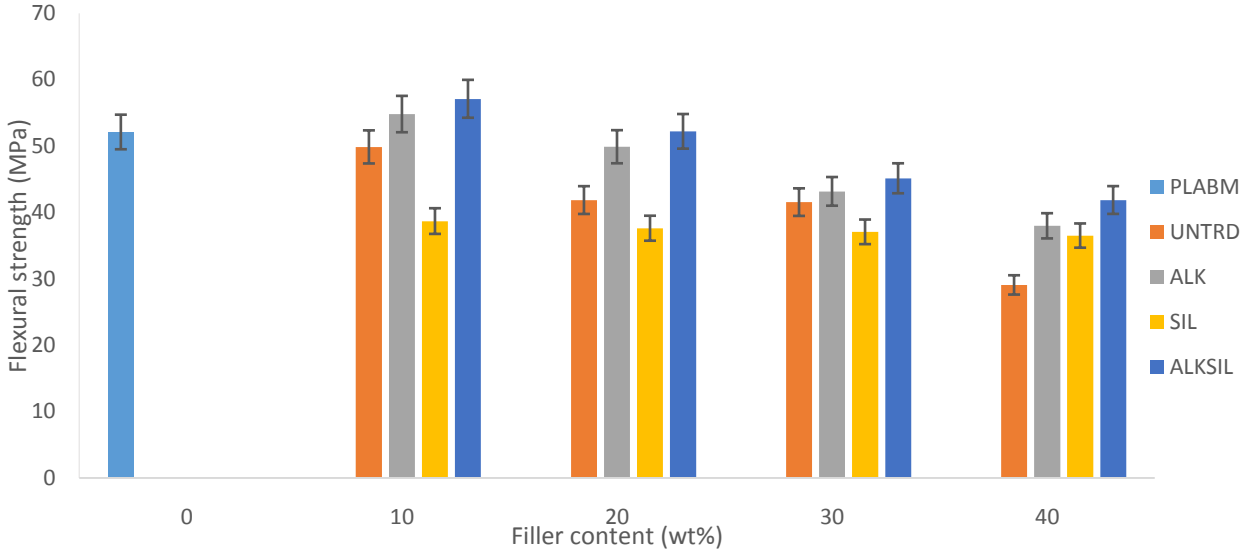


Figure 4.20: Flexural Strength of PLABM/GHP Composites against filler content for various treatments

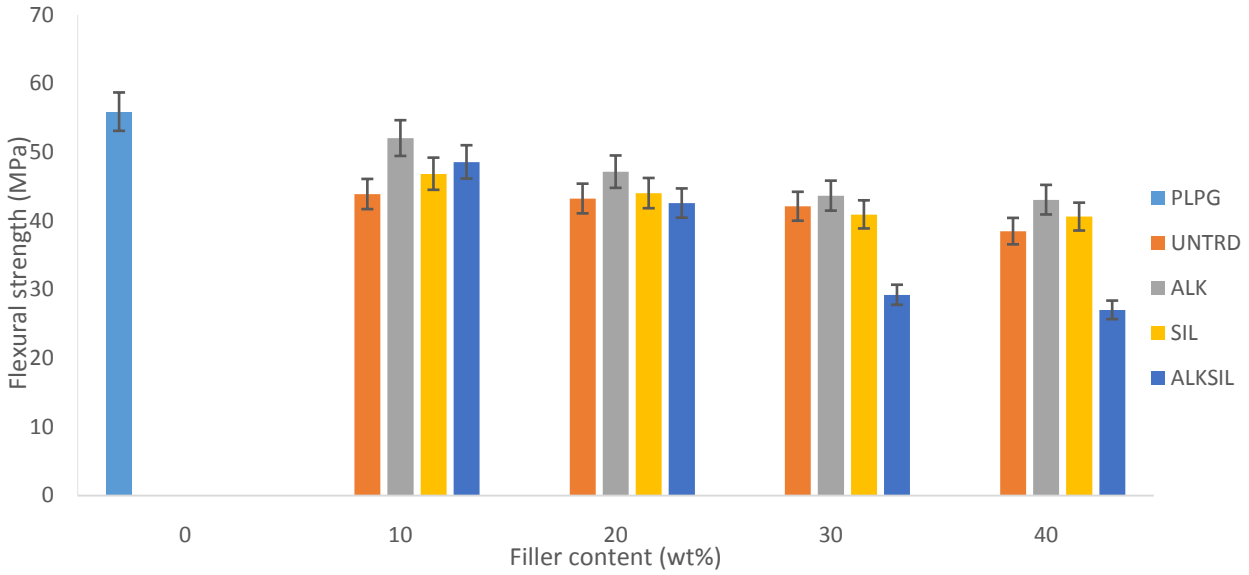


Figure 4.21: Flexural Strength of PLPG/GHP Composites against filler content for various treatments

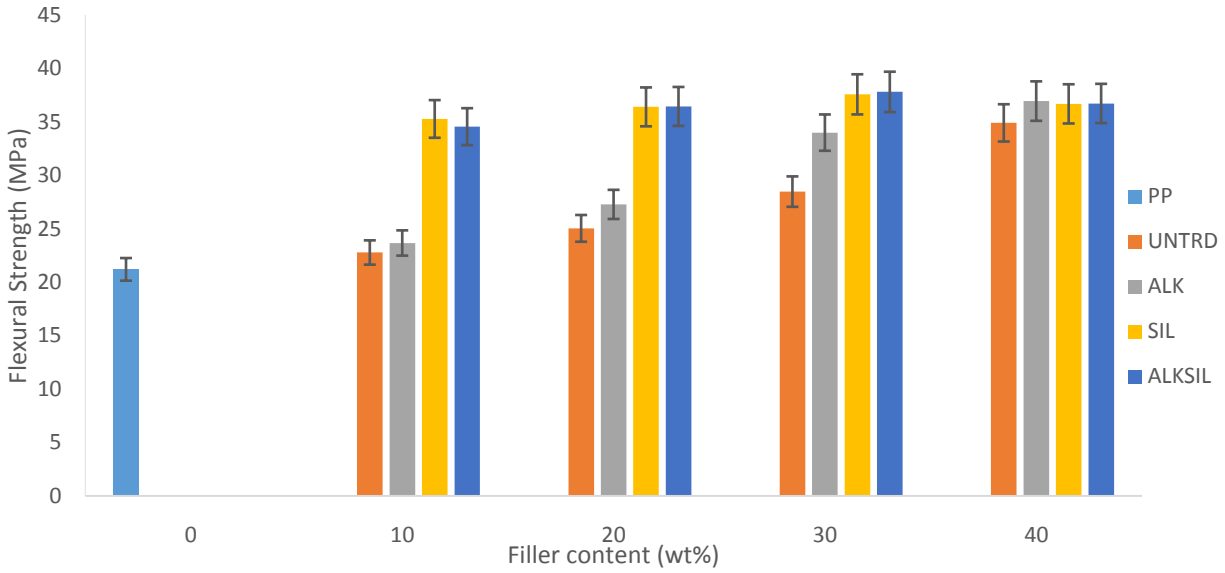


Figure 4.22: Flexural Strength of PP/GHP Composites against filler content for various treatments

From the results, the flexural strength of PLA matrices and their composites showed a general decrease with GHP loading. The results showed a similar trend as compared to the tensile strength results (Suardana *et al*., 2011; Baek *et al*., 2013) with respect to PLA matrices and their composites while PP and its composites showed an opposite trend whereby flexural strengths increase with increase in GHP content.

Figure 4.19 shows the results for flexural strengths of PLAP/GHP composites. The flexural strength of neat PLAP was 78.41MPa while those for its composites were lower and decrease with GHP loading. From the results, it was observed that ALKSIL treatment did not improve the flexural strength of the composites as lower values than even the UNTRD composites were recorded. However, the ALK treatment improved the flexural strength of the composites showing the highest strengths among the reinforced composites except at 10% GHP content where the SIL treated composites was the highest. At higher GHP contents (30% and 40%), the flexural strengths of UNTRD composites were higher than those of SIL treated by marginal values.

The flexural strength results of PLABM/GHP composites Figure 4.20 shows that PLABM matrix has a strength of 52.11MPa which decreases in value with increase in GHP loading. Similarly, the trend observed in this study were similar to those obtained in the tensile strength results where the order of increase in strength was ALKSIL > ALK > UNTRD > SIL. It was also observed that the flexural strengths of ALK and ALKSIL composites at 10% filler content and ALKSIL composites at 20% filler content were higher than that of the unreinforced matrix.

Figure 4.21 shows the flexural strength results of PLPG/GHP composites. Similar to the tensile strength results, the flexural strength of PLPG was 55.90MPa which is 7.27% higher than that of PLABM and 40% lower than that of PLAP matrices. The flexural strengths of the produced composites were lower than that of PLPG and decrease with GHP loading following the general trend obtained earlier from the other PLA matrices (Figures 4.19 and 4.20). The ALK treated composites had the highest flexural strengths at all filler contents with respect to the UNTRD and other treated composites. The SIL treated composites gave improved flexural strengths than the UNTRD composites; an observation which was contrary in the PLABM composites.

The ALKSIL treatment did not influence the flexural strength of PLPG composites since the UNTRD composites had higher values of flexural strengths than those of the ALKSIL treated ones.

Figure 4.22 shows the results of flexural strength for PP/GHP composites. The flexural strength of neat PP was 21.19MPa and those of its composites were higher and they increased with GHP loading.

Huda *et al*., (2006) who studied the flexural strength of PLA/kenaf composites reported a decrease with kenaf fibre addition and surface treated fibre composites had higher flexural strength than the untreated ones. But Shibata *et al*., (2003) stated that the high flexural strength exhibited by PLA makes it difficult to improve the strengths of its composites.

Koutsomipolou *et al*., (2014)reported that flexural strength decreases with filler loading. Suardana *et al*., (2011) reported that silane treatment did not affect the flexural strength of the composites as observed in their study. Thamae *et al*., (2009) reported that probably due to the

compressive component of flexural strength which is not interface dependent, they observed an improvement in flexural strength of their studied composites with flour loading. However, at higher flour content, there was a decrease probably due to agglomeration of the particles.

Ibrahim *et al*., (2012) who studied the flexural strength of Polyester/OPA composites reported a decrease with OPA loading possibly due to poor surface adhesion between Polyester and OPA. Due to limited quantity of matrix, polyester resin was not able to completely wet on the surface of filler.

Huda *et al*., (2006) who studied PLA/Wood fibre (WF) composites reported an increase in the flexural strength of composites in comparison to PLA but decrease with filler loading. Also, the flexural strength of PP/WF composites increase with increase in filler loading but PLA-based composites possessed higher flexural strengths than those of PP and PP-based composites.

Yussuf *et al*., (2010) produced PLA/kenaf fibre and PLA/RHF composites and observed a decrease in flexural strengths of the composites with addition of natural fillers. They attributed the decrease to the inability of the fillers, which are irregular in shape, to support stresses transferred from the polymer matrix.

4.2.2.5 Flexural Modulus

Figures 4.23 to 4.26 and Tables B1 to B4 (Appendix B) are the results for the flexural modulus of all the composite formulations.

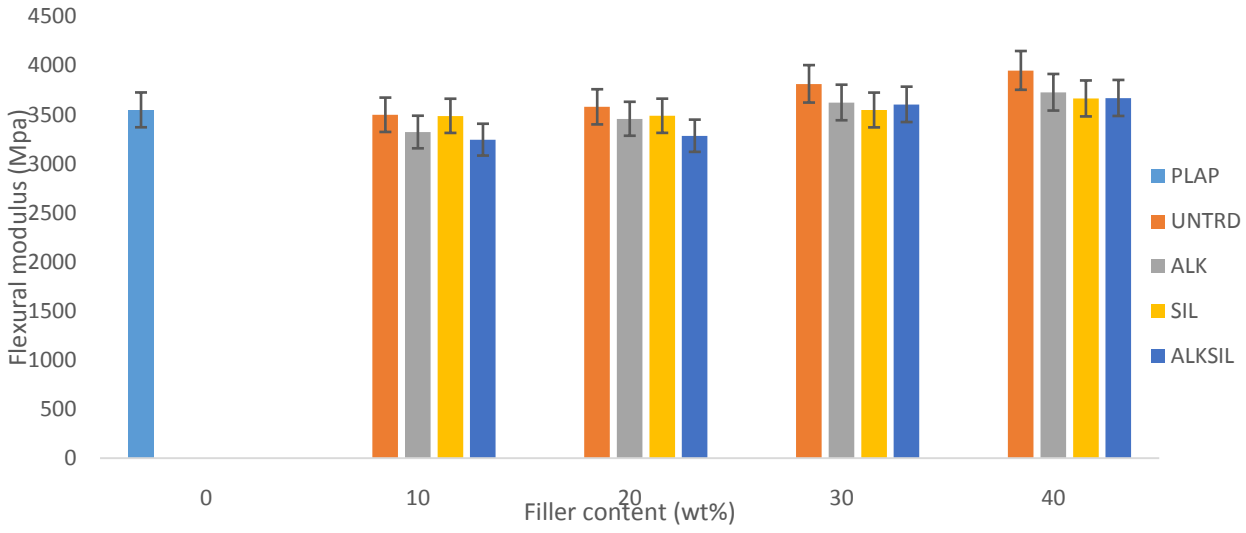


Figure 4.23: Flexural Modulus of PLAP/GHP Composites against filler content for various treatments

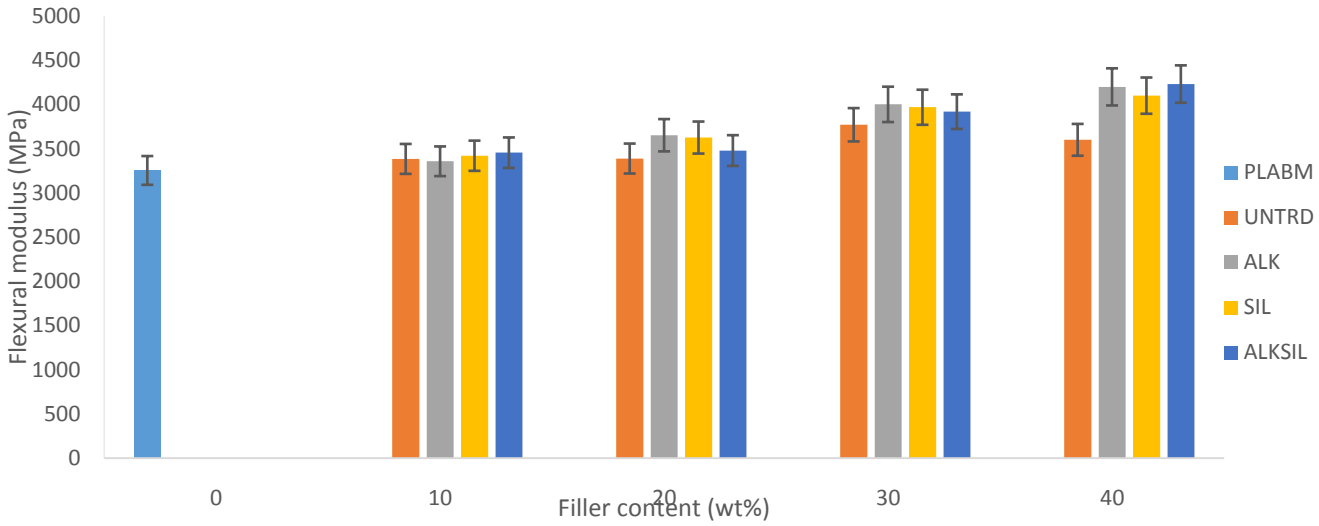


Figure 4.24: Flexural Modulus of PLABM/GHP Composites against filler content for various treatments

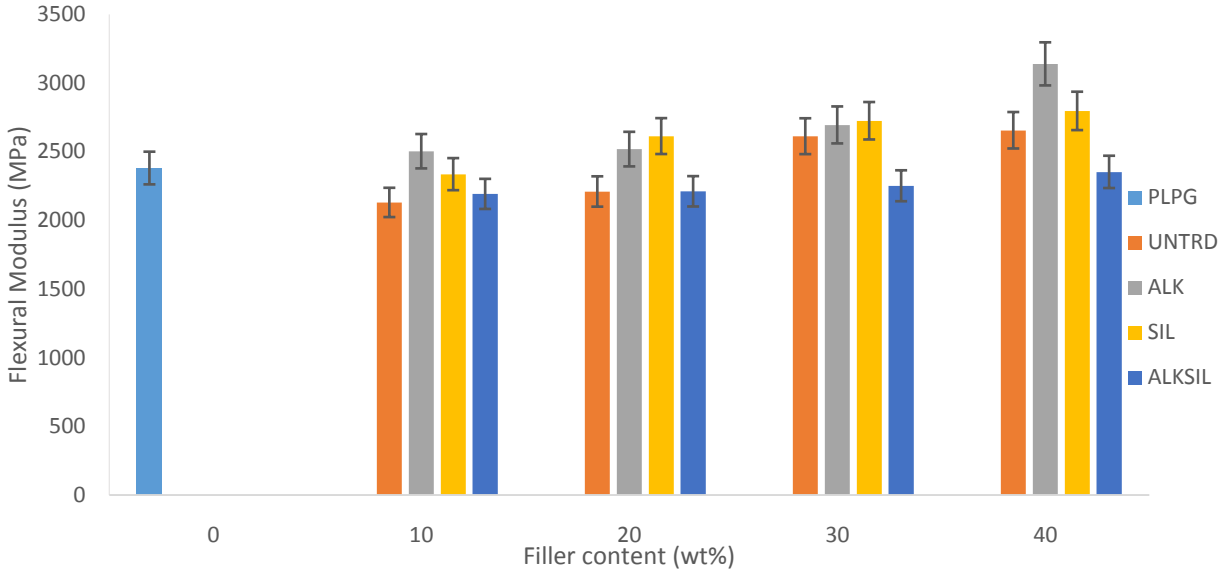


Figure 4.25: Flexural Modulus of PLPG/GHP Composites against filler content for various treatments

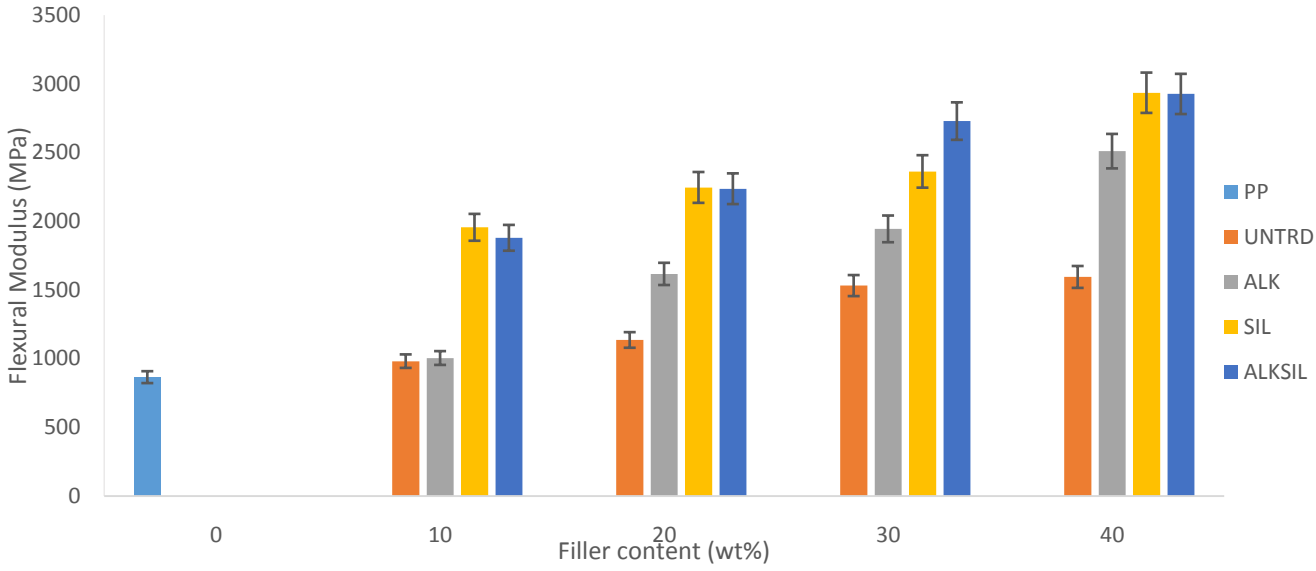


Figure 4.26: Flexural Modulus of PP/GHP Composites against filler content for various treatments

From the results shown, it was observed that, with GHP loading, there were increase in flexural moduli of the various composites produced. The flexural moduli of the unreinforced matrices were lower than those of their various composites in almost all the cases.

Figure 4.23 shows the results of flexural modulus for PLAP/GHP composites. The flexural modulus of the neat matrix was 3547.94MPa and even though various values were obtained for its composites, there was a progressive increase in flexural modulus with GHP loading. A very keen observation of the system showed that the flexural moduli of the UNTRD composites were higher than those of all the treated composites at all the GHP loadings indicating that the surface treatments applied in this system did not have influence on flexural modulus . Also, as compared to the PLAP matrix, flexural moduli of its composites were higher only at higher filler contents of 30 and 40%.

The flexural modulus results of PLABM/GHP composites with a value of 3255.53MPa for the unreinforced matrix are shown in Figure 4.24. It is indicated that there was an increase in flexural modulus with GHP loading and the moduli of all the composites were higher than that of the matrix. Unlike the results obtained for PLAP/GHP composites, the treated composites had higher moduli than those of the UNTRD. ALK treatment showed better flexural moduli indicating better interaction between filler and matrix. However, SIL treated composites had higher flexural modulus at 20 and 30% filler contents over the ALKSIL treated composites.

The flexural modulus results of PLPG/GHP composites are shown in Figure 4.25. Unlike the results obtained for tensile strengths and moduli as well as for flexural strength where the values obtained for PLPG were usually higher than those for PLABM, the flexural modulus of PLPG was lower in value than that of PLABM. The flexural modulus of PLPG was 2380MPa which was 49.07% and 36.71% lower than PLAP and PLABM respectively. The flexural moduli of the UNTRD composites were higher than that of the unreinforced matrix only at higher GHP contents of 30 and 40% while the ALKSIL treatment did not show any improvement in modulus as the values obtained were even lower than that of the matrix. The ALK and SIL treatments exhibited the highest moduli with ALK treatment giving the best influence.

The general trend of increase in modulus with GHP loading was also observed for PP/GHP composites as seen in Figure 4.26. The unreinforced PP had a flexural modulus of 864.73MPa and the flexural moduli of all its composites at all filler contents were higher than that of neat PP. The treated composites had higher flexural moduli than those of the untreated at all filler contents and the SIL and ALKSIL treated composites exhibited the best flexural moduli.

Ibrahim *et al*., (2012) defined flexural modulus as the ability of a material to maintain its dimensions before fracture and reported an increase in flexural modulus with addition of OPA fillers. Increase in modulus relates to the stiffness properties of the composites.

Huda *et al*., (2006) reported an increase in flexural modulus with addition of wood fibres in PLA matrix. They reported also that PLA and PLA-based composites possessed higher flexural strengths and moduli than PP and PP-based composites.

Yussuf *et al*., (2010) who reinforced PLA with Kenaf fibres reported higher flexural modulus of composites over the matrix due to the introduction of stiffer material in the soft matrix.

4.2.2.6 Hardness

The results for the hardness of the produced composites are presented in Figures 4.27 to 4.30 and Tables B1 to B4 in Appendix B.

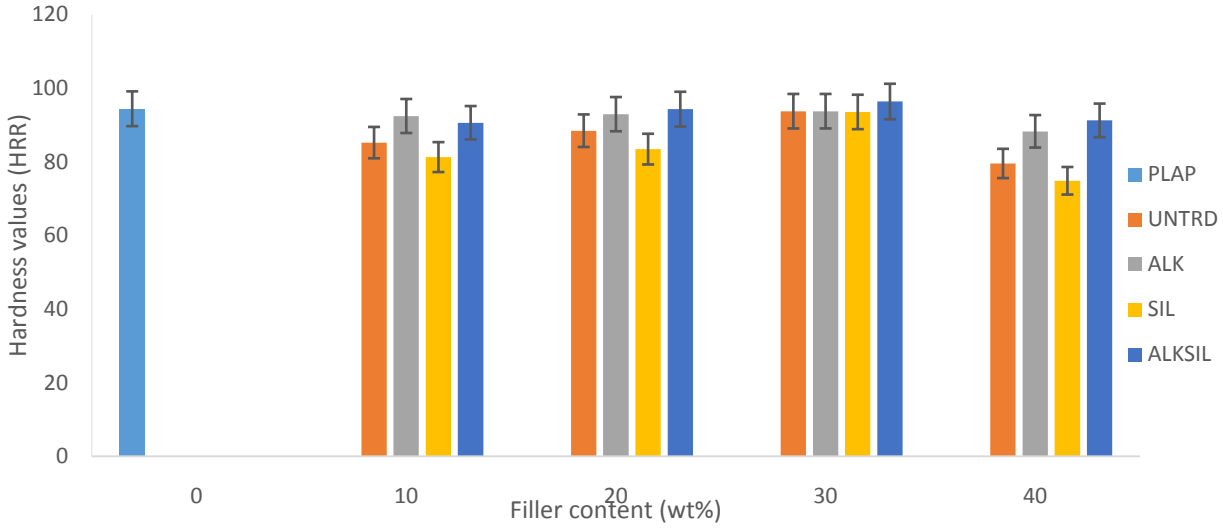


Figure 4.27: Rockwell Hardness values of PLAP/GHP Composites against filler content for various treatments

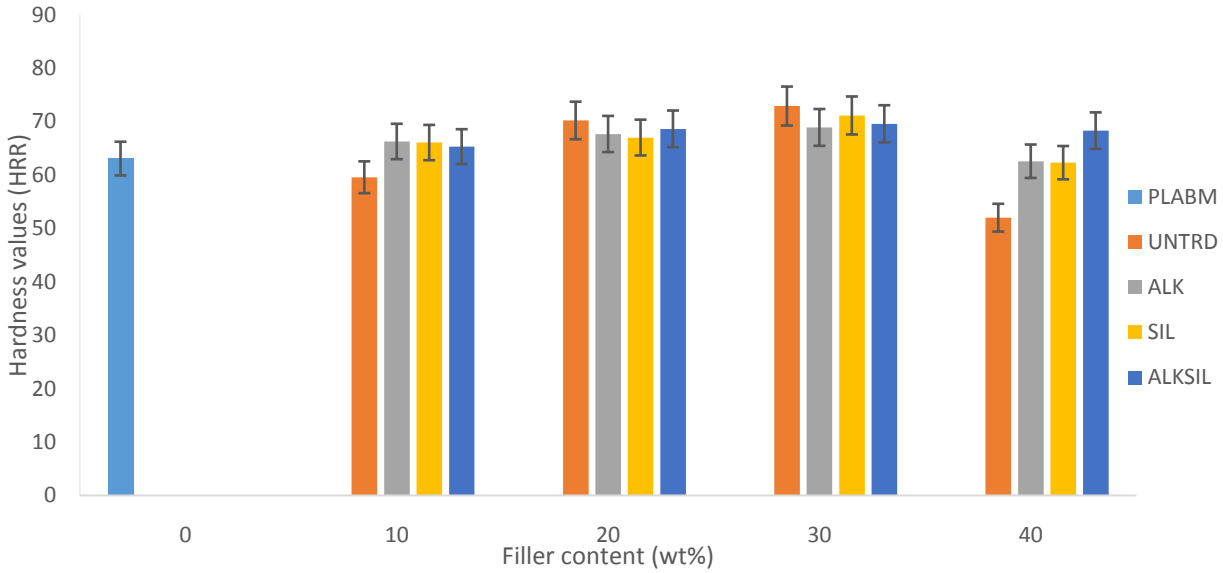


Figure 4.28: Rockwell Hardness values of PLABM/GHP Composites against filler content for various treatments

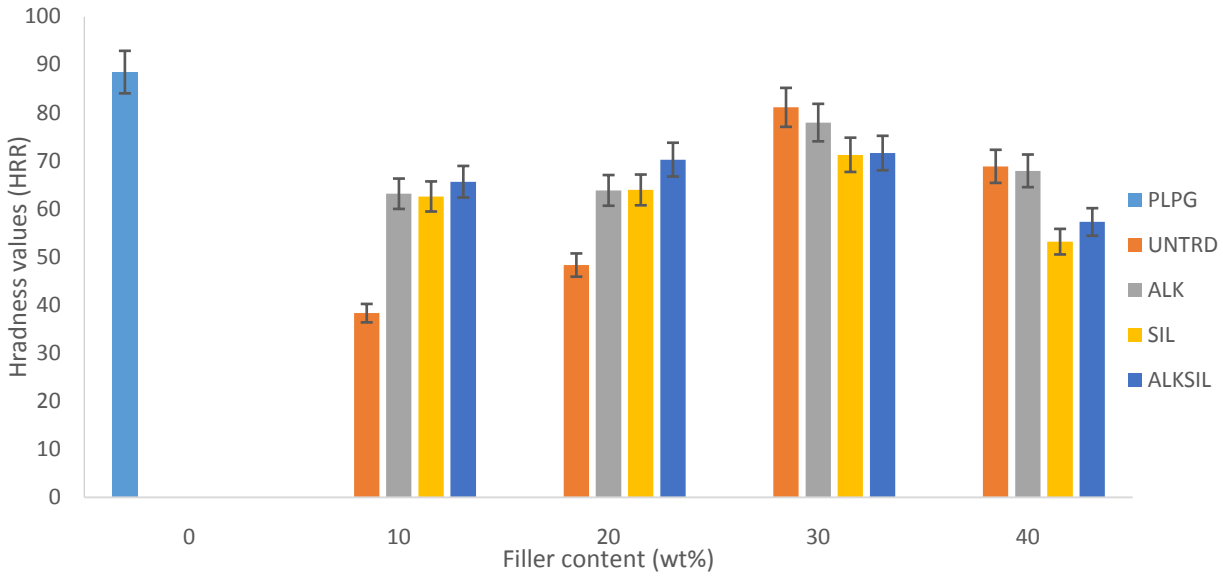


Figure 4.29: Rockwell Hardness values of PLPG/GHP Composites against filler content for various treatments

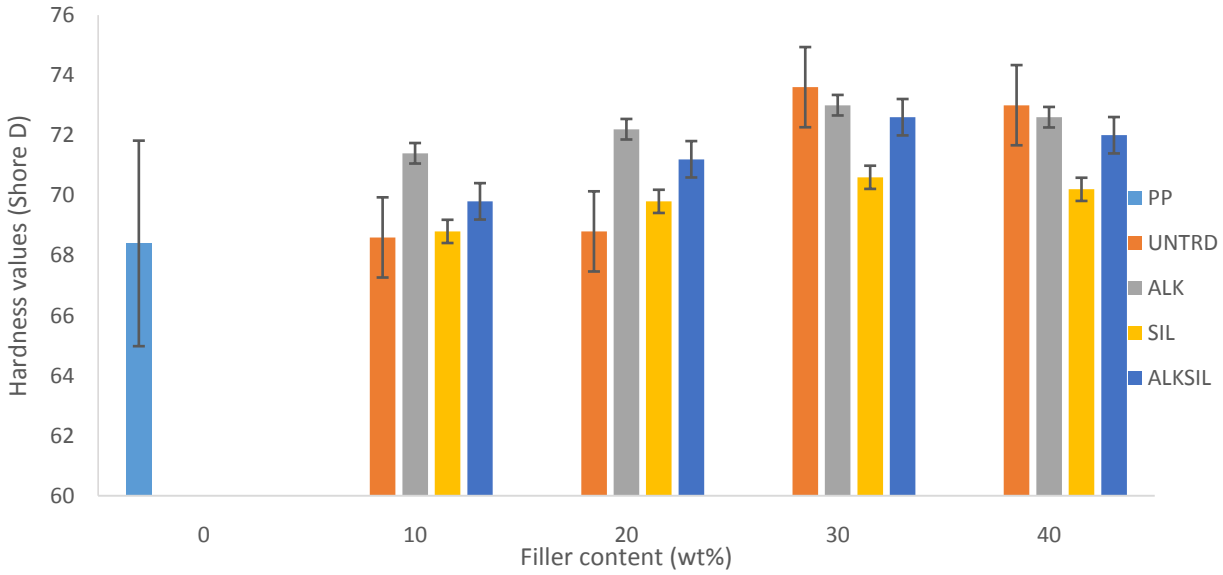


Figure 4.30: Shore D Hardness values of PP/GHP Composites against filler content for various treatments

The results showed a general increase in hardness with GHP loading for the composites. The increment occurred between 10 and 30% GHP contents and then decreased thereafter.

In Figure 4.27 the Rockwell hardness results for PLAP/GHP composites indicated that the matrix had the highest hardness value of 94.43HRR while the composites showed different values which were lower than that of the unreinforced matrix. However, the results showed a progressive increase in hardness with GHP loading up to 30% filler content but decreased afterwards for all the treated and untreated composites. ALK and ALKSIL treatments influenced the hardness as observed in the results but the SIL treatment did not improve the hardness of the composites with a range of values that lied between 81.30 and 74.87HRR as against those for the UNTRD which lied between 85.23 and 79.57HRR at GHP contents between 10% and 40% respectively.

The Rockwell hardness results for PLABM/GHP composites Figure 4.28 has the unreinforced matrix with a hardness value of 63.07HRR while higher values were recorded for its composites as against what was observed for PLAP/GHP composites where the unreinforced matrix had higher hardness over those of its composites. However, the hardness for the UNTRD composite at 10% GHP content with a value of 59.57HRR was lower than that of the unreinforced matrix. Surface treatments did not show significant improvement in the hardness of the composites as compared to the UNTRD composites. However, at 20 and 30% filler contents, the UNTRD composites with 70.2 and 72.9HRL respectively had the highest hardness.

The Rockwell hardness results for PLPG/GHP composites Figure 4.29 reveals that the hardness of the unreinforced matrix was 88.47HRR and various values were obtained for the composites even though they were lower than that of the matrix. Also, the hardness of the composites increased with GHP loading from 10 to 30% and decreased thereafter for all the treated and untreated composites. However, the treated composites exhibited higher hardness than the

untreated ones at 10 and 20% filler contents but they possessed lower hardness than the untreated ones at 30 and 40% filler contents.

The Shore D hardness results for PP/GHP composites 4.30 was also observed that hardness values increased with filler loading from 10 to 30% GHP content while the value decreased afterwards for all the treated and untreated composites. The PP/GHP composites possessed higher hardness than that of the unreinforced PP and surface treatments were not able to show significant improvement in hardness over the untreated composites.

Onuegbu and Igwe (2011) reported the hardness of PP/snail shell powder composites increased with increase in amount of filler incorporated which according to them, was an indication of abrasion enhancement.

Imoisili *et al*., (2012) reported an increase in hardness of composites with increase in filler level from 5% to 10% for both treated and untreated filler then the hardness decreased afterwards with increase in filler loading. Treated filler composites showed significant improvement in properties.

Saini *et al*., (2010) reported that hardness of PVC/Bagasse composites increased with filler loading but NaOH treatment did not change the hardness values of the composites. Hussein *et al*., (2011) reported that Shore D hardness of PP/egg shell composites decreased with increase in filler content. Hardness generally was considered to be a property of the surface. Egg shell leads to a decrease in the matrix surface resistance to indentation.

The increase in hardness with filler loading could be as a result of a more compact or rigid structure on the surface of the composite which leads to generation of greater resistance to penetration and consequently, higher hardness values are obtained for the composites with filler loading (Părpăriță *et al*., 2014) which could probably be the case in the present study.

4.2.2.7 Izod Impact Strength

The unnotced impact strength results of the produced composites are given in Figures 4.31 to 4.34 and Tables B1 to B4 in Appendix B.

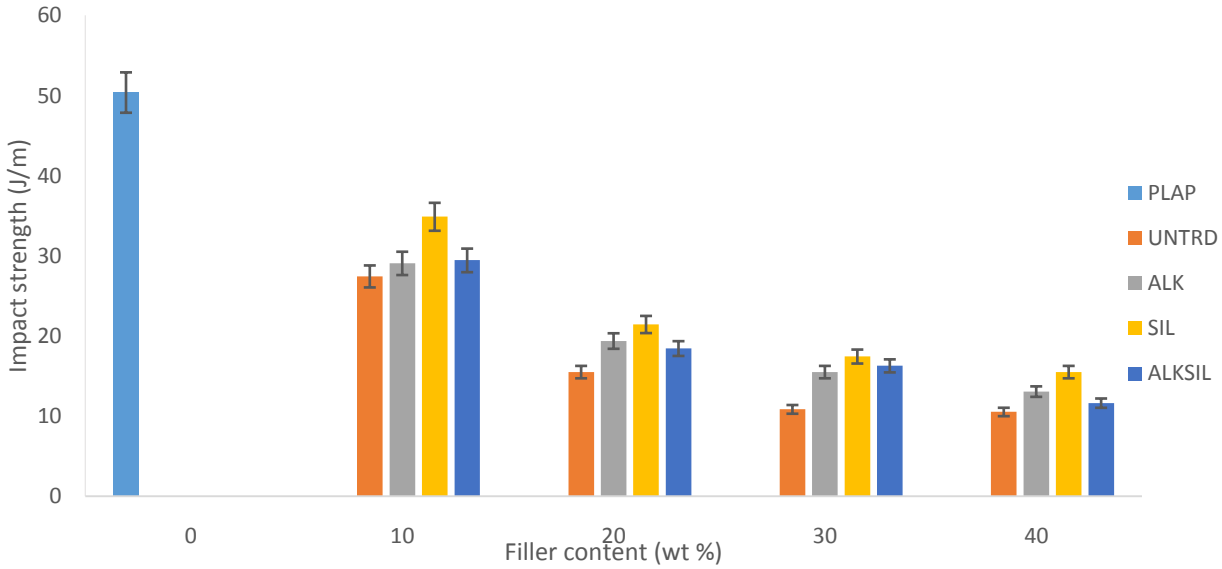


Figure 4.31: Izod Impact strength of PLAP/GHP Composites against filler content for various treatments

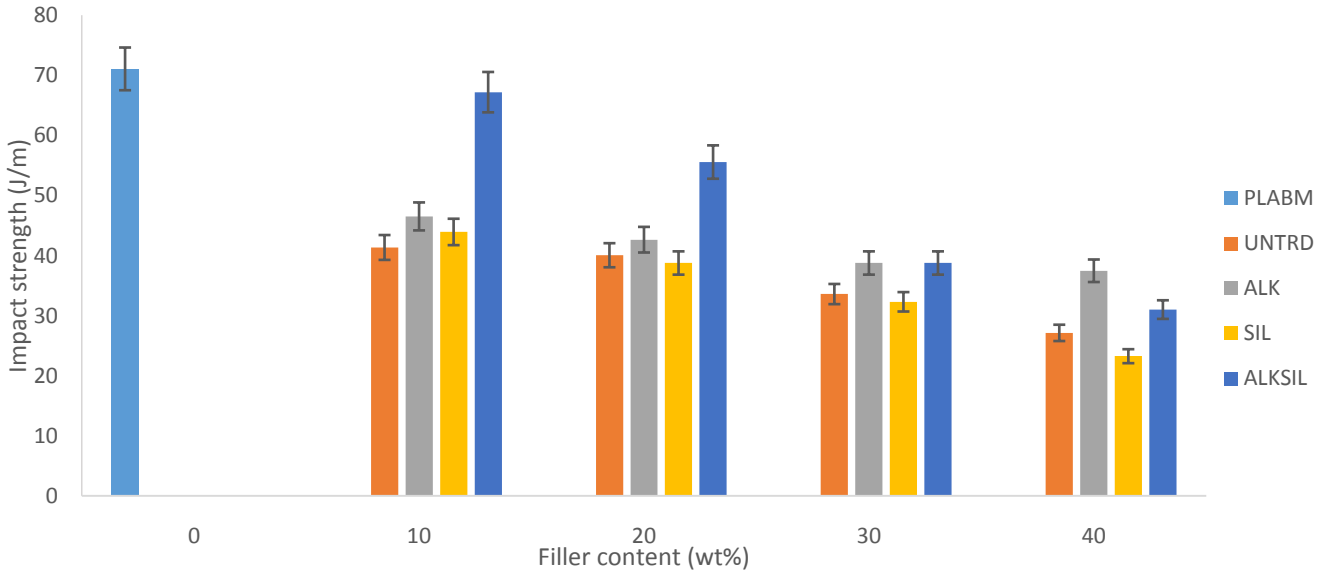


Figure 4.32: Izod Impact strength of PLABM/GHP Composites against filler content for various treatments

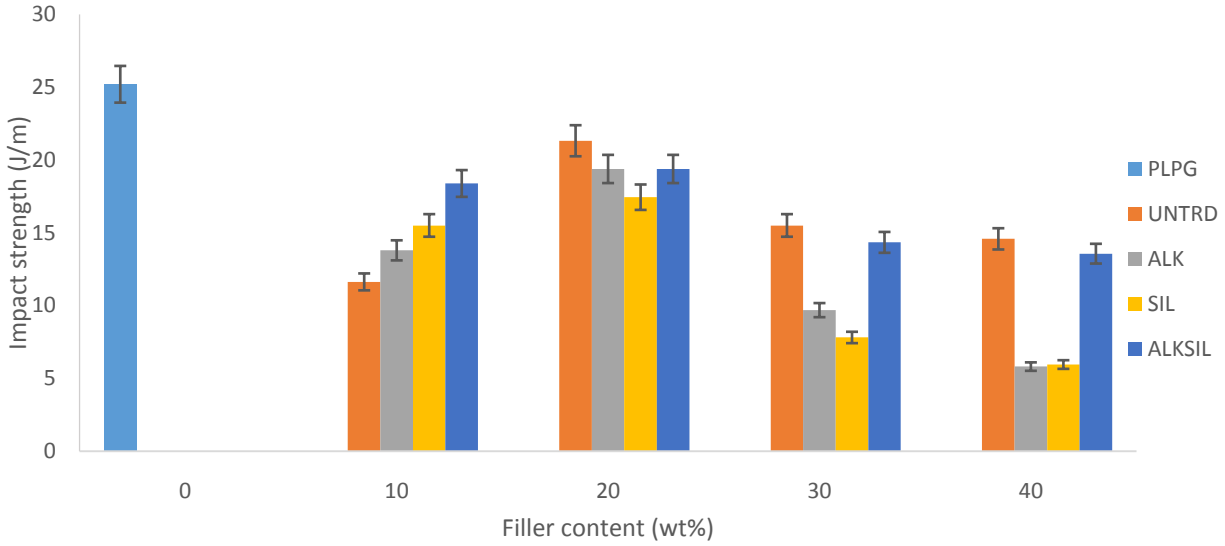


Figure 4.33: Izod Impact strength of PLPG/GHP Composites against filler content for various treatments

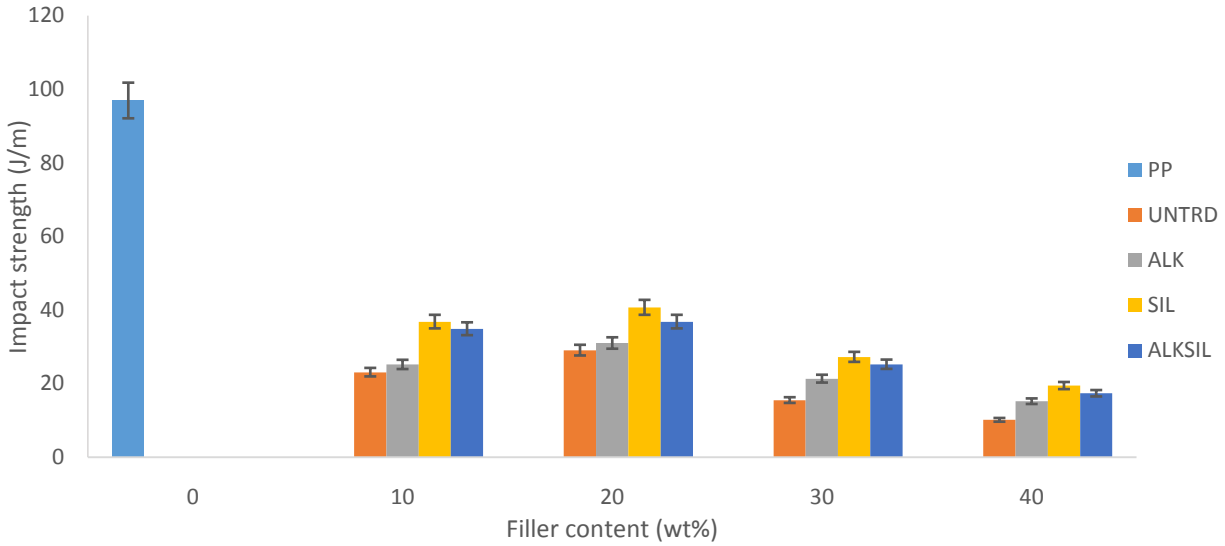


Figure 4.34: Izod Impact strength of PP/GHP Composites against filler content for various treatments

The results showed that the unreinforced matrices exhibited higher impact strengths than their respective composites and PLABM with a value of 71.06J/m. possessed the highest impact strength with respect to the other PLA matrices while PP with a value of 96.89J/m, recorded the highest impact strength amongst all the matrices even though the sample did not break. Also, it was observed that the impact strength decreased with GHP loading for all the composite systems.

Figure 4.31 indicates that the impact strength of unreinforced PLAP was 50.39J/m while its various composites at all filler loading possessed lower strengths and these decrease with GHP loading. It was observed also that the treated composites had better impact strengths than the untreated ones with the SIL treated composites exhibiting the highest impact strength at all the filler contents.

The results for the impact strength of PLABM/GHP composites in Figure 4.32 has the impact strength of the unreinforced matrix to be 71.06J/m. The impact strength for the composites decreased with filler loading and they were lower than those of the unreinforced matrix. The ALKSIL composites showed the highest impact strengths followed by those of the ALK treated composites at all filler contents while the UNTRD composites had higher impact strengths than those of the SIL treated ones except at 10% filler content where the SIL treated composite with impact strength of 43.93J/m was higher than that of the UNTRD which possessed an impact strength of 41.34J/m. The results obtained indicated that SIL treatment did not influence the impact strength of PLABM/GHP composites.

Figure 4.43 shows the impact strength results for the PLPG/GHP composites with a value of 25.19J/m for the unreinforced matrix. The impact strengths for the composites were lower than

that of the matrix and they increased between 10 and 20% GHP content and then subsequently decreased afterwards. It was observed also that the results obtained for this system were the lowest as compared to the other composite formulations. This could be attributed to the presence of PEG which probably have poor impact properties.At 10% GHP content, the impact strengths were 11.63J/m, 13.79J/m, 15.50J/m and 18.38J/m for UNTRD, ALK, SIL and ALKSIL treated composites respectively while at 40% filler content, the impact strengths were 14.58J/m, 5.81J/m, 5.95J/m and 13.57J/m for UNTRD, ALK, SIL and ALKSIL treated composites respectively. The results also showed that UNTRD composites exhibited higher impact strengths than the treated ones except at 10% filler content.

The results of impact strength for PP/GHP composites in Figure 4.34 reveals that the pure PP exhibited an impact strength of 96.90J/m while its composites exhibited lower impact strengths than the matrix (Bajpai *et al*., 2012) but the impact strengths increases initially from 10 to 20% filler content then decreased subsequently with filler loading. The SIL treated composites showed higher impact strengths than those of the untreated and other treated composites while the other treated composites possessed higher impact strengths than the untreated composites indicating that the surface treatments influenced the impact strengths of PP/GHP composites.

MatTaib *et al*., (2010) reported that the impact strength of PEG plasticized PLA/Kenaf fibre composites decreased with fibre loading. They attributed this behaviour to the presence of fibre ends inside the composites that can cause crack initiation and propagation and hence composite failure. PEG addition improved the impact strength of PLA/40%KF by19% from 5.9 to 7.0 kJ/m^2, the improvement, however, was not high enough to justify the use of PEG as a plasticizer for PLA/KF composites.

Khanjanzadeh *et al*., (2012) reported that typically, a polymer matrix with high loading of fillers has less ability to absorb impact energy. Fillers disturb matrix continuity and individual filler is a site of stress concentration, which can act as a micro-crack initiator. In light of nanoclay effect, contrary to flexural and tensile properties, impact strength slightly decreased with incorporation of nanoclay content. The higher the nanoclay content, the lower was the impact strength. With increasing nanoclay content in the mixture, the impact strength decreased.

Saini *et al*., (2010) reported that impact strength of PVC-bagasse composites decreased with increasing amount of filler. The decrease was significant at 40% filler content. On the other hand, impact strength increased significantly when alkali-treated bagasse powder was used as filler, but was still lower compared to PVC. Khanjanzadeh *et al*., (2012) also reported the decrease in impact strength of PP/Wood flour composite with increase in nanoclay content.

Părpăriță *et al*., (2014) reported that the impact strength of the PP containing various biomass as fillers decreased compared to PP matrix explaining that the biomass filler reduces the mobility of the polymer chains and in consequence the ability to absorb energy during fracture propagation. Therefore, the poor interfacial bonding can induce micro-cracks which further propagate easily and decreased the impact strength of the composites.

Yang *et al*., (2004) reported that the un-notched Izod impact strengths of the composites at different filler contents slightly decreased as the filler content increased probably due to microspaces between the filler and matrix polymer, and these cause numerous micro-cracks when impact occurs, which induce crack propagation easily and decrease the impact strength of the composites. Izod impact strength of the composite made of 100wt.% matrix polymer

(polypropylene) showed significantly high impact strength, which was drastically decreased at 10 wt.% filler loading. The un-notched impact behavior is controlled to a considerable extent by fracture initiation processes that, in turn, are controlled by stress concentrations at defects in the system.

The reduction of impact strength with filler loading could be attributed to the fact that fillers provide points of stress concentrations which could probably provide sites for crack initiation and potential composites failure (Pilla *et al*., 2008; Nourbakhsh *et al*., 2010). Another reason could be that addition of fillers could increase the probability of cellulosic fillers agglomeration which then create regions of stress concentration requiring less energy to elongate the crack propagation.

Furthermore, the rapid decline in impact strength with flour content could be attributed to the restriction in polymer chain mobility as a result of incorporation of stiffer fillers which then reduces the capacity of composites to absorb energy. Also, at regions of more filler-to-filler contact, stress concentration normally exist which leads to poor interface hence, the reduction of impact strength (Thamae *et al*., 2009)

4.2.2.8 Morphological studies

The SEM micrographs for tensile fractured surfaces of composite specimens are presented in Plates II to V

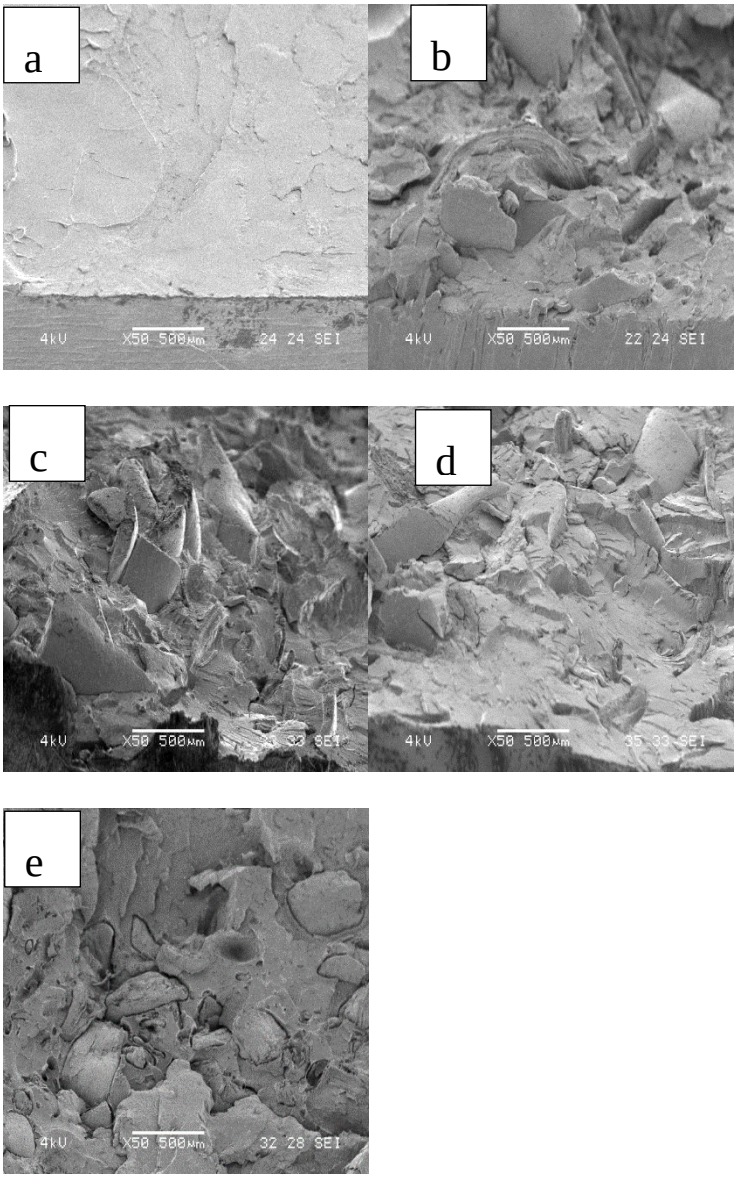


Plate II: SEM micrographs for tensile fractured surfaces of PLAP/GHP Composites at 10% GHP(a) Unreinforced PLAP (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated

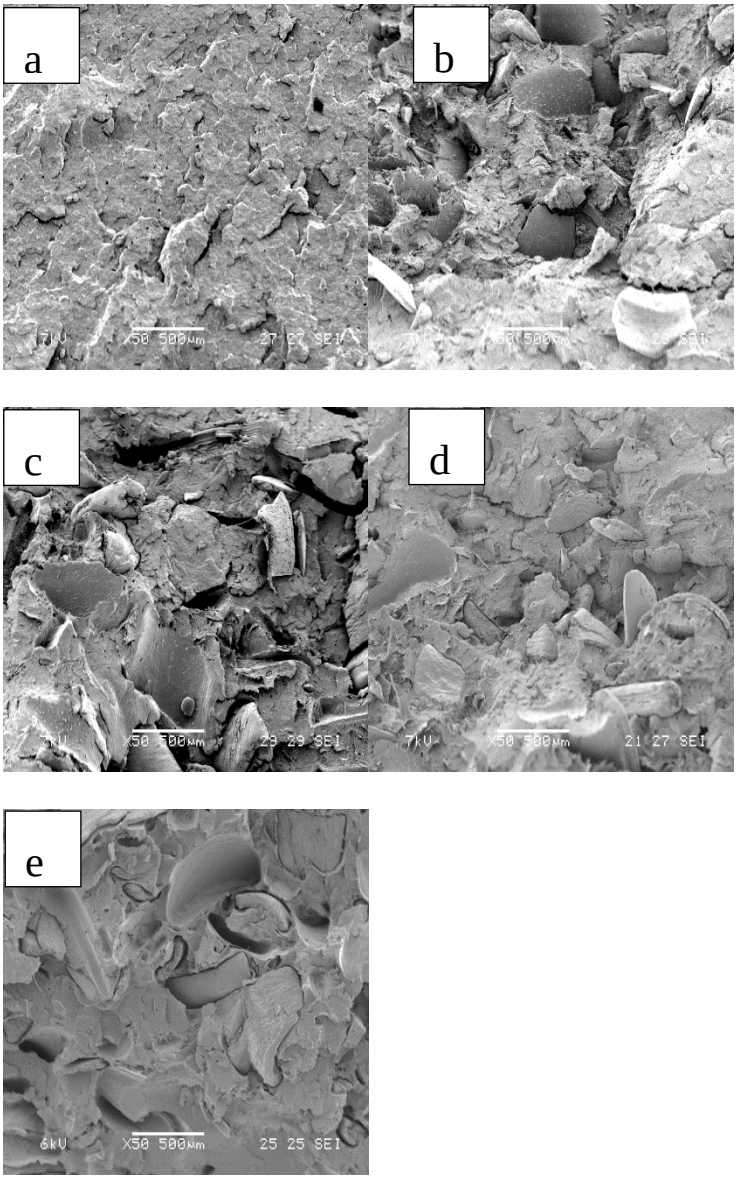


Plate III: SEM micrographs for tensile fractured surfaces of PLABM/GHP Composites at 10% GHP(a) Unreinforced PLABM (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated

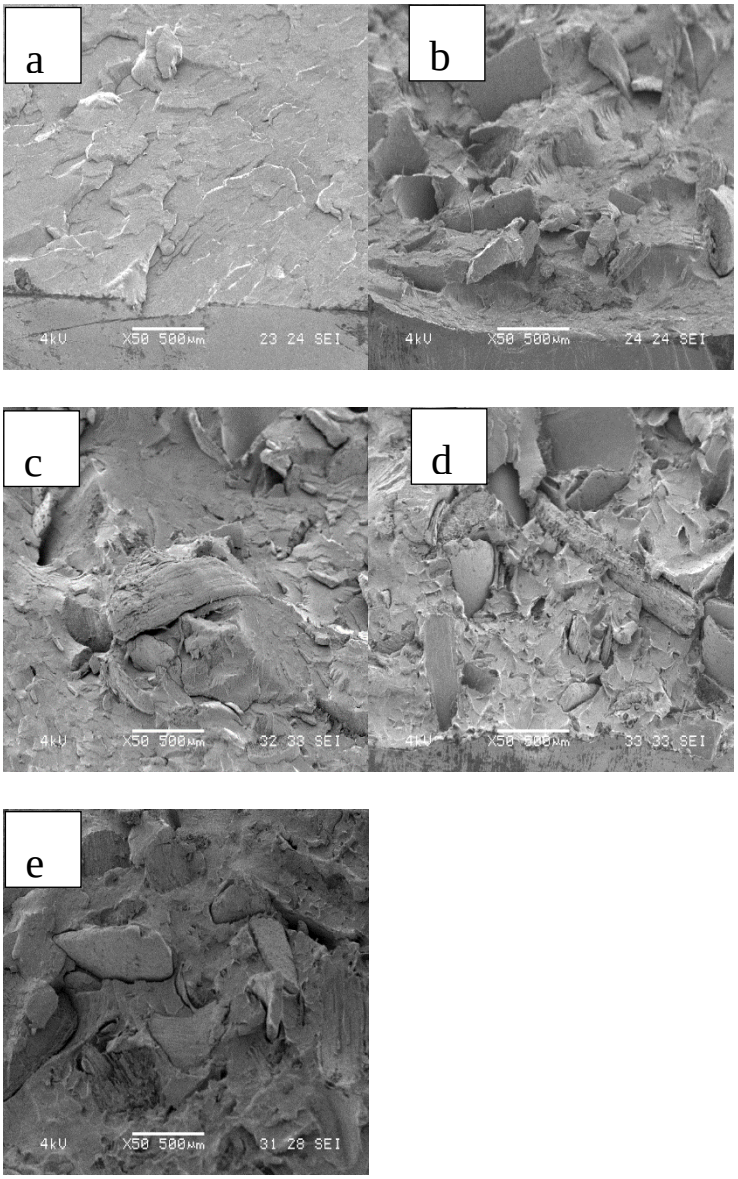


Plate IV: SEM micrographs for tensile fractured surfaces of PLPG/GHP Composites at 10% GHP(a) Unreinforced matrix (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated

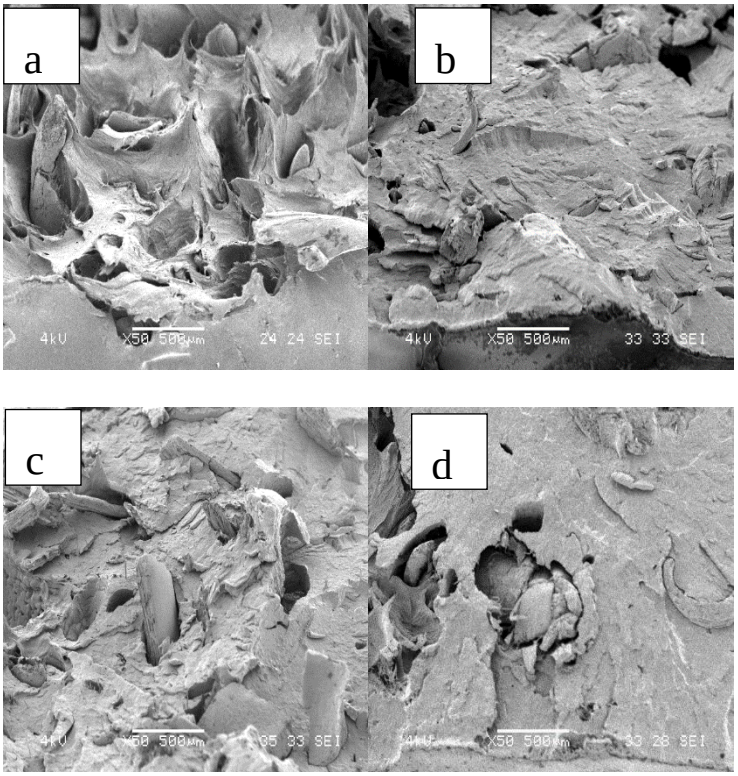


Plate V: SEM micrographs for tensile fractured surfaces of PP/GHP Composites at 10% GHP(a) UNTRD (b) ALK treated (c) SIL treated (d) ALKSIL treated

The SEM micrographs taken from the fractured surfaces of PLAP and its composites after the tensile test are shown in Plate II a-e. The fracture surface of PLAP matrix (a) showed a smooth surface indicating brittle failure. The surface for the UNTRD Specimen showed some little amount of voids due to pullout of fillers and also agglomeration of fillers. The ALK treated specimen showed a better distribution of filler within the matrix. The SEM image for SIL treated composite showed that the fracture actually occurred at the matrix since the matrix covered the filler surface showing or indicating good adhesion between the constituents. The ALKSIL treated specimen showed well bonded filler and matrix as only little amount of filler was seen in the SEM image.

SEM micrographs for PLABM/GHP composites are shown in Plate III a-e. The PLABM showed some tiny dots all over the surface which may probably be due to the Biomax Strong that was used as an impact modifier. The image for the UNTRD specimen showed numerous fillers with no matrix around which could be as a result of poor adhesion at the interface. As for the ALK treated filler specimen, a few voids were observed with failure taking place probably at the interface. The SIL treated specimen indicated that a layer of matrix had covered the filler which shows that failure took place at the filler itself indicating good adhesion. The ALKSIL treated specimen showed the least amount of filler and low amount of voids due to superior bonding between the constituents as a result, a better tensile strength was recorded.

Plate IV a-e shows the SEM micrographs for PLPG and its composites. The fracture surface of PLPG was smooth indicating a near ductile failure. The UNTRD specimen showed filler agglomeration and poor interfacial bonding suggesting that failure occurred along the interface which produced low tensile strength. The ALK specimen showed better interaction between the filler and the matrix thereby leading to good wetting of the filler. The SIL treated specimen showed many fillers suggesting debonding of the matrix from the fillers and lower mechanical property. Also, there was filler detachment from the matrix. The ALKSIL treated specimen showed the best interaction between filler and matrix as less fillers are seen in the micrographs suggesting a good wetting of the filler by the matrix.

As a result of lack of fracture for virgin PP, the SEM micrograph was not available but those of its composites are shown in Plate V a-e. Matrix drawing and fibrillation was observed in the PP/GHP composite which indicated ductile failure. However, the UNTRD specimen showed image that was characterized by filler pull-out which leads to voids generation within the

composite. Due to good distribution of filler, there was little or no agglomeration in the SEM image for ALK treated sample. The SIL treated specimen contained voids as a result of filler pull-out from the matrix even though this was not as pronounced as that observed in the UNTRD specimen. Here also, the ALKSIL treated specimen showed the best filler-matrix interaction. The failure was within the matrix.

4.2.3 Water absorption test

After 30 days of water absorption test for the composites, the results from Figure 4.35 to 4.39and Figures E1 to E16 in Appendix E show the water absorption profiles of the composites.

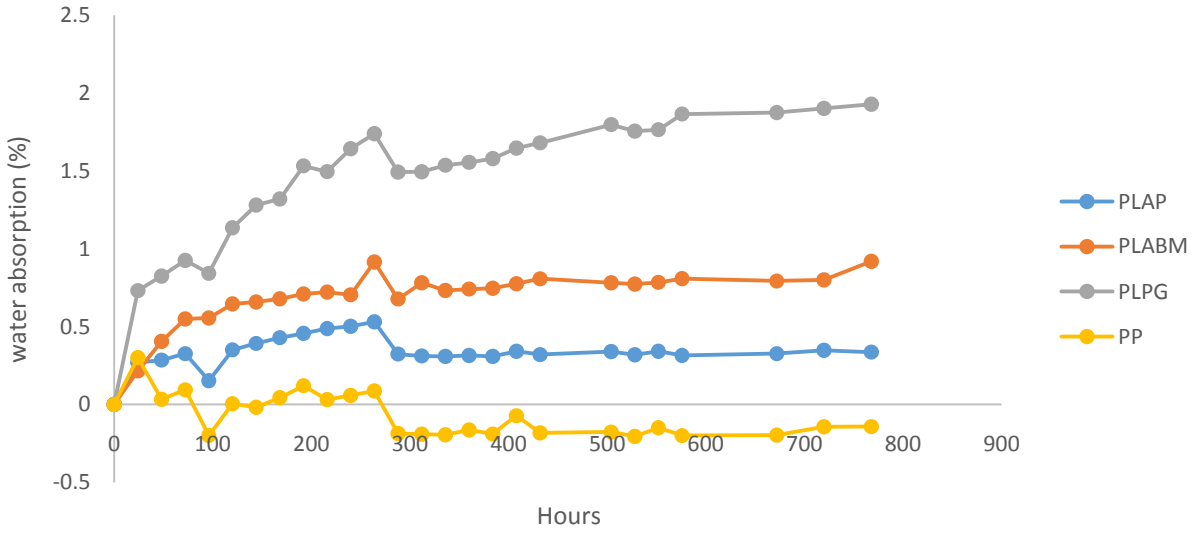


Figure 4.35: Water absorption curves of unreinforced matrices

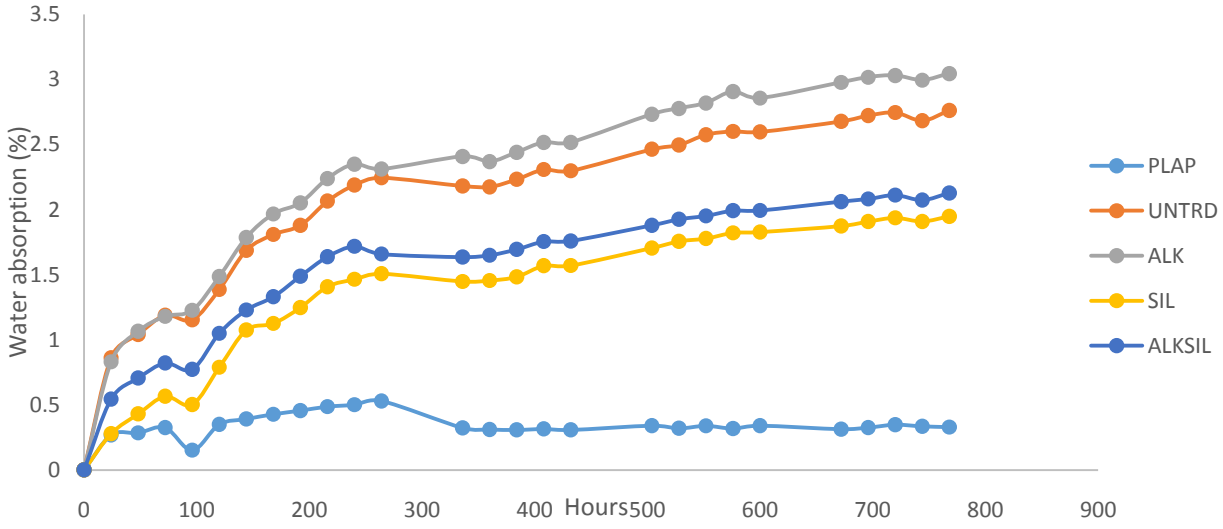


Figure 4.36a: Water absorption curves of PLAP/GHP Composites at 10% filler content

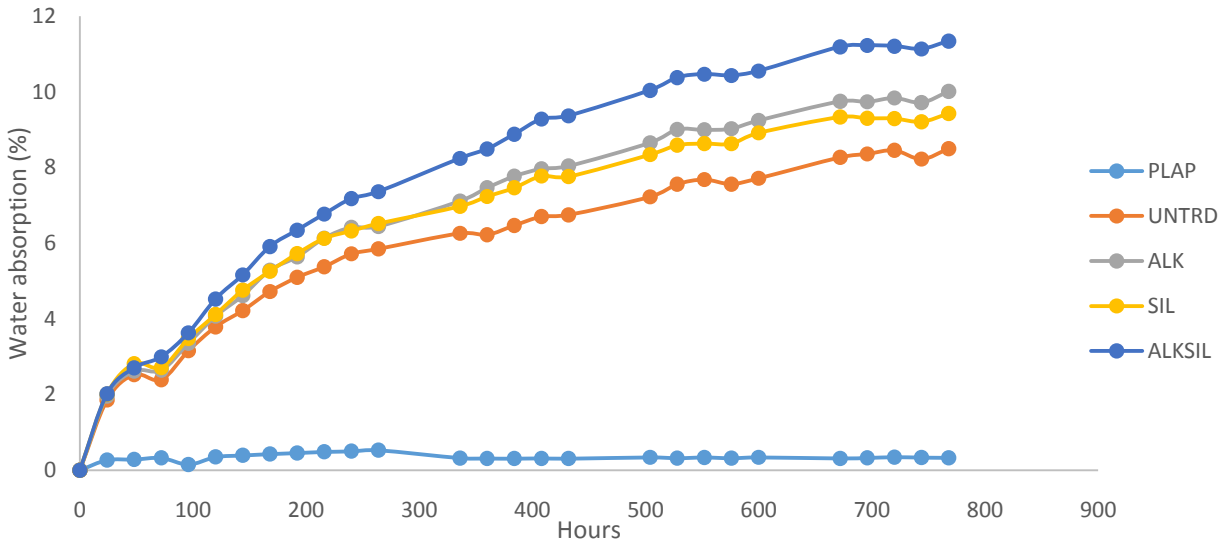


Figure 4.36b: Water absorption curves of PLAP/GHP Composites at 40% filler content

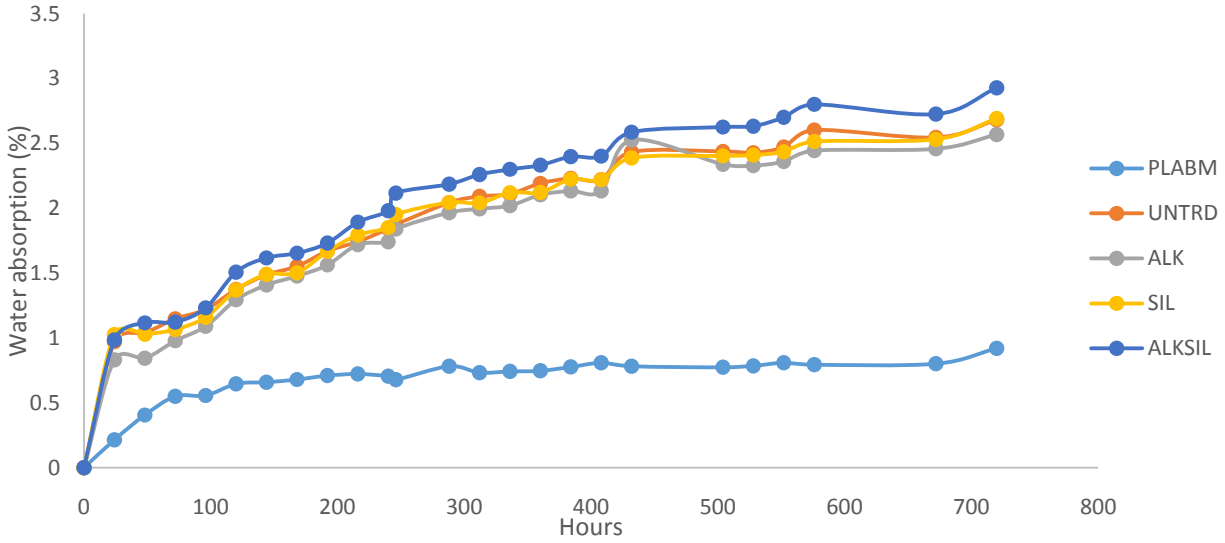


Figure 4.37a: Water absorption curves of PLABM/GHP Composites at 10% filler content

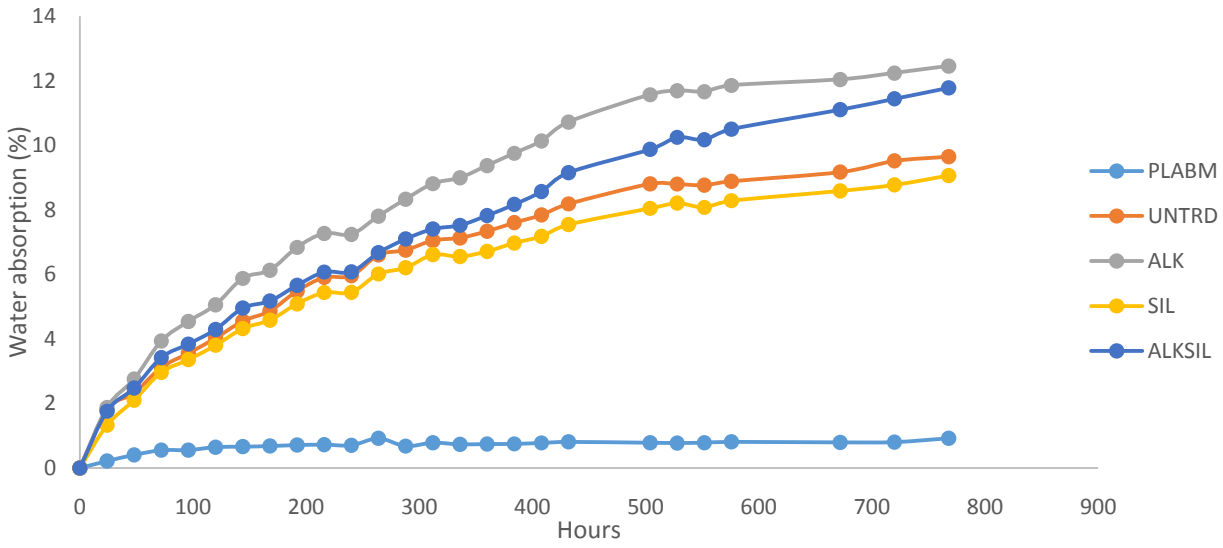


Figure 4.37b: Water absorption curves of PLABM/GHP Composites at 40% filler content

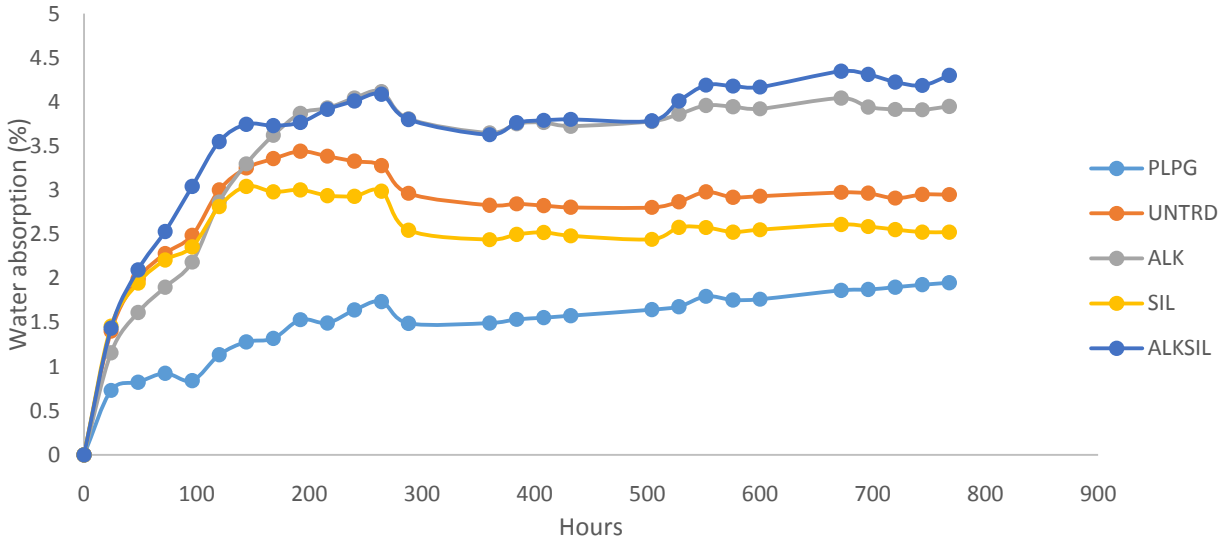


Figure 4.38a: Water absorption curves of PLPG/GHP Composites at 10% filler content

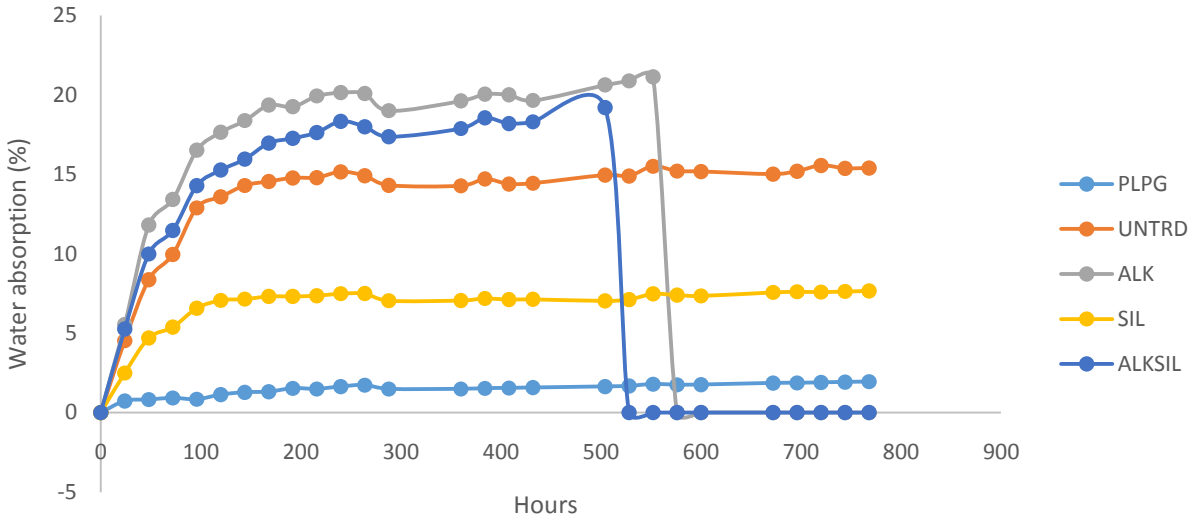


Figure 4.38b: Water absorption curves of PLPG/GHP Composites at 40% filler content

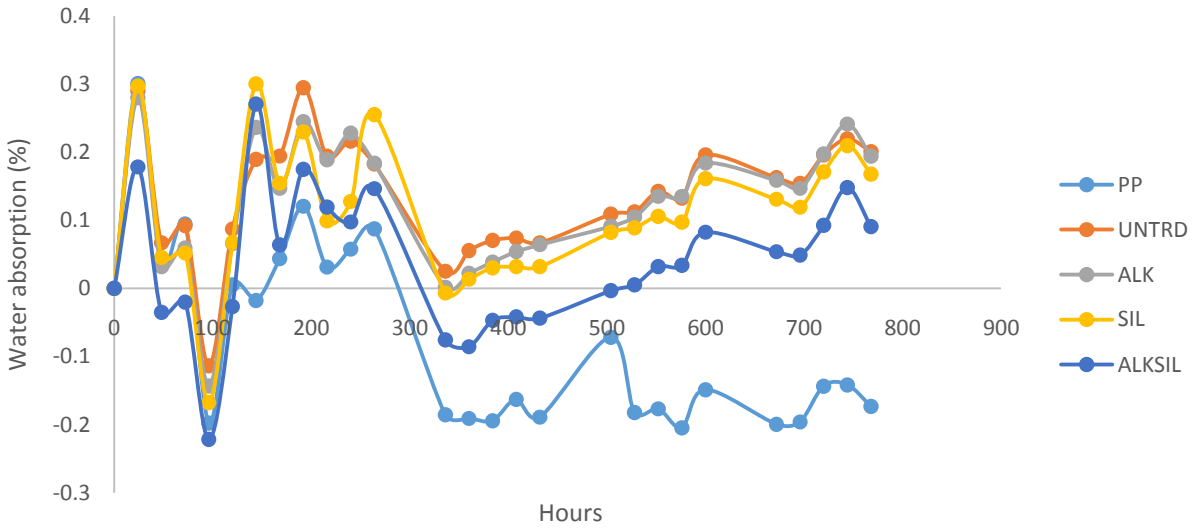


Figure 4.39a: Water absorption curves of PP/GHP Composites at 10% filler content

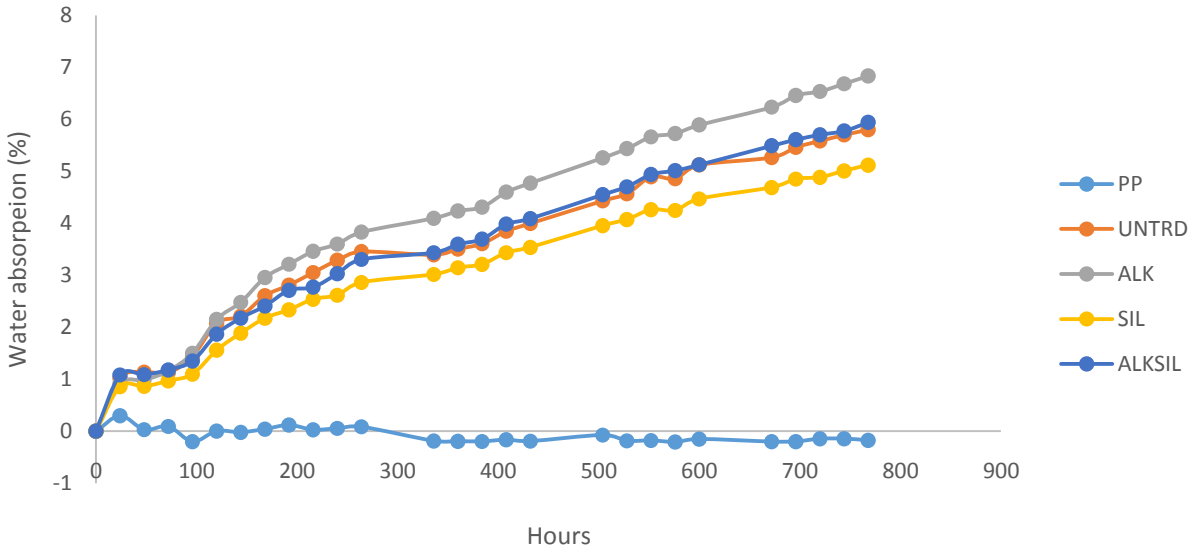


Figure 4.39b: Water absorption curves of PP/GHP Composites at 40% filler content

The results indicated that water absorption increased with filler loading (Gelfuso *et al*., 2011; Hardinnawirda and SitiRabiatull, 2012; Viet *et al*., 2012) and the water absorption values for the various matrices were all lower compared to their various composites. Also, the water absorption values of PP and PP-based composites were the least as compared to the values obtained for the various PLA matrices and their various composites.

The water absorption test results for the unreinforced matrices after 30 days in Figure 4.35 indicates that PP had the least water absorbed profile which generally showed negative value for the most part of the test. This is attributed to its stable and hydrophobic nature. However, the PLA matrices exhibited different degrees of water absorption with PLAP being the least to absorb water within the PLA matrices while PLPG absorbed water the most. The reason attributed to PLPG behaviour could be due to the PEG which is generally known to be water soluble or hydrophilic which contributed immensely in the water absorption behaviour. But over

a period of 30 days of immersion in water, the maximum water absorbed were about 0.5%, 0.9% and 1.8% for PLAP, PLABM and PLPG respectively.

The results for PLAP/10% GHP and PLAP/40% GHP composites after 30days of water absorption test are shown in Figures 4.36a and 4.36b respectively. At 10%GHP content, it was observed that SIL treated composites exhibited the least water absorption values while the ALK treated composites exhibited the highest water absorbed values with a maximum value of 3.05%.The order of increase in water absorption was SIL<ALKSIL<UNTRD<ALK.

The PLAP/40% GHP composites in Figure 4.36b indicated that the UNTRD composites absorbed water the least followed by SIL treated composites while the highest amount of water absorbed was exhibited by ALKSIL treated composites followed by ALK treated composites. The maximum water absorption of 11.36% was exhibited by the ALKSIL treated composites at the end of the test.

The results for the water absorption test for PLABM/10%GHP and PLABM/40% GHP composites after 30days are shown in Figures 4.37a and 4.37b respectively. The water absorption curves at 10%GHP showed that the ALKSIL treated composites possessed the highest amount of water absorbed values as compared to other treated and untreated composites but the values were not significant. The curves for UNTRD, SIL and ALK treated composites over- lapped one another. The maximum water absorption of 2.93% was exhibited by the ALKSIL treated composites.

PLABM/40% GHP composites after 30days of water absorption test in Figure 4.37b indicated that the least water absorbed composites were those for SIL treated composites while the

UNTRD composites exhibited slightly higher water absorbed values than the SIL treated composites. The ALK treated composites exhibited the highest water absorption while the ALKSIL treated composites showed slightly lower values than the ALK treated composites. The maximum amount of water absorbed was 12.46% by the ALK treated specimens at the conclusion of the test.

The water absorption test results for PLPG/10%GHP and PLPG/40% GHP composites after 30days are given in Figures 4.38a and 4.38b respectively. From the curves shown at 10% GHP, it was observed that SIL treated composites absorbed water the least while ALKSIL treated composites absorbed water the most. The maximum amount of water absorbed in the entire period of the test was 4.34% by the ALKSIL treated specimen.

The curves for 40% GHP composites shown in Figure 4.38b indicated that SIL treated composites exhibited the least water absorbed behaviour while the ALK treated composites exhibited the maximum water absorption of 21.12%. From the Figure (Figure 4.38b), the water absorbed values increased steadily and almost stable after 300hrs and seemed constant afterwards. Similar behaviour was exhibited by the UNTRD composite but at higher values than the SIL treated composites. The ALK and ALKSIL treated composites showed the maximum amount of water absorbed in the study with a maximum of about 20%. However, the ALK and ALKSIL treated composites specimen broke after 500hrs of the test which led to the termination of test for the two specimens.

After 30days of water absorption test for PP/10% GHP and PP/40% GHP composites, the results are shown in Figures 4.39a and 4.39b. The results showed that there was almost no water

absorbed at 10% GHP as the values were very low and maximum being 0.3% in the first few days. Negative values of water absorption were also obtained during the course of the test.

The results of water absorption test for PP/40% GHP composites after 30days as shown in Figure 4.39b also showed the SIL treated composites as exhibiting the least water absorption while the ALK treated composite exhibited the highest water absorption over the entire period of the test. The maximum amount of water absorbed for PP/40% GHP was 6.8%.

The water uptake of the composites could be attributed to the hydrophilic nature of the GHP which is known to be a lignocellulosic material. The extent of water uptake by lignocellulosic filler composites depends on the amount and nature of fillers and the matrix (Alvarez and Vázquez, 2004; Tserki *et al*., 2006a).

The increase in water uptake with filler loading maybe attributed to the fact that as filler content increases, there could probably be introduction of voids in the polymer matrix which results in a higher filler-to-filler interaction rather than filler-to-matrix interaction (Gelfuso *et al*., 2011).

The water absorption of PLPG/GHP composites was the highest of all the composites formulation. This could be attributed to the presence of PEG which is water soluble in nature. Being a water soluble material, the PEG could have been leached out from the matrix during the period of the test. PLA on the other hand, is easily hydrolyzed and as a result, voids could have been created in the material which provided sites for the accumulation of water molecules thereby generating internal stresses that led to micro-cracking (Mat Taib *et al*., 2010) of the matrix as seen in the SEM micrographs of Plate VIII.

On a general note, Polypropylene hardly absorbs water as a result of its strong hydrophobic nature (Rosa *et al*., 2009). However, GHP being hydrophilic in nature led to the absorption of water by the composites made with PP polymer. The results for the water absorption test indicated that increasing the filler content and water contact time translated to increased water absorption for the PP/GHP composites.

Saini *et al*., (2010) reported an increase in water uptake for PVC/BP composites with increasing amount of BP as well as immersion time. In their study, they reported that water uptake was within the range of 0.18 and 7.98%. The water absorption of lignocellulosic materials according to Mir *et al*., (2013) is because the hydroxyl (-OH) groups attached to these materials are responsible for the uptake of water because, with increase in the filler content, the number of (-OH) groups as well as micro-voids created in the composites increase which then leads to increase in water uptake of the composites.

It was also observed from the results presented that at low filler contents, the water absorption was also low. This could be as a result of full encapsulation of a greater percentage of the particles by the polymer matrices and except for those particles exposed on the composites surfaces, the encapsulated particles were not very much in contact with water. Therefore, the probability of such specimens taking part in the absorption of water was very low and it is believed that no significant change could occur in the microstructure of the composites. However, increase in filler content increases the chances of filler-to-filler interaction thereby forming agglomerates that subsequently form clusters which serve as passages for water movement (Yang *et al*., 2006; Thamae *et al*., 2009).

Surface treatments led to an increase or decrease in water absorption of the composites. From the results, it was observed that the SIL treated composites generally absorbed less water than the ALK and ALKSIL treated composites. Also, as observed from this study, the ALK treated composites generally absorbed water the most even above the UNTRD composites.

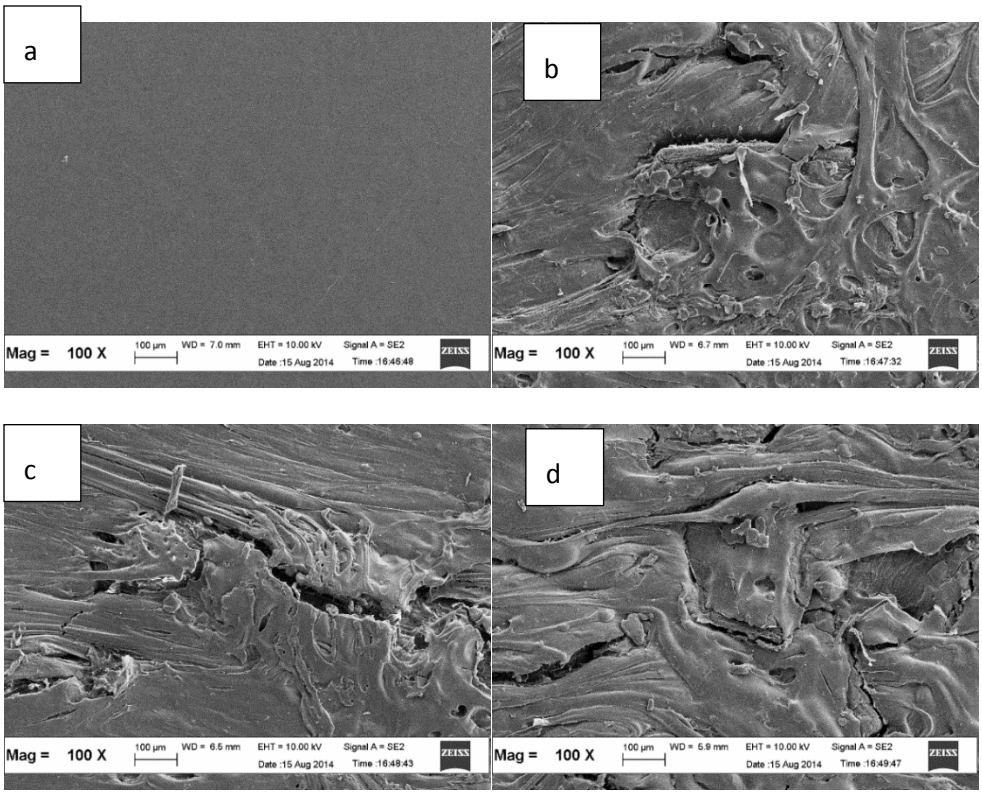
The findings in this study on ALK treated samples absorbing more water than silane treated and untreated samples goes contrary to what was reported by Ahmad *et al*., (2007) who submitted that composites with alkalized filler showed lower water absorption properties than that of the untreated ones. However, the finding was in agreement with some other literatures such as Gelfuso *et al*., (2011) who reported that alkalized samples presented higher water absorption (13%) than the ultrasonic shockwave samples (7%) due to the fact that alkali treatment was inefficient in removing the –OH groups on the fillers surface causing higher retention of water. Also, Sgriccia *et al*., (2008) reported that alkali treated kenaf and hemp composites absorbed more water than the silane or alkali/silane treated samples. In fact, they reported that the untreated, silane and alkali/silane treated samples had similar water absorption profiles. They explained that treatment with NaOH removes lignin, pectin, waxy substances as well as natural oils covering the surface of fibre cell walls which changes the fibre morphology by revealing the fibrils that probably created more voids for easy water penetration.

Furthermore, Alvarez *et al*., (2003) and ThaoTran *et al*., (2014) reported higher water absorption by alkaline treated composites than those of silane treated composites. While Alvarez *et al*., (2003) explained that the higher water absorption after alkaline treatment was because it rendered the fillers more hydrophilic by changing cellulose I to cellulose II. Thao Tran *et al*., (2014) reasoned that the decrease in water absorption after silane treatment was due to the fact

that silanes react with the hydroxyl groups on the glucose units of the cellulose molecules in the cell wall of the husk such that it weakened the ability of the husk to absorb water.

4.2.3.1 Morphological study after water absorption

The SEM micrographs after water absorption for 30 days are presented Plates VI to IX.



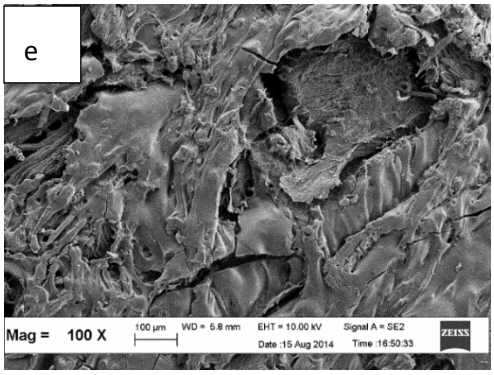
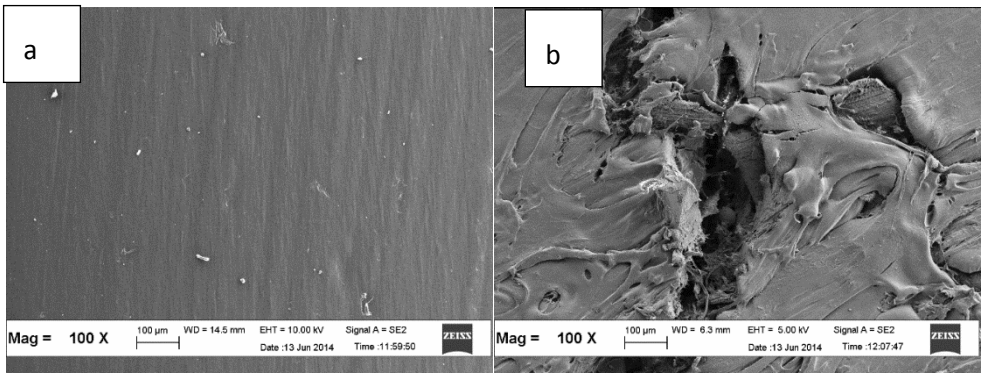
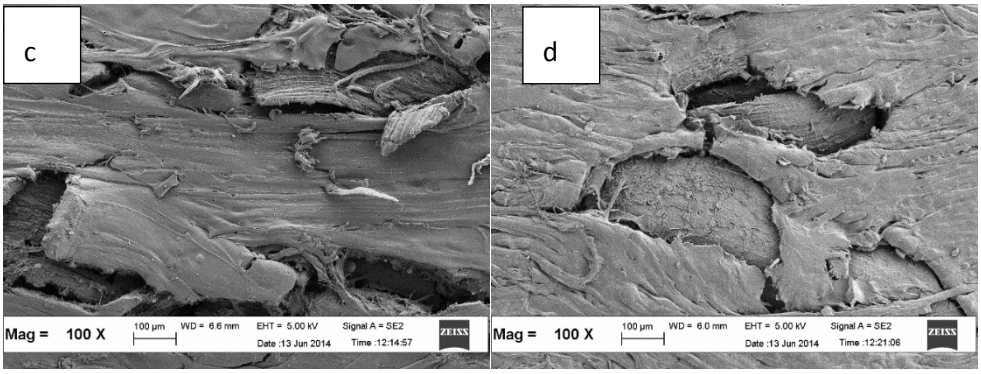


Plate VI: SEM micrographs showing surfaces of PLAP/40% GHP Composites after water absorption for 30 days(a) Unreinforced PLAP (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated





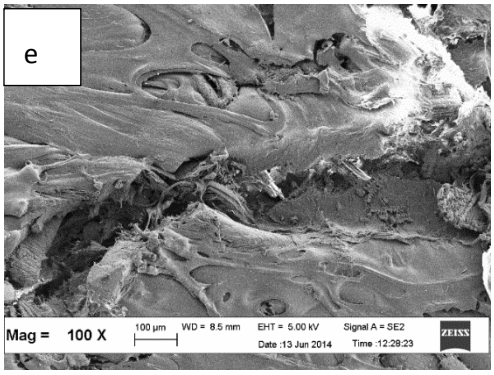
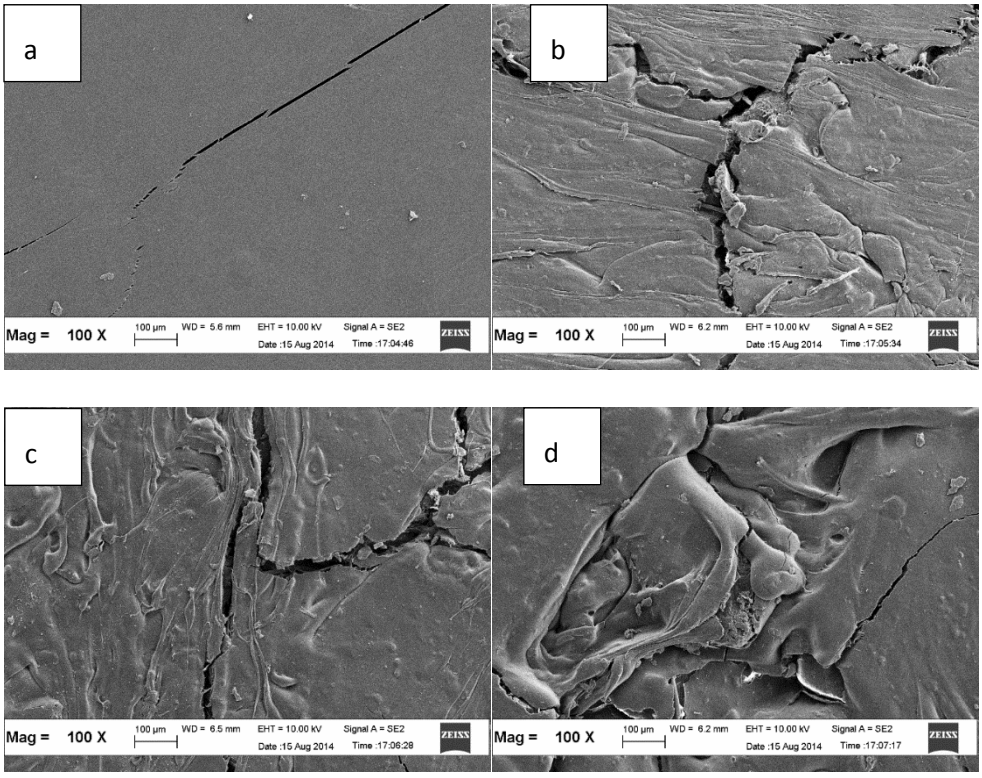


Plate VII: SEM micrographs showing surfaces of PLABM/40% GHP Composites after water absorption for 30 days(a) Unreinforced PLABM (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated



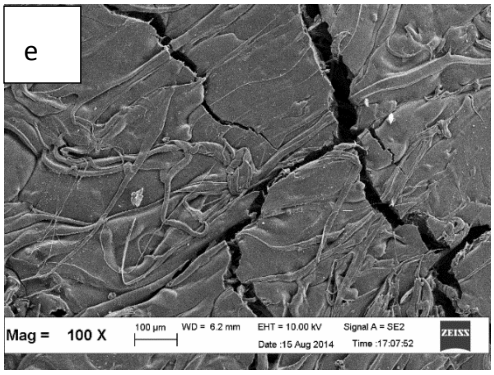
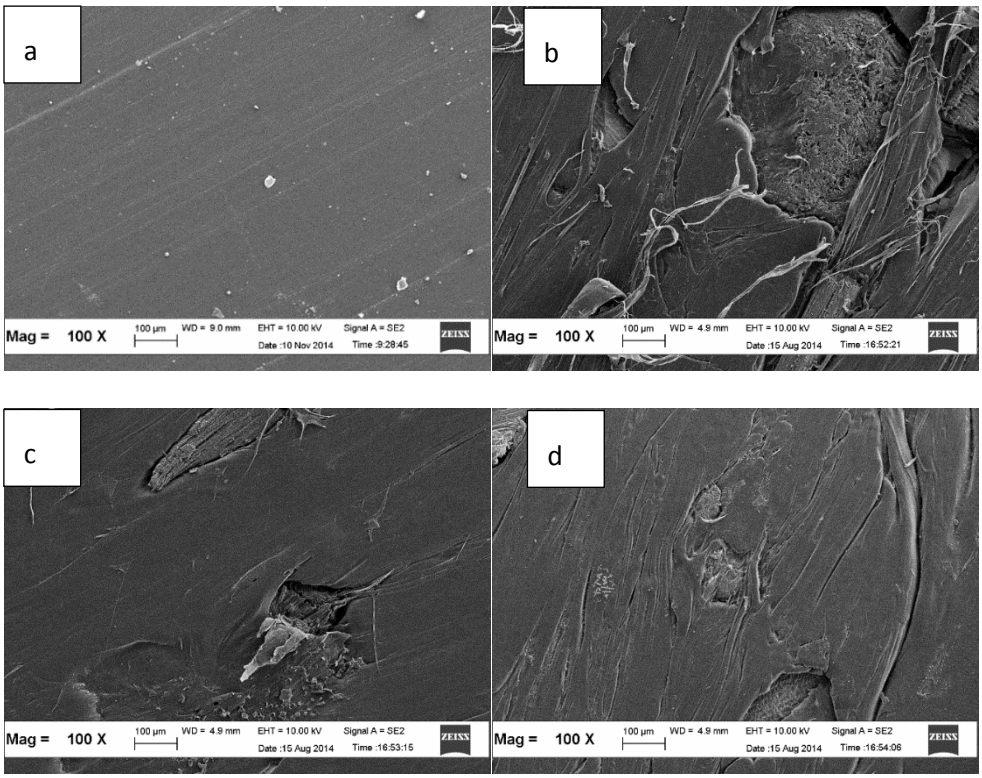


Plate VIII: SEM micrographs showing surfaces of PLPG/40% GHP Composites after water absorption for 30 days(a) Unreinforced PLAP (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated



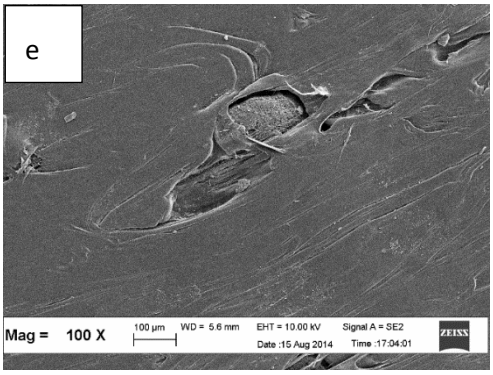


Plate IX: SEM micrographs showing surfaces of PP/40% GHP Composites after water absorption for 30 days(a) Unreinforced PP (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated

The surface of the PLAP matrix in Plate VIa was very smooth with no indication of any crack. On incorporation of filler, different surface morphologies were observed due to different treatments carried out.

The UNTRD specimen showed matrix tearing and warping with a few holes exposing the filler. Larger and more holes were observed for the ALK treated specimen from the SEM image. This suggests and clarifies why ALK treated samples absorbed more water than the untreated samples. More matrix warping were noticed on the SIL treated specimen as well as some cracking which could eventually lead water molecules into the matrix to interact with the filler. A more massive deterioration was observed in the ALKSIL treated specimen in addition to matrix cracking, fillers were visible which would lead to more water absorption.

The SEM micrographs after water absorption of PLABM/GHP composite in Plate VII a-e indicates that the surface of PLABM also looked intact with no holes or cracking of the matrix.

A deep hole and matrix cracking were observed in the UNTRD specimen. This was more pronounced in the ALK treated specimen while the SIL treated specimen showed matrix tearing leading to visibility of fillers. The most deteriorated specimen was that of the ALKSIL treated composite (Plate VII e). A deeper hole than that observed in ALK treated specimen was observed and serious warping of the matrix as well.

PLPG matrix showed micro-cracks in the SEM micrographs and various images are seen in its composites in Plate VIII. This, although contrary to the first two PLA matrices of Plates VI and VII, was probably due to the blending of PLA with PEG which is known to be hydrophilic on its own. The matrix cracking became larger for the UNTRD specimen. Also the ALK treated specimen showed more cracks and holes on the surface and also some warping while the SIL treated specimen exhibited the least surface cracking and holes but more warping and even a threshold for storing or holding water which could later penetrate into the matrix. The most affected by water in the study was ALKSIL treated specimen. Large matrix cracks which are more in number and also surface deformation were observed.

Plate IX a-e shows the SEM micrographs for water absorbed PP and its composites and it reveals surface of PPwas smooth without any form of crack. The UNTRD specimen showed "peeling" of the matrix surface to expose the filler for more water penetration. The ALK treated filler contained less and small matrix 'peeling' while the SIL treated specimen showed a dull surface and warping of the matrix. The dull surface could be due to silane treatment. The ALKSIL treated surface was not pronounced in matrix 'peeling' but had points on the surface that could lead to penetration of water molecules.

Mat Taib *et al*., (2010) reported warping of PEG-plasticized PLA/kenaf fibre composites which according to them suggested dimensional instability due to water absorption.

Tserki *et al*., (2006a) reported that water absorption could lead to rapid debonding, delamination and a loss of structural integrity which leads to deterioration of the material's mechanical properties.

Generally, water uptake in polymer composites happens in three different ways; firstly, there is the diffusion of water molecules inside the micro-voids in the polymer chains. Secondly, water flows by capillary action into the voids at the filler-matrix interface and thirdly, the transport of micro-cracks in the matrix resulting from the swelling of the fillers (Paul *et al*., 2015). Consequently, when GHP reinforced composites were exposed to moisture, the hydrophilic filler swells and then induces micro-cracks in the resin as seen in some of the SEM images and in others, warping were visible instead. The high GHP content further contributes to more water uptake as observed in the water absorption curves and led to cracking of the matrix. As the cracks get larger with immersion time, water molecules would attack the interface which would eventually lead to debonding of the matrix and filler (Paul *et al*., 2015) as observed in the SEM images (Plates VI to IX).

4.2.4 Mechanical properties after water absorption

4.2.4.1 Tensile strength

The tensile strengths results of composites after water absorption test for 30 days are presented in Figures 4.40 to 4.43 and Tables C1 to C4 in Appendix C.

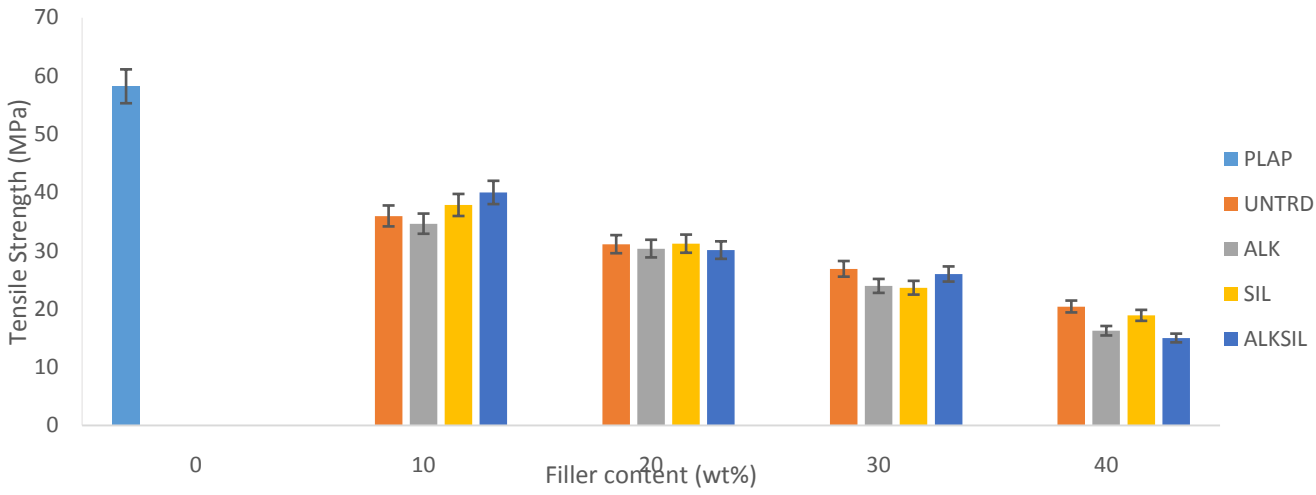


Figure 4.40: Tensile strength of PLAP/GHP Composites against filler content for various treatments after water absorption for 30 days

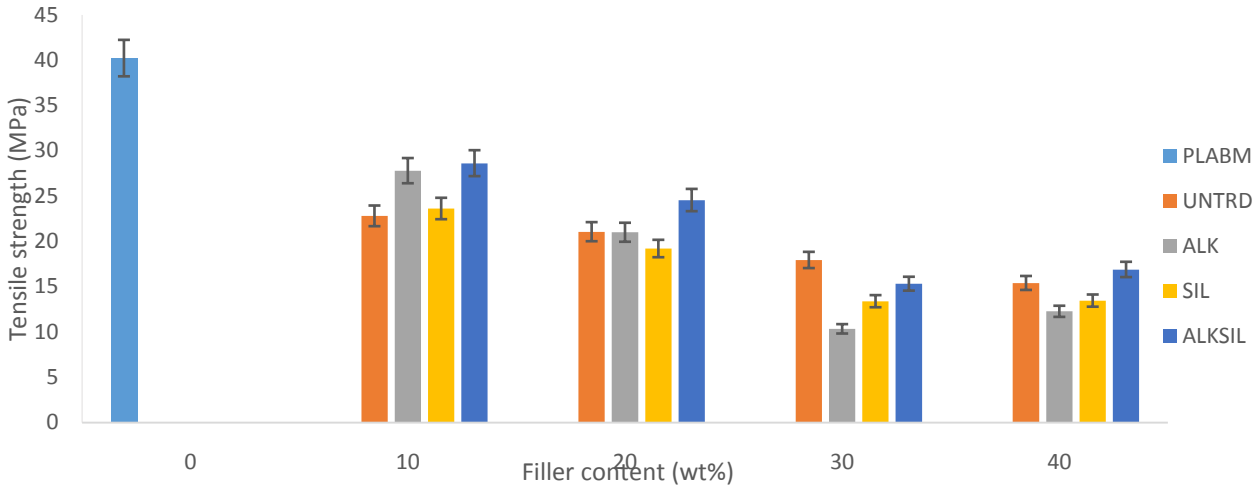


Figure 4.41: Tensile strength of PLABM/GHP Composites against filler content for various treatments after water absorption for 30 days

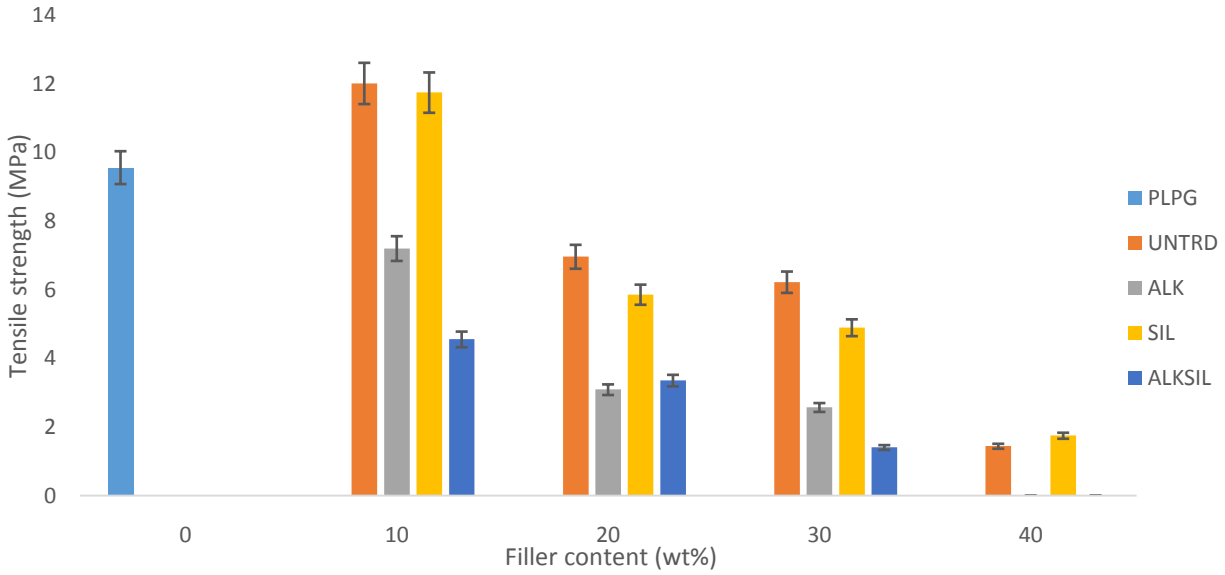


Figure 4.42: Tensile strength of PLPG/GHP Composites against filler content for various treatments after water absorption for 30 days

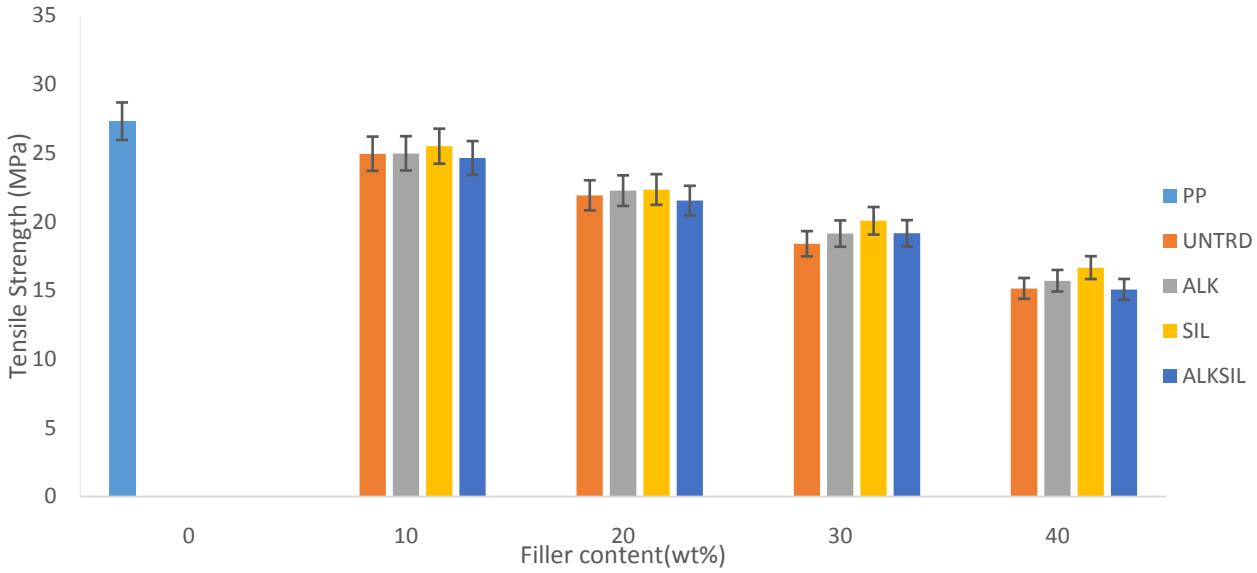


Figure 4.43: Tensile strength of PP/GHP Composites against filler content for various treatments after water absorption for 30 days

The results showed that the tensile strengths of the composites after water absorption decreased with increase in filler content as obtained in the results for the dry specimens but with lower values in most cases.

The tensile strength of PLAP/GHP composites after water absorption test for 30days in Figure 4.40indicated that the tensile strength of PLAP matrix was 58.20Mpa and various lower values were obtained for it composites. The PLAP matrix after water absorption test had slightly higher tensile strength than that of PLAP before water absorption test Figure 4.7.At 10% GHP content, the tensile strength of the composites were 35.95MPa, 34.62MPa, 37.98MPa and 39.83MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively. These showed that ALKSIL treated composites had the highest tensile strength among the other composites. At higher GHP

contents, the tensile strengths of UNTRD composites were higher than those of the treated composites.

The results for the tensile strength of PLABM/GHP composites after water absorption test for 30days in Figure 4.41 shows that the PLABM matrix had a tensile strength of 40.22MPa which is slightly less than that of PLABM before water absorption test with a value of 44.37MPa Figure 4.8.The tensile strength of the composites decreased with increase in GHP content. The tensile strength of ALKSIL treated composites were higher than those of UNTRD and other treated composites of 10,20 and 40% filler contents while the tensile strengths of SIL treated composites were the lowest of all the composites with exception of 10% filler content with 23.62 MPa which was higher than only the UNTRD composite with a value of 22.81MPa.

Figure 4.42 shows the tensile strength results of PLPG/GHP composites after water absorption for 30days. The results showed that PLPG had a tensile strength of 9.56MPa and various values of tensile strengths were obtained for its composites.From the results, the UNTRD composites showed the highest tensile strength values at all filler contents except at 40% GHP content where SIL treated composite had 1.75MPa over that of UNTRD with a value of 1.44MPa. There were no results for ALK and ALKSIL at 40% filler content because the specimens deteriorated and could not stand the tensile test.

PP and its composites exhibited different tensile strength results after water absorption for 30days as Figure 4.43 depicts. The tensile strength of pure PP was 27.32MPa which was 5.6% higher than that of the tensile strength of PP before water absorption Figure 4.10. The composites obtained had tensile strengths that were either slightly decreased or increased over

the tensile strengths of the dry PP-based composites. The behaviour could be attributed to the plasticization effect of water on the composites.

4.2.4.2 Tensile Modulus

Figures 4.44 to 4.47 and Tables C1 to C4 (Appendix C) are the results of tensile modulus of all the composites after water absorption for 30days.

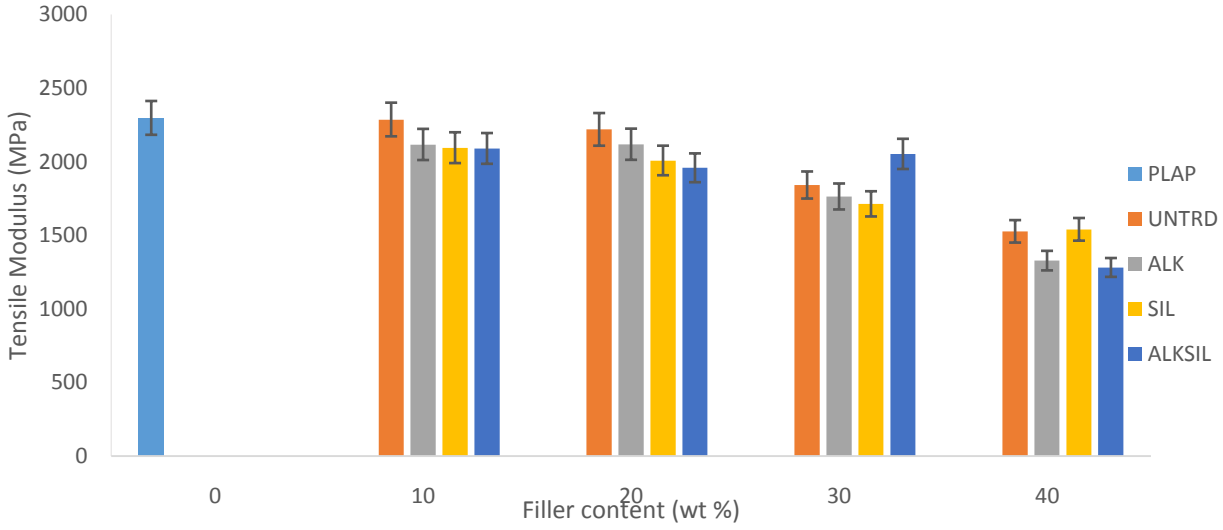


Figure 4.44: Tensile Modulus of PLAP/GHP Composites against filler content for various treatments after water absorption for 30 days

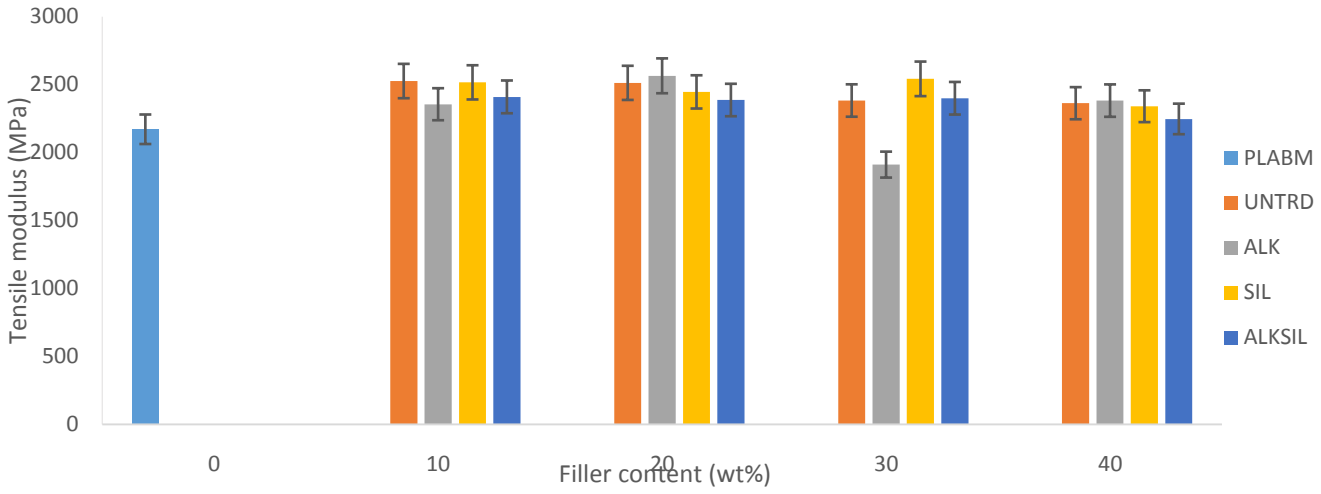


Figure 4.45: Tensile Modulus of PLABM/GHP Composites against filler content for various treatments after water absorption for 30 days

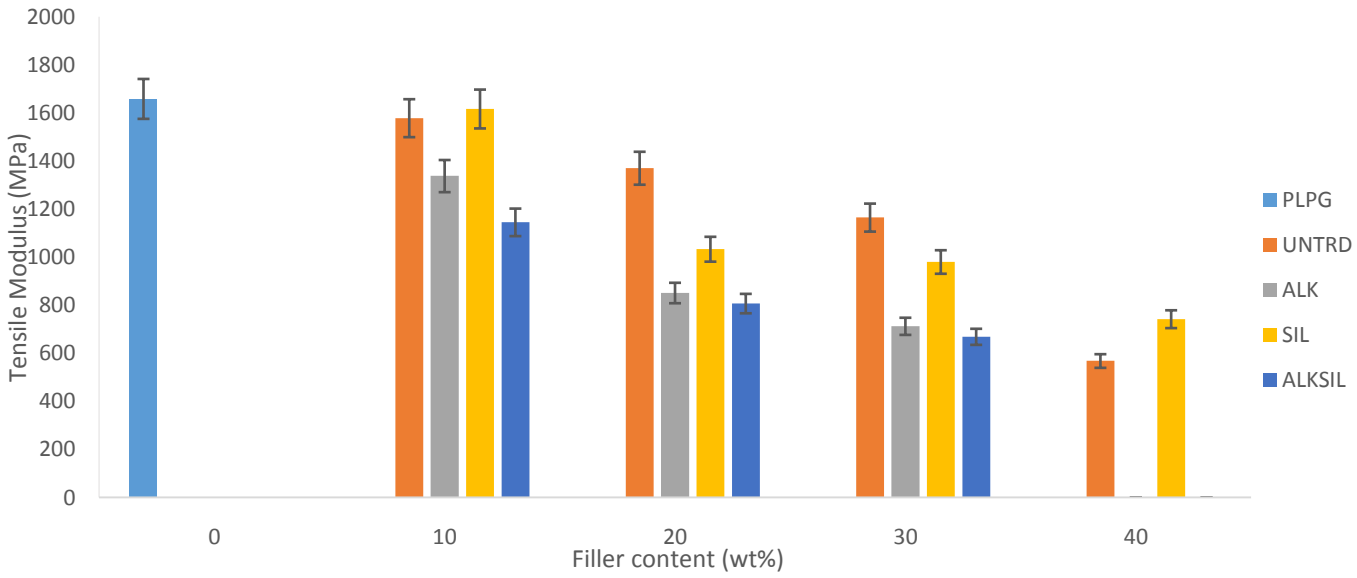


Figure 4.46: Tensile Modulus of PLPG/GHP Composites against filler content for various treatments after water absorption for 30 days

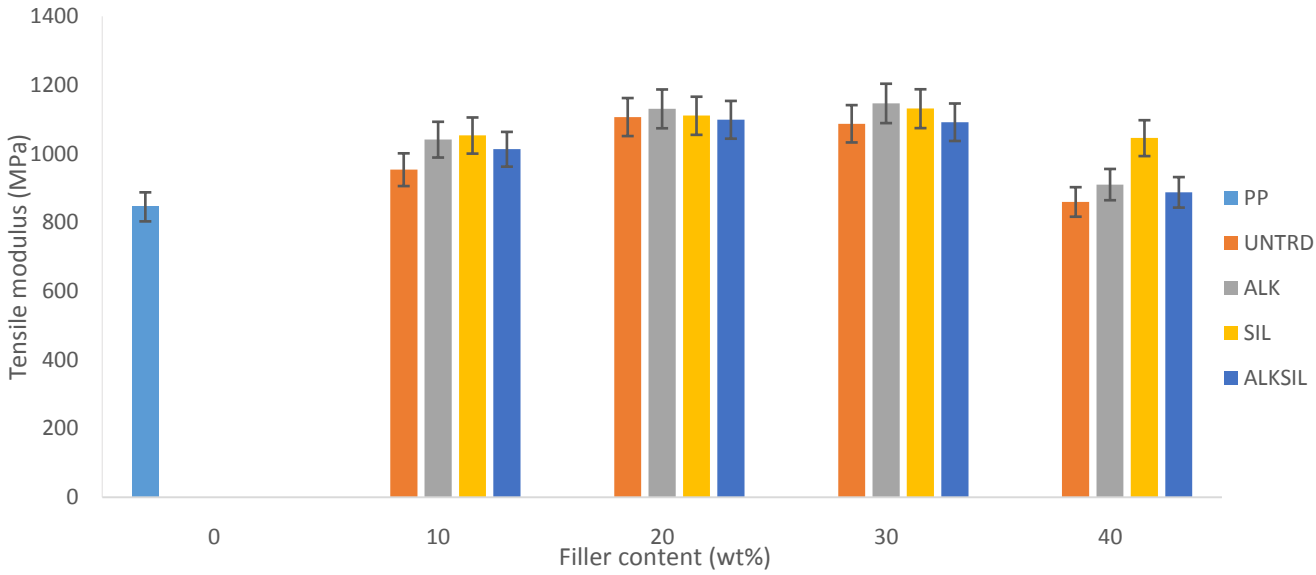


Figure 4.47: Tensile Modulus of PP/GHP Composites against filler content for various treatments after water absorption for 30 days

The tensile modulus results after water absorption test for 30days for PLAP/GHP composites in Figure 4.44 reveals that the tensile modulus of PLAP matrix was 2296.62MPa and slightly lower values were obtained by its composites. From the results, it was observed that the tensile modulus for the UNTRD composites were generally higher than those for composites with surface treatments. This was followed by ALK, then SIL treated composites while the ALKSIL treated composites exhibited the lowest tensile moduli results. At the same treatment and GHP content, the tensile moduli for the water absorbed specimen were significantly lower than those before water absorption test.

In results for tensile modulus of PLABM/GHP composites after water absorption for 30days shown in Figure 4.45, it was observed that the tensile moduli of the composites were higher than that of the matrix which had a modulus of 2171.48MPa except at 30% GHP content for ALK

treated composite with a value of 1911.41MPa. There was no definite trend observed in the results as different treatments and different GHP content possessed various values for tensile modulus. However, at the same filler content, ALKSIL treated composite apparently had the lowest tensile modulus values except at 30% filler content where its value was higher than those of UNTRD and ALK treated composite by 0.7% and 25.54% respectively.

It was apparent from the results obtained that tensile modulus for PLABM/GHP composite after water absorption test were either higher than those before water absorption test or slightly lower except at higher filler contents of 30% and 40% for SIL and ALKSIL treated composites which showed significantly higher values of tensile modulus over the ones after water absorption test. Generally, for the same treatment and filler contents especially for UNTRD and ALK treated composites, the tensile moduli for water absorbed specimens were higher than those before water absorption test. Even the unreinforced matrix of water absorbed specimen had higher tensile modulus than that of the dry specimen by 11.85%.

The tensile modulus results of water absorbed PLPG/GHP composites after 30 days of test in Figure 4.46 shows that the PLPG matrix had a tensile modulus of 1658.56MPa while various lower values were obtained for its composites which decreased with filler loading as expected. The tensile moduli obtained were much lower than those of the dry composites presented in Figure 4.13. The tensile moduli for UNTRD and SIL treated composites were higher than those obtained for ALK and ALKSIL treated composites. The PEG had a very significant effect in the tensile modulus as well since it is water soluble.

The results for tensile modulus of PP/GHP composites after water absorption for 30days are shown in Figure 4.47 with a value for the pure PP as 845.56MPa as against 733.44MPa obtained for the dry PP Figure 4.14. The tensile moduli for the composites were higher than that of the matrix and these generally increased with filler loading. Generally, the tensile moduli for SIL treated composites were higher than the other composites and at 40% filler content, the tensile moduli were least for the same treatment.

4.2.4.3 Elongation at break (EB)

The results for the elongation at break (EB) for all the composite formulations after water absorption for 30days are presented in Figures 4.48 to 4.51 and Tables C1 to C4 in Appendix C.

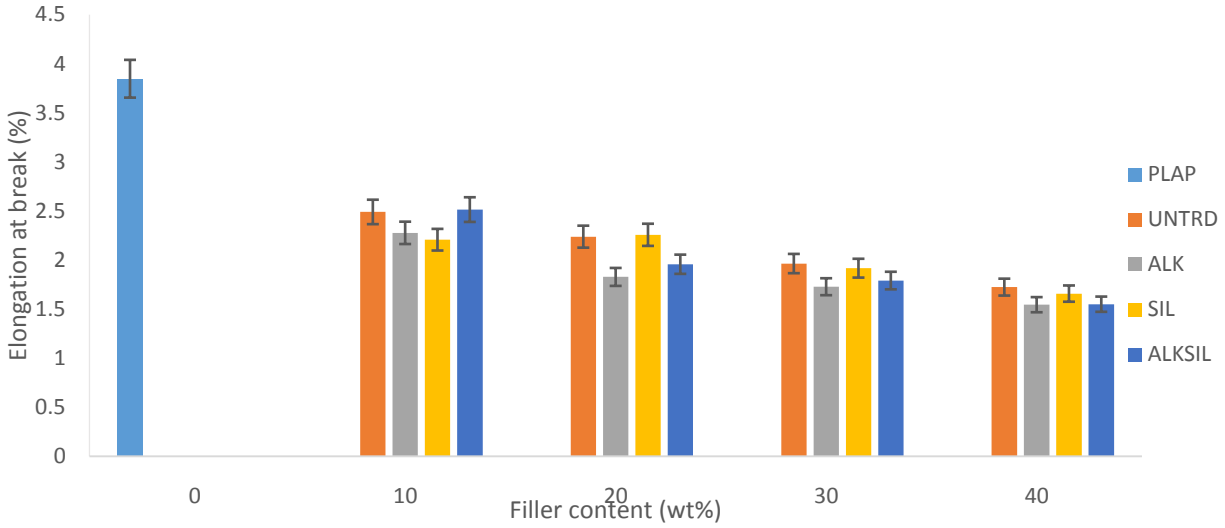


Figure 4.48: Elongation at Break of PLAP/GHP Composites against filler content for various treatments after water absorption for 30 days

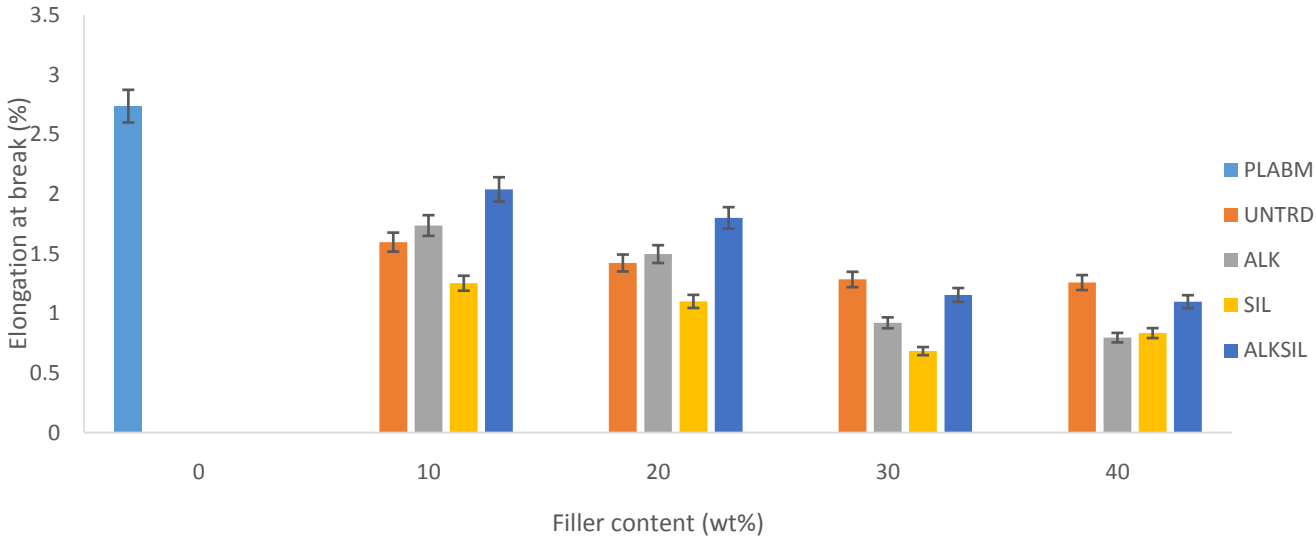


Figure 4.49: Elongation at Break of PLABM/GHP Composites against filler content for various treatments after water absorption for 30 days

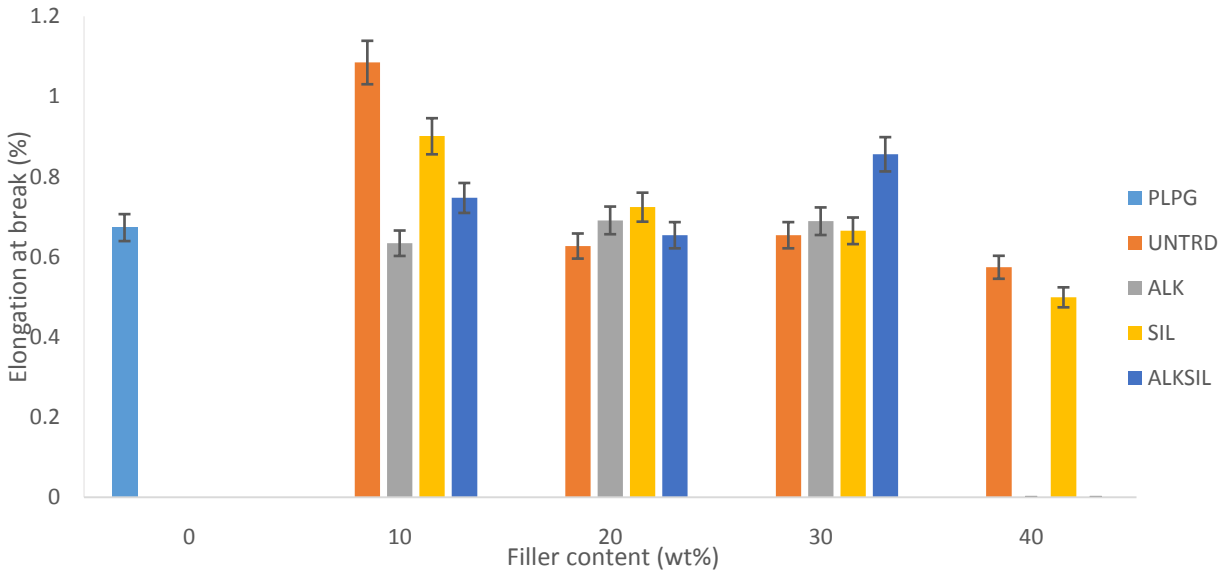


Figure 4.50: Elongation at Break of PLPG/GHP Composites against filler content for various treatments after water absorption for 30 days

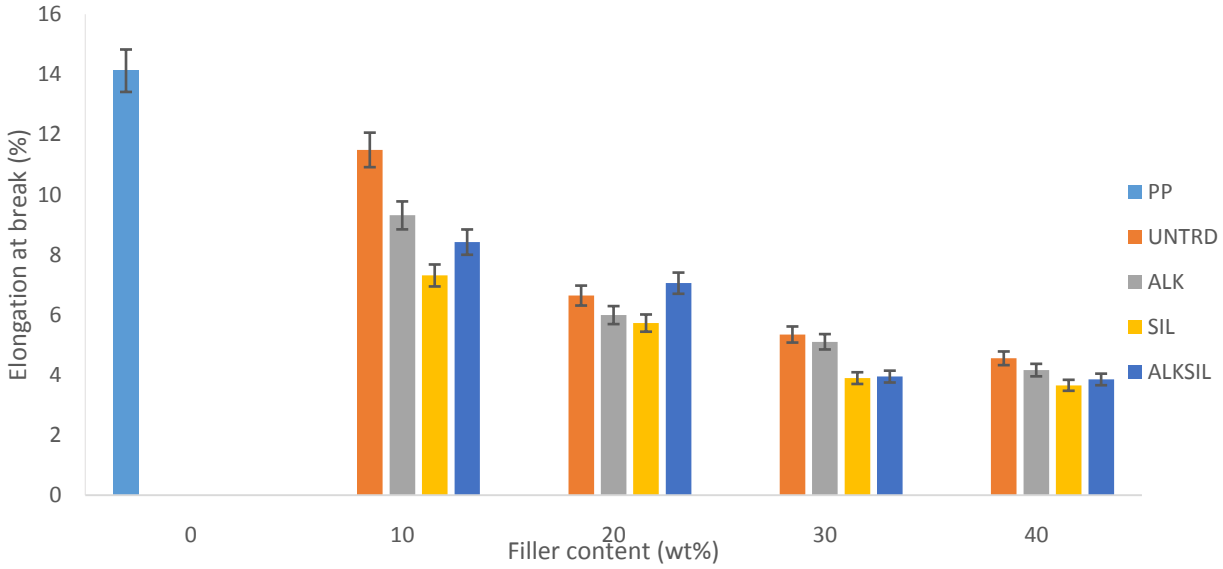


Figure 4.51: Elongation at Break of PP/GHP Composites against filler content for various treatments after water absorption for 30 days

Generally, there was decrease in EB with filler loading and the EB of the matrices exhibited the highest values over their various composites with the exception of PLPG matrix.

The EB results of PLAP/GHP composites after water absorption for 30 days as shown in Figure 4.48 reveals that PLAP matrix exhibited an EB of 3.85% while various lower values were obtained for its composites and these decrease with filler loading. It was observed from the results that, for the same filler content, the UNTRD and SIL treated composites exhibited the highest EB as compared to those exhibited by the ALK and ALKSIL treated composites except at 10% filler content where the EB was highest in ALKSIL followed by ALK treated composites with values of 2.51% and 2.28% respectively. Generally, the EB for the water absorbed composites were higher than those of the dry composites Figure 4.15. However, the EB for the dry matrix was higher than that of the water absorbed by 13.48%.

PLABM/GHP composites after water absorption test for 30days exhibited EB that progressively decreased with filler content Figure 4.49. Firstly, the results showed that the EB of PLABM matrix which had a value of 2.74% was higher than those of its composites. Secondly, the EB for the water absorbed specimens were all lower than those of the dry specimens Figure 4.16. The EB for ALK and SIL treated composites with 0.92% and 0.68% respectively at 30% filler content were significantly lower than those of the UNTRD and ALKSIL treated. The same observation was made at 40% filler content.

The results for the EB of PLPG/GHP composites after water absorption test for 30days presented in Figure 4.50 shows that the EB of PLPG and its composites after water absorption test were significantly lower than those obtained in the dry composites Figure 4.17.PLPG matrix exhibited

an EB of 0.67% and various values were obtained from its composites. At 10% GHP content, the EB were 1.09%, 0.63%, 0.90% and 0.75% for UNTRD, ALK, SIL and ALKSIL treated composites respectively.

The EB results of PP/GHP composites after water absorption test for 30days presented in Figure 4.51 shows a significant reduction in EB of composites after water absorption as compared to the dry specimens especially for the matrix Figure 4.18.The virgin PP exhibited an EB of 14.12% while the composites exhibited different values which were much lower than the matrix and they decreased with filler loading. As observed from the results also, for the same filler content, the EB for the UNTRD composites were higher than those of the treated composites except at 20% filler content where the ALKSIL treated composites had the highest value of EB.

4.2.4.4 Flexural Strength

The results of the flexural strengths of all the composites after water absorption test are presented in Figures 4.52 to 4.55 and Tables C1 to C4 in Appendix C.

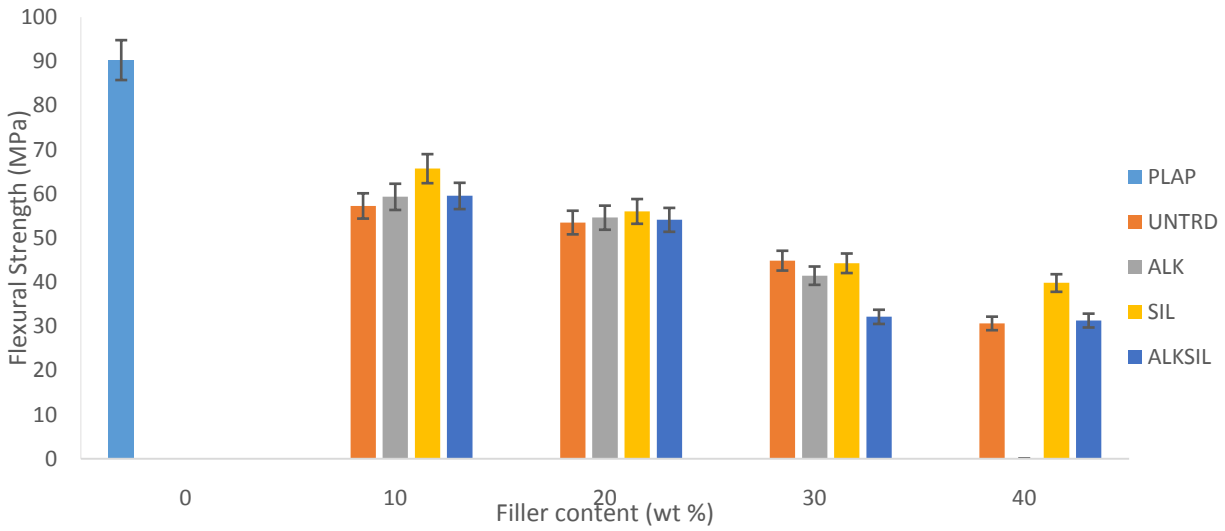


Figure 4.52: Flexural Strength of PLAP/GHP Composites against filler content for various treatments after water absorption for 30 days

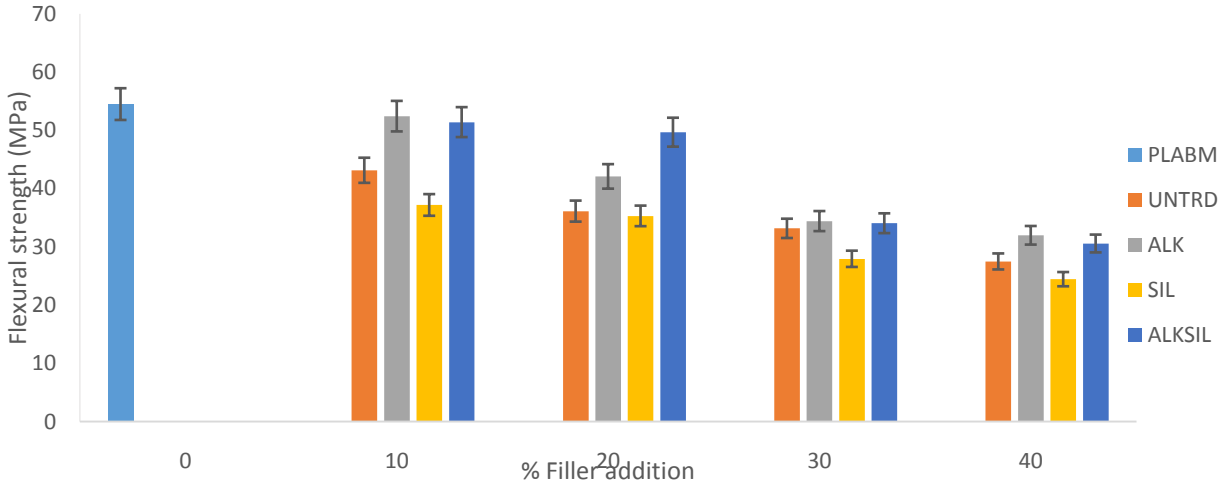


Figure 4.53: Flexural Strength of PLABM/GHP Composites against filler content for various treatments after water absorption for 30 days

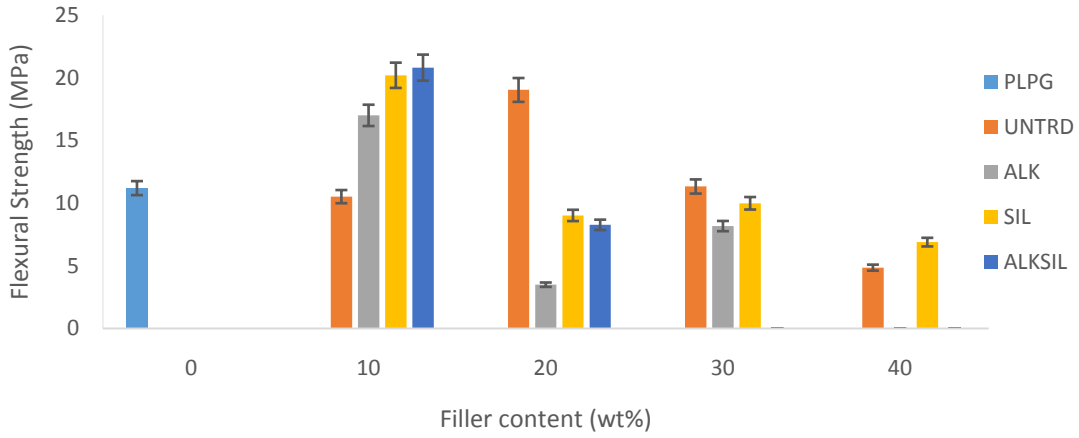


Figure 4.54: Flexural Strength of PLPG/GHP Composites against filler content for various treatments after water absorption for 30 days

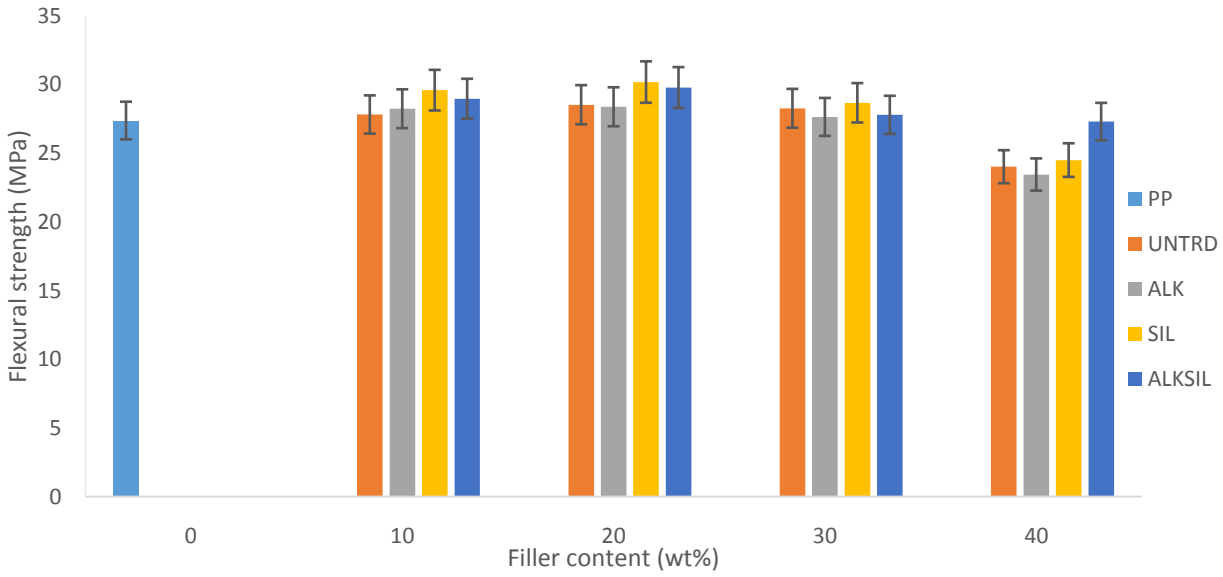


Figure 4.55: Flexural Strength of PP/GHP Composites against filler content for various treatments after water absorption for 30 days

The results of flexural strength for PLAP/GHP composite after water absorption for 30days Figure 4.52 indicates that the PLAP matrix exhibited a flexural strength of 90.29MPa while various lower values were obtained for its composites and these values decreased with increasing filler loading. There was no result for ALK treated composite at 40% filler content because the specimen broke before the end of the test.The flexural strength of the PLAP matrix after water absorption was significantly higher than that obtained before the test while, even though lower values were obtained for the composites, they were not very much different from those obtained before water absorption test Figure 4.19.

The treated composites exhibited higher flexural strengths over the untreated composites except at 30% filler content where the flexural strength of UNTRD composite was 44.88MPa which was just slightly higher than that of the SIL treated composite with 44.29MPa. The effect of SIL treatment was observed after the water absorption test as it possessed the highest flexural strength at all filler content with the exception at 30% filler content.

Figure 4.53 shows that the flexural strength of neat PLABM after water absorption for 30days was 54.4MPa and lower values were exhibited by its composites. At 10% filler content, the ALK treated composite exhibited the highest flexural strength followed by ALKSIL treated composite while the SIL treated composites exhibited the least flexural strength for all the filler contents. The flexural strength for PLABM before water absorption test was slightly lower than that obtained after water absorption test (Figures 4.20 and 4.53).

The flexural strength results for PLPG/GHP composites after water absorption for 30days presented in Figure 4.54 shows very low values in themselves and as compared to those obtained

before water absorption test. There were no results for ALK treated composites at 40% filler content and ALKSIL treated composite at 30 and 40 % filler contents due to the fact that the specimens seriously deteriorated and broke before the end of the test.

At 10% GHP content, the flexural strengths of the treated composites were higher than that of the matrix which had a value of 11.2MPa whereas the treated ones were 17.01MPa, 20.21MPa and 20.82MPa for ALK, SIL and ALKSIL treated composites respectively.However, at 20 and 30% GHP contents, the flexural strengths of UNTRD composites were 19.04 and 11.33MPa as against 3.49MPa and 8.17MPa, 9.02 and 9.99MPa and then 8.27MPa for ALK, SIL and ALKSIL treated composite respectively. It indicated that the flexural strength of UNTRD composites at the mentioned filler contents were higher than those for the treated composites.

The flexural strength results for PP/GHP composites after water absorption test for 30days presented in Figure 4.55 indicated that PP matrix had a flexural strength of 27.38MPa. Marginal increment in flexural strengths for all treatments and at all filler levels were observed from the results.While the flexural strengths of PP/GHP composites before water absorption increased with filler loading Figure 4.22, the strengths obtained after 30days of water absorption test initially increased at 10 and 20% filler contents and subsequently decreased with higher filler loadings of 30 to 40% for all treated and untreated composites.

The SIL treated composites exhibited slightly higher flexural strengths at all but 40% filler content where the ALKSIL treated composite exhibited the highest flexural strength with a value of 27.30MPa as against 24.02MPa, 23.45MPa and 24.5MPa exhibited by the UNTRD, ALK and SIL treated composites respectively.

4.2.4.5 Flexural Modulus

The results for the flexural modulus of all the composite formulations after water absorption test for 30days are shown in Figures 4.56 to 4.59 and Tables C1 to C4 in Appendix C.

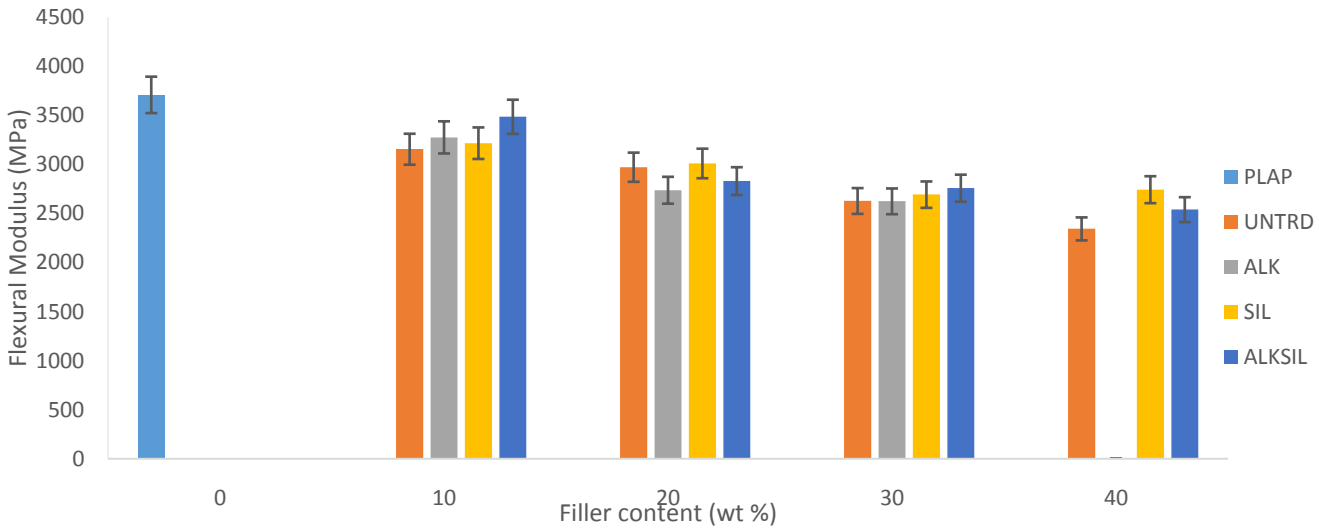


Figure 4.56: Flexural Modulus of PLAP/GHP Composites against filler content for various treatments after water absorption for 30 days

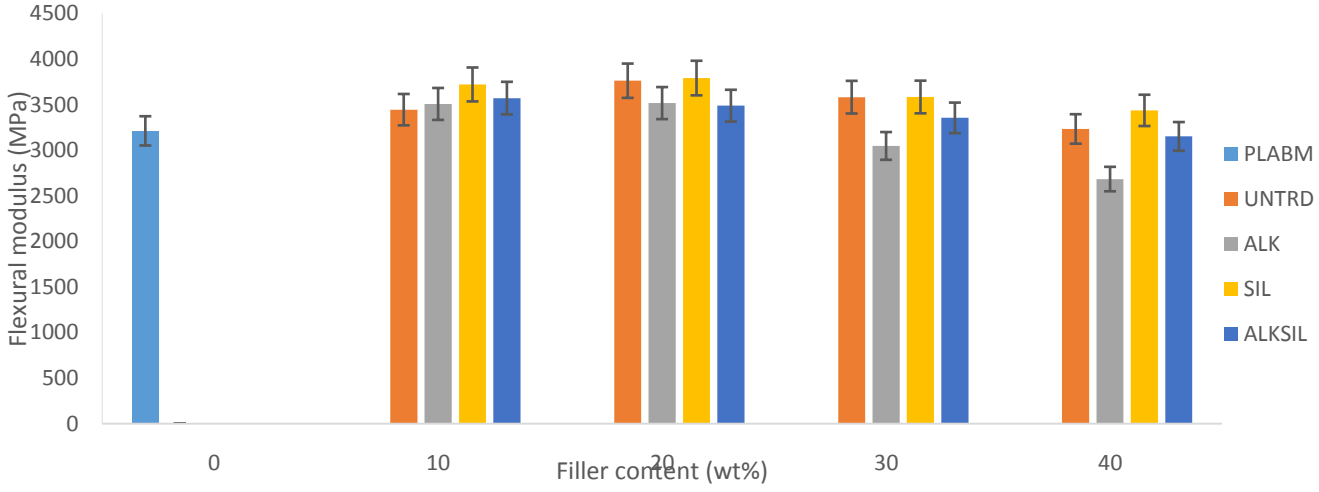


Figure 4.57: Flexural Modulus of PLABM/GHP Composites against filler content for various treatments after water absorption for 30 days

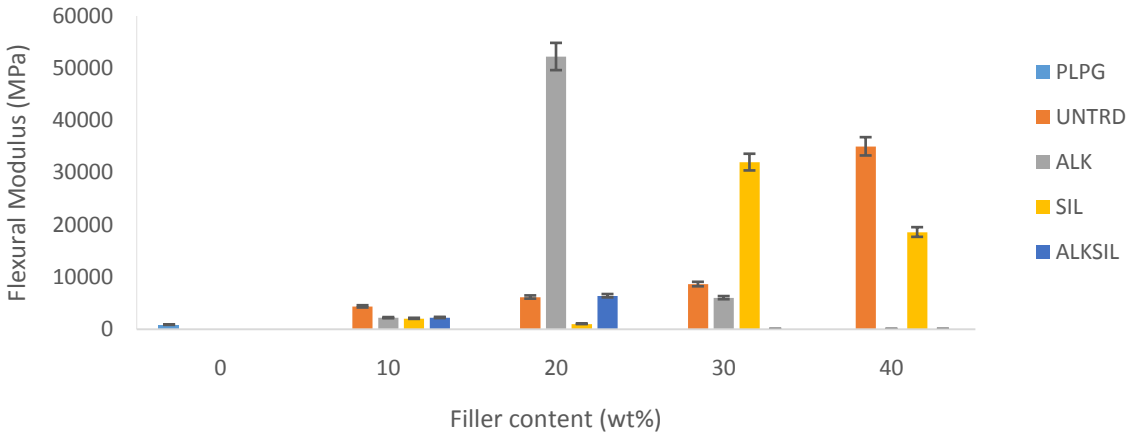


Figure 4.58: Flexural Modulus of PLPG/GHP Composites against filler content for various treatments after water absorption for 30 days

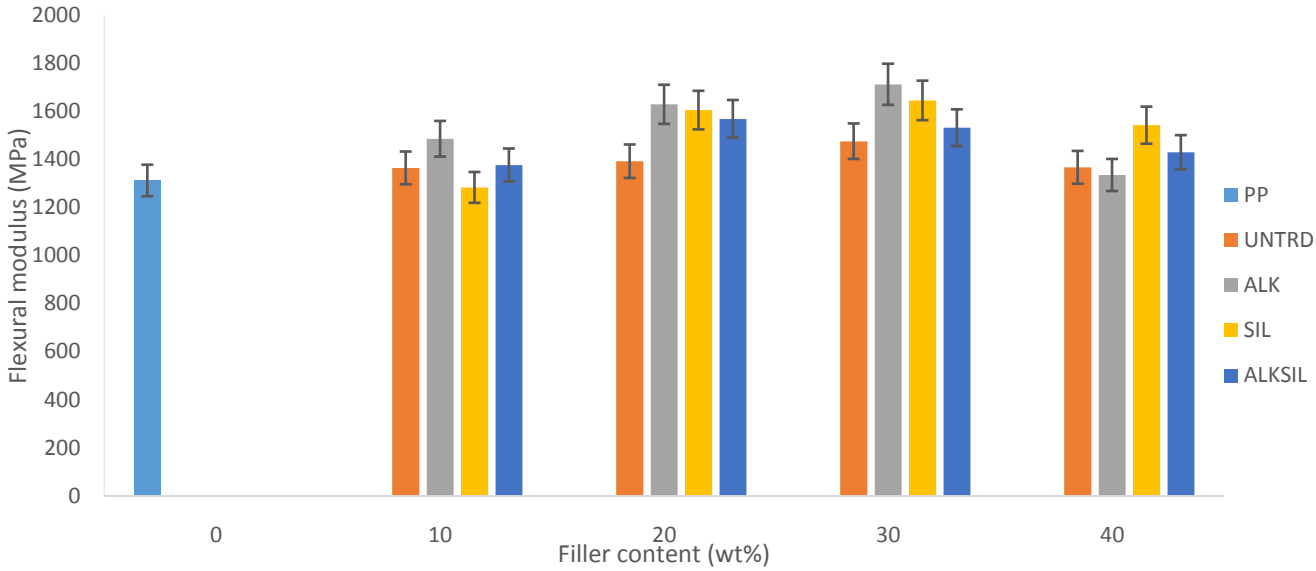


Figure 4.59: Flexural Modulus of PP/GHP Composites against filler content for various treatments after water absorption for 30 days

Figure 4.56 indicates that the flexural modulus after water absorption for 30days of PLAP matrix was 3708.6MPa with lower values obtained for its composites which progressively decreased with filler loading.The flexural modulus for the unreinforced matrix for the water absorbed specimen was higher than that of matrix before water absorption test Figure 4.23. However, the flexural modulus of the composites after water absorption were lower than those obtained before water absorption. The composites at 10% filler content possessed flexural modulus of 3154.99MPa, 3275.54MPa, 3216.19MPa and 3485.06MPa indicating that the ALKSIL treated composite exhibited the highest flexural modulus. Similar behaviour was observed at 30% filler content while at 20% filler content, SIL treated composite with a flexural modulus of 3010.13MPa and at 40% filler content with a flexural modulus of 2742.71MPa exhibited the highest flexural modulus as compared to the other composites.

After 30 days of water absorption test, the flexural modulus results for PLABM/GHP composites presented in Figure 4.57 indicates thatthe matrix had a modulus of 3211.77MPa with higher values obtained inalmost all of its composites. The flexural moduli of the composites initially increased at 10% and 20% filler contents as compared to the unreinforced matrix then it decreased at 30% filler content and further decreased at 40% filler content. The flexural moduli of SIL treated composites were higher than those of the UNTRD and other treated composites at all filler contents. The flexural moduli of the UNTRD composites at 20, 30 and 40% filler contents on the other hand, were higher than those obtained for ALK and ALKSIL treated composites.

The flexural modulus of PLABM after water absorption test with a value of 3211.77MPa was slightly lower than that of the matrix before water absorption test which had a value of

3255.53MPa Figure 4.24.As for the composites, the flexural moduli of PLABM/GHP composites after water absorption test at 10% and 20% filler contents were higher than those obtained for PLABM/GHP composites before water absorption test. However, at 30 and 40% filler contents, the flexural moduli for PLABM/GHP composites before water absorption test were higher than those obtained after water absorption test. The only exception however, was observed at 20% filler content for ALK treated composites where the flexural strength of the composite before water absorption test was higher than that obtained after water absorption test.

PLPG and its composites after water absorption test for 30days have flexural modulus resultspresented in Figure 4.58. The flexural modulus for PLPG matrix was 849.59MPa and different values were obtained for it composites. The results did not follow the general trend observed earlier especially 40% GHP for UNTRD, 20%GHP for ALK 30 and 40% GHP for SIL treated composites.

The flexural modulus results for PP/GHP composites after water absorption for 30days in Figure 4.59 showed that PP matrix had a modulus of 1311.42MPa. The flexural moduli of PP-based composites increased initially up to 20% filler content then decreased with filler content for UNTRD and ALKSIL treated composites while it increased up to 30% filler content before decreasing at 40% filler content for ALK and SIL treated composites. In most cases, the PP/GHP composites before water absorption exhibited flexural moduli that were higher than those obtained after water absorption test. However, it was clear that the flexural modulus of the PP matrix after water absorption was higher than that obtained for PP matrix before water absorption test (Figure 4.26).

4.2.4.6 Izod Impact strength

The results presented in Figures 4.60 to 4.63 and Tables C1 to C4 (Appendix C) are those of the un-notched Izod impact strengths of all the composite formulation after water absorption test for 30days.

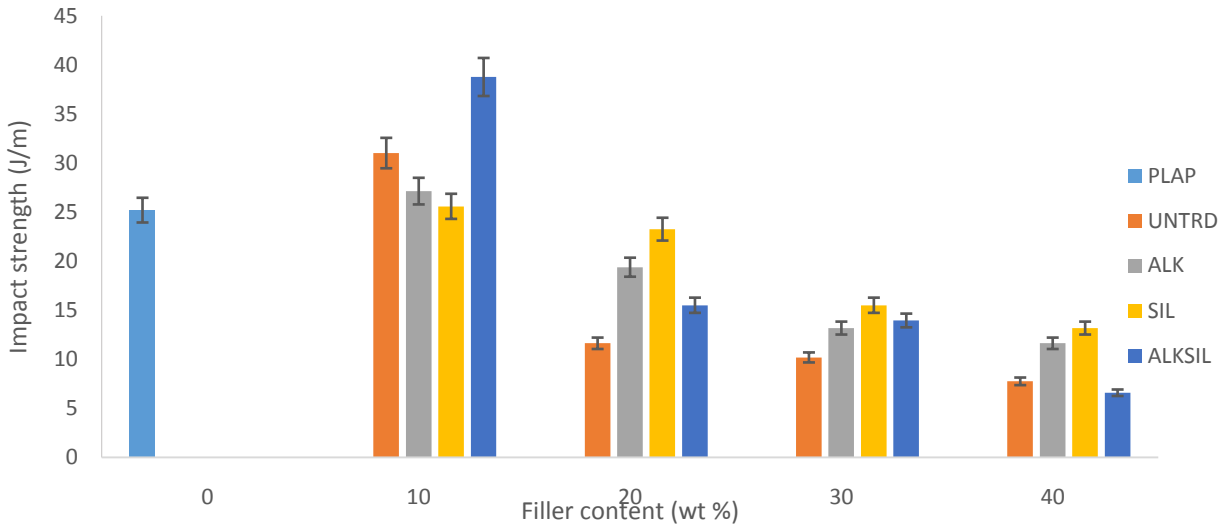


Figure 4.60: Izod Impact strength of PLAP/GHP Composites against filler content for various treatments after water absorption for 30 days

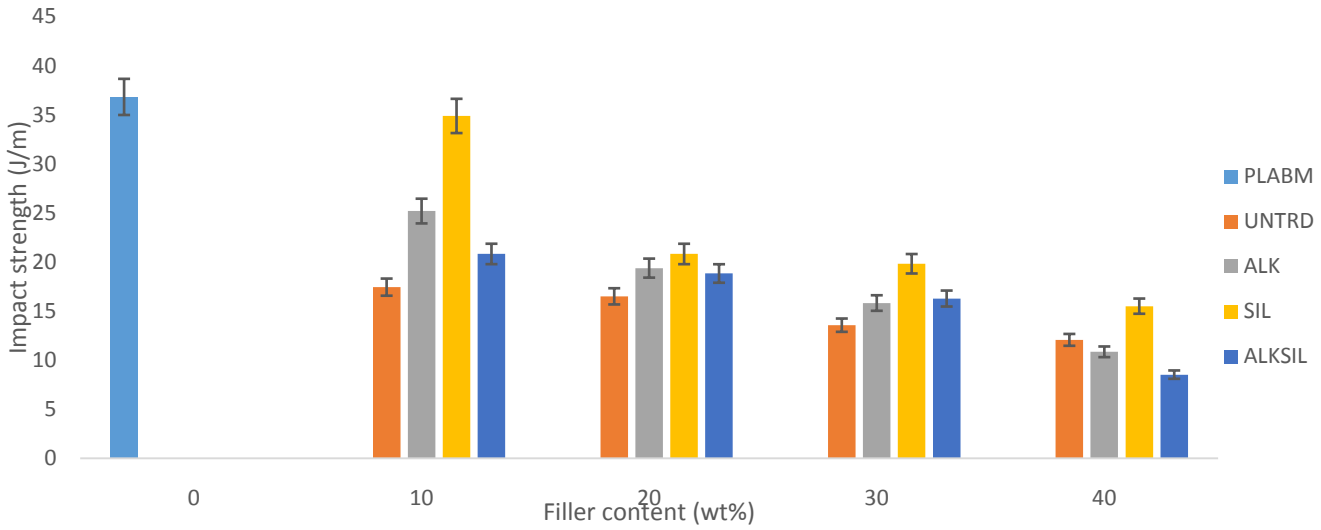


Figure 4.61: Izod Impact strength of PLABM/GHP Composites against filler content for various treatments after water absorption for 30 days

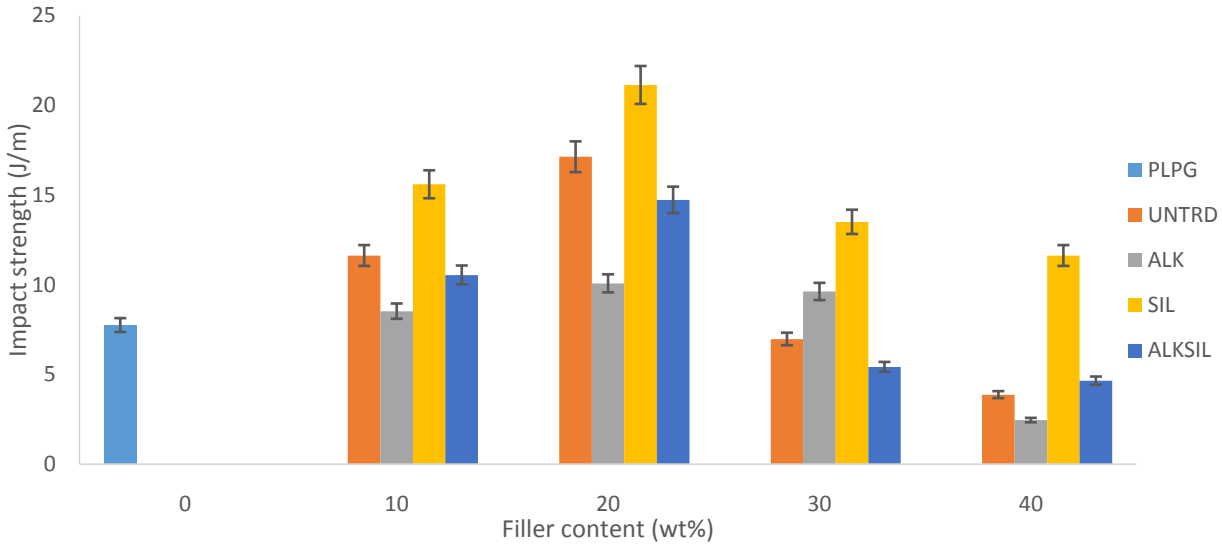


Figure 4.62: Izod Impact strength of PLPG/GHP Composites against filler content for various treatments after water absorption for 30 days

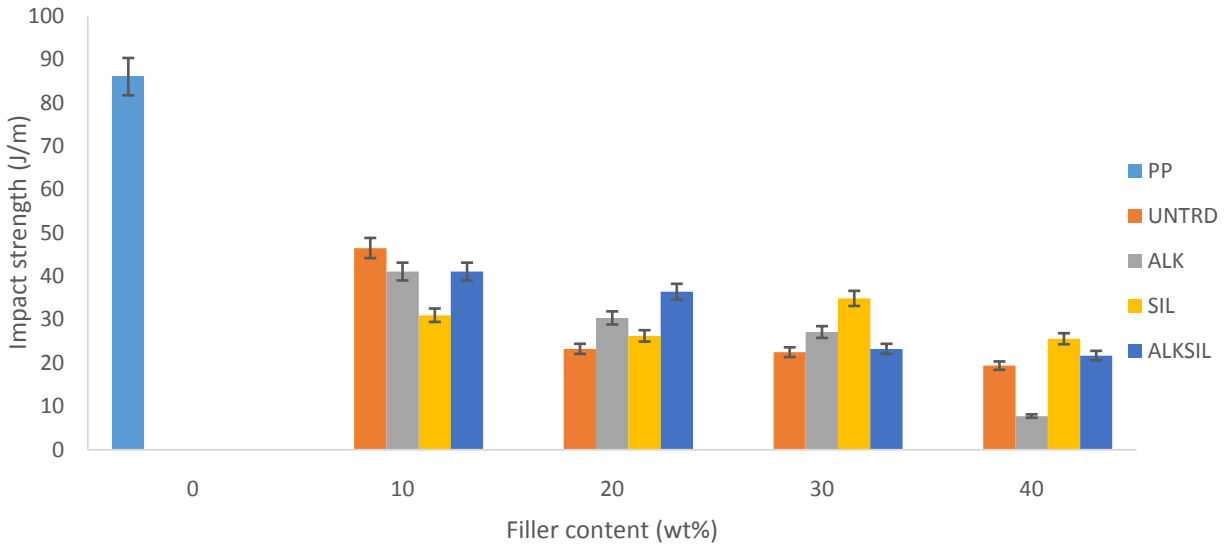


Figure 4.63: Izod Impact strength of PP/GHP Composites against filler content for various treatments after water absorption for 30 days

The results showed a general reduction of Izod impact strengths with GHP loading for the various composites.

The Izod impact strength results for PLAP/GHP composites after water absorption test for 30days Figure 4.60 indicates that PLAP matrix had an impact strength of 25.19J/m with an initial increment observed at 10% filler content for both the treated and untreated composites. The values then decreased significantly at first, then progressively with filler loading. The impact strength for SIL treated composites at all filler contents except at 10% filler content had the highest impact strength. The results showed that the surface treated composites had higher impact strength than the untreated composites.

The impact strength of the unreinforced matrix after water absorption was 25.19J/m and that obtained before water absorption was 50.39J/m while at the same filler contents, the impact strengths for PLAP/GHP composites before water absorption test were higher than those obtained after absorption test (Figures 4. 31 and 4.60).

The Izod impact strength results for PLABM/GHP composites after water absorption test for 30days are presented in Figure 4.61. The Izod impact strengths of the unreinforced matrix was 36.82J/m and various values were obtained for its composites which decreased with filler loading. For all the filler contents, the SIL treated composites exhibited the highest impact strength while the other treated composites (ALK and ALKSIL) exhibited higher impact strengths than the UNTRD composites except 40% filler content where the UNTRD composites with impact strength of 12.08J/m exhibited higher impact strength than the ALK (10.85J/m) and ALKSIL (8.53J/m) treated composites.

In comparison with the impact strength of PLABM/GHP composites before water absorption test Figure 4.32, the impact strength after water absorption test Figure 4.61 were much lower and in most cases they were 50% lower in values.

The Izod impact strength results of PLPG/GHP composites after water absorption for 30days in Figure 4.62 shows thatthe composites with different values of impact strength exhibited higher impact strength than the matrix with the exception of the value obtained at 30 and 40% filler contents for UNTRD and 40% filler content for ALK and ALKSIL treated composites. It was also observed that SIL treated composites exhibited the highest impact strength at all filler

contents. The results showed an initial increase in impact strength at 10% and 20% filler contents before decreasing with filler loading for all treated and untreated composites.

The Izod impact strength results of PP/GHP composites after water absorption test for 30days in Figure 4.63 indicates that the PP matrix had an impact strength of 86.05J/m while it composites exhibited much lower impact strengths which reduced with filler loading.The impact strength of UNTRD composite at 10% filler content was 46.51J/m indicating that it had the highest impact strength while the least impact strength was exhibited by SIL treated composite with a value of 31.01J/m. At higher filler contents, the treated composites exhibited higher impact strength than the UNTRD composites except ALK treated composite with a very low impact strength of 7.75J/m.The impact strength of PP matrix before water absorption was higher than after water absorption. However, at almost all the filler contents, the impact strength of PP/GHP composites after water absorption were generally higher than those before water absorption as observed in the results.

Generally, moisture absorption leads to the degradation of filler-matrix interface which creates poor stress transfer efficiencies resulting in the reduction of mechanical properties (Rashdi *et al*., 2010; Rassiah *et al*., 2012). Therefore, with increase in immersion time of composites in water, it was expected and believed that tensile strength would decrease as reported by (Tserki *et al*., 2006a). Another reason for the general decrease in mechanical properties is the fact that natural fillers such as GHP is hydrophilic due to the presence of –OH groups which exhibit low moisture resistance. This then leads to dimensional variations of composites and poor interfacial bonding between the filler and matrix thereby causing a decrease in mechanical properties (Dhakal *et al*., 2007).

It was reported that flexural strength decreased with filler loading after water absorption (Dhakal *et al*., 2007) but flexural modulus was not adversely affected by moisture absorption and the effect of filler is less critical for flexural failures than tensile failure because the failure in flexural mode is due to a combination of compression, shear and tensile mode (Dhakal *et al*., 2007).

Tensile modulus on the other hand, is affected by water absorption and this is attributed to the fact that modulus is a filler sensitive property in composites. For higher filler content, the stress transfer capability between filler and matrix gets sharply reduced due to excess water absorption (Dhakal *et al*., 2007).

The effect of water absorption was not really felt on the unreinforced matrices. Infact some properties were increased after water immersion for 768hrs. This is also reported in Dhakal *et al*., (2007) for unsaturated polyester matrix.

It was expected that the mechanical properties of composites would decrease with water absorption as compared to dry specimens. Interestingly however, it was observed that water absorbed specimens exhibited higher properties in some compositions over the dry specimens. This could be attributed to the fact that high amount of water causes swelling of fillers which could eventually fill the gaps between the fillers and matrix and subsequently, it could lead to increase in mechanical properties (Dhakal *et al*., 2007). Another reason for higher mechanical properties of water absorbed specimens over the dry specimens could be attributed to the plasticization effect of water in composite (Alvarez and Vázquez, 2004; Dhakal *et al*., 2007**)**. Also, it is possible that there are other mechanisms taking place which enhance the material's

properties or a good filler-matrix bonding that decreases the amount of water absorbed by the composites could lead to improved mechanical properties of water absorbed specimens over the dry specimens (Dhakal *et al*., 2007; Patel *et al*., 2012).

4.2.5 Soil burial test

Figures 4.64 to 4.67 and Table D1 in Appendix D present the soil burial test results in terms of weight loss after three months for all the composite formulations produced.

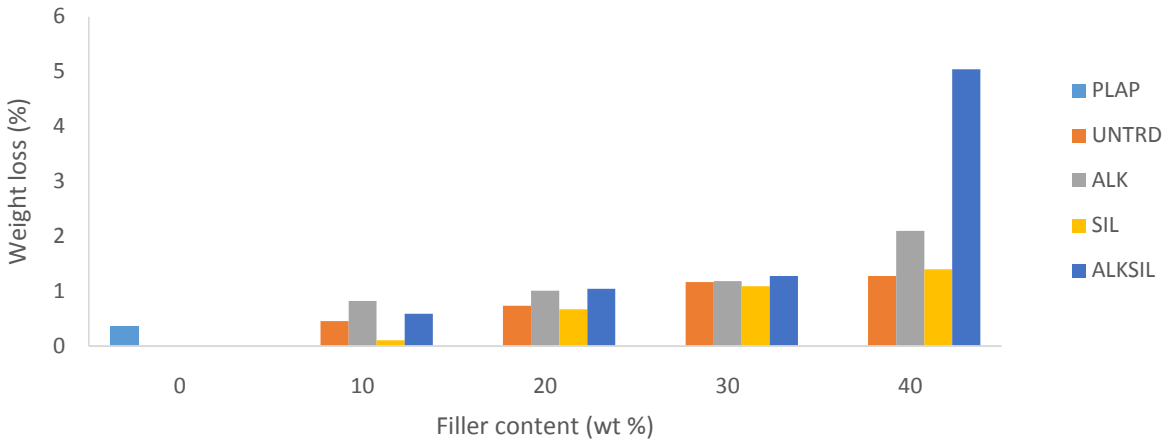


Figure 4.64: Weight loss against filler content of PLAP/GHP Composites due to soil burial after 3 months

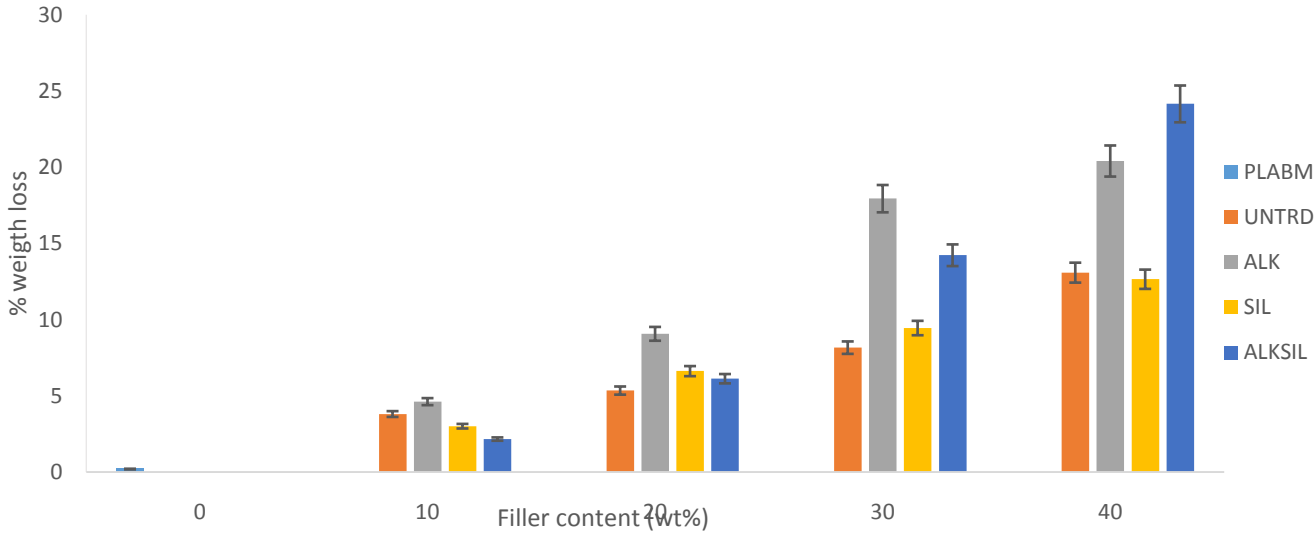


Figure 4.65: Weight loss against filler content of PLABM/GHP Composites due to soil burial after 3 months

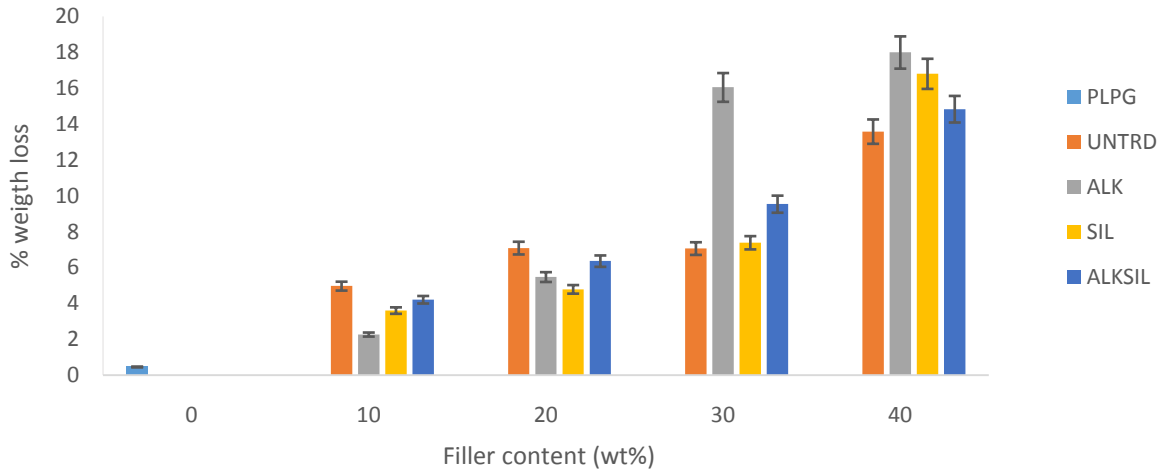


Figure 4.66: Weight loss against filler content of PLPG/GHP Composites due to soil burial after 3 months

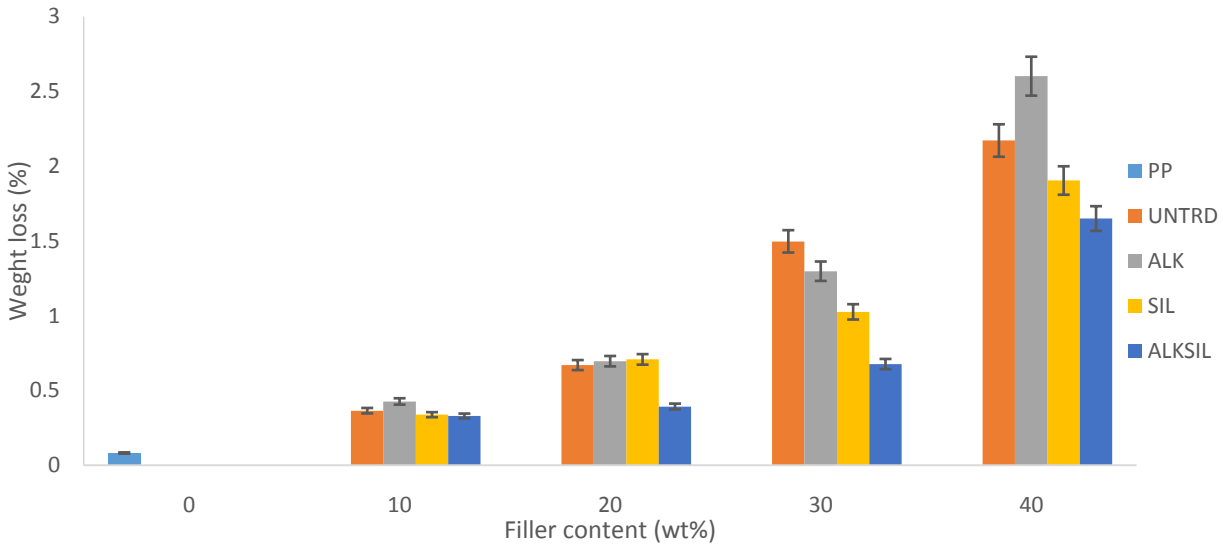


Figure 4.67: Weight loss against filler content of PP/GHP Composites due to soil burial after 3 months

It was observed from the results that the various matrices degraded less than their respective composites as obtained from their various weight losses and that the degradation of the composites increased with GHP loading.

Figure 4.64 is the weight loss for PLAP/GHP composites after three months of soil burial and that of the matrix was 0.36%. The weight loss of the composites increased with filler loading indicating that degradation increased as filler content increased. The weight loss lied between 0.45% and 1.28%, 0.82% and 2.10%, 0.10% and 1.40% and then 0.59% and 5.05% for UNTRD, ALK, SIL and ALKSIL treated composites at 10 and 40% filler contents respectively. It was apparent from the results that ALK and ALKSIL treated composites degraded most in comparison to the UNTRD and SIL treated composites. With the exception of GHP content at 10%, the weight loss of SIL treated composites was higher than those of the UNTRD composites.

Figure 4.65 shows the results of the soil burial test for PLABM/GHP composites after three months. The results also showed a progressive increment in degradation of the composites with filler loading as evidenced from the weight loss values. The weight loss of the PLABM matrix was 0.2% after three months while higher values which increased with filler loading were obtained for its composites. At filler contents of 10 and 20%, the composites weight loss were 3.80% and 5.35%, 4.62% and 9.07%, 3.01% and 6.62% and then 2.17% and 6.13% for UNTRD, ALK, SIL and ALKSIL treated composites respectively. The results indicated that ALK and ALKSIL treated composites exhibited higher degradation rates than the SIL treated and UNTRD composites while those for the SIL treated composites were higher than those of the UNTRD composites at 20 and 30% filler contents only.

The results of the soil burial test for PLPG/GHP composites after three months presented in Figure 4.66 reveals that the PLPG matrix had degradation rate of 0.46% while its various composites exhibited different degradation rates which obviously increased with filler loading. The results indicated that the UNTRD composites had higher weight loss than the treated ones at 10 and 20% filler contents while the treated composites showed higher weight loss over the UNTRD ones at 30 and 40% filler contents. It was apparent that PEG, being hydrophilic, contributed to the degradation of the composites by possibly absorbing moisture together with the GHP unlike the Biomax strong which is a rubbery substance and not water soluble in nature.

The degradation results of PP/GHP composites after three months of soil burial are presented in Figure 4.67. The results also showed increment in weight loss with filler loading but with much less values in comparison to the various PLA matrices and their various composites. The weight loss of pure PP was only 0.08% after three months of soil burial and this increased to a maximum of 2.60% for ALK treated composite at 40% filler content. Contrary to the results obtained for PLA –based composites, ALKSIL treated composites exhibited the lowest degradation rate as compared to the untreated and other treated composites. The reason for the very low degradation of PP/GHP composites is attributed to the resistance in microbial attack of PP which is known to be non-biodegradable and the increment in weight loss was attributed to the incorporation of filler in the PP matrix which was possibly selectively attacked by the microorganisms in the soil and as the filler content increased, the polymer content reduced leaving a high surface area consisting mostly of filler than polymer.

It was observed from the results that degradation increased with filler loading because the fillers could easily be attacked by microorganisms (Kim *et al*., 2006). This is attributed to the fact that

lignocellulosic materials, being hydrophilic, transferred water by capillary means into the composites (Tserki *et al*., 2006a) and as the filler content increased, the degradation increased due to the growth of microorganisms which are more in higher filler contents. The degree of biodegradation according to Patel and Sen (2011), varies with temperature, matrix stability and available oxygen. Humid environment also promotes the growth of microorganisms in the soil (Tserki *et al*., 2006a) and most microorganisms need light, water, oxygen and favourable temperature to assist in the biodegradation process (Patel and Sen, 2011). Favourable conditions for microbial activities will result to physical disintegration and serious reduction in molecular weights of the composites and these lower molecular weights and small fragments would then be amenable to biodegradation (Patel and Sen, 2011).

The results indicated that the addition of GHP enhanced the biodegradability of the various polymer matrices as seen in the Figures because of the increase in polymer surface created after GHP consumption by microorganisms (Kim *et al*., 2006). However, the biodegradability of PP and its composites were obviously and expectedly the least due to its highly hydrophobic nature.

The natural soil burial test is obviously a slow process but, it is worthy of note that the test reflects a real-life condition better than other known types of tests (Kim *et al*., 2005a). This could be attributed to the fact that in soil, fungi are majorly responsible for the degradation of organic matters including polymers. The biodegradation rate of biopolymers depends on filler content, biodegradability of each constituent and then quality of the filler-matrix interface (Behjat *et al*., 2009). Furthermore, filler addition generally increased the degradation rate of composites and alkaline treatment of fillers resulted in a slight increased rate of degradation (Behjat *et al*., 2009).

4.2.5.1 Surface morphology after soil burial

The SEM micrographs shown in Plates X to XIII are those of the surface morphologies of the composites after three months of burial in the soil.

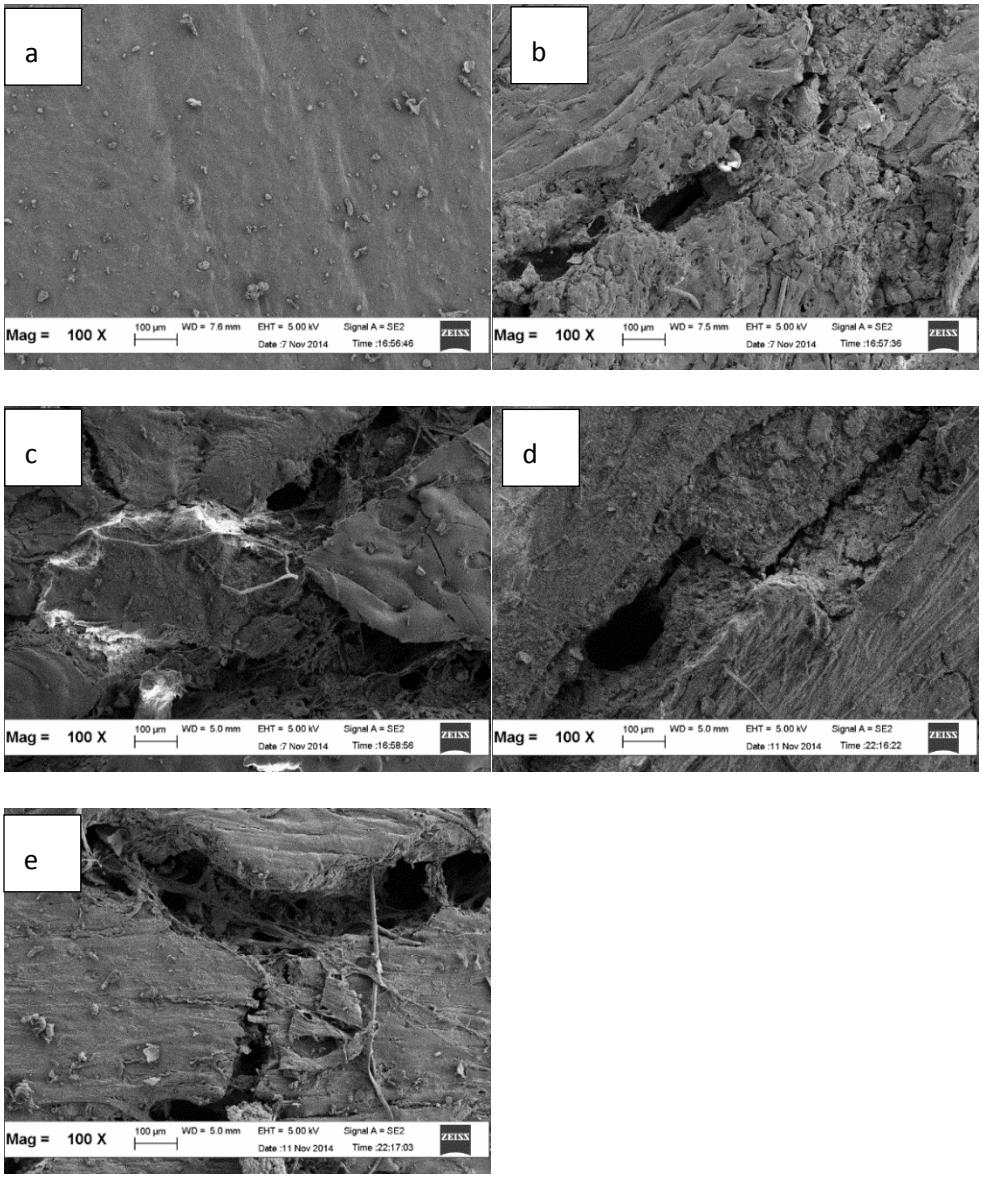


Plate X: SEM micrographs of PLAP/40% GHP Composites after three months of soil burial(a) Unreinforced PLAP (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated

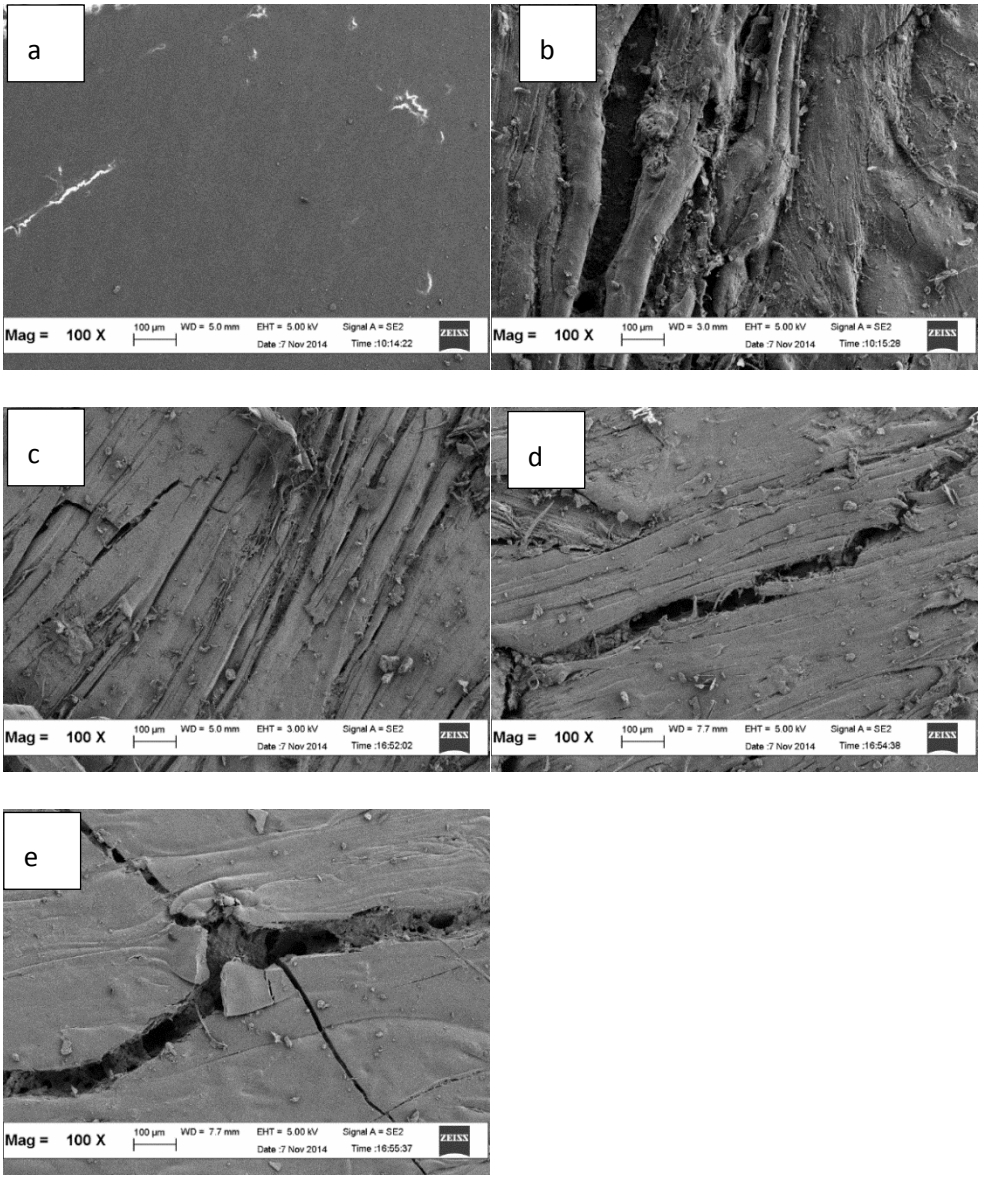


Plate XI: SEM micrographs of PLABM/40% GHP Composites after three months of soil burial(a) Unreinforced PLABM (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated

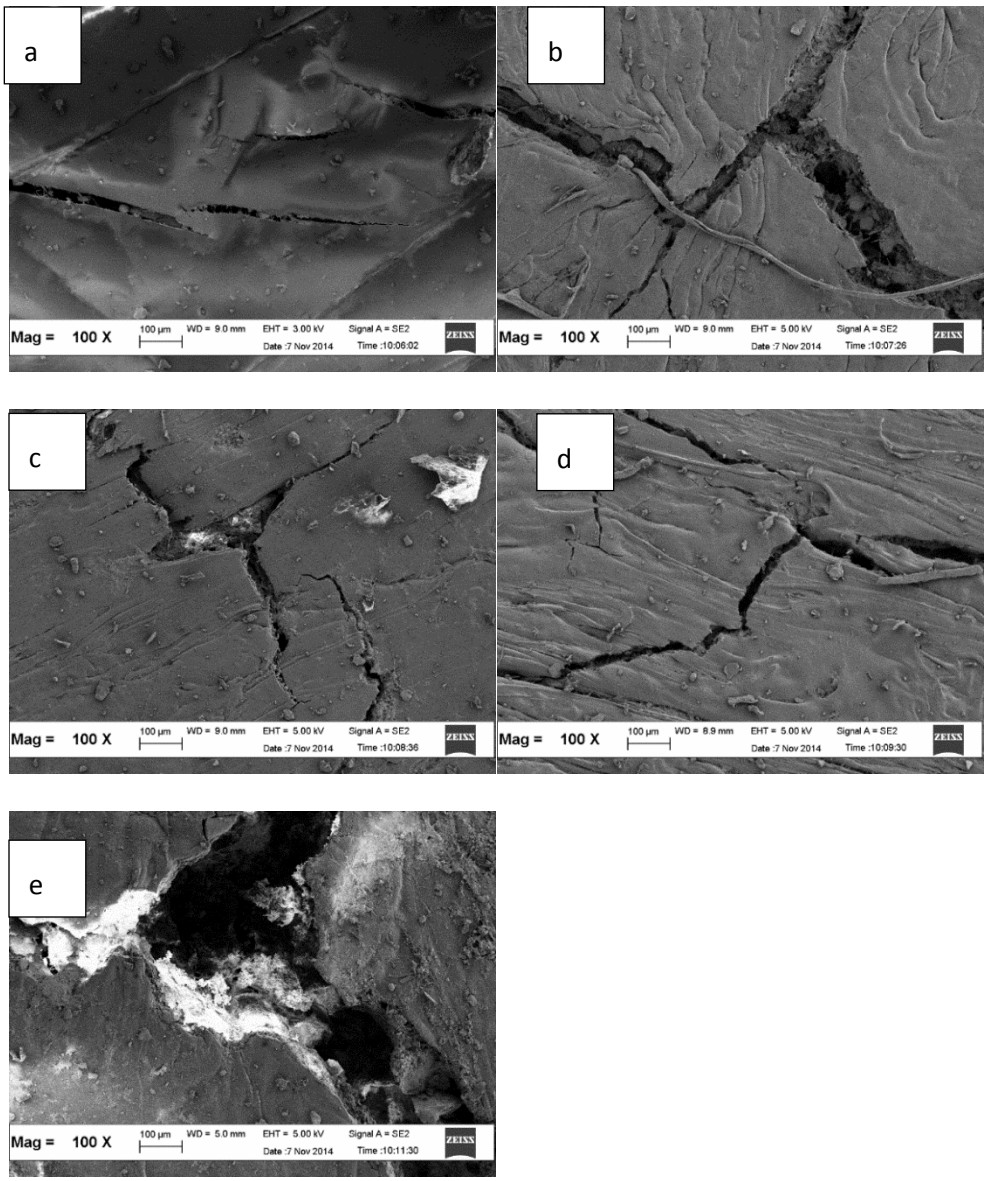


Plate XII: SEM micrographs of PLPG/40% GHP Composites after three months of soil burial(a) Unreinforced PLPG (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated.

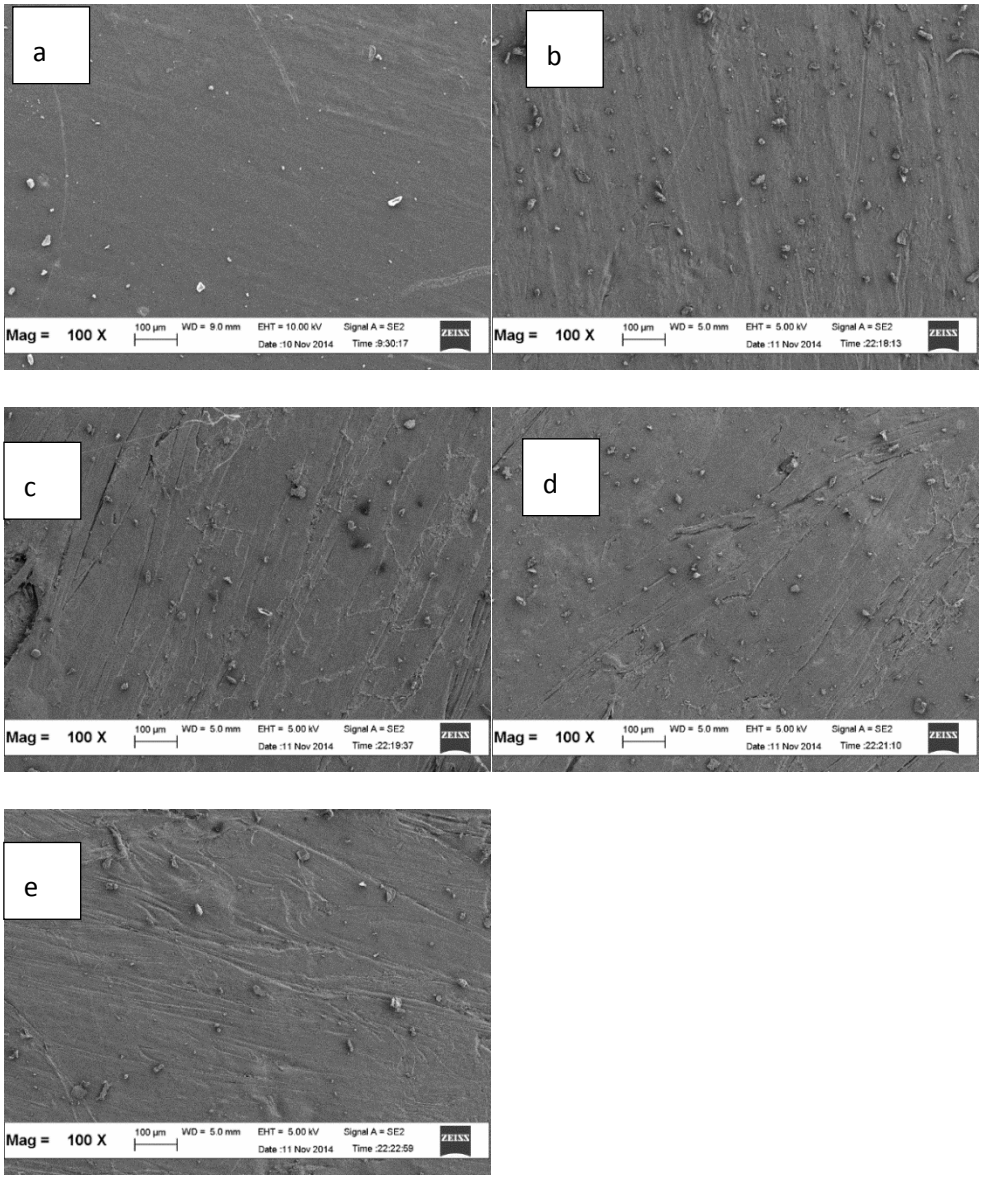


Plate XIII: SEM micrographs of PP/40% GHP Composites after three months of soil burial(a) Unreinforced PP (b) UNTRD (c) ALK treated (d) SIL treated (e) ALKSIL treated.

The surfaces of PLAP and its composites are shown in Plate X a-e. The matrix exhibited a dull surface which may have been as a result of the microorganisms in the soil. But the time was not long enough for any meaningful attack. The surface of the UNTRD specimen eroded significantly showing the activities of microbes on the specimen. ALK treated specimen

exhibited holes and surface deterioration due to microorganism activities while the SIL treated specimen showed deterioration but not as pronounced as that obtained in Plates X b and X c. The deterioration was most observed on the ALKSIL treated specimen (Plate X e) showing deep holes and surface tearing.

The SEM images for PLABM/GHP composite after three months of soil burial are shown in Plate XI a-e. The matrix was looking clean as if there was no deterioration. This could be due to the presence of Biomax strong which is a rubbery substance and could stand degradation. The filled composites exhibited different degrees of degradation due to activities of the microorganisms in the soil. That of the UNTRD seems to be the worst followed by that of the ALKSIL treated specimen which exhibited cracking with deep holes.

The degraded surfaces after soil burial for PLPG and its composites are shown in Plate XII a-e. Generally, PLPG and its composites exhibited the greatest deterioration probably due to the influence of PEG in the composite.

The PLPG matrix showed cracks at various points on the surface. The UNTRD and SIL treated specimens were similar in surface texture and colour but the UNTRD had deep holes as a result of cracks that abound on the surface. The worst degradation was exhibited by the ALKSIL treated specimen which may have completely disintegrated in the soil if left a little longer.

The SEM image for PP and its composites after soil burial for three months are shown in Plate XIII a-e. Generally, PP is resistant to the attack of microorganisms so it did not show any appreciable deterioration. PP/GHP composites showed surface roughening with some

degradation lines being visible especially on the treated specimens. The deterioration could and most probably be due to the filler which is a good food for the microorganism in the soil.

It was observed from the SEM images that the degraded samples showed heterogeneous erosion and exhibited irregular surfaces with a number of holes of different depths and sizes and finally damaged completely by the microorganisms in the soil. This was also observed in the study of Tserki *et al*., (2006a). The observation indicated that the degradation surfaces of the GHP filled polymer composites were attacked by microorganisms. Also, there was indication that addition of GHP led to selective hydrolysis which created localized micro-pores in the composites giving rise to increased surface areas and concomitant increase in rate of degradation.

The degradation mechanism observed from the SEM images include debonding and cracking as observed also by Abdulkhalil *et al*., (2010). Their explanation was that the factor responsible for such was moisture absorption within the samples. The high water uptake is attributed to the hydrophilic nature of GHP which permitted the colonization by microorganisms. The microbes depend on the nutrients provided by the filler and resins resulting in their being susceptible to degradation.

Also, the micro-voids may result in poor interface between the matrices and the fillers which may create a new surface for water penetration and bacterial growth which will then lead to gradual degradation of the matrices (Petinakis *et al*., 2010).

The results obtained from the water absorption and soil burial tests point to the fact that the biodegradable composites in this study could be used in such applications as (Patel and Sen, 2011):

i. disposable items such as packaging and catering items (cutlery, pots, bowls, straws etc)
ii. Organic waste bags such that they can be composted together with the food or green wastes. Also for trays and containers for fruits, vegetables, eggs, bottles for soft drinks and dairy products
iii. agriculture as mulch films, planting cups etc

4.2.6 Thermal properties

4.2.6.1 Differential Scanning Calorimetry (DSC)

The DSC curves of PLABM and its composites are shown in Figures 4.68 and 4.69 a-d and the DSC data are summarized in Table 4.2.

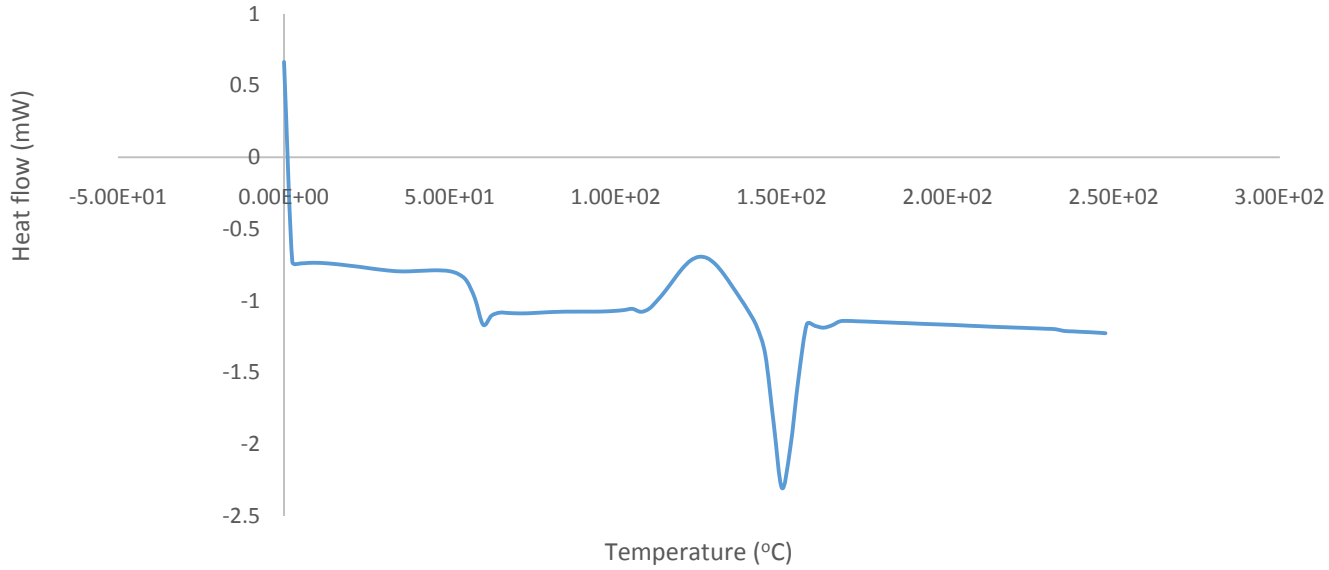


Figure 4.68: DSC thermogram for unreinforced PLABM

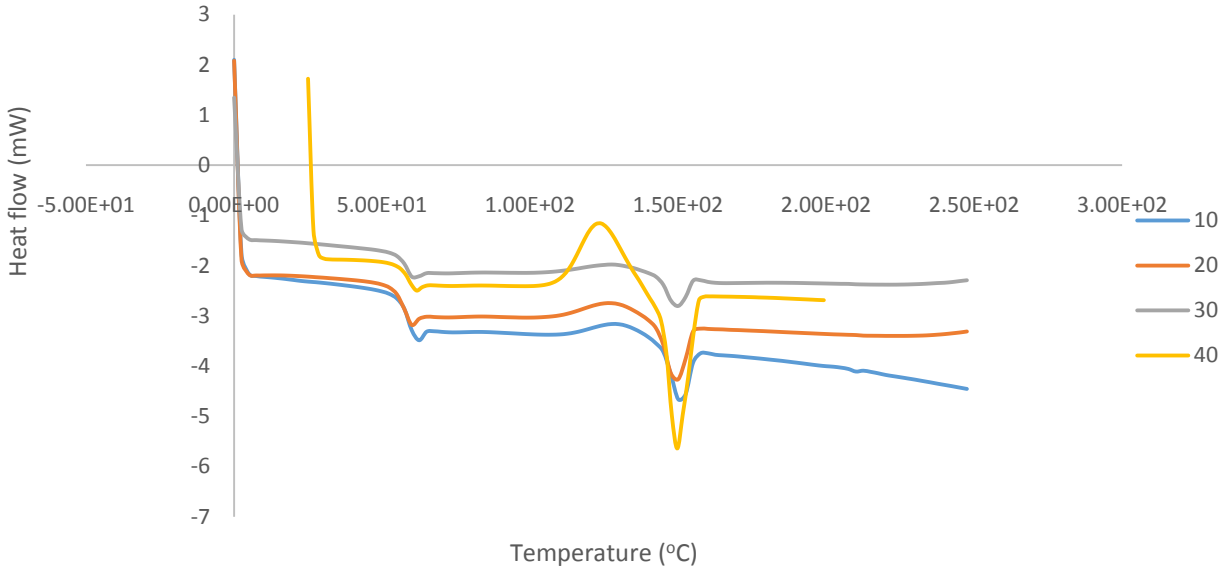


Figure 4.69a: DSC thermograms for UNTRD PLABM/GHP Composites

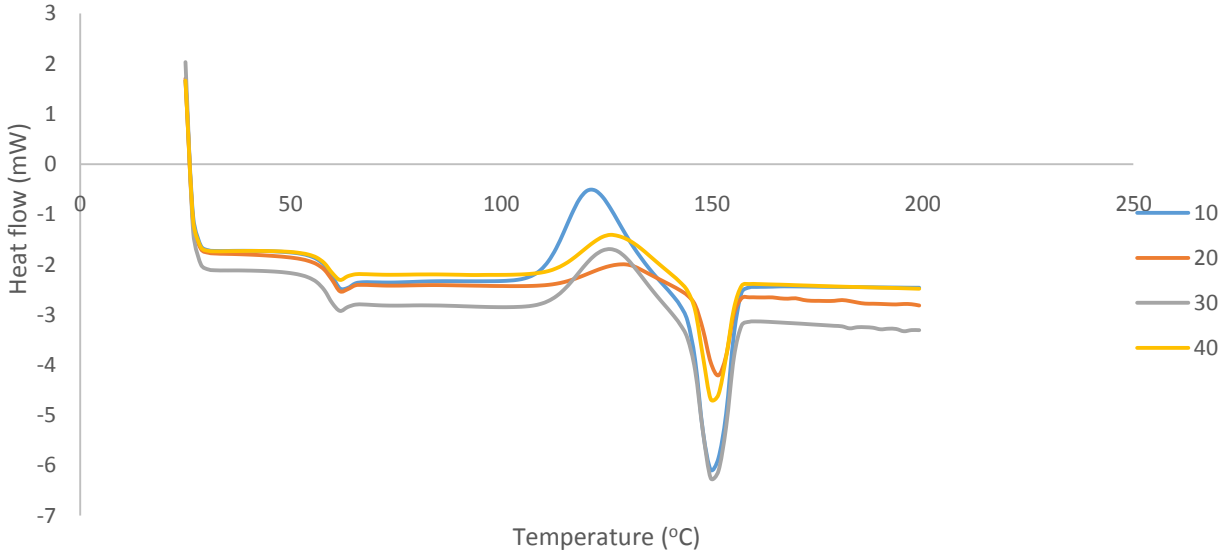


Figure 4.69b: DSC thermograms for ALK treated PLABM/GHP Composites

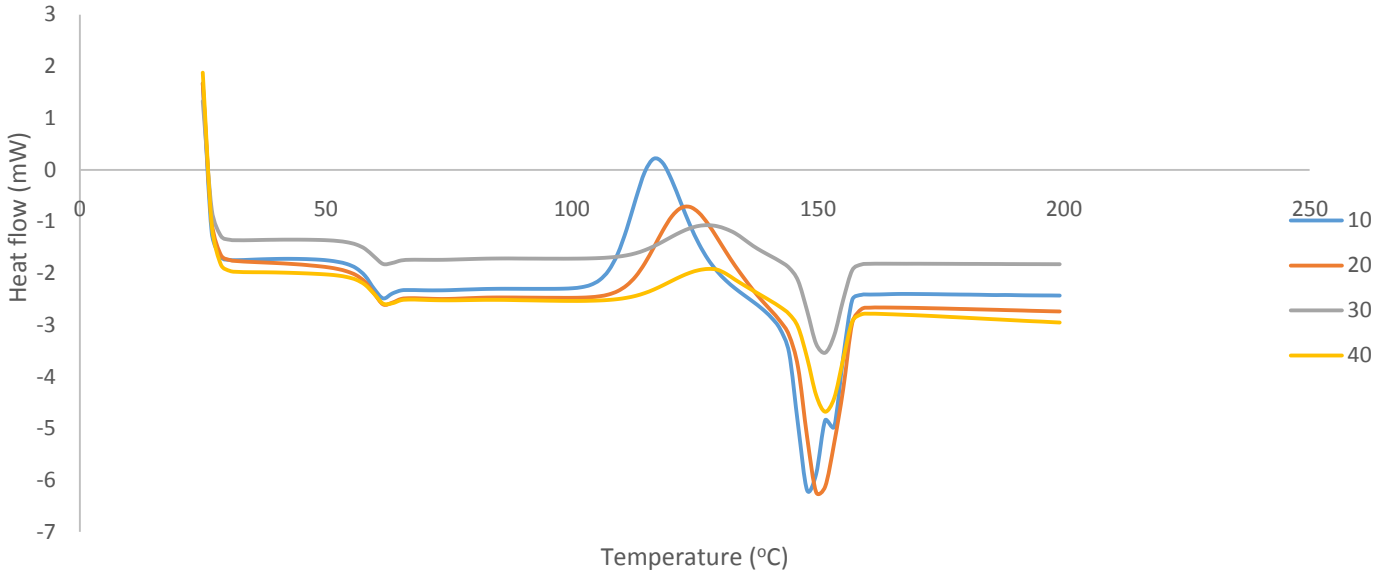


Figure 4.69c: DSC thermograms for SIL treated PLABM/GHP Composites

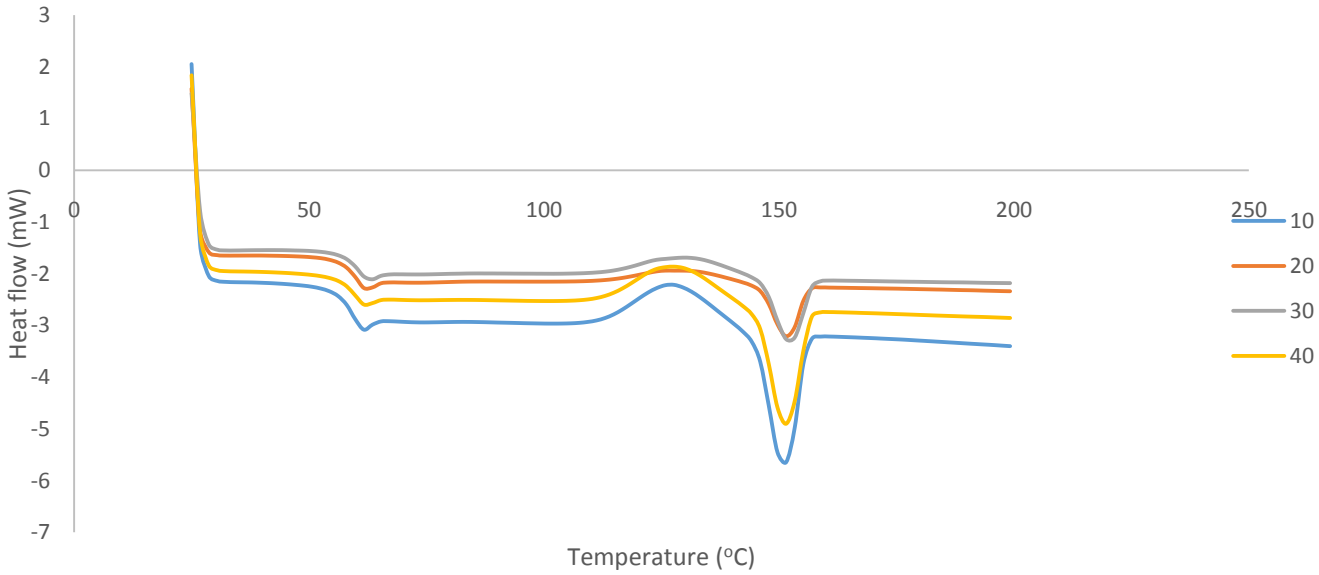


Figure 4.69d: DSC thermograms for ALKSIL treated PLABM/GHP Composites

Table 4.2: Summary of DSC data for PLABM/GHP Composites

SPECIMEN	Tg (^{o}C)	Tc (^{o}C)	Tm (^{o}C)	Xc (%)
PLABM	60.00	127.50	150.01	12.66
PLABM/10UGHP	62.50	132.51	150.01	4.46
PLABM/20UGHP	60.00	130.01	150.01	5.25
PLABM/30UGHP	60.00	130.01	150.01	4.03
PLABM/40UGHP	61.67	124.01	149.68	20.66
PLABM/10AGHP	61.67	122.18	149.68	20.56
PLABM/20AGHP	61.67	129.51	151.51	8.88
PLABM/30AGHP	61.67	127.68	149.68	18.66
PLABM/40AGHP	61.67	127.68	149.68	18.98
PLABM/10SGHP	61.67	118.51	147.85;153.35	24.20
PLABM/20SGHP	61.67	124.01	149.68	22.32
PLABM/30SGHP	61.67	129.51	151.51	9.18
PLABM/40SGHP	63.53	129.51	151.51	14.19
PLABM/10ASGHP	61.67	127.68	151.51	11.42
PLABM/20ASGHP	61.67	129.51	151.51	6.04
PLABM/30ASGHP	63.50	131.34	151.51	8.29
PLABM/40ASGHP	61.67	129.51	151.51	15.60

U: Untreated; A: Alkali-treated; S: Silane-treated; AS: Alkali and Silane treated; GHP: Guineacorn Husk Particulate; PLABM: PLA/Biomax strong.

From Figures 4.69a-d, addition of GHP did not affect the glass transition temperature (Tg) and melting temperature (Tm) as there was no significant changes observed. Similar observation was reported by (Finkenstadt *et al*., 2007ab; Lee *et al*., 2009). It was also observed that the peaks of the crystallization temperature (Tc) were most pronounced with the SIL treated composites (Figure 4.69c) while these peaks were almost absent in the ALKSIL treated composites (Figure 4.69d). On a general note, the Tc broadened, decreased in peak size and shifted to higher temperatures with GHP loading.

Table 4.2 showed that the Tg of PLABM was 60^{o}C and Tm was 150 ^{o}C and the degree of crystallinity was 12.66%. The low degree of crystallinity exhibited by PLABM could be either because the PLA was amorphous or that the plasticizer used may have decreased the molecular segmental mobility of PLA thereby reducing the ability of PLA to crystallize during processing. The melting temperature of Biomax strong was not observed in the DSC curves probably because the heat flow associated with the melting of the plasticizer was too low to be detected by the equipment. This was also the observation made by (Mat Taib *et al*., 2012).

Generally, as observed from Table 4.2, the degree of crystallinity for treated composites were higher than those for the untreated ones which is also reported by Chun *et al*., (2012). The increase in crystallinity could be ascribed to the enhancement of nucleating effect from the GHP contents due to improved interfacial bonding between the constituents (Chun *et al*., 2012). Fillers are responsible for the increase in PLA crystallinity but the low values obtained in this study could be as a result of interference from the Biomax strong that was used as a plasticizer and the low Xc values indicated less crystallites (MatTaib *et al*., 2012, Battegazzore *et al*., 2014).

4.2.6.2 Dynamic Mechanical Analysis (DMA)

The DMA curves for unreinforced PLABM and loss modulus curves for PLABM and its composites are shown in Figures 4.70 and 4.71 a-d and the data are summarized in Table 4.3.

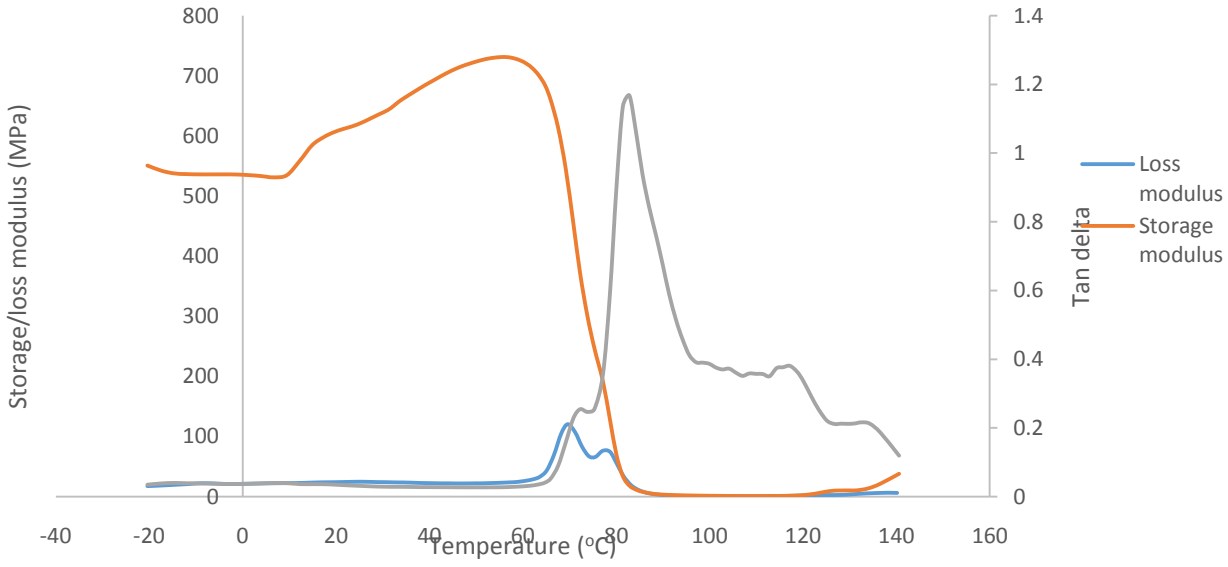


Figure 4.70: DMA curves for unreinforced PLABM

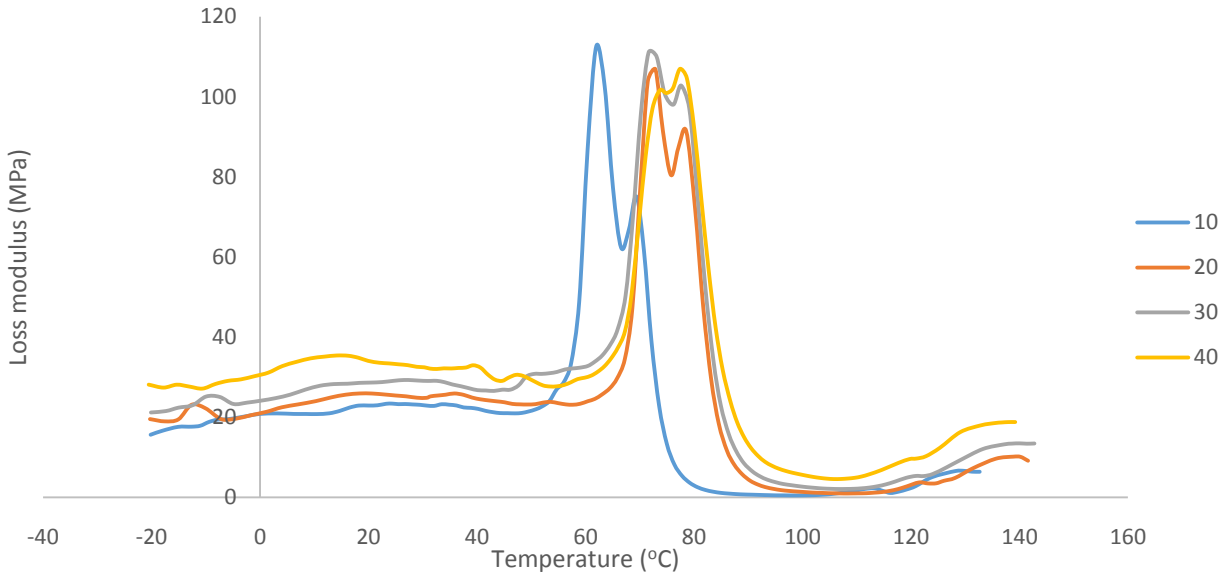


Figure 4.71a: Loss modulus against temperature of UNTRD treated PLABM/GHP Composites

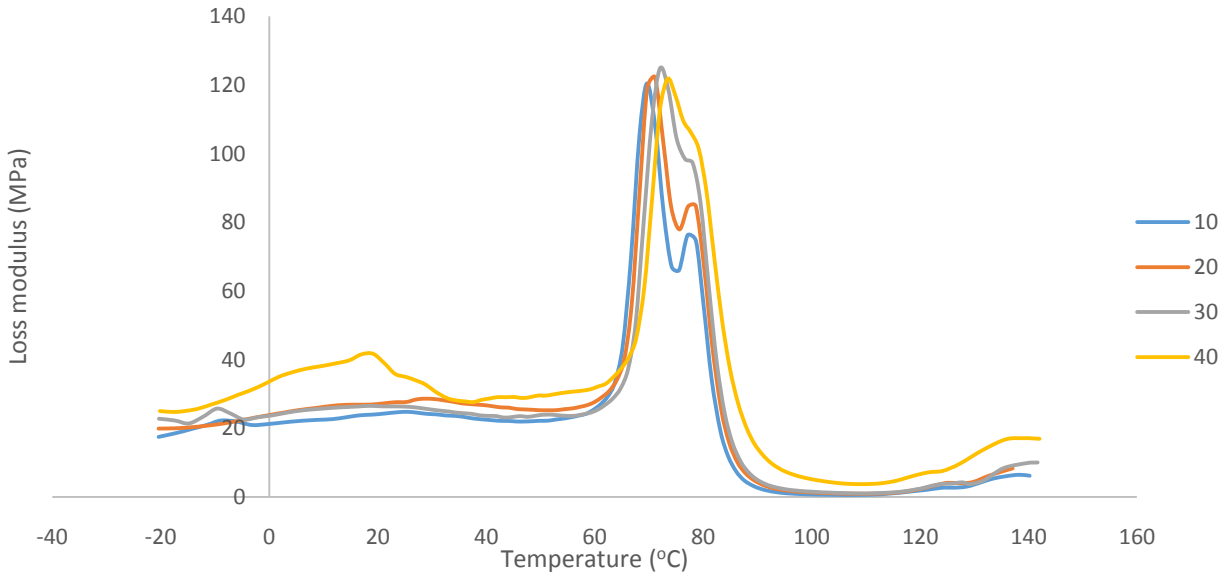


Figure 4.71b: Loss modulus against temperature of ALK treated PLABM/GHP Composites

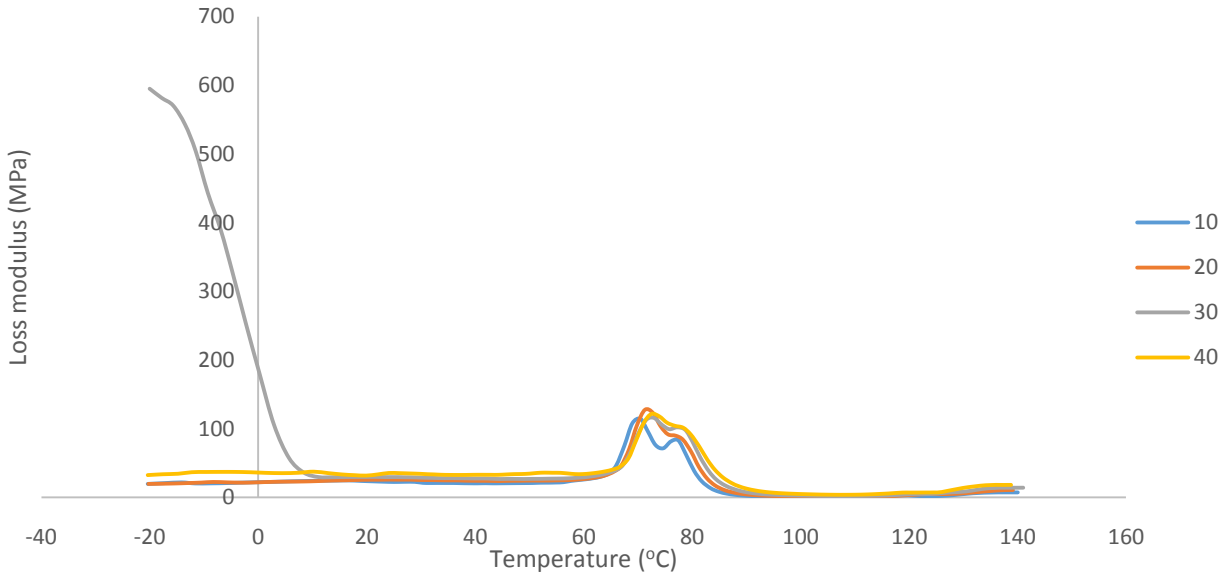


Figure 4.71c: Loss modulus against temperature of SIL treated PLABM/GHP Composites

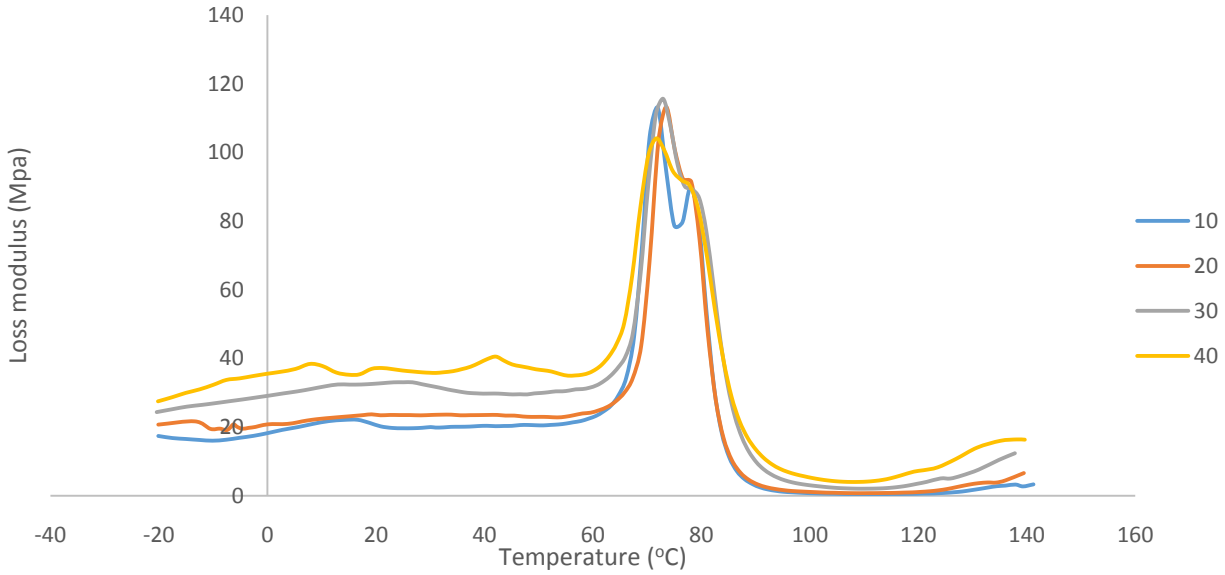


Figure 4.71d: Loss modulus against temperature of ALKSIL treated PLABM/GHP Composites

Table 4.3: Summary for the loss modulus curves of PLABM/GHP composites

Specimen	Tg (^{o}C)
PLABM	69.63; 78.67
PLABM/10UGHP	61. 98; 69.40
PLABM/20UGHP	72.91; 78.57
PLABM/30UGHP	73.11; 77.63
PLABM/40UGHP	74.90; 77.40
PLABM/10AGHP	69.63; 78.67
PLABM/20AGHP	71.12; 78.67
PLABM/30AGHP	72.05
PLABM/40AGHP	73.45
PLABM/10SGHP	70.49; 77.46
PLABM/20SGHP	71.29
PLABM/30SGHP	72.93
PLABM/40SGHP	72.49
PLABM/10ASGHP	71.95; 78.01
PLABM/20ASGHP	73.55
PLABM/30ASGHP	72.96
PLABM/40ASGHP	71.70

The results for the storage modulus of PLABM and its composites as a function of temperature are shown in Figure 4.72 a-d while the data at 30^{o}C are summarized in Table 4.4.

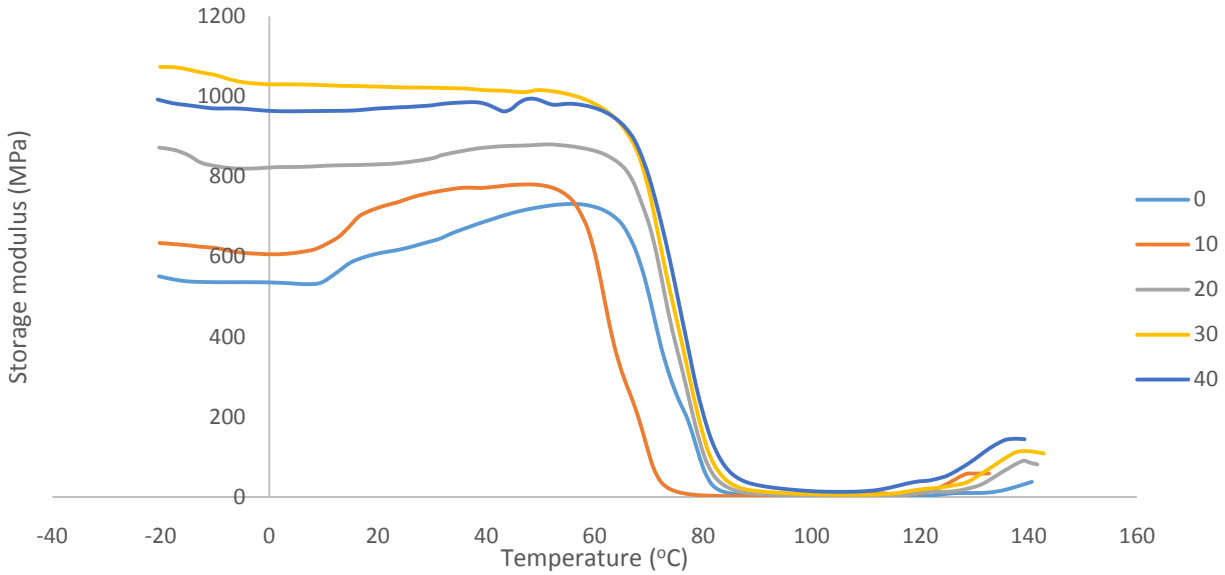


Figure 4.72a: Storage modulus against temperature of UNTRD PLABM/GHP Composites

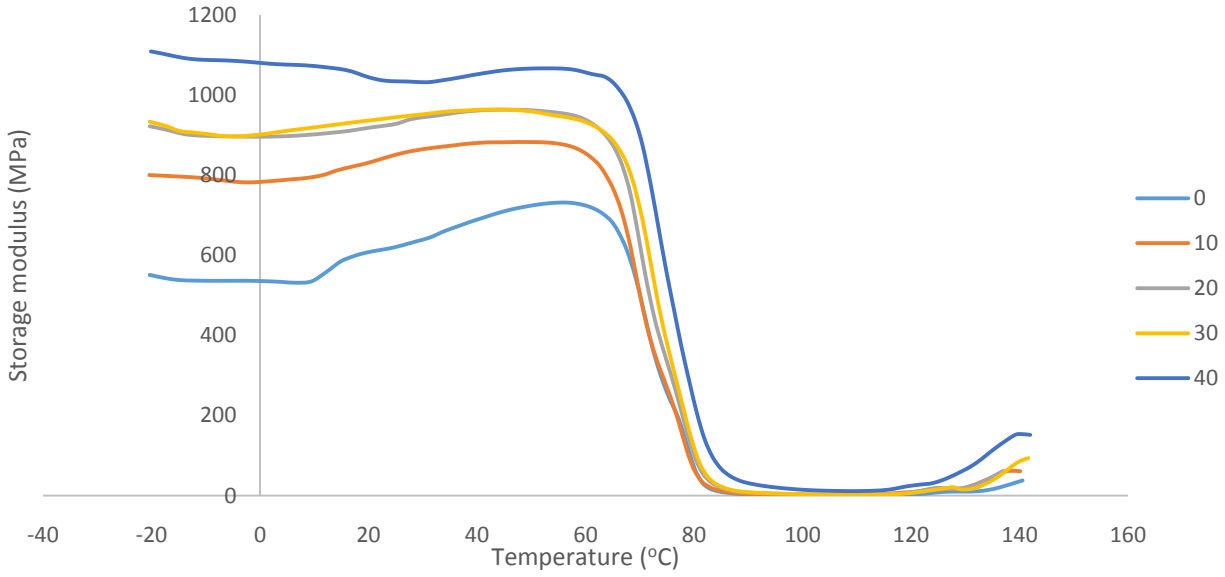


Figure 4.72b: Storage modulus against temperature of ALK treated PLABM/GHP Composites

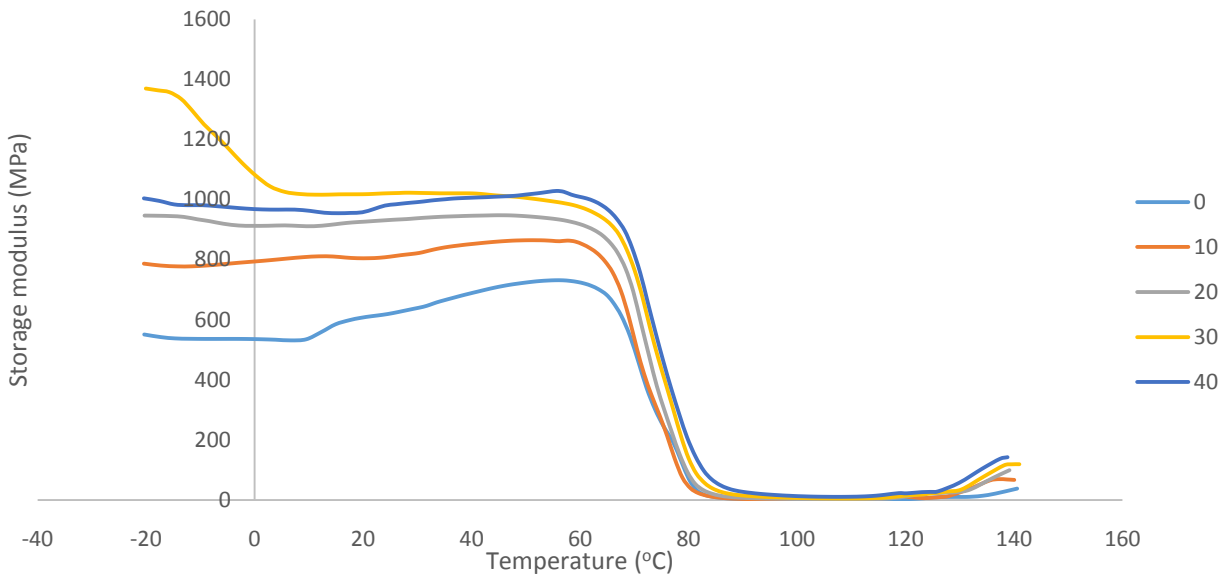


Figure 4.72c: Storage modulus against temperature of SIL treated PLABM/GHP Composites

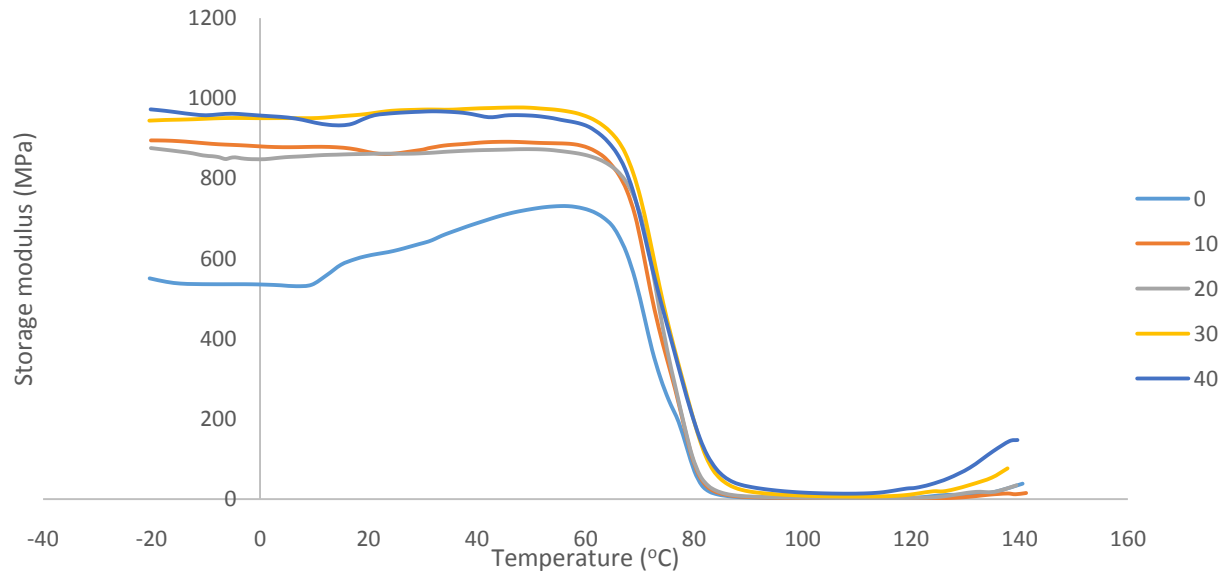


Figure 4.72d: Storage modulus against temperature of ALKSIL treated PLABM/GHP Composites

Table 4.4: Summary for the storage modulus of PLABM/GHP composites at 30 (^{o}C)

Specimen	Storage modulus (MPa)
PLABM	642.96
PLABM/10UGHP	761.81
PLABM/20UGHP	848.07
PLABM/30UGHP	1021.58
PLABM/40UGHP	978.32
PLABM/10AGHP	866.42
PLABM/20AGHP	945.79
PLABM/30AGHP	952.40
PLABM/40AGHP	1032.01
PLABM/10SGHP	822.85
PLABM/20SGHP	939.21
PLABM/30SGHP	1022.53
PLABM/40SGHP	991.49
PLABM/10ASGHP	875.34
PLABM/20ASGHP	863.24
PLABM/30ASGHP	972.12
PLABM/40ASGHP	966.87

The observation from the curves indicated that, for almost all the specimens, there was a shift of the curves to higher temperatures with GHP loading indicating that loss modulus increased with GHP loading (Figure 4.71a-d). This was also observed and reported by (Huda *et al*., 2006; MatTaib *et al*., 2010; Yu *et al*., 2010; Paul *et al*., 2015). This was ascribed to the decreased mobility of PLABM chain as a result of GHP addition.

The peaks of the loss modulus curves are interpreted as the Tg of the materials (Lee *et al*., 2008) and though the values here are higher than those obtained from the DSC experiment because DMA being a dynamic method normally yields higher Tgs than DSC , the results were similar in the sense that the difference in Tg were not so pronounced. Splitting peaks were observed in the DMA experiment for the loss modulus but these peaks were close and had similar and single bases which indicated the blend of PLA and Biomax strong being two different polymers, were very much compatible. The fact that double peaks were observed in the loss modulus curves unlike in the DSC experiment is an indication that the DMA equipment is much more sensitive than the DSC equipment and the heating rates for both experiments were quite different with that of the DMA being lower which would allow detection of any small changes occurring within the materials. Also, the double peaks obtained could probably be due to the fact PLA and Biomax strong being a polymer-polymer blend, are compatible with themselves.

Moreover, the fact that the peaks were close and not far apart and the bases were not broad is an indication of high compatibility between the GHP and PLABM.

From Figure 4.72a-d of the storage modulus results, it was observed that the composites exhibited higher storage modulus as compared to the unreinforced matrix and they increased

with GHP loading (Kim *et al*., 2005b; Huda *et al*., 2006; Lee *et al*., 2009; Yu *et al*., 2010; Baek *et al*., 2013). The increment was up to 30% GHP content and decreased at 40% GHP composites for UNTRD, SIL and ALKSIL treated composites while for ALK treated composites, the increment was even up to 40% GHP content.

The increase in storage modulus with GHP loading is attributed to the stiffness imparted by the filler on the composites which allows a greater degree of stress transfer at the interface from the matrix to the filler (Kim *et al*., 2005b). Generally, the result of the storage modulus is in agreement with tensile modulus results (Pilla *et al*., 2008) and this is an indication that GHP, being an agro-flour increased the rigidity of the composites as its content is increased.

Generally, the composites with surface treatments exhibited higher storage modulus as compared to the untreated composites. This suggests better adhesion and higher compatibility between the surface treated GHP and PLABM than with the untreated GHP. Similar results were obtained and reported by (Huda *et al*., 2008b; Lee *et al*., 2009; Yu *et al*., 2010).

From the data of storage modulus at 30^{o}C presented in Table 4.4, it can be seen that the storage modulus of PLABM matrix was 642MPa while those of its composites at 10% were 761MPa, 866MPa, 822MPa and 875MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively. While at 40% GHP loading, the storage modulus were 978MPa, 1032MPa, 991MPa and 966MPa for UNTRD, ALK, SIL and ALKSIL treated composites respectively.

As the temperatures increased towards the Tg, the storage modulus generally decreased as a result of increased polymer chain mobility of the matrix at higher temperatures (Kim *et al*., 2005b; Pilla *et al*., 2008; MatTaib *et al*., 2010; Yu *et al*., 2010).

4.2.6.3 Thermogravimetric Analysis (TGA)

The TGA and DTG curves and TGA results for PLABM and its composite are shown in Figures 4.73 and 4.74 a-d and the TGA data are summarized in Table 4.5.

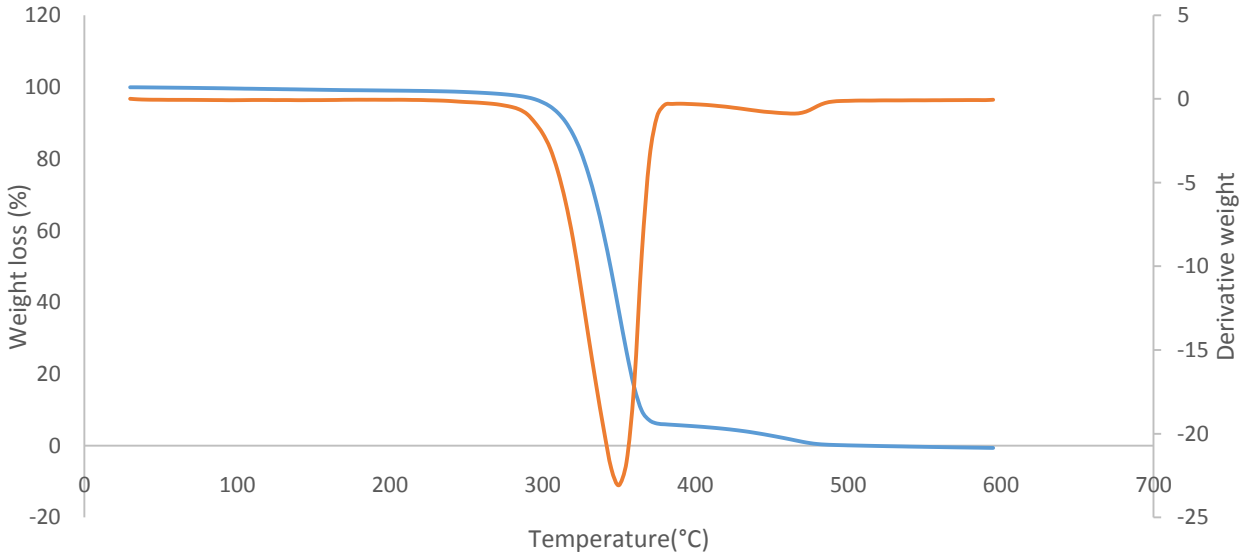


Figure 4.73: Weight loss and derivative weight of unreinforced PLABM against temperature

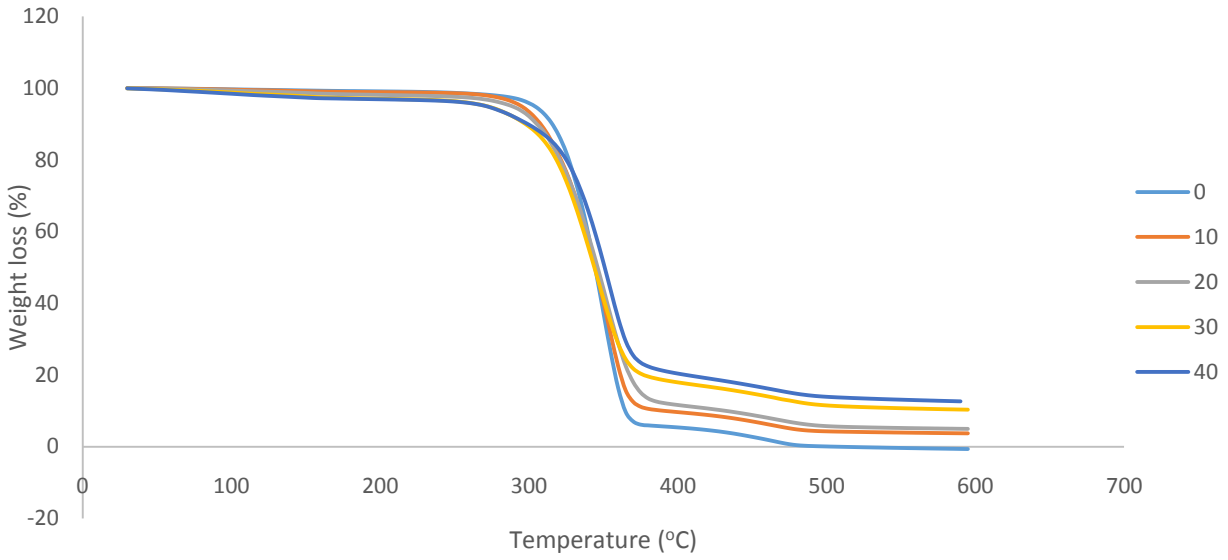


Figure 4.74a: Weight loss of UNTRD PLABM/GHP Composites against temperature

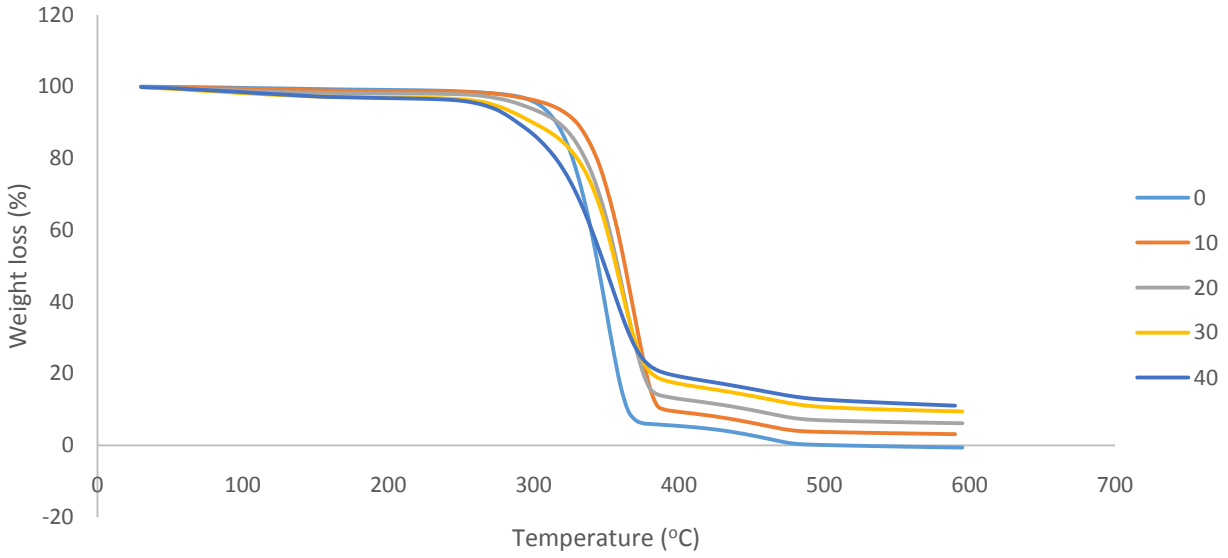


Figure 4.74b: Weight loss of ALK treated PLABM/GHP Composites against temperature

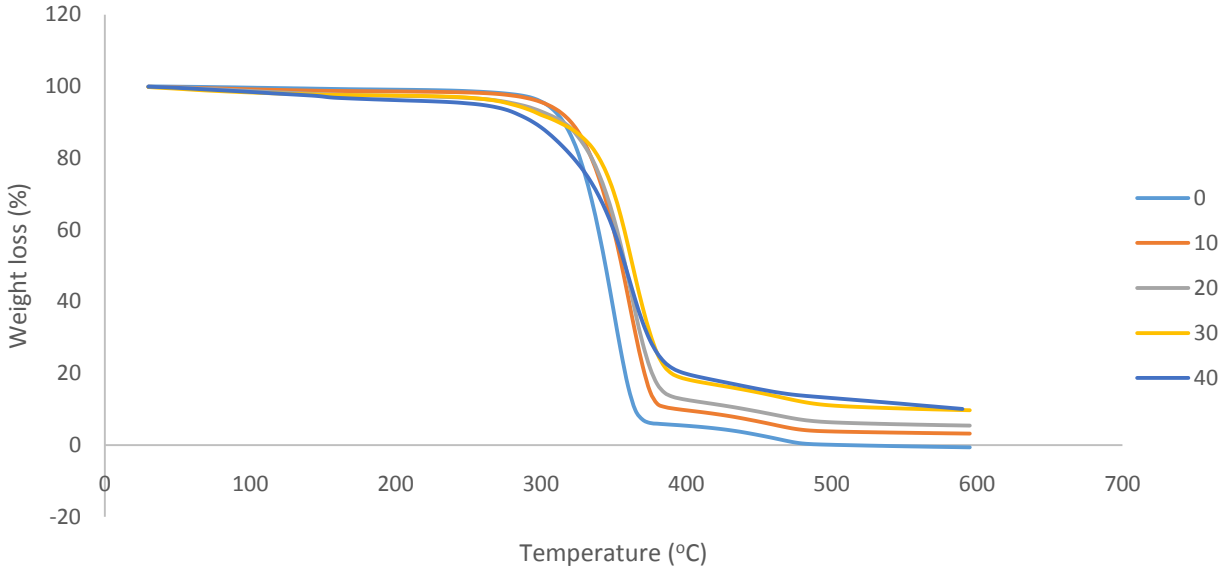


Figure 4.74c: Weight lossof SIL treated PLABM/GHP Composites against temperature

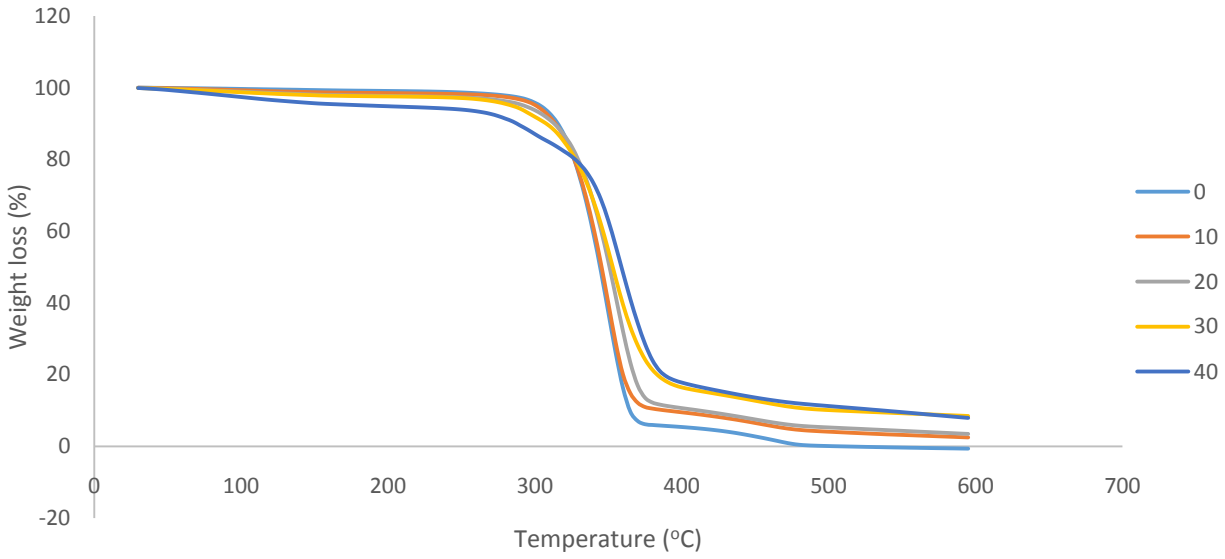


Figure 4.74d: Weight lossof ALKSIL treated PLABM/GHP Composites against temperature

Table 4.5: Summary of TGA data of PLABM/GHP Composites

Specimen	Onset (^{o}C)	Endset (^{o}C)	Dmax (^{o}C)	Residue (%)
PLABM	295	375	350	-
PLABM/10UGHP	275	370	355	3.69
PLABM/20UGHP	275	385	350	4.92
PLABM/30UGHP	265	375	345	10.29
PLABM/40UGHP	260	375	355	12.66
PLABM/10AGHP	280	390	370	3.12
PLABM/20AGHP	270	385	360	6.15
PLABM/30AGHP	265	385	360	9.40
PLABM/40AGHP	265	380	360	11.07
PLABM/10SGHP	285	385	360	3.21
PLABM/20SGHP	275	385	360	5.45
PLABM/30SGHP	275	395	365	9.69
PLABM/40SGHP	270	390	360	10.01
PLABM/10ASGHP	285	370	350	2.43
PLABM/20ASGHP	280	380	355	3.45
PLABM/30ASGHP	275	395	355	8.42
PLABM/40ASGHP	270	390	360	7.86

It was observed from the TGA curves in Figures 4.73 and 4.74a-d that the matrix and its composites exhibited one- step decomposition. Similar observation was made by (Salmah *et al*., 2011; Chun *et al*., 2012; Baek *et al*., 2013; Fakhrul *et al*., 2013; ThaoTran *et al*., 2014). This is an indication of high compatibility between the matrix and its reinforcement because the decomposition stages of GHP as shown in Figure 4.2a was overlapped with that of PLABM (Chun *et al*., 2012).

The TGA of PLABM curve with its derivative (DTG) shown in Figure 4.73 indicated that the blend of PLA and Biomax strong was miscible and compatible as well. Also, PLABM contained no decomposition end-products which ascertains its purity. The same observation was made by Fakhrul *et al*., (2013) on the TGA of PP. The effect of the filler was observed in the residues or ash contents at 600^{o}C as it increased with filler loading (Kim *et al*., 2005b; Lee *et al*., 2008; Chun *et al*., 2013a) and the residues obtained from the UNTRD composites were higher than those obtained for the treated composites as shown in Table 4.5.

The onset, endset and maximum degradation (dmax) temperatures are shown in Table 4.5. The Onset temperature indicates the extent of a material's stability with temperature and from the data, it was observed that the unreinforced matrix exhibited a higher thermal stability as compared to its composites and the stability decreased with GHP loading. The reduction in thermal stability with filler loading was also reported by a number of researchers (Lee *et al*., 2009; Dean *et al*., 2010; Salmah *et al*., 2012; Essabir *et al*., 2013a; Koutsomitopoulou *et al*., 2014; Thao Tran *et al*., 2014) and this could be attributed to the fact that natural fillers are less thermally stable than polymers and their addition to polymers leads to the replacement of some

portions of the polymer as the fillers increase in content thereby decreasing the thermal stability of the resulting composites (Yussuf *et al*., 2010).

From Table 4.5, it was observed that for the same GHP content, treated composites exhibited higher thermal stability than the untreated composites (Lee *et al*., 2009; Yu *et al*., 2010; Salmah *et al*., 2011) with that of SIL treated being higher than ALK treated (Yu *et al*., 2010; Thao Tran *et al*., 2014) while the ALKSIL treated composites exhibited the highest thermal stability as observed in the Table. This could be due to enhanced interfacial adhesion between the constituents and the stability of the interfacial bond for the ALKSIL treated GHP could be more effective than for the SIL treated GHP and ALK treated GHP as well.

The thermal stability of the composites as observed in the TGA curves (Figure 4.74a-d) and Table 4.5 indicated that the composites were all stable at their processing temperatures during compounding and injection moulding.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The research focused on the development and characterization of PLA/GHP composites produced using single screw extruder for compounding and injection moulding for production. At the end of the study, the following conclusions were drawn based on the results obtained;

1. PLA/GHP composites of different formulations as well as PP/GHP composites were successfully produced.
2. The tensile strength, flexural strength and Impact strength generally decreased with GHP loading.
3. The SEM micrographs for tensile fractured surfaces were generally characterized by agglomeration, debonding and filler pull-out while those for water absorption and soil burial were characterized by matrix cracking, warping and massive deterioration.
4. The tensile modulus, flexural modulus and hardness generally increased with GHP loading.
5. The water absorption test showed increase in water uptake with GHP loading.
6. Plasticization effect of water was observed.
7. The soil burial test showed increase in degradation with GHP loading.
8. The composites produced were biodegradable and environmentally friendly.
9. The SIL treated composites showed the least water absorption and degradation amongst all the treated and untreated composites while the ALK and ALKSIL treated composites exhibited highest deterioration and degradation.

10. The mechanical properties of the PLA/GHP composites were higher than those for PP/GHP composites but the reverse was the case with the result for elongation at break.
11. The loss modulus of PLABM/GHP composites increased with GHP loading and to higher temperatures.
12. The storage modulus of PLABM/GHP composites increased with GHP loading up to 30% GHP and decreased thereafter.
13. The thermal degradation of GHP showed a three –step degradation suggesting the evaporation of moisture, degradation of cellulosic contents and degradation of non-cellulosic contents.
14. The degradation of PLABM and its composites showed one-step degradation which suggested high compatibility between the two polymers and the filler.
15. The residues after thermal degradation at 600^{o}C increased with GHP content
16. The composites produced were stable at their processing temperatures during compounding and injection moulding processes.
17. The composites produced were of low density.
18. The systems could be best used indoors, in applications in which high strength is not a requirement or in applications requiring single use before disposal.

5.2. Recommendation

Based on the results and conclusion, the following recommendations can be given:

1. Studies on blending of PLA with other polymers and plasticizers should be carried out to improve its toughness without sacrificing its biodegradability.
2. The soil degradability test should be carried out for longer periods so as to establish the period of complete degradation and evaluate the effect of season on its degradation.
3. The effect of natural weather on the composites should be studied.
4. The water absorption test should be carried out for longer periods.
5. Studies on other forms of degradation other than soil burial should be carried out.
6. Compounding of the composites could be carried out through other means such as the use of twin screw extruder and internal mixer so as to evaluate their effects with respect to using single screw extruder.
7. The use of other types of surface treatments for the filler should be studied.
8. The study of rheological properties of PLA and its composites should be carried out.
9. The use of GHP on other biodegradable polymers as well as using GHP with other lignocellulosic fibres for hybrid composites production should be studied.

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Appendix A: Density values of the composite formulations

Table A 1: Density of composites

	Density (g/cm^3)			
GHP	PLAP	PLABM	PLPG	PP
0	1.2552	1.2807	1.2902	0.9351
10% UNTRD	1.3244	1.2935	1.3233	0.9717
20% UNTRD	1.3488	1.3107	1.3381	1.0159
30% UNTRD	1.3743	1.3383	1.3744	1.0649
40% UNTRD	1.3854	1.3544	1.3885	1.1236
10% ALK	1.3176	1.1700	1.3325	0.9645
20% ALK	1.3403	1.3204	1.3566	1.0034
30% ALK	1.3676	1.3480	1.3765	1.0568
40% ALK	1.3734	1.3574	1.3906	1.0920
10% SIL	1.3600	1.3170	1.3272	0.9765
20% SIL	1.3618	1.3196	1.3404	1.0090
30% SIL	1.3923	1.3443	1.3590	1.0708
40% SIL	1.4019	1.3596	1.4036	1.1160
10% ALKSIL	1.3265	1.2901	1.3389	0.9771
20% ALKSIL	1.3338	1.3120	1.3382	1.0251
30% ALKSIL	1.3619	1.3427	1.3838	1.0484
40% ALKSIL	1.4028	1.3617	1.4084	1.1170

Appendix B: Mechanical Properties of Composites

Table B 1: Mechanical properties of PLAP and PLAP/GHP composites

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Hardness (HRR)	Impact strength (J/m)
PLAP	57.130	2294.148	4.446	78.41	3547.94	94.433	50.388
PLAP/10UGHP	40.637	2380.541	2.158	61.42	3498.04	85.233	27.442
PLAP/20UGHP	36.401	2521.919	1.738	56.25	3579.01	88.467	15.504
PLAP/30UGHP	33.220	2831.801	1.471	53.70	3813.13	93.767	10.853
PLAP/40UGHP	31.594	2915.201	1.279	48.59	3950.03	79.567	10.527
PLAP/10AGHP	41.431	2519.459	1.736	64.76	3322.46	92.467	29.070
PLAP/20AGHP	38.348	3004.887	1.529	62.86	3457.47	92.967	19.380
PLAP/30AGHP	36.493	3035.870	1.359	58.75	3623.27	93.767	15.504
PLAP/40AGHP	32.945	3270.689	1.059	52.80	3727.36	88.300	13.070
PLAP/10SGHP	40.555	2638.260	1.926	66.00	3487.24	81.300	34.884
PLAP/20SGHP	35.006	2768.047	1.596	62.40	3487.82	83.467	21.442
PLAP/30SGHP	31.279	2981.562	1.319	52.44	3546.80	93.567	17.442
PLAP/40SGHP	30.770	3206.920	1.133	47.70	3664.36	74.867	15.504
PLAP/10ASGHP	45.483	2553.805	2.033	58.38	3244.54	90.633	29.442
PLAP/20ASGHP	40.059	2722.247	1.601	50.32	3284.33	94.333	18.442
PLAP/30ASGHP	39.068	2888.357	1.433	49.29	3604.11	96.400	16.279
PLAP/40ASGHP	37.565	3068.875	1.209	44.23	3669.37	91.267	11.628

PLAP: unplasticized PLA; GHP: Guineacorn husks particulates; U: Untreated; A: Alkali treated; S: Silane treated; AS: Alkali and Silane treated; EB: Elongation at break.

Table B 2: Mechanical properties of PLABM and PLABM/GHP composites

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Hardness (HRR)	Impact strength (J/m)
PLABM	44.367	1941.459	3.477	52.11	3255.53	63.067	71.059
PLABM/10UGHP	31.195	2322.633	2.289	49.86	3386.09	59.567	41.344
PLABM/20UGHP	26.349	2411.000	2.251	41.85	3390.06	70.200	40.052
PLABM/30UGHP	22.578	2455.282	2.031	41.54	3772.60	72.900	33.592
PLABM/40UGHP	19.777	2505.906	1.837	29.07	3602.09	52.000	27.132
PLABM/10AGHP	31.243	2146.117	2.136	54.80	3359.35	66.267	46.512
PLABM/20AGHP	28.159	2150.311	1.840	49.88	3654.03	67.667	42.636
PLABM/30AGHP	23.659	2367.667	1.824	43.16	4003.33	68.900	38.760
PLABM/40AGHP	20.491	2371.333	1.596	37.97	4201.56	62.567	37.468
PLABM/10SGHP	29.098	2361.832	2.036	38.69	3421.92	66.067	43.928
PLABM/20SGHP	24.078	2414.802	2.023	37.61	3627.78	67.000	38.760
PLABM/30SGHP	22.193	2667.246	1.701	37.07	3970.82	71.133	32.300
PLABM/40SGHP	17.683	2519.752	1.129	36.50	4102.25	62.300	23.256
PLABM/10ASGHP	32.086	2379.114	2.785	57.10	3456.18	65.300	67.183
PLABM/20ASGHP	29.501	2512.341	2.414	52.20	3480.62	68.633	55.556
PLABM/30ASGHP	25.441	2679.705	1.807	45.13	3920.98	69.567	38.760
PLABM/40ASGHP	21.710	2804.772	1.759	41.86	4233.51	68.300	31.008

PLABM: PLA plasticized with Biomax strong 100; GHP: Guineacorn husks particulates; U: Untreated; A: Alkali treated; S: Silane treated; AS: Alkali and Silane treated; EB: Elongation at break.

Table B 3: Mechanical properties of PLPG and PLPG/GHP composites

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Hardness (HRR)	Impact strength (J/m)
PLPG	47.881	2045.439	2.632	55.90	2380.00	88.467	25.194
PLPG/10UGHP	28.504	1787.020	3.257	43.91	2129.64	38.333	11.628
PLPG/20UGHP	24.850	1877.908	2.580	43.25	2209.29	48.333	21.318
PLPG/30UGHP	23.986	2216.021	1.695	42.13	2611.74	81.133	15.504
PLPG/40UGHP	21.503	2424.759	1.819	38.51	2654.99	68.867	14.583
PLPG/10AGHP	34.896	2113.607	1.854	52.05	2502.35	63.167	13.794
PLPG/20AGHP	28.722	2177.726	2.243	47.16	2517.84	63.867	19.380
PLPG/30AGHP	24.229	2359.850	1.692	43.67	2693.83	77.967	9.690
PLPG/40AGHP	20.170	2560.422	1.178	43.08	3138.23	67.933	5.814
PLPG/10SGHP	32.071	1890.940	2.196	46.86	2335.48	62.600	15.504
PLPG/20SGHP	28.516	2013.238	2.316	44.04	2612.54	63.967	17.442
PLPG/30SGHP	23.163	2216.405	1.724	40.94	2724.18	71.267	7.814
PLPG/40SGHP	21.776	2471.338	1.595	40.62	2795.80	53.200	5.955
PLPG/10ASGHP	31.587	1719.633	2.429	48.58	2191.62	65.667	18.385
PLPG/20ASGHP	24.585	1802.112	1.121	42.59	2210.59	70.267	19.380
PLPG/30ASGHP	24.424	2057.734	2.066	29.24	2251.00	71.633	14.341
PLPG/40ASGHP	16.857	2223.953	2.104	27.04	2352.00	57.300	13.566

PLPG: PLA plasticized with Polethylene glycol (PEG); GHP: Guineacorn husks particulates; U: Untreated; A: Alkali treated; S: Silane treated; AS: Alkali and Silane treated; EB: Elongation at break.

Table B 4: Mechanical properties of PP and PP/GHP composites

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Hardness (SHORE D)	Impact strength (J/m)
PP	25.880	733.441	54.718	21.19	864.73	68.40	96.899
PP/10UGHP	22.878	915.578	11.398	22.77	981.21	68.60	23.084
PP/20UGHP	21.140	1054.520	7.309	25.03	1135.49	68.80	29.070
PP/30UGHP	18.663	1138.389	4.903	28.47	1531.25	73.60	15.504
PP/40UGHP	15.225	1249.034	3.033	34.90	1594.08	73.00	10.132
PP/10AGHP	23.214	909.754	11.800	23.66	1004.07	71.40	25.186
PP/20AGHP	20.605	1050.808	6.885	27.27	1616.28	72.20	31.008
PP/30AGHP	18.169	1102.970	5.849	33.99	1944.09	73.00	21.318
PP/40AGHP	15.684	1226.328	3.247	36.94	2509.72	72.60	15.194
PP/10SGHP	23.454	947.199	9.902	35.27	1955.34	68.80	36.822
PP/20SGHP	21.223	1055.967	6.269	36.40	2245.82	69.80	40.698
PP/30SGHP	19.630	1186.578	5.576	37.57	2362.28	70.60	27.242
PP/40SGHP	17.131	1279.393	3.078	36.68	2934.93	70.20	19.442
PP/10ASGHP	23.373	950.643	8.882	34.55	1878.96	69.80	34.884
PP/20ASGHP	20.590	1060.200	5.602	36.44	2236.33	71.20	36.822
PP/30ASGHP	19.461	1192.015	6.300	37.80	2728.61	72.60	25.236
PP/40ASGHP	16.626	1282.365	3.910	36.72	2926.31	72.00	17.357

PP: Polypropylene; GHP: Guineacorn husks particulates; U: Untreated; A: Alkali treated; S: Silane treated; AS: Alkali and Silane treated; EB: Elongation at break.

Appendix C: Mechanical properties after water absorption test

Table C 1: Mechanical properties of PLAP and PLAP/GHP composites after water absorption

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Impact strength (J/m)
PLAP	52.202	2296.618	3.847	90.29	3708.60	25.194
PLAP/10UGHP	35.951	2285.791	2.490	57.27	3154.99	31.008
PLAP/20UGHP	31.103	2218.693	2.238	53.51	2971.78	11.628
PLAP/30UGHP	26.868	1840.763	1.964	44.88	2627.59	10.186
PLAP/40UGHP	20.405	1526.154	1.724	30.67	2343.21	7.752
PLAP/10AGHP	34.623	2116.304	2.277	59.33	3275.54	27.132
PLAP/20AGHP	30.345	2117.851	1.828	54.61	2737.10	19.380
PLAP/30AGHP	23.937	1762.904	1.728	41.48	2623.95	13.178
PLAP/40AGHP	16.243	1327.229	1.545	-	-	11.628
PLAP/10SGHP	37.832	2094.421	2.207	65.71	3216.19	25.581
PLAP/20SGHP	31.189	2007.537	2.257	56.03	3010.13	23.256
PLAP/30SGHP	23.623	1712.857	1.917	44.29	2692.02	15.504
PLAP/40SGHP	18.882	1539.810	1.658	39.82	2742.71	13.178
PLAP/10ASGHP	39.981	2089.335	2.514	59.53	3485.06	38.760
PLAP/20ASGHP	30.085	1957.790	1.957	54.12	2830.24	15.504
PLAP/30ASGHP	25.982	2052.143	1.791	32.16	2757.85	13.953
PLAP/40ASGHP	14.997	1280.868	1.550	31.32	2539.31	6.589

Table C 2: Mechanical properties of PLABM and PLABM/GHP composites after water absorption

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Impact strength (J/m)
PLABM	40.220	2171.482	2.736	54.49	3211.77	36.822
PLABM/10UGHP	22.810	2526.242	1.597	43.13	3444.28	17.442
PLABM/20UGHP	21.063	2512.853	1.422	36.12	3762.06	16.504
PLABM/30UGHP	17.943	2382.918	1.284	33.16	3581.51	13.566
PLABM/40UGHP	15.405	2363.096	1.258	27.48	3232.84	12.070
PLABM/10AGHP	27.798	2355.657	1.736	52.42	3507.13	25.194
PLABM/20AGHP	21.001	2564.712	1.496	42.08	3516.61	19.380
PLABM/30AGHP	10.343	1911.408	0.920	34.41	3046.53	15.823
PLABM/40AGHP	12.277	2382.391	0.796	31.97	2683.11	10.853
PLABM/10SGHP	23.622	2516.563	1.252	37.18	3720.88	34.884
PLABM/20SGHP	19.206	2446.261	1.100	35.30	3791.26	20.821
PLABM/30SGHP	13.393	2542.332	0.683	27.93	3583.28	19.823
PLABM/40SGHP	13.459	2340.894	0.834	24.44	3436.59	15.504
PLABM/10ASGHP	28.626	2409.809	2.039	51.40	3571.42	20.823
PLABM/20ASGHP	24.556	2386.668	1.800	49.67	3487.95	18.832
PLABM/30ASGHP	15.324	2399.570	1.154	34.04	3354.35	16.279
PLABM/40ASGHP	16.898	2247.550	1.097	30.56	3150.84	8.527

Table C 3: Mechanical properties of PLPG and PLPG/GHP composites after water absorption

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Impact strength (J/m)
PLPG	9.557	1658.564	0.673	11.20	849.59	7.752
PLPG/10UGHP	12.008	1578.463	1.085	10.52	4350.65	11.628
PLPG/20UGHP	6.961	1370.21	0.627	19.04	6140.02	17.132
PLPG/30UGHP	6.220	1164.879	0.654	11.33	8622.92	6.977
PLPG/40UGHP	1.444	568.330	0.574	4.85	35016.77	3.876
PLPG/10AGHP	7.200	1337.562	0.634	17.01	2184.23	8.527
PLPG/20AGHP	3.091	851.195	0.691	3.49	52226.00	10.078
PLPG/30AGHP	2.573	712.708	0.689	8.17	6018.09	9.624
PLPG/40AGHP	-	-	-	-	-	2.457
PLPG/10SGHP	11.741	1616.618	0.901	20.21	2052.39	15.597
PLPG/20SGHP	5.857	1033.315	0.724	9.02	1001.57	21.132
PLPG/30SGHP	4.895	980.230	0.665	9.99	31996.22	13.504
PLPG/40SGHP	1.750	742.286	0.499	6.89	18595.50	11.628
PLPG/10ASGHP	4.555	1145.087	0.747	20.82	2219.72	10.544
PLPG/20ASGHP	3.356	807.276	0.654	8.27	6390.68	14.729
PLPG/30ASGHP	1.407	669.017	0.856	-	-	5.426
PLPG/40ASGHP	-	-	-	-	-	4.651

Table C 4: Mechanical properties of PP and PP/GHP composites after water absorption

Specimen	Tensile strength (MPa)	Tensile Modulus (MPa)	EB (%)	Flexural strength (MPa)	Flexural Modulus (MPa)	Impact strength (J/m)
PP	27.315	845.557	14.124	27.38	1311.42	86.047
PP/10UGHP	24.948	953.766	11.489	27.82	1363.75	46.512
PP/20UGHP	21.920	1107.051	6.642	28.53	1391.57	23.256
PP/30UGHP	18.394	1087.472	5.346	28.27	1474.95	22.481
PP/40UGHP	15.144	859.878	4.554	24.02	1366.19	19.380
PP/10AGHP	24.975	1041.228	9.310	28.24	1484.84	41.085
PP/20AGHP	22.261	1130.906	5.992	28.38	1628.23	30.388
PP/30AGHP	19.134	1146.736	5.104	27.64	1711.62	27.132
PP/40AGHP	15.702	910.410	4.162	23.45	1334.32	7.752
PP/10SGHP	25.495	1053.242	7.311	29.59	1282.55	31.008
PP/20SGHP	22.342	1110.779	5.726	30.18	1604.27	26.243
PP/30SGHP	20.065	1131.381	3.895	28.67	1644.52	34.884
PP/40SGHP	16.656	1045.635	3.656	24.50	1541.62	25.581
PP/10ASGHP	24.637	1013.258	8.421	28.97	1375.64	41.085
PP/20ASGHP	21.536	1099.059	7.054	29.78	1567.80	36.434
PP/30ASGHP	19.156	1092.010	3.946	27.79	1530.95	23.256
PP/40ASGHP	15.078	887.877	3.851	27.30	1428.56	21.705

Appendix D: Composites degradation by soil burial test after 3months

Table D 1: Weight losses of all the composite formulations

	Weight loss (%)			
GHP	PLAP	PLABM	PLPG	PP
0	0.3563	0.1996	0.4617	0.0814
10% UNTRD	0.4547	3.8082	4.9690	0.3643
20% UNTRD	0.7321	5.3484	7.0893	0.6693
30% UNTRD	1.1670	8.1640	7.0627	1.4966
40% UNTRD	1.2760	13.0857	13.5838	2.1709
10% ALK	0.8249	4.6218	2.2683	0.4261
20% ALK	1.0093	9.0718	5.4748	0.6954
30% ALK	1.1822	17.9401	16.0490	1.2970
40% ALK	2.0978	20.4094	17.9959	2.6012
10% SIL	0.1038	3.0100	3.6061	0.3375
20% SIL	0.6690	6.6237	4.7884	0.7073
30% SIL	1.0885	9.4513	7.3872	1.0251
40% SIL	1.3968	12.6525	16.8064	1.9035
10% ALKSIL	0.5887	2.1658	4.2095	0.3285
20% ALKSIL	1.0463	6.1268	6.3616	0.3921
30% ALKSIL	1.2779	14.2265	9.5391	0.6765
40% ALKSIL	5.0460	24.1577	14.8339	1.6493

UNTRD: Untreated; ALK: Alkali treated; SIL: Silane treated; ALKSIL: Alkali and Silane treated.

Appendix E: Water absorption test after 30 days

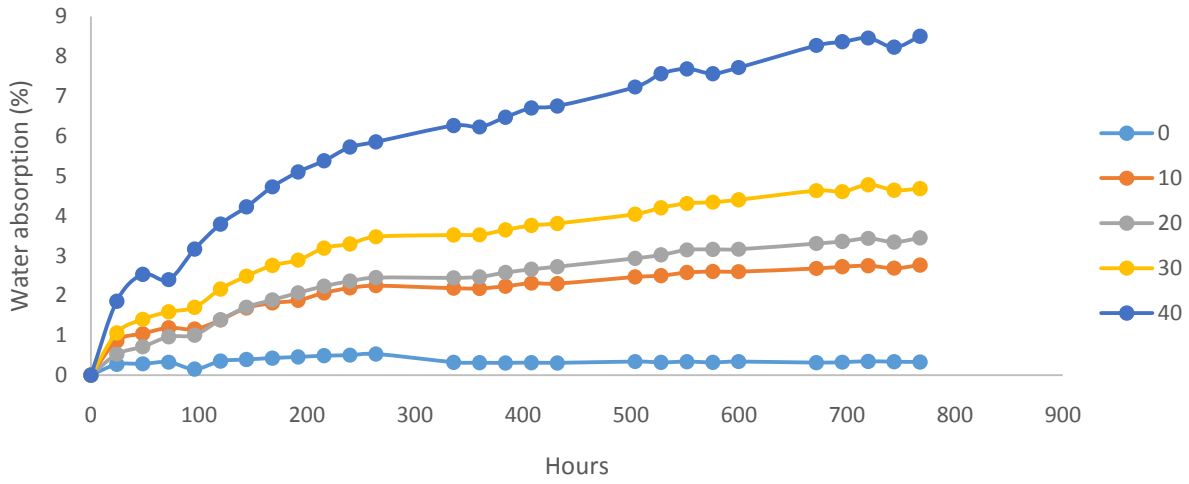


Figure E 1: Water absorption of PLAP/GHP Composites for UNTRD samples

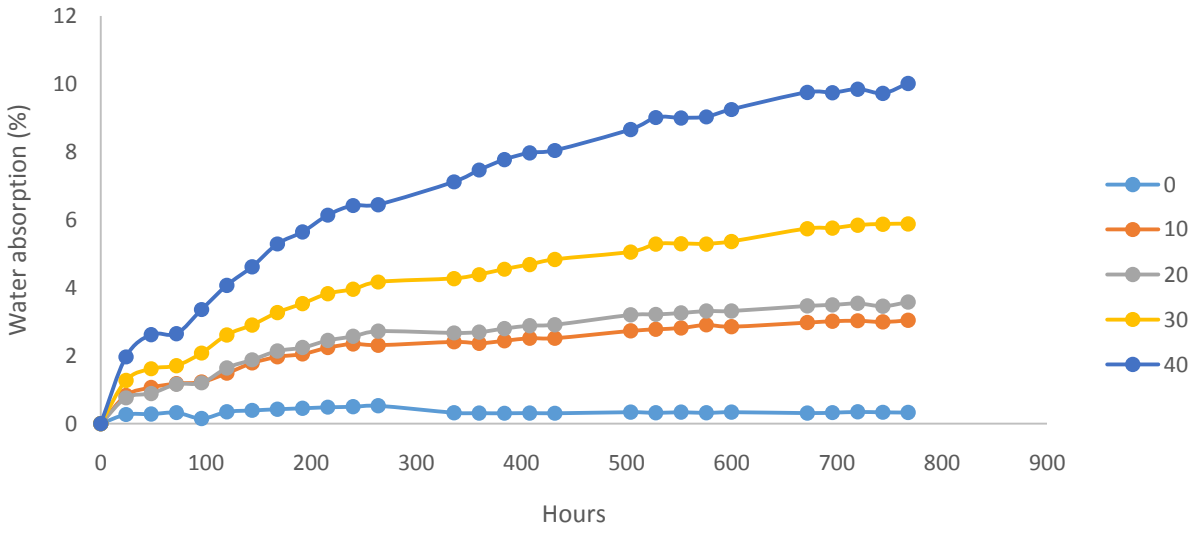


Figure E 2:Water absorption of PLAP/GHP Composites for ALK treated samples

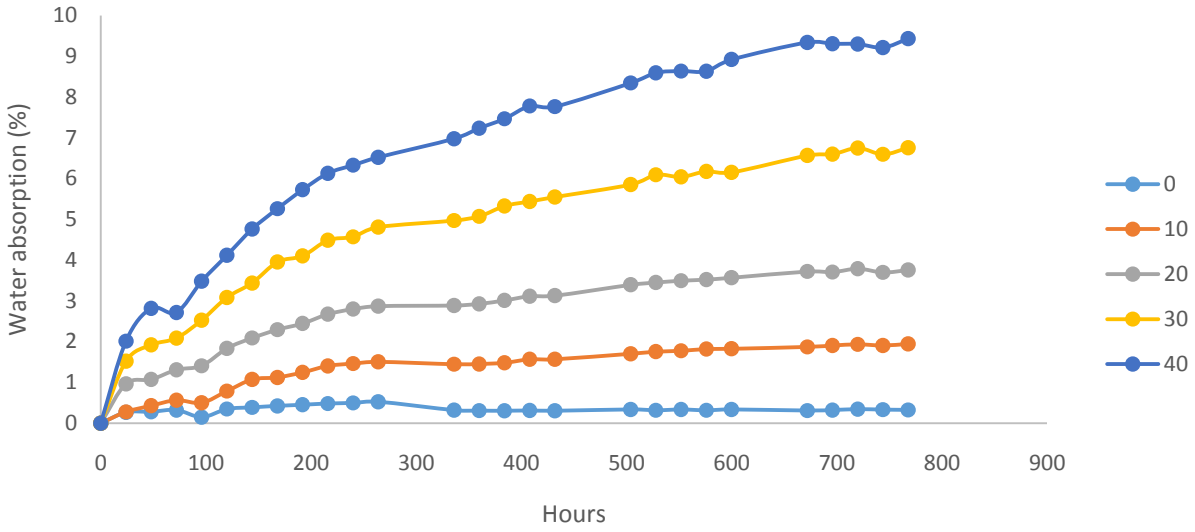


Figure E 3: Water absorption of PLAP/GHP Composites for SIL treated samples

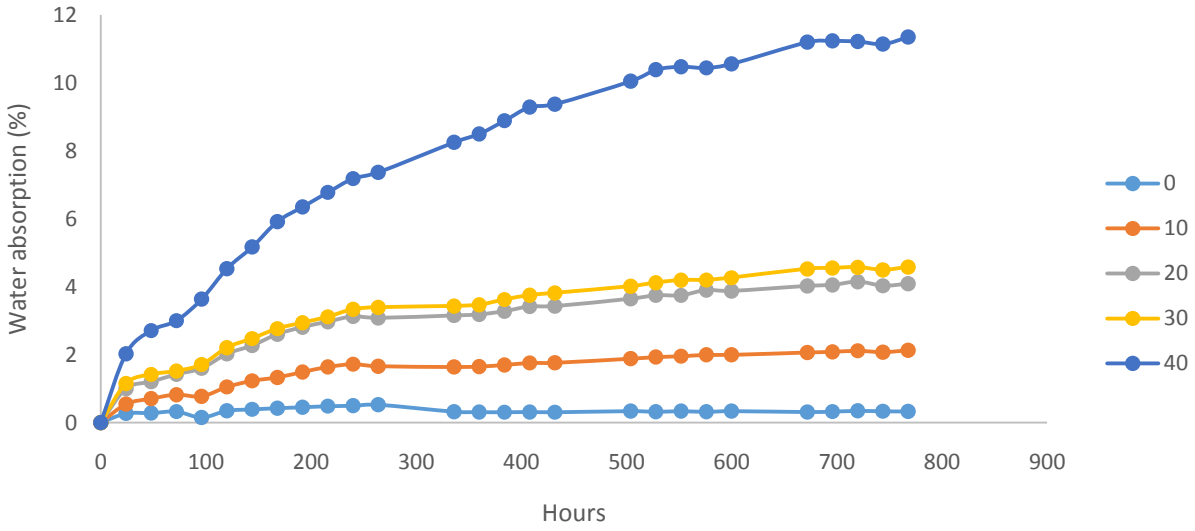


Figure E 4: Water absorption of PLAP/GHP Composites for ALKSIL treated samples

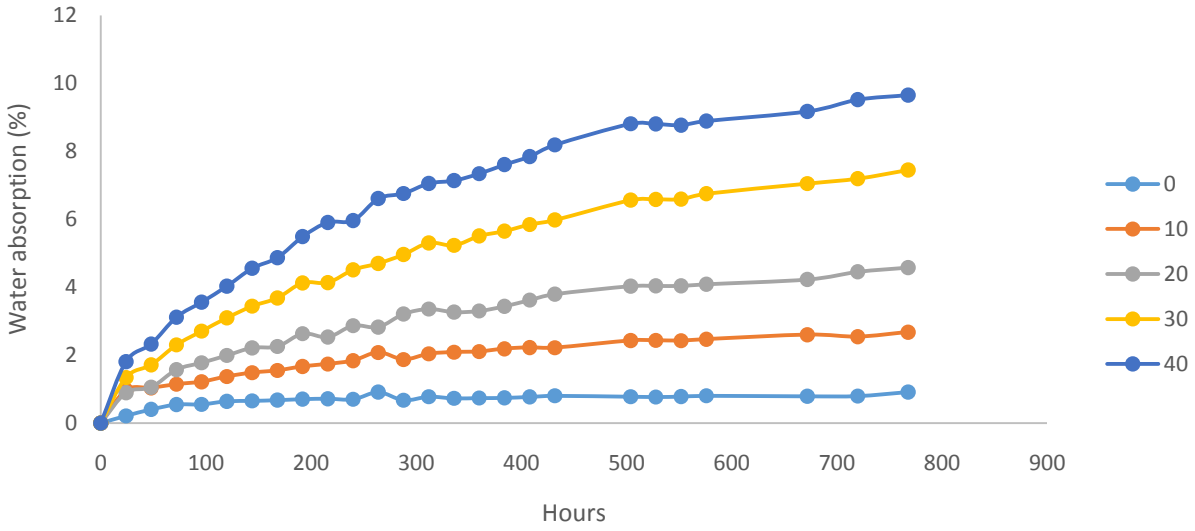


Figure E 5: Water Absorption of PLABM/GHP Composites for UNTRD samples

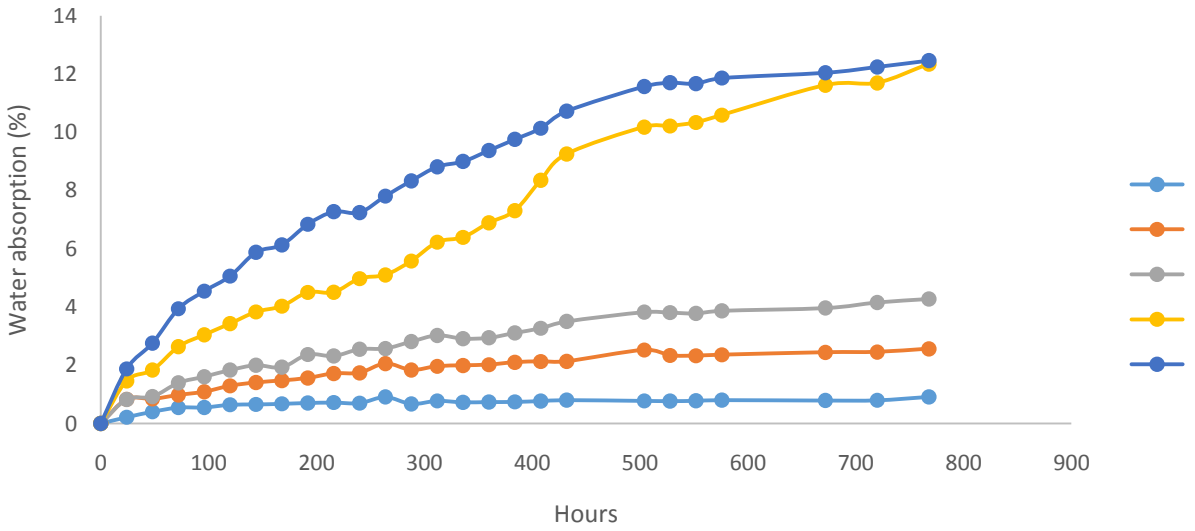


Figure E 6: Water Absorption of PLABM/GHP Composites for ALK samples

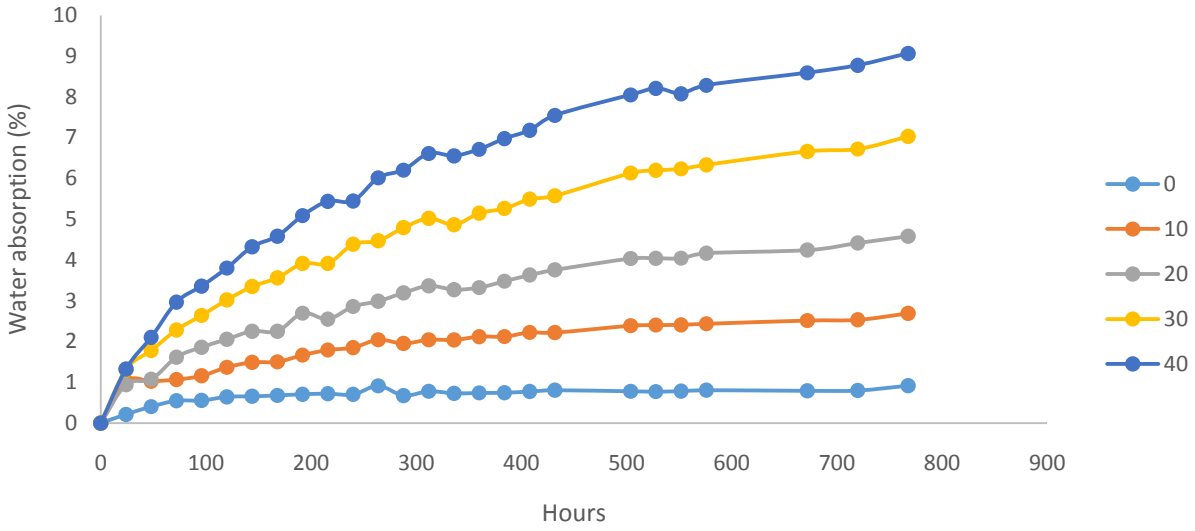


Figure E 7: Water Absorption of PLABM/GHP Composites for SIL samples

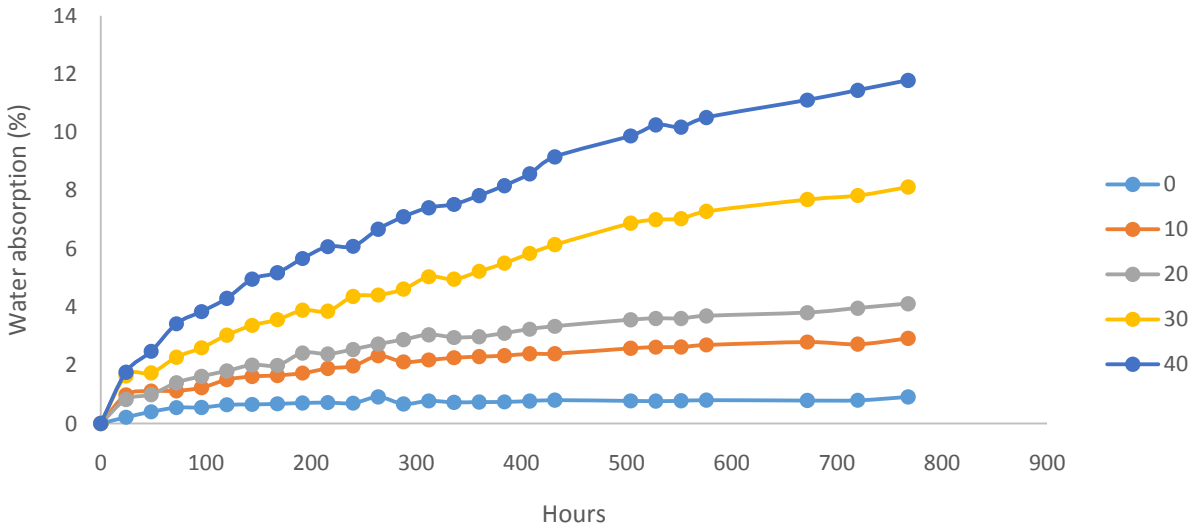


Figure E 8: Water Absorption of PLABM/GHP Composites for ALKSIL samples

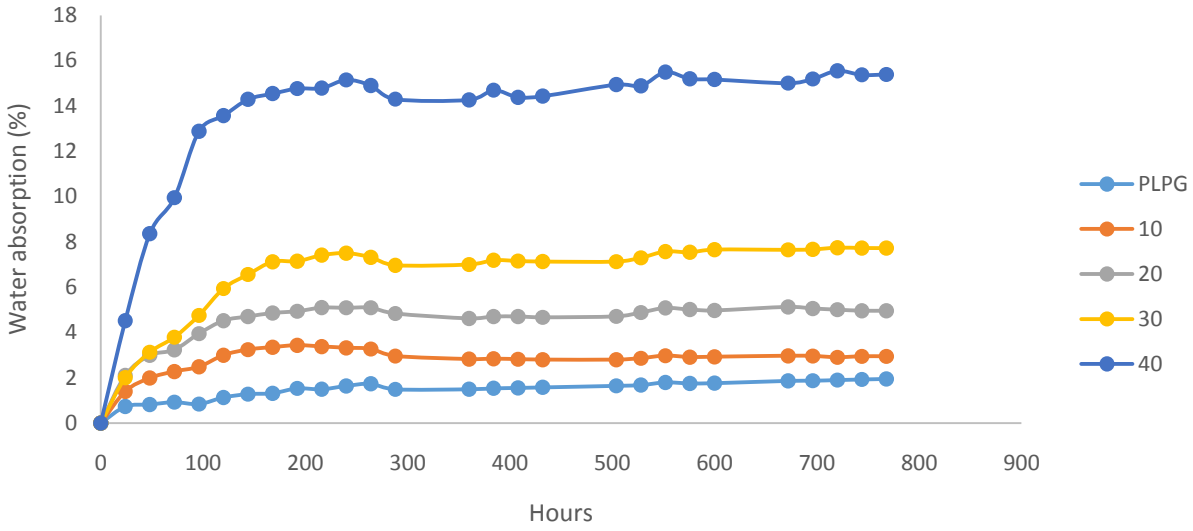


Figure E 9: Water absorption of PLPG/GHP Composites for UNTRD samples

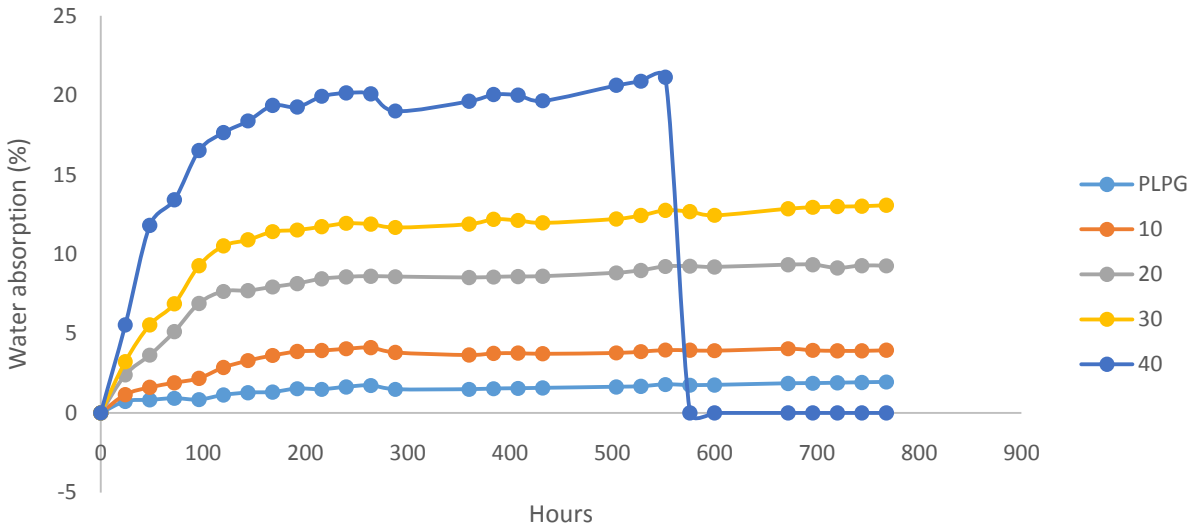


Figure E 10: Water absorption of PLPG/GHP Composites for ALK samples

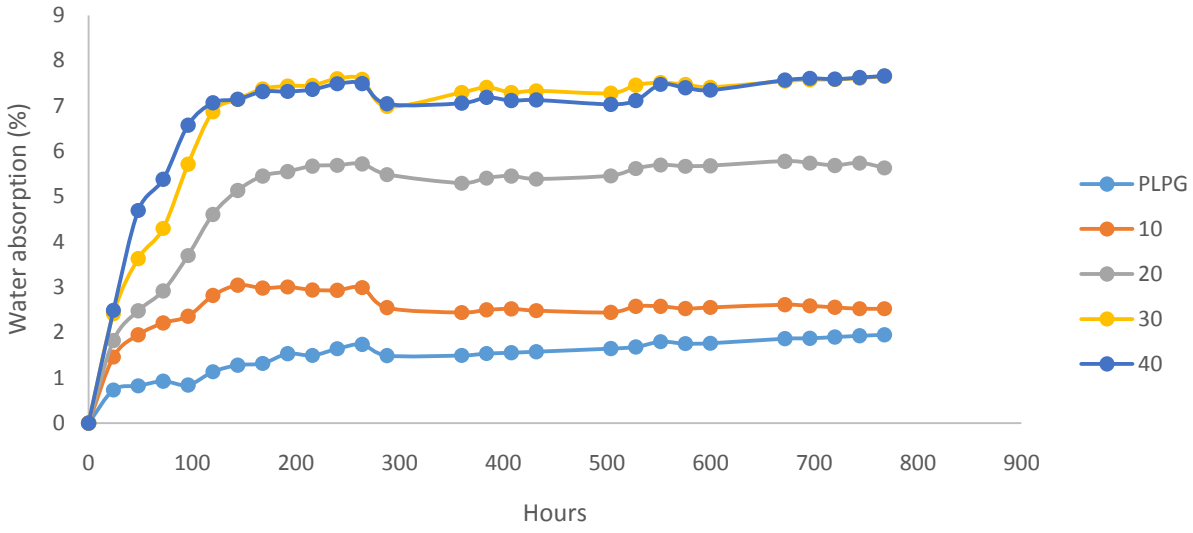


Figure E 11: Water absorption of PLPG/GHP Composites for SIL samples

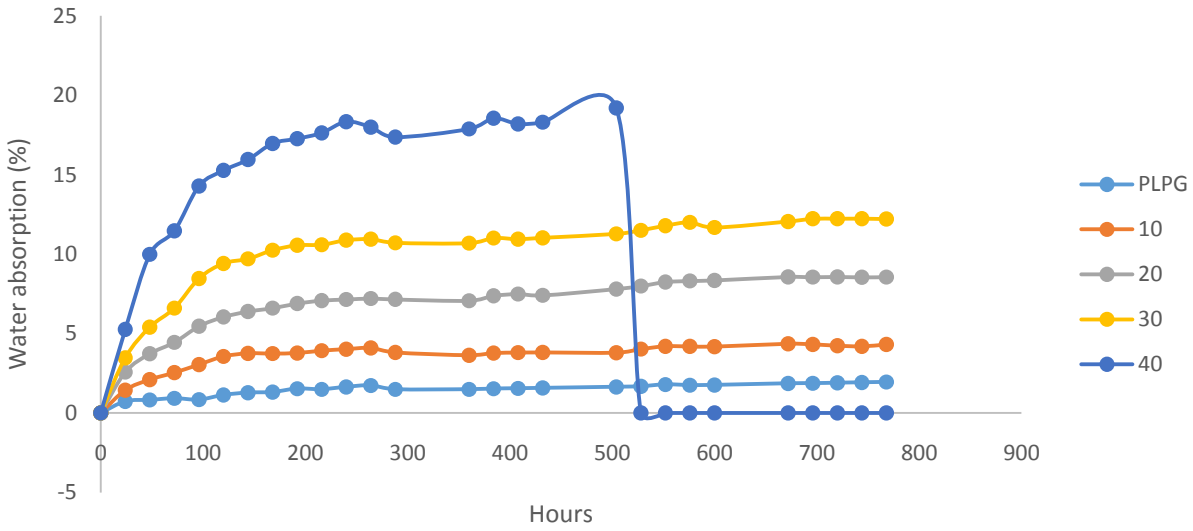


Figure E 12: Water absorption of PLPG/GHP Composites for ALKSIL samples

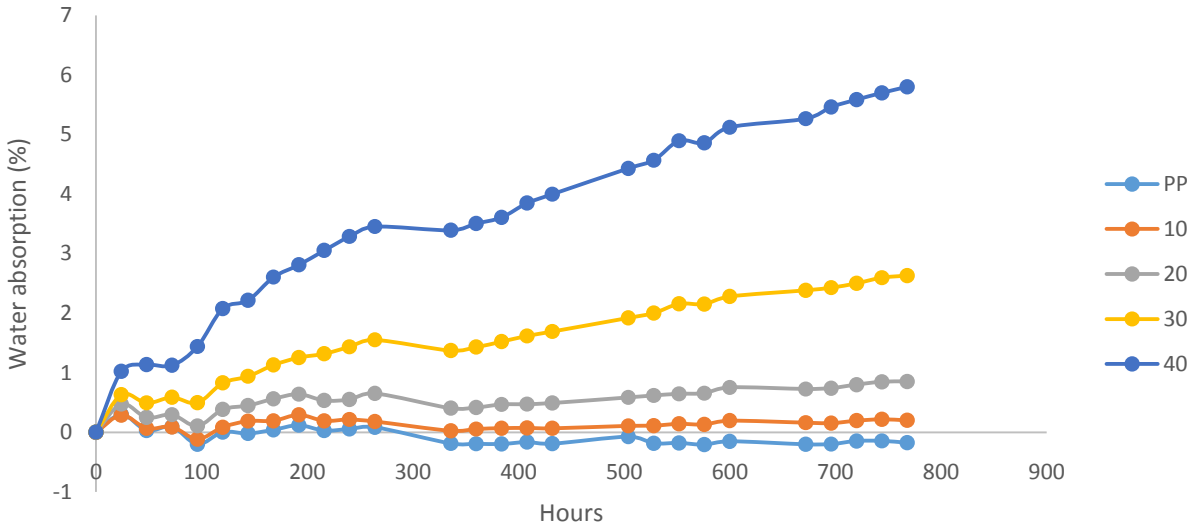


Figure E 13: Water absorption of PP/GHP Composites for UNTRD samples

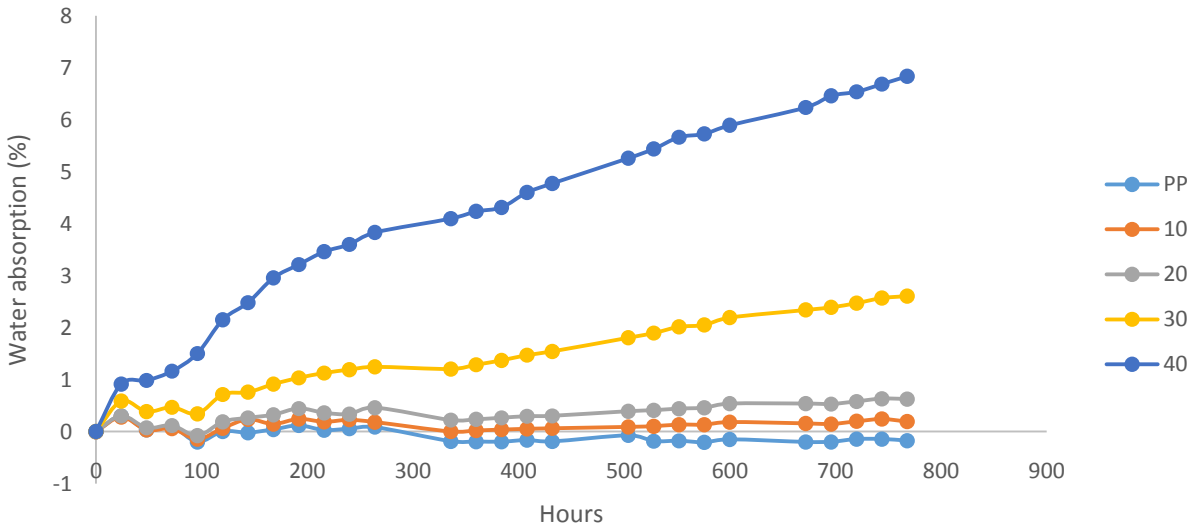


Figure E 14: Water absorption of PP/GHP Composites for ALK samples

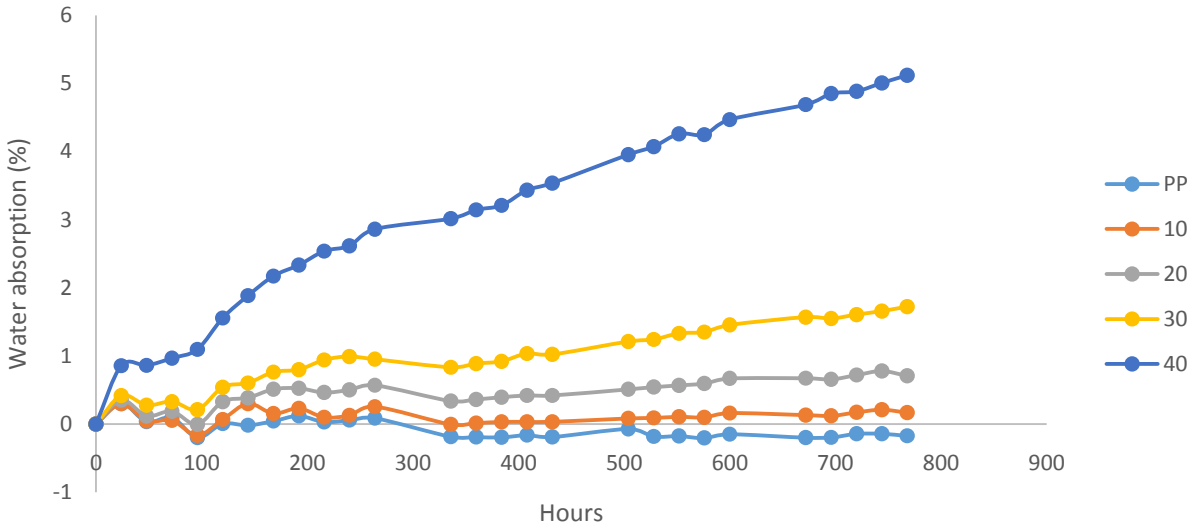


Figure E 15: Water absorption of PP/GHP Composites for SIL samples

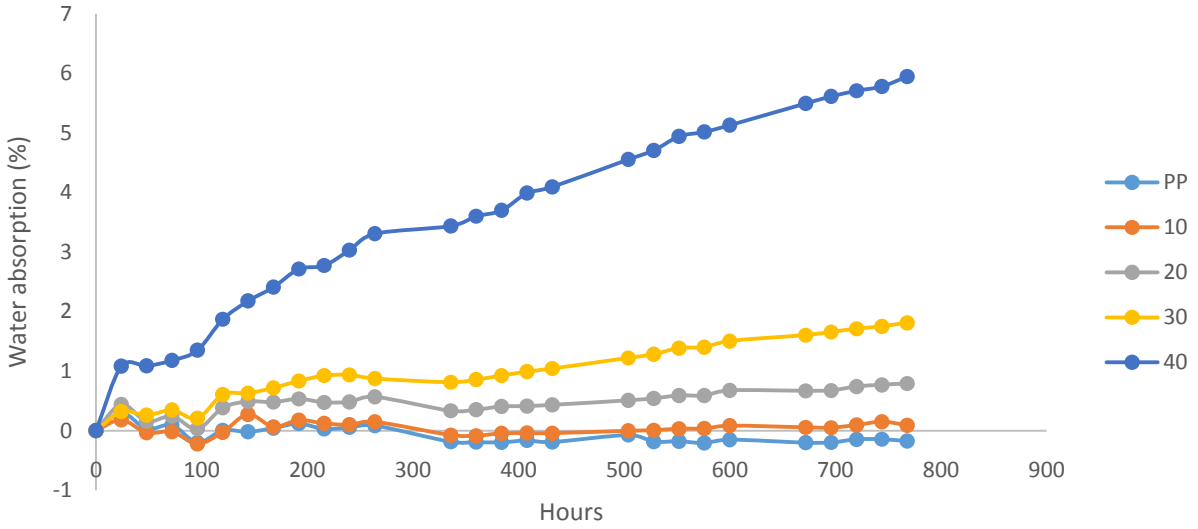


Figure E 16: Water absorption of PP/GHP Composites for ALSKIL samples