

**A STUDY OF THE DEVELOPMENT, CHARACTERISATION AND DEGRADABILITY
OF POLYESTER/NANO-LOCUST BEAN *PODS* ASH COMPOSITE**

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BY

**Babatunde Oyebode ARAOYE, B. ENG. (FUTA) 2010
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JUNE, 2015

DECLARATION

I declare that the work in this thesis entitled “A STUDY OF THE DEVELOPMENT, CHARACTERISATION AND DEGRADABILITY OF POLYESTER/NANO-LOCUST BEAN *PODS* ASH COMPOSITE” has been carried out by me in the Department of Metallurgical and Materials Engineering, under the supervision of Dr. Auwal Kasim and Dr. M. Abdulwahab. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis has been presented for another degree or Diploma at this or any other Institution.

Araoye, Babatunde Oyebode

Signature

Date

CERTIFICATION

This thesis entitled A STUDY OF THE DEVELOPMENT, CHARACTERISATION AND DEGRADABILITY OF POLYESTER/NANO-LOCUST BEAN *PODS* ASH COMPOSITE by Oyebo Babatunde ARAOYE meets the regulations governing the award of the degree of Master of Science of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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TABLE OF CONTENT

	Page
Title Page.....	i
Cover Page.....	ii
Declaration.....	iii
Certification.....	iv
Acknowledgement.....	v
Dedication.....	vi
Table of Content.....	vii
List of Figures.....	x
List of Tables.....	xi
List of Plates.....	xiii
Abbreviations, Definitions, Glossary And Symbols.....	xv
Abstract.....	xvi
CHAPTER ONE.....	1
1.0 Introduction.....	1
1.1 Background Information/Justification.....	2
1.2 Aim and Objectives.....	3
1.3 Scope of Study.....	3
1.4 Contribution to Knowledge.....	3
CHAPTER TWO.....	4
2.0 Literature Review.....	4
2.1 Composite Materials.....	4
2.1.1 Advantages and disadvantages of composites.....	5
2.1.2 Advantages of thermoset resin composites.....	6
2.1.3 Disadvantages of thermoset resin composites.....	7
2.1.4 Advantages of thermoplastic resin composites.....	7
2.1.5 Disadvantages of thermoplastic resin composites.....	8
2.1.6 Classification of composites.....	8
2.1.7 Particulate reinforced polymers.....	12
2.1.8 Fiber reinforced polymers.....	13

2.4	Engineering Composites Materials	14
2.5	Thermosetting	17
2.6	Thermoplastics	17
2.7	Polyester	18
2.8	Method of Polymer Composite Fabrication	19
2.9	Locust Bean	20
2.9.1	Locust Bean Pod	20
2.10	Nanotechnology	21
2.10.1	Nanoparticles	21
2.10.2	Nanomaterials	22
2.10.3	Nanocomposites	22
2.11	Nanoparticle Production Processes	23
CHAPTER THREE		31
MATERIALS AND METHODS		31
3.0	Introduction	31
3.1	Materials	31
3.2	Equipment	31
3.3	Methodology	31
3.3.1	Preparation of locust bean pod ash (LBPA) Nanosized Particles by Sol-gel Method	31
3.3.2	Composite preparation	32
3.3.3	Degradability test	32
3.3.5	Characterisation of test samples.....	34
3.3.6	Water absorption test	34
CHAPTER FOUR		35
RESULTS		35
4.0	Introduction	35
4.1	Mechanical Tests Results	35
4.2	Impact Strength	36
4.3	Tensile Properties	38
4.4	Flexural Properties	42

4.5	Hardness	46
4.6	Water Absorption	48
4.7	Weight Loss	49
4.8	Nanoparticle Determination	52
4.9	Correlation between Properties and Microstructure of the Produced Nano-Composite	53
CHAPTER FIVE		56
5.0	SUMMARY, CONCLUSIONS AND RECOMMENDATIONS	56
5.1	Summary	56
5.2	Conclusions	57
5.3	Recommendations	58
REFERENCES		59
APPENDIX A		67

List of Figures

	Page
Figure 4.1: Impact strength profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	36
Figure 4.2: Impact strength profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.....	36
Figure 4.3: Tensile strength profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	38
Figure 4.4: Tensile strength profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.....	39
Figure 4.5: Tensile modulus profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	39
Figure 4.6: Tensile modulus profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.....	40
Figure 4.7: Flexural strength profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	42
Figure 4.8: Flexural strength profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.....	43
Figure 4.9: Flexural modulus profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	43
Figure 4.10: Flexural modulus profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.....	44
Figure 4.11: Hardness profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	46
Figure 4.12: Hardness profile of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.....	47
Figure 4.13: Percent Water absorption profile of polyester/Nano-LBPA composite after 24hour.....	48
Figure 4.14: Weight loss profile of impact test samples after degradation.....	49
Figure 4.15: Weight loss profile of tensile test samples after degradation.....	49
Figure 4.16: Weight loss profile of flexural test samples after degradation.....	50
Figure 4.17: Weight loss profile of hardness test samples after degradation.....	50

List of Tables

	Page
Table 2.1:Chemical composition of LBPA.....	21
Table A.1: Impact strength (J/m) of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	67
Table A.2: Impact strength (J/m) of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.....	67
Table A.3: Impact strength values of non-degraded polyester/Nano-LBPA composite.....	67
Table A.4: Tensile strength values of polyester/Nano-LBPA composite subjected to weathered condition for 30 days.....	68
Table A.5: Tensile strength values of polyester/Nano-LBPA composite subjected to weathered condition for 60 days.....	68
Table A.6: Tensile strength values of polyester/Nano-LBPA composite subjected to weathered condition for 90days.....	69
Table A.7: Tensile strength values of polyester/Nano-LBPA composite subjected to soil burial for 30 days.....	69
Table A.8: Tensile strength values of polyester/Nano-LBPA composite subjected to soil burial for 60 days.....	70
Table A.9: Tensile strength values of polyester/Nano-LBPA composite subjected to soil burial for 90 days.....	70
Table A.10: Tensile modulus values of polyester/Nano-LBPA composite subjected to weathered for 30, 60, 90 days.....	71
Table A.11: Tensile modulus values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60, 90 days.....	71
Table A.12: Tensile strength values of non-degraded polyester/Nano-LBPA composite.....	72
Table A.13: Tensile modulus values of non-degraded polyester/Nano-LBPA composite.....	72
Table A.14: Flexural strength values of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	73
Table A.15: Flexural strength values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.....	73
Table A.16: Flexural modulus values of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	74

Table A.17: Flexural modulus values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.....	74
Table A.18: Flexural strength values of non-degraded polyester/Nano-LBPA composite.....	75
Table A.19: Flexural modulus values of non-degraded polyester/Nano-LBPA composite.....	75
Table A.20: Hardness values of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.....	75
Table A.21: Hardness values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.....	76
Table A.22: Hardness values of non-degraded polyester/Nano-LBPA composite.....	76
Table A.23: Water absorption Values of polyester/Nano-LBPA Composite after 24hours.....	76
Table A.24: Percentage weight loss values of impact test samples after degradation.....	77
Table A.25: Percentage weight loss values of tensile test samples after degradation.....	77
Table A.26: Percentage weight loss values of flexural test samples after degradation.....	78
Table A.27: Percentage weight loss values of hardness test samples after degradation.....	78

List of Plates

	Page
Plate I: SEM micrographs of the Nanoparticles developed from LBPA particle. A, B, C and D shows the particle size at different agglomerate formed.....	52
Plate II: SEM micrographs of the polyester/Nano-LBPA composite exposed to natural weather for 90days (at 3%LBPA) showing a rough surface (a) 500x (b) 1000x.....	53
Plate III: SEM micrographs of the polyester/Nano-LBPA composite exposed to natural weather for 90days (at 9%LBPA), showing a rougher surface compared to Plate II, (C) 1000x (D) 5000x.....	54
Plate IV: SEM micrographs of the polyester/Nano-LBPA composite after water absorption test for 24hours, showing agglomerate of particles within the matrix phases (E) 1000x (F) 5000x.....	54

Appendix

APPENDIX A: Tables.....	67
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Abbreviations, Definitions, Glossary and Symbols

Abbreviations

LBPA	Locust Bean <i>Pod</i> Ash
SEM	Scanning Electron Microscope
Wt	Weight

Symbols

%	Percent
°C	Degree Celsius
HRF	Rockwell Hardness, Scale F

Glossary

Sol-gel – a method used in the synthesis of Nanoparticles

Refluxing –a step in sol-gel used in achieving gelation.

ABSTRACT

This study produced locust bean pods ash, synthesized from it nanoparticles which were subsequently used for the production of polyester matrix composite. It characterized the synthesized particulates and the composite produced. It also evaluated the effects of degradation of the composite subjected to different agents on mechanical properties such as hardness, tensile, flexural and impact strength. This was with a view to determining the degradability of the composite. Scanning Electron Microscopy (SEM) was used to characterize the synthesized nanoparticles and some test samples (composite). The minimum average Particle size of the synthesized LBPA Nanoparticles was 52.4nm, which falls within the range of 1 – 100nm, the recommended particle size required for a material to be classified as Nanomaterial. The mechanical properties of the control samples increased as the reinforcement was increased from 0%LBPA – 12%LBPA; the impact, tensile and flexural strengths increased from 0.03 – 0.37J/m, 4.30 – 6.84MPa and 10.75 – 14.17MPa, respectively. The mechanical properties of buried and weathered samples decreased with increase in reinforcement (from 0%LBPA – 12%LBPA) and exposure time (90days). The impact, tensile, flexural and hardness values of the buried samples decreased from 0.04 – 0.023J/m, 32 – 10MPa, 47.27 – 16.47MPa and 8.7 – 6.5HRF indicating 43, 69, 65 and 25% decrease, respectively. Similarly, decreases were observed in the impact, tensile, flexural and hardness values of the weathered samples from 0.05 – 0.023J/m, 28 – 12MPa, 62.13 – 8.73MPa and 11.6 – 6.6HRF indicating a decrease of 54, 57, 86 and 43% decrease, respectively. It was noted that the composite became more susceptible to degradation with increase in reinforcement. The swelling and shrinking of natural filler when exposed to natural weather and activities of microorganisms in the soil might have been responsible for the decrease in their properties. The rate of moisture absorption of the composite samples increased with increase in reinforcement; the highest value of 1.42% was obtained at 12%LBPA. The percentage by weight losses for the impact, tensile, flexural and hardness test samples after soil burial and weathering were respectively, 0.55, 1.01, 0.09, 0.77 and 0.35, 0.93, 0.14, 0.42% after 90days of exposure. SEM examinations of the weathered and buried samples showed roughened surfaces with some voids and pits observed on the soil buried samples.

CHAPTER ONE

INTRODUCTION

1.0

The continuous growth in modern technology calls for materials with unusual combination of properties that cannot be met by most of the conventional metals, alloys, ceramics and polymeric materials. This is especially true for materials needed for the aerospace, underwater and transportation applications. Most industries are increasingly searching for materials that are light, strong, stiff, abrasion and impact resistant and are not easily corroded as may be required in the aerospace industry (Mishra *et al.*, 2002).

Over the last three decades, composites materials, plastic and ceramics have been the dominant emerging materials. The number of applications of composites particularly polymeric composites reinforced with synthetic fibers such as glass, carbon and aramid has grown steadily due to their unique properties of high stiffness and strength-to-weight ratio (Mishra *et al.*, 2002).

Furthermore, polymers have substituted many conventional materials. They are used in many applications due to the advantages they have over conventional materials; ease of processing, high performance, low cost and versatility. However, for some specific uses, some mechanical properties such as strength and toughness of polymer materials are inadequate. Various approaches have been developed to improve such properties. In most of these applications, the properties of polymers are modified using fillers and fibers to suit the high strength/high modulus requirements. In polymer matrix composites, fibrous materials e.g. synthetic or natural fibers, serve either as filler or reinforcement by giving strength and stiffness to the base material; while the polymer matrix serves as the adhesive to hold the fibers in place (Taj, 2011).

The shift of composite application from aircraft to other commercial uses has become prominent in recent years, increasingly enabled by the introduction of newer polymer resin matrix materials

and high performance reinforcement fibers of glass, carbon and aramid. The industrial uses of these advanced materials have witnessed a steady expansion in usage and volume (Tudu, 2009). High performance synthetic fiber reinforced polymer composites have been used in such diverse applications as composite armoring designed to resist explosive impacts, fuel cylinders for natural gas vehicles, windmill blades, industrial drive shafts and paper making rollers (Passipoularidis and Philippidis, 2009; Tudu, 2009).

1.1 Background Information/Justification

The widespread use of synthetic fiber reinforced polymer composites has a tendency to decline because of high initial costs and, more importantly, their adverse environmental effect (Mohanty and Drzal, 2001; Mishra *et al.*, 2002). Today, the growing environmental awareness throughout the world has triggered a paradigm shift from synthetic fibers and their composites towards composites made from natural reinforcing constituents; natural fiber and natural particulate fillers which are more environmentally friendly (Wretfors and Svennerstedt, 2006). It is obvious that large amounts of agricultural produce wastes are generated annually across the country and the potential uses of these byproducts have not been effectively utilized. In recent time, the trend in developing a composite material using this byproduct as reinforcement has been a worthy area of interest because of their easy access, low cost and biodegradability. Njoku *et al.* (2011); Hassan *et al.*, (2012) and other scholarly researches have reported on the strengthening effect of carbonized particulate and improvement of interfacial bonding between the reinforcement and the matrix. Researchers around the world have stepped further in using microsize to nanosize particulate due to the better mechanical properties they proffer. Therefore, these byproducts can be used to benefit a country's economy and human race at large. Hence, the potential uses of nanosized Locust Bean *Pods* Ash (LBPA) particle as reinforcement has not been explored. Therefore, there is need for research consideration that will investigate into the possibility of

using Nano-sized LBPA in polymer matrix particulate composite for industrial applications. The present research work is focused on the utilization of LBPA nanosized particulate filler to produce polymer matrix composite.

1.2 Aim and Objectives

The aim of this research is to develop and characterize polyester/nanosized locust bean *pod*sash composite. The Specific objectives of the research are:

- a. Synthesis of locust bean pod ash (LBPA) nanoparticles and the production of polyester matrix composite;
- b. Microstructural and property characteristics study of LBPA nanoparticles and polyester matrix composite produced in (a); and
- c. Determination of the effects of soil and natural weathering on the degradability of the polyester composite produced in (a).

1.3 Scope of Study

The research work involves synthesis of LBPA particulate reinforced polyester composite using nanosized particles of locust bean pods ash. Assessment of the degradation of the composite after soil burial and exposure to natural weathering for 90days, mechanical properties and morphological evaluation of the composite were also carried out.

1.4 Contribution to Knowledge

To the best of my knowledge, no previous work has been carried out on Nanosized LBPA reinforced polyester composite. In this light, the study has established that the polyester/LBPA composite developed is biodegradable and eco-friendly; this is in accordance with the current global trend towards the use of ecofriendly materials.

CHAPTER TWO

2.0

LITERATURE REVIEW

2.1

Composite Materials

A composite material can be defined as a combination of two or more materials that results in better properties than those of the individual components used alone. In contrast to metallic alloys, each material retains its separate chemical, physical, and mechanical properties. The two constituents are reinforcement and a matrix (Campbell, 2010).

Composite broadly refers to a material system which is composed of a discrete constituent (the reinforcement) distributed in a continuous phase (the matrix), and which derives its distinguishing characteristics from the properties of its constituents, from the geometry and architecture of the constituents, and from the properties of the boundaries (interfaces) between different constituents (Clyne, 2000; Ikechukwu, 1997).

A composite material is made by combining two or more materials – often the ones that have very different properties. The two materials work together to give the composite unique properties. A more restrictive definition is used by industries and materials scientists, a composite is a material that consists of constituents produced via a physical combination of pre-existing ingredient materials to obtain a new material with unique properties compared to the monolithic material properties (Surappa and Rohatgi, 1981).

In its most basic form, a composite material is one which is composed of at least two elements working together to produce material properties that are different from those of a single element. In practice, most composites consist of a bulk material (matrix) and a reinforcement of some various kinds, added primarily to increase the strength and stiffness of the matrix (White and Ansell, 1993). The main advantages of composite materials are their high strength and stiffness, combined with low density, when compared with bulk materials, allowing for a weight reduction of the finished part (Campbell, 2010).

Polymer composite materials are being used in a wide range of structural applications in the aerospace, construction and automotive industries due to their lightweight and high specific stiffness and strength (Anon, 1999).

2.1.1 Advantages and disadvantages of composites

Composite parts have both advantages and disadvantages when compared to the metal parts they are being used to replace.

(a) Advantages of composites

- i. A higher performance for a given weight leads to fuel savings. Excellent strength-to-weight and stiffness-to-weight ratios can be achieved by composite materials. This is usually expressed as strength divided by density and stiffness (modulus) divided by density. These are so-called “specific” strength and “specific” modulus characteristics.
- ii. Laminate patterns and ply buildup in a part can be tailored to give the required mechanical properties in various directions.
- iii. It is easier to achieve smooth aerodynamic profiles for drag reduction. Complex double-curvature parts with a smooth surface finish can be made in one manufacturing operation.
- iv. Part count is reduced.
- v. Production cost is reduced. Composites may be made by a wide range of processes.
- vi. Composites offer excellent resistance to corrosion, chemical attack, and outdoor weathering; however, some chemicals are damaging to composites (e.g., paint stripper), and new types of paint and stripper are being developed to deal with this. Some thermoplastics are not very resistant to some solvents.

(b) Disadvantages of composites

- i. Composites are more brittle than wrought metals and thus are more easily damaged. Cast metals also tend to be brittle.

- ii. Repair introduces new problems, for the following reasons:
 - Materials require refrigerated transport and storage and have limited shelf lives
 - Hot curing is necessary in many cases, requiring special equipment
 - Curing either hot or cold takes time. The job is not finished when the last rivet has been installed.
- iii. If rivets have been used and must be removed, this presents problems of removal without causing further damage.
- iv. Repair at the original cure temperature requires tooling and pressure.
- v. Composites must be thoroughly cleaned of all contamination before repair
- vi. Composites must be dried before repair because all resin matrices and some fibers absorb moisture.

2.1.2 Advantages of thermoset resin composites

Thermoset resin composites have advantages and disadvantages when compared to thermoplastic resin composites. The advantages of thermoset resin composites over thermoplastic resin composites include the following:

- a. Thermosets will cure at lowest temperatures than most thermoplastics will melt. Therefore, thermosets can be manufactured at lower temperatures than thermoplastics.
- b. Two-part systems can be cured at room temperature, and their cure can be speeded by heating to approximately 80°C (176°F).
- c. A range of curing temperatures, particularly with epoxy systems, allows repair at lower temperatures than the original cure.

- d. Tooling can be used at lower temperatures than with thermoplastics.
- e. Chemical resistance is generally good, but check for resistance to any chemicals that may come into contact with the part. For example, some epoxies are more resistant to chemicals than others.

2.1.3 Disadvantages of thermoset resin composites

- a. Slow to process (cold store/thaw/cure).
- b. Can be associated with health hazards.
- c. Slow to repair.

2.1.4 Advantages of thermoplastic resin composites

The advantages of thermoplastics resin composites over thermoset resin composites include the following:

1. Thermoplastic resin composites are much tougher than thermosets and offer fast processing times and good environmental performance, except against certain solvents in some cases. Again, check each material and its response to each solvent likely to be encountered.
2. No health hazards.
3. More closely match fiber performance.
4. Good fire/smoke performance (interiors and fuel tanks and engines parts).
5. Good fatigue performance.
6. Primary structure usage.
7. High temperature uses polyetheretherketone (PEEK) 250 to 300^oC (482 to 572^oF).
8. Commercial applications include helicopter rotor blades, some high-strength interior parts and fairing panels on civil aircraft.

9. Future possibility of resin transfer molding (RTM) around reinforcing fiber or use in conventional application mode (i.e., pre-preg stacking). Single crystal growth versions could be used for engine parts.

2.1.5 Disadvantages of thermoplastic resin composites

1. Cost.
2. New process methods.
3. Long-term fatigue characteristics unknown.
4. Temperature to melt for repairs is very high in some cases. This could cause curious problems for *in-situ* repairs to primary or secondary structures, especially if being done near fuel tanks or hydraulic systems.
5. Polyimides suffer micro cracking (Tuttle, 2006).

2.1.6 Classification of composites

Classification of composite is based on two distinct levels, Matrix and Reinforcement.

Classification based on matrix

- i. Polymer Matrix Composite (PMCs)
- ii. Metal Matrix Composite (MMCs)
- iii. Ceramic Matrix Composite (CMCs)
- iv. Carbon-Carbon Composite (CCCs)

Classification based on reinforcement materials

- i. Particulate reinforcement
- ii. Whisker reinforcement
- iii. Fabrics reinforcement
- iv. Structural reinforcement

A variety of materials are being used ranging from lower performance glass fiber/polyester used in small sail boats and domestic products, to high performance carbon fiber epoxy systems used in military aircrafts and spacecrafts. In these sectors, where the use of composite materials offer great potential in reducing vehicle weight, thus increasing fuel efficiency and reducing CO₂ emissions. In additions to weight reduction, the number of individual parts can be significantly reduced, making the high volume composite car concept cost effective (Mishra *et al.*, 1999; Jeffrey, 2000).

(i) Polymer matrix composites

Polymer matrix composites are normally composed of a matrix reinforced with a synthetic or natural fiber (Monterio *et al.*, 2009).

The composite materials are chemically cured to a highly cross-linked, three-dimensional network structure. These cross-linked structures are highly solvent resistant, tough and creep resistant (Ticolau *et al.*, 2010).

Polymer resins have been divided broadly into two categories: Thermosetting and Thermoplastics (Taj *et al.*, 2007).

Both thermoset and thermoplastics are attractive as matrix materials for composites. In thermoset composites, formulation is complex because a large number of components are involved such as base resin, curing agents, catalysts, flowing agents and hardeners.

Thermoplasts offer many advantages such as low processing costs, design flexibility and ease of molding complex parts over thermosets. Thermoplastic composites are flexible, tough and exhibit good mechanical properties (Ticolau *et al.*, 2010).

(ii) Metal-matrix composites

As the name implies, for metal-matrix composites (MMCs) the matrix is a ductile metal. These materials may be utilized at higher service temperatures than their base metal counterparts;

furthermore, the reinforcement may improve specific stiffness, specific strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability. Some of the advantages of these materials over the polymer-matrix composites include higher operating temperatures, nonflammability, and greater resistance to degradation by organic fluids. Metal-matrix composites are much more expensive than PMCs, and, therefore, their (MMC) use is somewhat restricted. The superalloys, as well as alloys of aluminum, magnesium, titanium, and copper, are employed as matrix materials. The reinforcement may be in the form of particulates, both continuous and discontinuous fibers, and whiskers; concentrations normally range between 10 and 60 volume percent. Continuous fiber materials include carbon, silicon carbide, boron, aluminum oxide, and the refractory metals. On the other hand, discontinuous reinforcements consist primarily of silicon carbide whiskers, chopped fibers of aluminum oxide and carbon, and particulates of silicon carbide and aluminum oxide (Callister, 2006).

Some matrix–reinforcement combinations are highly reactive at elevated temperatures. Consequently, composite degradation may be caused by high-temperature processing or by subjecting the MMC to elevated temperatures during service. This problem is commonly resolved either by applying a protective surface coating to the reinforcement or by modifying the matrix alloy composition. Normally the processing of MMCs involves at least two steps: consolidation or synthesis (i.e., introduction of reinforcement into the matrix), followed by a shaping operation. A host of consolidation techniques are available, some of which are relatively sophisticated; discontinuous fiber MMCs are amenable to shaping by standard metal-forming operations e.g., forging, extrusion, rolling (Callister, 2006).

(iii) Ceramic matrix composites

Ceramic materials are inherently resilient to oxidation and deterioration at elevated temperatures; were it not for their disposition to brittle fracture, some of these materials would be ideal

candidates for use in high-temperature and severe-stress applications, specifically for components in automobile and aircraft gas turbine engines. Fracture toughness values for ceramic materials are low and typically lie between 1 and 5MPa. The fracture toughness of ceramics have been improved significantly by the development of a new generation of ceramic-matrix composites (CMCs) - particulates, fibers, or whiskers of one ceramic material that have been embedded into a matrix of another ceramic. Ceramic-matrix composite materials have extended fracture toughness to between about 6 and 20MPa. In essence, this improvement in the fracture properties results from interactions between advancing cracks and dispersed phase particles. Crack initiation normally occurs with the matrix phase, whereas crack propagation is impeded or hindered by the particles, fibers, or whiskers. One particularly interesting and promising toughening technique employs a phase transformation to arrest the propagation of cracks and is aptly termed 'transformation toughening'. Other recently developed toughening techniques involve the utilization of ceramic whiskers, often SiC or Si₃N₄. These whiskers may inhibit crack propagation by deflecting crack tips, forming bridges across crack faces, absorbing energy during pull-out as the whiskers debond from the matrix, and/or causing a redistribution of stresses in regions adjacent to the crack tips. Furthermore, there is a considerable reduction in the scatter of fracture strengths for whisker-reinforced ceramics relative to their unreinforced counterparts. In addition, these CMCs exhibit improved high-temperature creep behavior and resistance to thermal shock (i.e., failure resulting from sudden changes in temperature). Ceramic-matrix composites may be fabricated using hot pressing, hot isostatic pressing, and liquid phase sintering techniques (Callister, 2006).

(iv) Carbon-carbon composites

One of the most advanced and promising engineering material is the carbon fiber reinforced carbon-matrix composite, often termed a carbon-carbon composite; as the name implies, both

reinforcement and matrix are carbon. These materials are relatively new and expensive and, therefore, are not currently being utilized extensively. Their desirable properties include high-tensile moduli and tensile strengths that are retained to temperatures in excess of resistance to creep, and relatively large fracture toughness values. Furthermore, carbon-carbon composites have low coefficients of thermal expansion and relatively high thermal conductivities; these characteristics, coupled with high strengths, give rise to a relatively low susceptibility to thermal shock. Their major drawback is a propensity to high temperature oxidation. The carbon-carbon composites are employed in rocket motors, as friction materials in aircraft and high-performance automobiles, for hot-pressing molds, in components for advanced turbine engines, and as ablative shields for re-entry vehicles. The primary reason that these composite materials are so expensive is the relatively complex processing techniques that are employed (Callister, 2006).

2.1.7 Particulate reinforced polymers

Particulate fillers used as reinforcements in polymer systems may be classified as natural and synthetic. Natural fillers include minerals such as calcium carbonate, Kaoline, Mica, Talc and some agro-byproducts, while synthetic fillers include processed mineral products such as carbon black, fumed silica, aluminium hydroxide etc (Zurale and Bhide, 1998; Leng, 2008). The size of particulate fillers range from 0.1 μm to about 2mm. Nowadays, research in polymer science and technology is mainly focused on composites made from renewable resources (Mohanty *et al.*, 2000).

Generally, Bio-composites are suitable materials for use in various fields due to their biodegradable nature/ecofriendly advantages. Bio-composites are manufactured using biopolymer as binder and natural fiber as a reinforcement material (Ning *et al.*, 2010).

2.1.8 Fiber reinforced polymers

Common fiber reinforced composites are composed of fibers and a matrix. Fibers are the reinforcement and the main source of strength while matrix glues all the fibers together in shape and transfers stresses between the reinforcing fibers. The fibers carry the loads along their longitudinal directions. Sometimes, filler might be added to smoothen the manufacturing process, impart special properties to the composites, and/or reduce the product cost. Common fiber reinforcing agents include asbestos, carbon/graphite fibers, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminium oxide, glass fibers, polyamide, natural fibers etc. Similarly, common matrix materials include epoxy, phenolic, polyester, polyurethane, polyetheretherketone (PEEK), vinyl ester etc. Among these resin materials, PEEK is most widely used. Epoxy, which has higher adhesion and less shrinkage than PEEK, comes in second for its high cost (Tudu, 2009).

2.2 Advantages of Polymer Matrix

Polymer composites consist of reinforcement embedded in a resilient plastic matrix. The reinforcement provides the strength for the composite material, and the matrix provides the support. Polymer composites are light and resist heat and corrosion better than conventional plastics or natural composites. Other advantages can be seen in its strength, weight and resilience, material properties and cost (Khan and Armes, 2000).

2.3 Application of Polymer Composite

Polymer composites have wide applications which include Boat decking (boat hulls, submersibles pressure hull, propeller shafts, masts, bulkheads, rudders) and Transportation (car and rail body panels, bumper fascia, radiator grills, instrument panels, engine components, fuel lines, armored vehicles). They are also used in Aerospace (General and military aviation fuselage, bulkhead and floor, cargo liner, wings, landing gear, doors, rotor blades and hubs,

satellite structure aircraft wings) and Sports (bike frames, canoes, fishing rods, archery bows, golf clubs, ski poles and skis, surf boards, racquets). Other applications include light transmitting panes, construction of light, but tough and strong armour including bullet proof vest, support beam for highway beam, windmill blades and industrial drive shafts (Passipoularidis and Philippidis, 2009).

2.4 Engineering Composites Materials

Researchers in diverse fields of sciences and engineering have devised innovative interdisciplinary techniques for synthesizing, analyzing, and manufacturing new generations of engineered materials. These new classes of engineered synthetic materials comprising ceramics, plastics and composites have had a major impact on our lifestyles in areas as diverse as those utilizing the more traditional naturally-occurring materials (Gandhi and Thompson, 1992).

Mathew and Rawling (2005) opined that in pursuing the quest for improved performance, which may be specified by various criteria including less weight, more strength and lower cost, engineers and scientists are always striving to produce either improved traditional materials or completely new materials. Composites are examples of the latter category. Several reports agree that composite materials have better strength-weight ratio, materials properties etc. when reinforced with particulate fillers.

According to Leng (2008) and Kim *et al.*, (2008), particulate filler imparts equal strength in all directions compared to fillers that offer unidirectional reinforcement. Their incorporation in polymers lead to increase in stiffness, high resistance to distortion by heat, low shrinkage, low coefficient of thermal expansion and high resistance to permeation of gases and liquids (Zurale and Bhide, 1998 and Kim *et al.*, 2008).

Patricio Toro *et al.*, (2007) evaluated the use of eggshell (ES) as a new bio-filler for polypropylene composites. The work proved that reinforcement with ES produced composite

with lower modulus of Elasticity. It was established that ES could replace talc up to 75%, while maintaining a similar stiffness and modulus of elasticity compared to the talc composites.

Abdullahi *et al.*, (2011) studied the water absorption and mechanical properties of high-density polyethylene/eggshell composite and reported that the addition of eggshell powder to the polymer leads to decrease in the tensile strength and modulus of elasticity; hardness on the other hand, increased along with the percentage elongation and impact strength. Water absorption of the composites as function of days was also investigated and it increased with increasing exposure time for the same filler content and weight percent of eggshell at constant exposure time.

Njoku *et al.*, (2011) reported that the tensile strength of a carbonized periwinkle shell reinforced Polyester matrix composite increased with decreasing particle size and that both tensile strength and young modulus of the composite material increased with increasing weight fraction of periwinkle particles in the composite laminate.

Shehu *et al.*, (2014) studied the effect of particle size on the properties of polyester/palm kernel shell (PKS) particulate composite and reported that 300 μm sieve size PKS/polyester composites had the most steady/definite properties, gave best tensile strength values as compared to those of other sieve sizes, and had better interaction with the polyester resulting in better mechanical and physical properties.

It has been established that the carbonization process has a great effect on the final product, and careful selection of carbonization parameters is important. The purpose of carbonization process is to enrich the carbon content and to create an initial porosity in the carbonized particle. It has been shown that high carbonization temperature would result in a great amount of volatiles being released from the raw material and eventually influencing the product yield and porosity (Wei *et al.*, 2008). Nasihu (2014) reported an increase in hardness of a produced locust bean reinforced

polyester composite while the tensile strength decreases but impact and flexural strength were not stable.

Hassan *et al.*, (2012) reported that carbonized reinforcement gives better interfacial bonding between the carbonized particles and polymer matrix (polyester), hence strengthening the composite. Consequently, the grain size and particle size of nanoparticle powders decreased the increasing volume fraction of the reinforcement of the produced Al-2wt% Cu alloy composite reinforced by Boron Carbide (B_4C) Nanoparticles (Alizadeh and Tahere, 2012). Alireeza *et al.*, (2013) worked on the preparation and characterization of Bagasse/HDPE composites using multi-walled carbon nanotubes carbohydrate polymers and reported that physical and mechanical properties of the composites were improved with increase in coupling agent content, due to better interfacial bonding.

Parida *et al.*, (2012) worked on the mechanical analysis of Bio-Nanocomposite prepared from Luffa cylindrical and reported that crystallinity and crystalline size of the composites decrease with increase in weight percent of fiber in the resin and also that the mechanical properties of the composite depend on adhesion between fibers and resin as well as fiber loading. In another work (Atuanya and Aigbodion, 2014) titled; evaluation of Al-Cu-Mg alloy/bean pods ash (BPA) nanoparticles synthesized by double layer feed-stir casting method, it has been reported that density of the composite decreases as the BPA nanoparticles weight percent increases and improvement in mechanical properties is due to uniform distribution of the BPA nanoparticles in the composite.

Faraz *et al.*, (2014) studied the structure-property relationships and modeling of the mechanical properties of a high-temperature resistant thermoset nanocomposite and reported that incorporation of clay particles improves thermo-mechanical properties, elastic modulus and heat deflection temperature with increasing concentration of clay particles and they used Halpin-Tsai

model to fit stiffness data of the nanocomposites to determine the aspect ratio of the clay particles and explain the structure present in the nanocomposites thus, the model reproduced reasonable experimental data. In similar work(Deepthi *et al.*, 2014), it was reported that the incorporation of silicon nitrate (SN) increase the tensile strength and modulus of elasticity of the produced Nanocomposite. Nanoclay addition further enhances the properties due to improved adhesion between HDPE and SN but optimal compatilization was observed at 10% addition.

2.5 Thermosetting

Thermosetting is a hard and stiff cross-linked material that does not soften or become mouldable when heated. Thermosets are stiff and do not stretch the way elastomers and Thermoplasts do. Several types of thermoset polymers are epoxy resins, unsaturated polyester resins (as in fiberglass), vinyl ester, phenolics, Novolac and polyamide. Unsaturated polyesters are extremely versatile in properties and applications and have been popular thermosets used as polymer matrix in composites. They are widely produced industrially due to many advantages compared to other thermosetting resins. These include room temperature cure capability, good mechanical properties and transparency (Taj *et al.*, 2007).

2.6 Thermoplastics

Thermoplastics are polymers that require heat to make them processable. After cooling, such materials retain their shape. In addition, these polymers may be reheated and reformed often without significant changes in their properties. Some of the thermoplastics which have been used as matrix for natural fiber reinforced composites include High density Polyethylene (HDPE), Low density polyethylene (LDPE), Chlorinated polyethylene (CPE), Polypropylene (PP), Normal Polystyrene (PS), Polyvinyl Chloride (PVC), mixture of polymers and Recycled thermoplastics (Taj *et al.*, 2007).

In recent decades, the uses of natural fibers as an alternative reinforcement in polymer composites have attracted the attention of many researchers and scientist due to their advantages over conventional glass and carbon fibers. These natural fibers include flax, hemp, jute, sisal, kenaf, coir, kapok, banana, henequen and many others. The various advantages of natural fibers over man-made glass and carbon fibers are low cost, low density, comparable specific tensile properties, non-abrasive to the equipment, non-irritation to the skin, reduced energy consumption, less health risk, renewability, recyclability and bio-degradability (Ku *et al.*, 2011).

2.7

Polyester

The term 'polyesters' is applied to different types of resins. Hydrocarbon resins can be made in unsaturated and saturated forms. Unsaturated polyester resins are less flexible and less compatible with aromatic cross-linking agents. These polyesters are primarily used in composite structures where they can be reinforced with fillers such as glass fibers. Polyester resins made by polyesterification of maleic and phthalic anhydrides and propylene glycol increase resin flexibility. Unsaturated glycols can be used to increase the rigidity of the cured resin by permitting additional cross-linking. Saturated polyester resins are most frequently used in the manufacture of fibers and films. The most prevalent of these polyesters is poly(ethylene terephthalate). This is a linear polyester that is prepared by transesterification of the dimethylester of terephthalic acid and ethylene glycol. The resulting polymer is chemically resistant to moisture, acids and organic solvents. Polyesters have a relatively simple structure composed of Carbon, Oxygen and Hydrogen atoms in a benzene ring with $-CH_2$ attached via carbon-oxygen bonds. Upon thermal decomposition, the gaseous products are hydrocarbon compounds and oxygenated hydrocarbons as well as CO , CO_2 and water. The addition of cross-linking agents, fillers and flame retardants modify the nature of the combustion products (Emil and Barbara, 1986).

Polyester is produced when dihydric alcohol, like ethylene glycol, reacts with an aromatic acid like phthalic acid to produce a polymeric ester (Njoku *et al.*, 2011).

Properties of polyester

Polyester resins are, across the board, pale in colour. This could be a pale gray colour to a dull and diluted white. All polyester resins are thermosetting, that is, they are malleable until they are heated at which time they permanently harden, even when exposed to the same heat a second time. Polyester resins are pretty resistant to both water and ultra violet (UV) rays. This is another reason why they are often employed in the marine industry. Because of the thermosetting nature of polyester, they can be fairly brittle because of their resistance to being bent or changed. When enough pressure is applied, they can crack or shatter. Polyester resins are generally viscous. In order to lessen their viscosity, styrene is added. However, styrene may create fumes that can endanger those who work with polyester resins (Khanna, 2010).

2.8 Method of Polymer Composite Fabrication

Polyester resin can be readily processed without pressure by using cheap moulds to produce a wide variety of finished products with the range of possible moulding processes available. They can be made from similar wide variety of materials including wood, plaster, epoxies, polyester resins, non-ferrous metals, steels or a combination of these. Two general methods are available for composite development; the open mould and close mould process.

Open mould process, which could be by hand lay-up, produces composite whose surface are all smooth, while the close mould process involves complex machinery and equipment. The technology is not readily available but produces composite with better mechanical properties than the open mould process (Khan and Armes, 2000).

2.9

Locust Bean

The African locust bean tree, *Parkia biglobosa* is a perennial tree legume which belongs to the sub-family *mimosoideae* and family *leguminosae* (now family *fabaceae*). It grows in the savannah region of West Africa up to the southern edge of the Sahel zone (Campbell-Platt, 1980). A matured locust bean tree (20 - 30 years) can bear about a tone and above of harvested fruits. From experience, the tree can start to bear fruits from five to seven years after planting (Musa, 1991). The most important use of African locust bean is found in its seed (Karwa-Hausa; Ngin-Ham; Iyere - Yoruba). It has other food and non-food uses, especially the seeds which serve as source of useful ingredients for consumption (Campbell-Platt, 1980). It has also been reported that the husks and *Pods* are good food for livestock (Douglass, 1996; Obiazoba, 1998). The fruit shell is traditionally used to extract a substance that helps to harden the natively made house floors and can be an important source of tannin for leather tanning.

2.9.1 Locust bean pod

Locust bean pods are waste byproduct of agricultural processing of the African locust bean fruit. Substantial quantities can be found across northern Nigeria during the harvest season. Across the globe, much research efforts in recent times are geared towards possible ways of recycling these wastes for reuse to keep the environment clean and safe (Adama and Jimoh, 2011).

Locust bean pod, which is a waste agricultural biomass (WAB) obtained from the fruit of the African locust bean tree (*Parkia Biglobosa*), is the material resource required for the production of locust bean pod ash (LBPA). The harvested fruits are riped open while the yellowish pulp and seeds are removed from the pods. The empty pods are the needed raw material. The pods make up 39% of the weight of the fruits while the mealy yellowish pulp and seeds make up 61% (Adama and Jimoh, 2011). Table 2.1 shows the chemical composition of LBPA:

Table 2.1:Chemical composition of LBPA

Chemical composition	Na ₂ O	K ₂ O	MgO	Pb ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	LoI
Percentage %wt by weight	1.21	5.62	2.01	5.82	11.51	13.05	15.71	39.01	6.00

(Source: Adama and Jimoh, 2011). LoI: losses on Ignition.

2.10 Nanotechnology

Nanotechnology is a broad interdisciplinary area of research, development and industrial activity which has been growing rapidly worldwide for the past decade. It is a multidisciplinary grouping of physical, chemical, biological, engineering, and electronic, processes, materials, applications and concepts in which the defining characteristic is one of size. It is important to note that nanotechnology is concerned with items of small size where the size factors relates to their “novel properties and/or functions”; the “novelty” is usually noticeable in some manner from a macro point of view (Charles, 2009). Nanotechnology offers new ways to create materials promising a degree of property control not previously possible and offer multiple property enhancements (Kear and Strutt, 1995).

2.10.1 Nanoparticles

Nanoparticles are particles with at least one dimension smaller than 1 micron and potentially as small as atomic and molecular length scales (~0.2 nm). Nanoparticles can have amorphous or crystalline form and their surfaces can act as carriers for liquid droplets or gases. To some degree, nanoparticulate matter should be considered a distinct state of matter, in addition to the solid, liquid, gaseous, and plasma states, due to its distinct properties (large surface area and quantum size effects). Examples of materials in crystalline nanoparticle form are fullerenes and carbon nanotubes, while traditional crystalline solid forms are graphite and diamond. Nanoparticles are the end products of a wide variety of physical, chemical and biological processes some of which are novel and radically different. Nanoparticle products include

nanotubes, nanowires, quantum dots and “other” nanoparticles (HSE, 1999). In general, the size of a nanoparticle spans the range between 1 and 100 nm (Satoshi and Nick, 2013).

2.10.2 Nanomaterials

Nanomaterials are materials that have structural components smaller than 1 micrometer in at least one dimension. While the atomic and molecular building blocks (~0.2 nm) of matter are considered nanomaterials, examples such as bulk crystals with lattice spacing of nanometers but macroscopic dimensions overall, are commonly excluded. Many authors limit the size of nanomaterials to 50 nm or 100 nm, the choice of this upper limit being justified by the fact that some physical properties of nanoparticles approach those of bulk when their size reaches these values. However, this size threshold varies with material type and cannot be the basis for such a classification. A legitimate definition extends this upper size limit to 1 micron, the sub-micron range being classified as nano (Cristina *et al.*, 2007).

Nanomaterials are classified into Nanostructured materials and Nanophase/Nanoparticles materials. The former refers to condensed bulk materials that are made of grains with grain sizes in the nanometer range, while the latter are usually the dispersive particles. Nanomaterials are a bridge that links single elements with single crystalline bulk structure (Zhong, 2009).

2.10.3 Nanocomposites

Nanocomposites are materials that combine two or more components and are designed to exhibit overall the best properties of each component (mechanical, biological, optical, electric, or magnetic). Nano-composites containing carbon nanotubes (CNT) and polymers used to control their conductivity are interesting for a wide range of applications, such as supercapacitors, sensors, solar cells, etc (Cristina *et al.*, 2007).

2.11

Nanoparticle Production Processes

Nanoparticles, even from the same material, can be synthesized utilizing a variety of methods. Different methods are used in order to optimize specific properties of the materials. These properties include, but are not limited, to size (diameter, length, volume), size distribution, symmetry, surface properties, surface coating, purity, ease of manipulation, yield and suitability for scaling up. Methods used for the commercial or deliberate manufacture of nanoparticles may be divided into four main groups. These are;

- (i) Gas phase processes including flame pyrolysis, high temperature evaporation and plasma synthesis.
- (ii) Vapour deposition synthesis.
- (iii) Colloidal or liquid phase methods in which chemical reactions in solvents lead to the formation of colloids.
- (iv) Mechanical processes including grinding, milling and alloying.

For all of these processes the recovery stage may be quite similar and is likely to comprise of mainly powder or slurry handling techniques (HSE, 1999).

(i) Gas phase synthesis methods

Gas phase processes may be used to produce a wide range of materials. Most (but not all) nanoparticle synthesis methods in the gas phase are based on homogeneous nucleation of a supersaturated vapour and subsequent particle growth by condensation, coagulation and capture. Gas phase synthesis methods have been reviewed by several authors including Kruis *et al.*, (1998) and Swihart (2003). Multiple approaches can be used to generate the supersaturated vapour dependant on the materials (precursors) used and the form of materials to be produced. In general, the formation of the vapour occurs within an aerosol reactor at elevated temperatures. The most straight forward method of achieving super saturation is to heat a solid and evaporate it

into a background gas. This method is well suited for the production of metal nanoparticles in particular. By including a reactive gas such as oxygen, oxides or other compounds of the evaporated material can be produced. This method has also been used to prepare composite nanoparticles and to control the morphology of single component nanoparticle. The precursor materials are introduced into the reactor as solids, powders, liquids or gases. In some cases, the precursors are nanoparticles, produced by a separate process. In the reactor, the precursors are heated and mixed with a carrier gas. The supersaturated vapour is produced by cooling or by chemical reaction or by some combination of these. Cooling may be induced by expansion, mixing with a cooler gas or by heat transfer to the surroundings. Chemical reactions used are usually decomposition reactions. The supersaturated vapour nucleation process is initiated by the formation of very small particle embryos from the molecular phase. These nuclei subsequently grow surface growth mechanisms (heterogeneous condensation, surface reaction) and by collision and coagulation. Further collisions can result in the formation of loosely bound agglomerates or chain like, dendritic forms. The details of the overall process depend on the amount of available condensable gaseous materials, their thermodynamic and chemical properties as well as on the process conditions.

The methods can be categorised by the heating or evaporation process used (Kruis *et al.*, 1998).

These include;

- flame pyrolysis
- furnace flow reactors
- laser induced pyrolysis
- laser vaporisation
- thermal plasma
- microwave plasma

- sputtering
- laser ablation
- droplet evaporation

(a) Flame pyrolysis methods are the basis of production for many of the existing industrial processes used to generate bulk quantities of nanomaterials such as carbon black and fumed silica. In flame pyrolysis, nanoparticles are produced by using the flame heat to initiate the chemical reactions. This is a relatively inexpensive, potentially high volume method which is used in the production of fumed silica (SiO_2) and ultrafine TiO_2 . These materials are generated by the oxidation of titanium tetra chloride (TiCl_4) or silicon tetra chloride (SiCl_4) in a methane / oxygen flame. The disadvantage of this method is that it usually yields agglomerated particles. More complex products can also be synthesised using this method. For example, Zachariah *et al.*, (1995) described the production of iron oxide (Fe_3O_4) particles embedded in SiO_2 host particles.

(b) Furnace flow reactors are the simplest systems used to produce saturated vapour for substances having a large vapour pressure at intermediate temperatures. In these systems a crucible containing the source material is placed in a heated flow of inert carrier gas. Materials with low vapour pressure can be fed in as suitable precursors, such as organometallics or metal carbonyls into the furnace. This method has been used to produce nanoparticles such as silver (Ag), gallium (Ga), and galena (PbS). Maisels *et al.*, (2000) prepared composite nanoparticles of PbS with Ag by separate evaporation and condensation of the two materials followed by coagulation of oppositely charged particles. Ohno (2002) described the production of various composite nanoparticles including indium, lead (Pb), silicon (Si), germanium (Ge) and aluminium (Al).

- (c) In the laser pyrolysis technique, a flowing reacting gas is heated rapidly with an infra-red laser. The source molecules are heated selectively by absorption of the laser energy whereas the carrier gas is not. Decomposition of the precursors takes place due to the temperature increase and super saturation is created resulting in nanoparticle formation. This process has been used to produce Si nanoparticles from silane (SiH_4) (Canon *et al.*, 1982) and Fe nanoparticles from iron pentacarbonyl (FeCO_5) (Majima *et al.*, 1994).
- (d) Plasma reactors can also be used to deliver the energy required to cause evaporation or initiate chemical reactions. They can achieve temperatures of the order of $10,000^\circ\text{C}$. Powder feeds can also be decomposed by the plasma. The main types of plasma used are Direct Current (DC) plasma jet, DC arc plasma and Radio-Frequency (RF) induction plasma (Young and Pfender, 1985). Commercial quantities of metal and metal oxide nanoparticles are produced using this method by QinetiQ Nanomaterials in what is described as “the UK’s first production facility dedicated to the volume production of specialist nanomaterials”.
- (e) Sputtering is a method of vaporising materials from a solid surface by bombardment with high velocity ions of inert gas e.g. Argon (Ar) or Krypton (Kr) causing an ejection of atoms. Sputter sources such as an ion gun or hollow cathode plasma sputter are normally used in the vacuum systems. Urban *et al.*, (2002) demonstrated formation of nanoparticles of a dozen different metals by magnetron sputtering of metal targets. This process needs to be carried out at low pressure which limits its effectiveness for further processing of nanoparticles in aerosol form and in the scaling up of this process.

Gas phase synthesis methods are considered to be able to produce improved specification and control in aspects such as particle size, crystallinity, degree of agglomeration, porosity, chemical

homogeneity, purity and stoichiometry (Kruis *et al.*,1998) and are generally considered to offer good possibilities for scaling up to industrial level processes.

(ii) Vapour deposition methods

Chemical Vapour Deposition (CVD) methods are based on well established methods for the manufacture of semiconductors (Van Zant, 2000). These systems have conventionally been used to deposit thin films of silicon and other semiconductors on to semiconductor wafers. Vapour is formed in a reaction chamber by pyrolysis, reduction, oxidation and nitridation. Deposited film growth, in several stages beginning with nucleation as the first few atoms, deposit on the surface. These first atoms form islands which spread and coalesce into a continuous film. After this transition film is formed, growth continues until thicker film develops. Areas of growth on the wafer is controlled using various patterning processes (also known as photolithography or photomasking) in which deposition patterns are etched on to the surface layers of the wafers. CVD methods have been used to produce nanoparticles from many different materials including TiO_2 (Nakaso *et al.*,2003), ZNO (Lee and Mukund,2001) and SiC (Honda *et al.*,2003). However the most important application is the synthesis of carbon nanotubes where CVD is considered to offer one of the most effective routes for scaling up to industrial production (Singh *et al.*,2003).

(iii) Colloidal methods

The third major group are the colloidal methods. These are well established “conventional” wet chemistry precipitation processes in which solutions of the different ions are mixed under controlled conditions of temperature and pressure to form insoluble precipitates. Colloidal methods provide a simple route to the synthesis of nanoparticles. This approach enables the relatively straightforward production of significant quantities of nanoparticle material at modest capital cost. As with other approaches, much of the recent emphasis has been on the development of more monodisperse particles with better defined shape.

The earliest reported colloids were metals. Preparation of metallic colloids dates back several centuries, but scientific investigation of their preparation and properties were first reported by Faraday (1857) in his experiments with gold. Development of colloidal theory, processes and methods have been ongoing since that time. Many comprehensive reviews are available including Hodgson *et al.*, (1993), Hiemenz and Rajagopalan (1997), and Holmberg (2002) which describe this science in great detail. Nanomaterials produced by colloidal process include metals, metal oxides, organics, and pharmaceuticals.

An important and rapidly expanding sub-set of colloidal methods are sonochemistry methods, in which acoustic cavitation is used to control the process (Gedanken, 2004). In this process, molecular precursors undergo chemical reactions due to the application of ultrasound radiation. The main event in sonochemistry is the creation, growth and rapid collapse of a bubble that is formed in the liquid. High temperatures and high cooling rates accompany the collapse of the bubble and nucleation centres formed whose growth is limited by the rapid collapses. This method has been used to generate a wide range of nanoparticles including chalcogenides, metals and alloys including gold, cobalt and nickel as well as carbon and titania nanotubes. Nanoparticles produced by these wet chemical methods can remain in liquid suspension for distribution and use or may be used as slurries. They may also be collected by filtering or by spray drying to produce a dry powder.

(iv) Attrition methods

The final group of methods are the mechanical attrition methods. In contrast to the previous three groups where nanoparticles were built “bottom-up” from individual molecules, in attrition methods nanoparticles are produced top down from larger particles. Size reduction by grinding and milling is a very well established industrial process used to produce progressively finer forms of materials including minerals such as clay, coal and metals. Production rates of materials can be

of the order of tonnes per hour. Production of the finest grades of material was previously referred to as micronising. Production of particles in the nanometer size range is referred to as ultrafine grinding (Mende *et al.*, 2003) or nanosizing (Merisko-Liversidge *et al.*, 2003).

The process involves wet milling in high shear media mills. Mende *et al.*, (2003) used a stirred media mill to produce suspensions of fused carborundum with a median per hole size of 50nm. The milling chamber comprised rotating perforated plates. Alumina suspensions were also produced. Due to increasing particle – particle interactions in this process, it was necessary to stabilise the suspension by adjustment of the pH to prevent particle recombination. Merisko-Liveridge *et al.*, (2003) used a similar process (described as Nanocrystal Technology) to produce nanometre size drug particles of poorly-water-soluble compounds. Against stabilisation was required to prevent recombination of the particles. Milligramme quantities of the drug were produced although it is understood that higher production rates can be achieved in commercial systems. Particles with a diameter of 147 nm were produced by this method.

2.12 Sol-gel processing

In this method nanoparticles are produced top down from larger particles; is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel). In this process, the particle will firstly be disintegrated to smaller size via grinding and milling before the chemical stage of the process. Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel). After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order to favour further polycondensation and enhance mechanical properties.

Advantages of sol-gel technique

- Able to get uniform and small sized powder
- It is cheap
- Can have low temperature sintering capability, usually 200-600 °C
- Can easily shape materials into complex geometries in a gel state.

Disadvantages of sol-gel technique

- Non-uniform thermal expansion

Applications

- Glasses lenses
- Nanopowder for dental and biomedical application (HSE, 2013).

CHAPTER THREE

MATERIALS AND METHODS

3.0 Introduction

This chapter highlights and explains the materials, equipment and methods used in this research. The different mechanical tests carried out such as; impact, tensile, flexural and hardness were also elucidated as well as the water absorption test, percentage weight loss and SEM characterization of the produced nano-composite.

3.1 Materials

The materials used in this research include: Locust bean pods ash (*Pakiabiglobosa*) particulates, liquid polyester resin, HCl, NaOH, ethanol, Cobalt accelerator and methyl-ethyl ketone catalyst.

3.2 Equipment

The equipment used in this research include: set of sieve, ball milling machine, grinding machine, mould, measuring cylinder, oven, Hardness testing machine, impact testing machine, Tensometer and Scanning Electron Microscope (SEM),

3.3 Methodology

3.3.1 Preparation of locust bean pod ash (LBPA) nanosized particles by Sol-gel method

The locust bean *Pods* (*Pakia biglobosa*) were sourced locally, washed to remove dirt and sun dried. The *Pods* were ground and then ashed at 600⁰C for 2hours. The nanosized particles of LBPA were produced by sol-gel technique. The ash particles were dissolved in a prepared solution and then poured into a round bottom flask attached to a condenser. The mixture was then placed on a Hot-magnetic stirrer and stirred continuously at a specified temperature and time which was then refluxed. After refluxing (gelation), the particulate was then removed, filtered, washed with distilled water, dried and heated in a furnace at a required temperature.

In this work, the produced ash was mixed with 2.5M NaOH solution, boiled for 3hours at 90⁰C with constant stirring. The particulate was then filtered and mixed thoroughly with 2% HCl solution; refluxing of the mixture followed for 4hours at 90⁰C; the particles were then removed, filtered, washed with distilled water and dried. The dried particles were then heated in a heat-treatment furnace at 600⁰C for 5hours. Scanning Electron microscopy (SEM) was used to establish the size of the particle.

3.3.2 Composite preparation

The polyester resin was first thoroughly mixed with the cobalt accelerator (10%) and methyl-ethyl ketone catalyst (10%). Petroleum jelly was used as releasing agent inside the mould cavity. The polyester resin was mixed with and without reinforcement, after addition of the hardener and catalyst. The nano-LBPA was varied in the polyester from 3wt% to 12wt% (at interval of 3wt%) to produce the polyester/nano-LBPA particulate composite. The mixture was poured into the mould and left at room temperature until it settled. After cooling and solidification, it was removed from the mould, cured by heating in an oven at 70⁰C for 2hours and then cooled in still air. The dimension and shape of the cavities were varied according to the required test sizes of tensile, impact, hardness, flexural and water absorption.

3.3.3 Degradability test

Degradability test of the synthesized composite was carried out by assessing the influence of soil burial and exposure to natural weather. The samples for both soil buried and natural weather were prepared according to the required test sizes of tensile, hardness, impact and flexural. Some specimens were then buried in the soil (at a depth of 20cm) while others were exposed to natural weather using the customized weather racks method (samples were suspended with the aid of a copper wire) for 90days (from August to October) in the Department of Metallurgical and Materials Engineering, A.B.U. main campus, Samaru, Zaria. After 30 days, each set of samples

were removed and their properties evaluated using the aforementioned tests; their weight loss were also computed.

3.3.4 Mechanical tests

The following mechanical tests were carried out on the test samples:

- i. **Impact Test:** The impact energy test of the composite samples was determined using Charpy impact testing machine. The procedure used was in accordance with that recommended by ASTM 256 as reported by Satheesh *et al.*, (2013). Samples were sectioned to 10×10×10mm dimensions using hacksaw, mounted on the machine and a swinging pendulum released, under gravity, to hit the sample(s). The energy at impact was read directly from a dial indicator of the machine and the results obtained are given in Tables A.1 – A.3 (Appendix A).
- ii. **Tensile Test:** The test was performed in accordance with standard procedure specified in ASTM D638, using the Hounsfield Tensometer. Samples were sectioned to 120×15×3mm with gauge dimension 40×10×3mm. Each sample was then tested and maximum stress and strain values recorded for tensile strength computation. The Tensile values are given in Tables A.4 – A.13 (Appendix A).
- iii. **Flexural Test:** Flexural strength tests were carried out on a Tensometer. Samples were prepared to dimension of 120×60×10mm. The Samples were subjected to bending by supporting them at both ends and a midpoint load applied until failure as recommended in ASTM D790. The results obtained are presented in TablesA.14 – A.19 (Appendix A).
- iv. **Hardness Test:** The Hardness tests of the samples were carried out using a Rockwell hardness testing machine on F scale (HRF). The test was carried out in accordance with the procedure described by ASTM D785. The samples were sectioned to dimensions 100×10×10mm using hacksaw and then mounted on the machine. Minor load (10kgF)

was applied followed by the major (60KgF). The hardness value of each sample, digitally displayed, was recorded. Tables A.20 – A.22 (Appendix A) showed the hardness values obtained.

3.3.5 Characterisation of test samples

Characterization of the samples was carried out using Scanning Electron Microscope (SEM – model: Phenom ProX) examination of the samples were carried out to reveal the surface morphologies and to establish whether the synthesized Locust Bean *Pod* Ash (LBPA) produced by sol-gel technique have attained nanoscale.

3.3.6 Water absorption test

Samples of the different compositions of the synthesized composite were sectioned, weighed (initial weight, W_1) and immersed in distilled water for 24 hours. The samples were removed from the distilled water, cleaned and dried with blotting paper and weighed again (final weight, W_2). This was in accordance with the procedure recommended by ASTM D570; Standard Test Method for Water Absorption of Plastics. The percentage moisture content was evaluated using the equation below:-

$$\% \text{ Moisture Content} = \frac{W_2 - W_1}{W_1} \times 100 \quad (3.1)$$

3.3.7 Weight loss evaluation

The tests samples used were weighed before (initial weight, W_0) and after (final weight, W_t) degradation and the percentage weight loss evaluated using the equation below:-

$$\% \text{ Weight loss} = \frac{W_0 - W_t}{W_0} \times 100 \quad (3.2)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Introduction

The results obtained from the mechanical tests (impact, tensile, flexural and hardness), water absorption, percentage weight loss and SEM image of the samples before and after degradation test are presented and discussed in this chapter.

4.1 Mechanical Tests Results

The results for the impact strength, tensile strength, tensile modulus, flexural strength, flexural modulus and hardness of the polymer/nano-LBPA composite under varying reinforcements for both degraded (soil-buried and weathered samples) and non-degraded samples; and of the percentage weight loss after degradation are presented in tabular form; Tables A.1 – A.27 (Appendix A). These results are represented graphically in Figures 4.1 – 4.17. The micrographs (SEM) are shown on Plates I -IV.

4.2

Impact Strength

The impact strength of the polyester/nano-LBPA composite was determined to assess the shock absorbing properties of the composites before and after degradation.

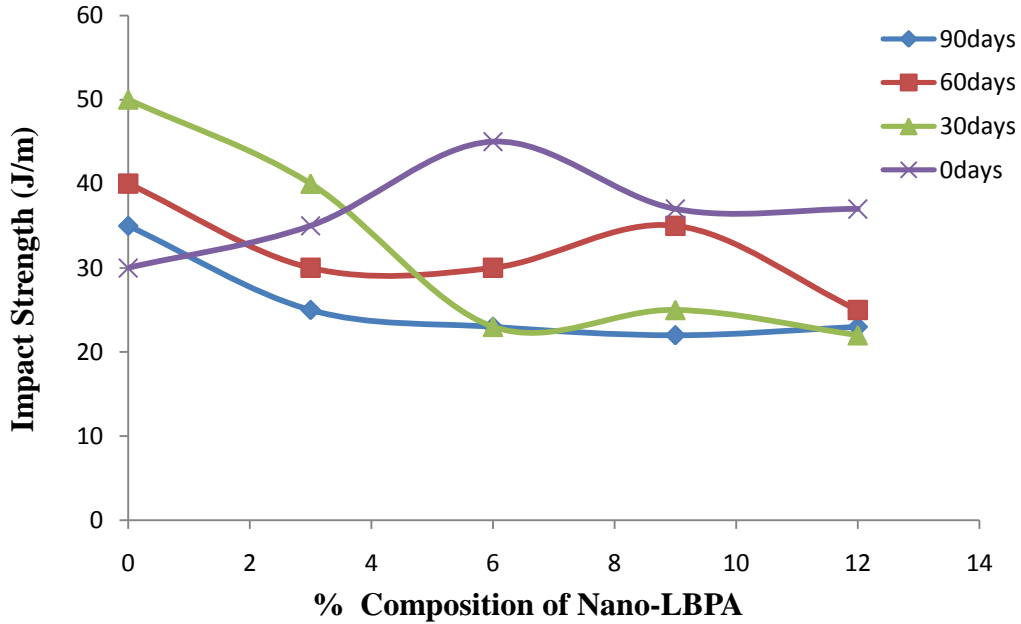


Figure 4.1: Impact strength profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

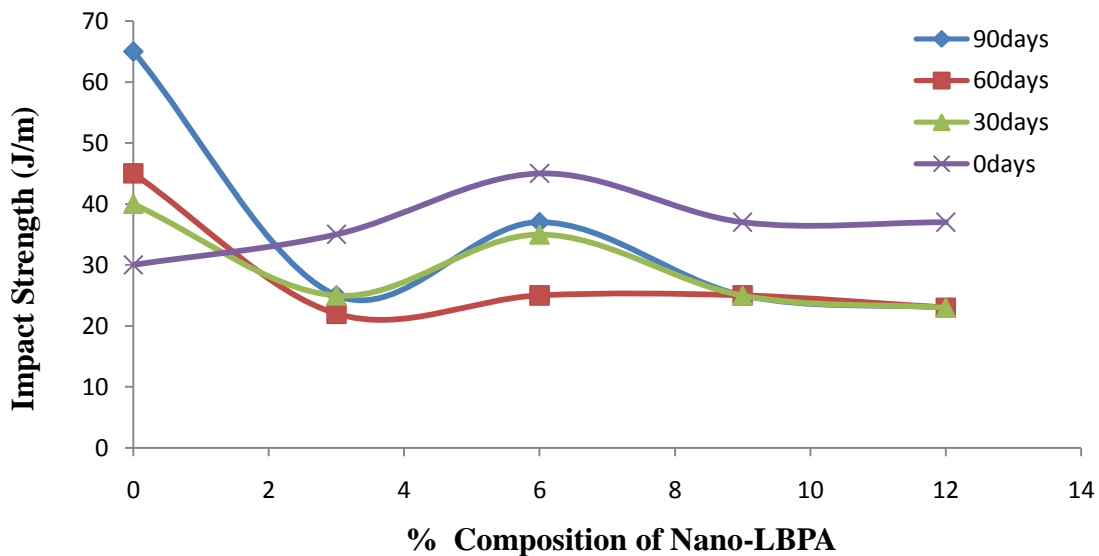


Figure 4.2: Impact strength profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.

Figures 4.1 and 4.2 show the impact strength profile of the produced polyester/Nano-LBPA composite after exposure to natural weather and soil. From the Figures, it could be seen that a decrease in impact strength was observed with corresponding increase in percentage LBPA reinforced polyester composite. It was also observed that the impact strength of the weathered composite dropped sharply from 50 J/m (at 0%LBPA) after 30days to a value of 23 J/m (at 12%LBPA); approximately 54% decrease after 90days. The same scenario was observed for composite samples buried in the soil; the impact strength value decreased from 40 J/m (at 0%LBPA) after 30days to a value of 23 J/m (at 12%LBPA); approximately 42% reduction after 90days. The addition of LBPA enhanced the biodegradability of the polyester mainly because of the increased polymer surface created after LBPA consumption by microorganisms and the atmospheric effect due to natural weathering. This is in accordance with a report elsewhere (Kim *et al.*, 2006 and Singh *et al.*, 2003).

Fluctuations were observed with an increase in impact strength value from 23 J/m (at 6%LBPA) to a maximum value of 25 J/m (at 9%LBPA) approximately 8% rise in value after 30days, from 30 J/m (at 6%LBPA) to a value of 35 J/m (at 9%LBPA) approximately 16% after 60days, and from 22 J/m (at 9%LBPA) to a value of 23 J/m (at 12%LBPA) approximately 4% increase after 90days of exposure to natural weather. Similarly, there was also an observed increase in impact strength value at 3%LBPA and 6%LBPA for the entire period of exposure to soil as evident from Figure 4.2, this could be due to the fact that their were better dispersion of the particulate in the matrix phase which could have contributed to the better mechanical properties observed for these composite samples. The impact strength of the non-degraded composite samples was found to increase with increase percentage reinforcement (at 0%LBPA to 12%LBPA) – approximately 18%, but 6%LBPA was noted to exhibit the highest impact strength value (see Table A.3). This is similar to earlier report (Shenoy and D'melo, 2007; Karmakar andHoffmann, 1994 in Rashdi

et al., 2009). However, there was general decrease in impact strength values of the composite samples with increase in LBPA addition after degradation. This result indicates that the degradation of LBPA is faster than that of polyester matrix; this might be because weathering has induced cracks, possibly due to the swelling and shrinkage of the particles and weakening of the bonds between particles-polyester matrix and/or might be because the cellulosic materials were easily attacked by microorganisms as earlier established (Kim *et al.*, 2006 and Cao *et al.*, 2002).

4.3 Tensile Properties

The figures below shows the tensile strength and tensile modulus of the degraded tensile test sample after 90 days of study.

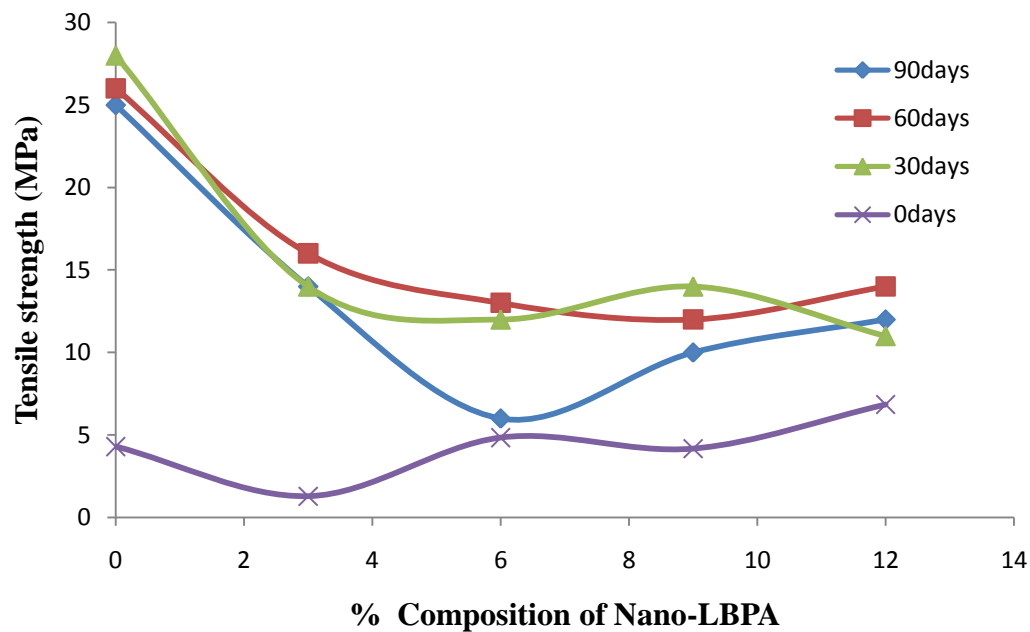


Figure 4.3: Tensile strength profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

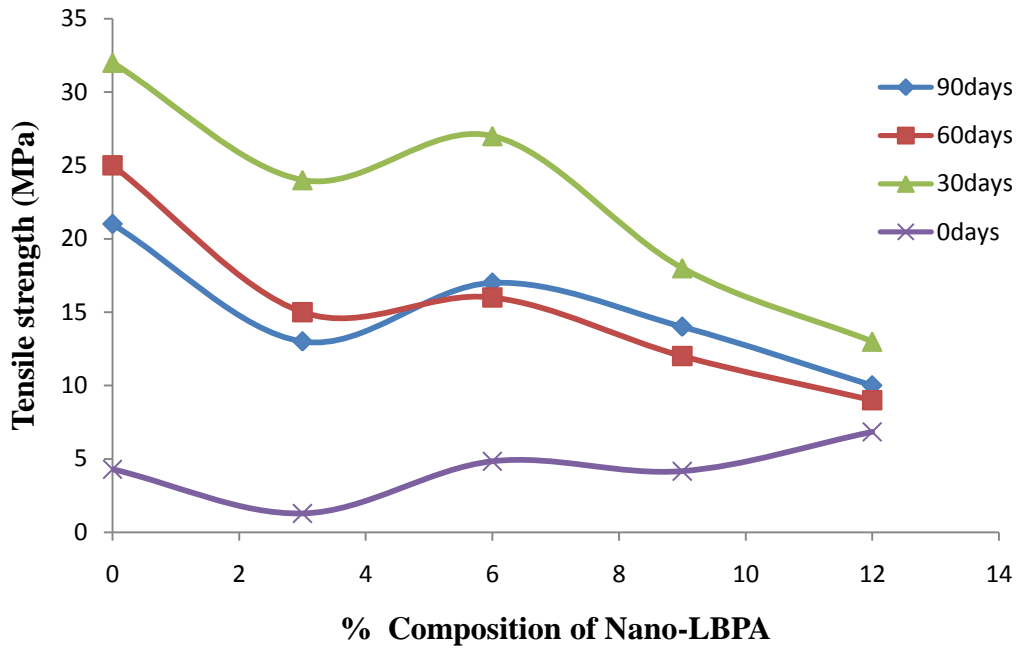


Figure 4.4: Tensile strength profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.

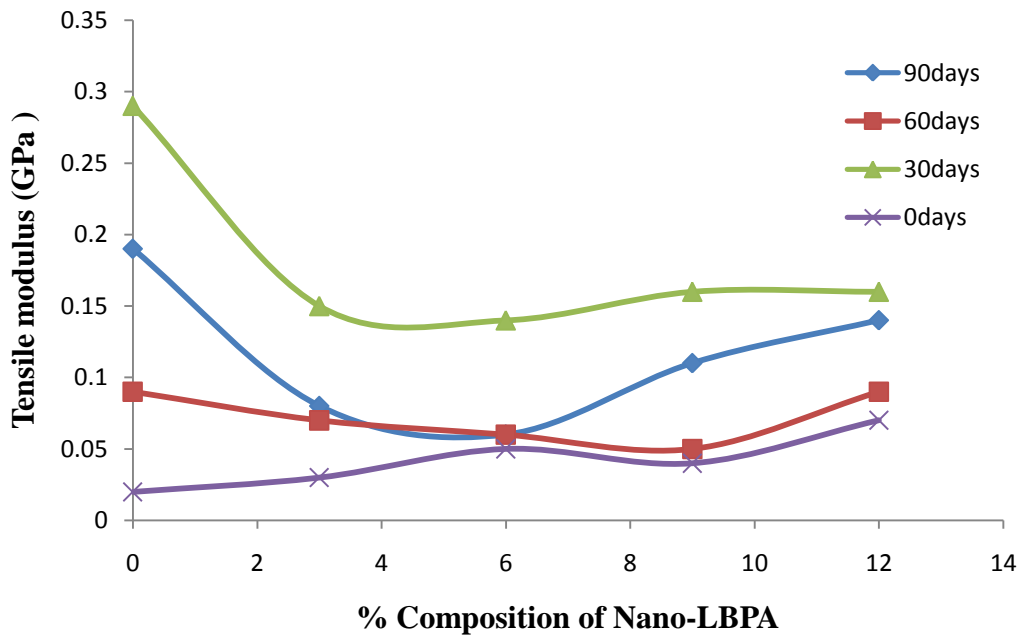


Figure 4.5: Tensile modulus profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

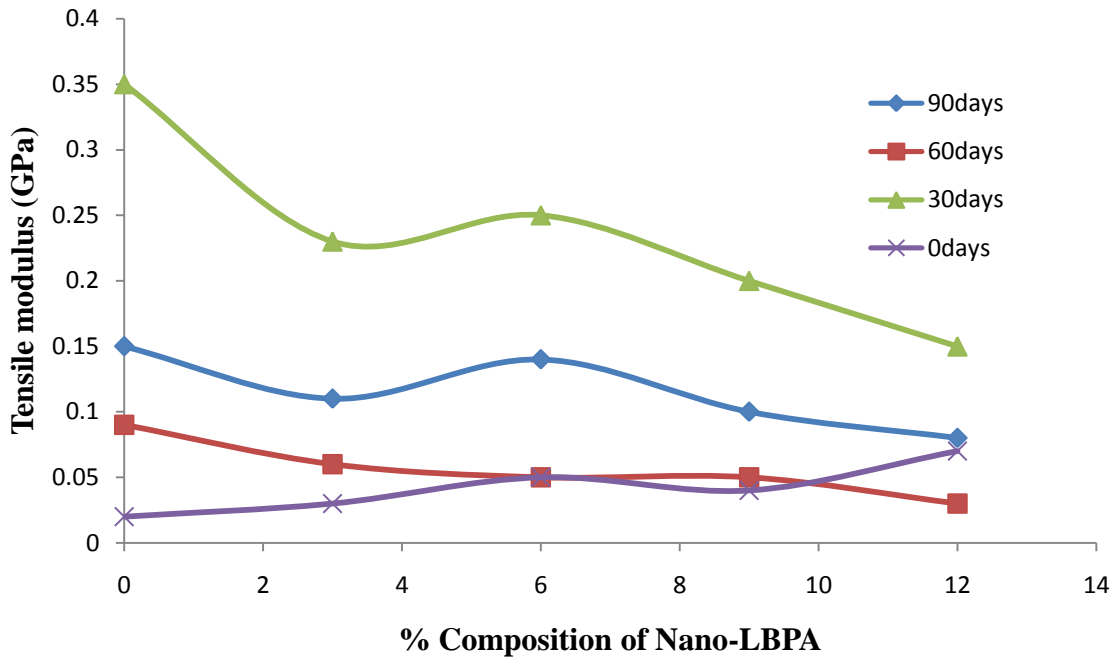


Figure 4.6: Tensile modulus profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.

The tensile properties values of the degraded polyester composite were generally observed to decrease with increase in LBPA addition.

Figures 4.3 and 4.4 illustrate the effect of soil exposure and natural weather on the tensile properties of polyester/nano-LBPA composites. The tensile strength and modulus of the samples decreased marginally from 28 MPa to 25 MPa and 0.2 GPa to 0.19 GPa (at 0%LBPA), respectively with maximum reduction found to be approximately 11% and 35%, respectively after exposure to natural weather for 30 – 90days. At 12%LBPA, the least tensile strength value of 9 MPa was obtained after 60days of exposure to soil. From Figure 4.4, it is obvious that the tensile strength of the polyester samples dropped from 32 MPa to 21 MPa (at 0%LBPA), approximately 34% reduction, with tensile modulus found to decrease approximately up to 57% (see Table A.11), after exposure to soil within this period. This may be due to the fact that when the composite is exposed to moisture, the hydrophilic LBPA swelled as a result of stress exerted

by the particles on the matrix, micro-cracking of the brittle thermosetting resin occurred; an external load applied leads to the timely failure of the composite. This indicated that the samples continuously degrade with increase in the exposure time and also the microorganisms has consumed the LBPA and created pores in the matrix, leading to its higher water absorption and low mechanical properties as established (Obasi, 2012). The presence of voids might also be a contributing factor for the drop in tensile strength (Rashdi *et al.*, 2010; Facca *et al.*, 2006; Hill *et al.*, 2000). General reduction was observed in the tensile modulus value of the degraded samples. The drop in modulus was found to be approximately 51% after exposure to natural weather at 0%LBPA for 30 – 90days and approximately 77%, for samples exposed to soil at 0%LBPA to 12%LBPA for 30 – 90days (see Table A.10 and A.11). Some fluctuations were observed in the tensile strength values; from 12 MPa (at 6%LBPA) to 14 MPa with approximately 17% increase (at 9%LBPA) after 30days, 12 MPa (at 9%LBPA) to 14 MPa approximately 17% (at 12%LBPA) after 60days, and finally from 6 MPa (at 6%LBPA) to 12 MPa (at 12%LBPA) after 90days exposure to natural weather. The same trend was also observed in increased tensile strength values at 6%LBPA for the entire period of exposure to soil. This indicated that there were some degree of interactions between the particle and the polymer matrix of the composite which might be responsible for the anomalous increase in tensile strength value. This agrees with earlier report (Shenoy and D'melo, 2007).

The tensile strength and modulus of non-degraded samples were enhanced with particle loading. This might be due to increased surface area that is possible from fine particles compared to large ones as reported elsewhere (Oladele and Adewole, 2013). Except for 3%LBPA (tensile strength) and 9%LBPA (modulus of elasticity) which exhibit decrease in property probably due to poor interfacial adhesion between the matrix and reinforcement as established earlier (Abdul Khalil, *et al.*, 2010).

However, atmospheric effect due to natural weathering and the effect of water absorption due to soil burial might be responsible for the changes in mechanical properties of the polyester/nano-LBPA composites. These changes might have occurred due to property and structural changes in the matrix phase, reinforcement and the interface between them as established (Rashdi *et al.*, 2010).

4.4 Flexural Properties

The flexural strength and flexural modulus behaviour of the test samples before and after degradation are presented in Figures 4.7 – 4.10.

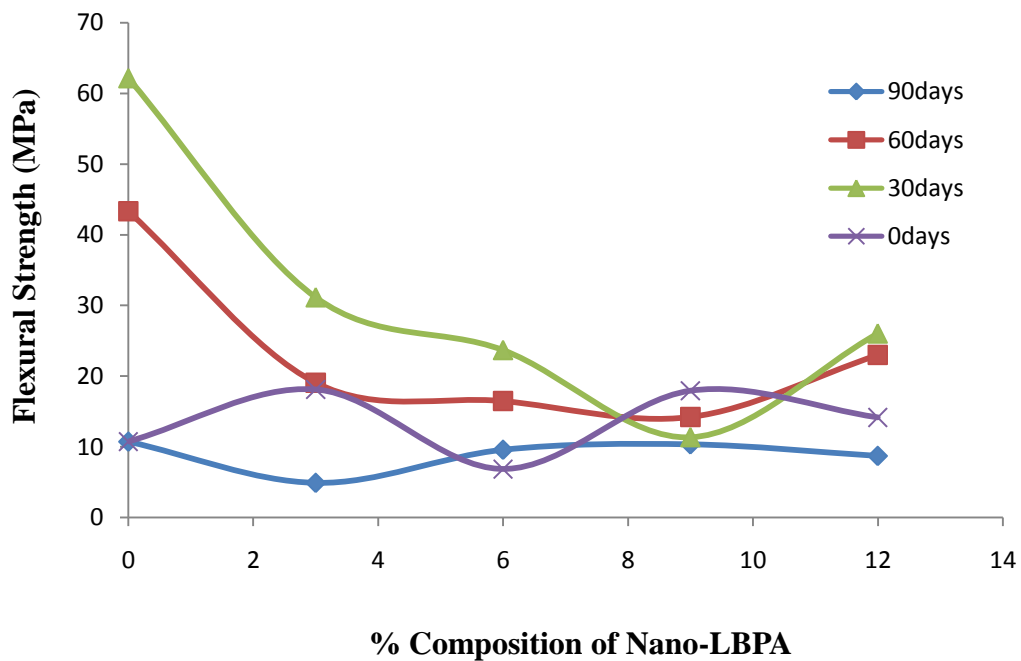


Figure 4.7: Flexural strength profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

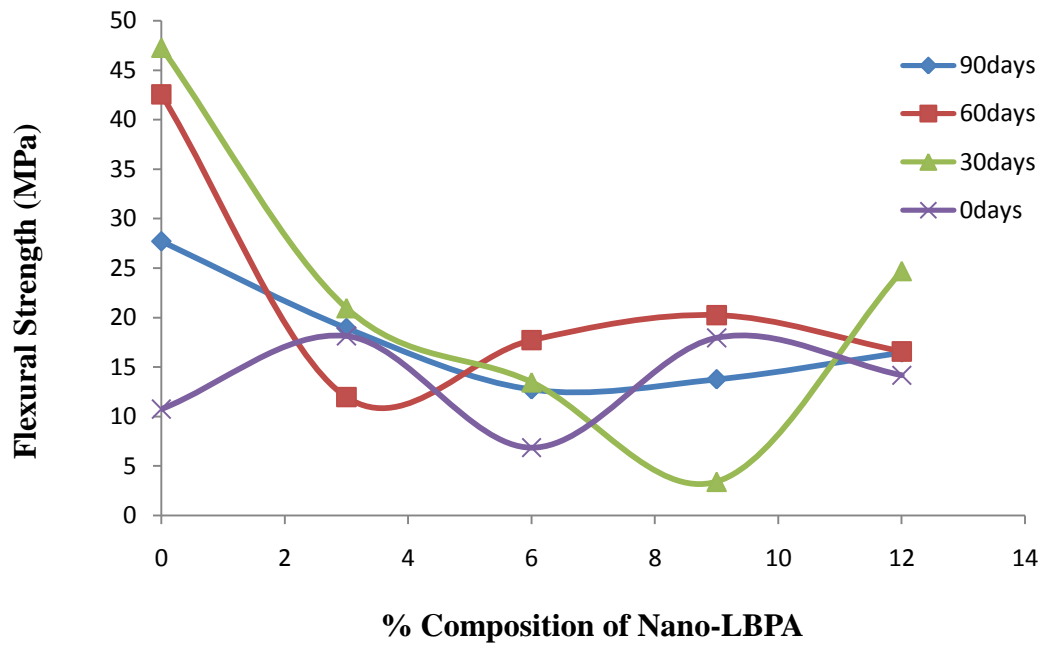


Figure 4.8: Flexural strength profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.

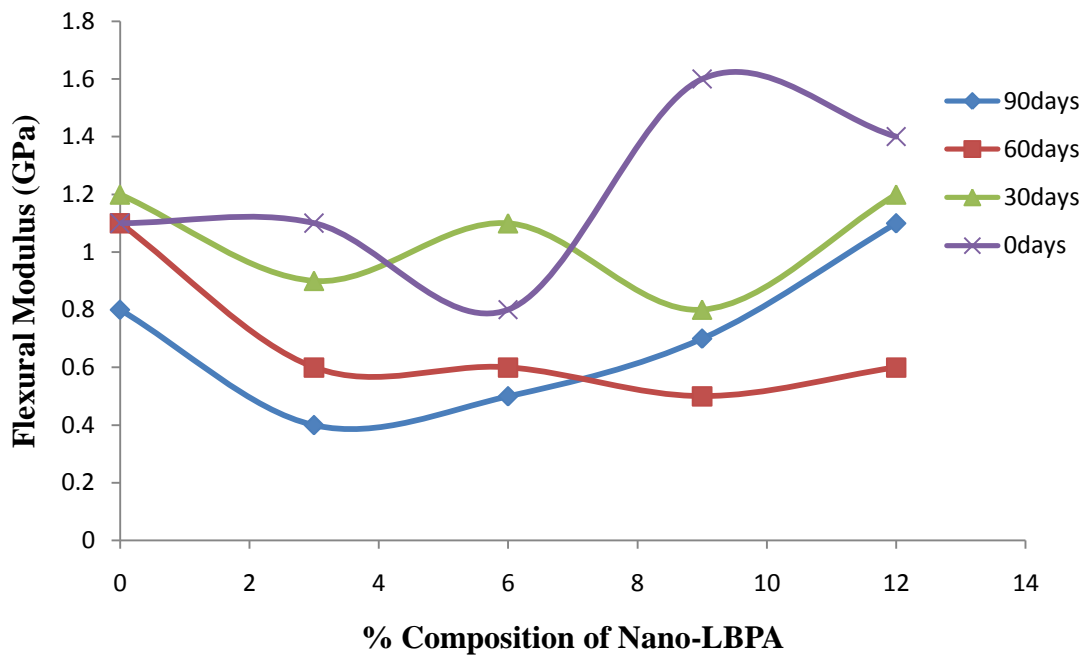


Figure 4.9: Flexural modulus profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

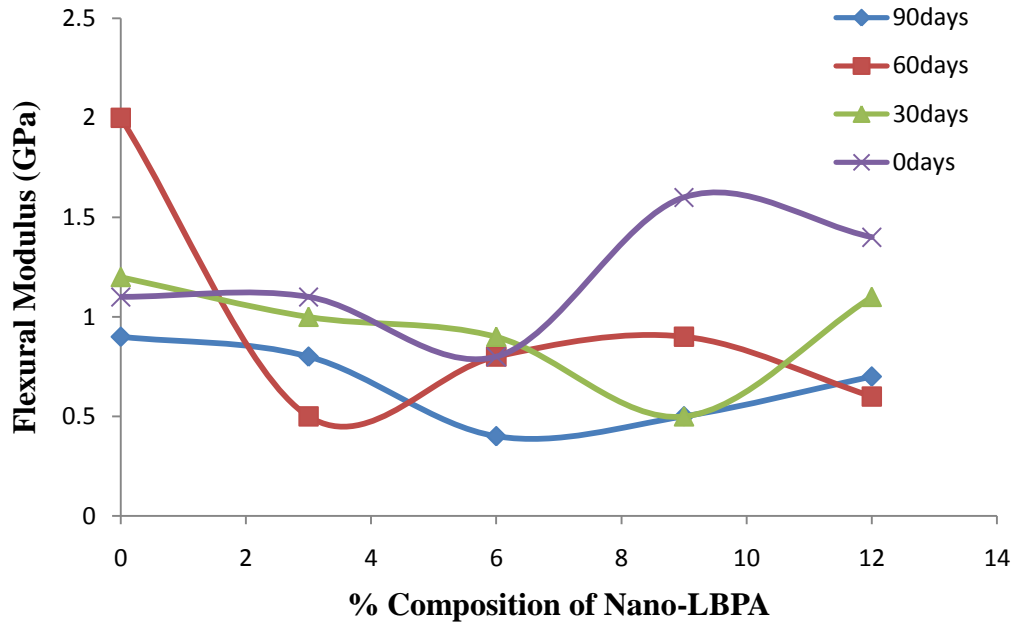


Figure 4.10: Flexural modulus profile of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.

The flexural strength decreased with an increase in LBPA addition from 62.13 MPa (at 0%LBPA) after 30days to 8.73 MPa (at 12%LBPA) – approximately 86% reduction after 90days exposure to weather; with their respective modulus found to be 1.2 GPa to 1.1 GPa – approximately 8% (see Figure 4.9). The lowest flexural strength and flexural modulus value of 4.92 MPa and 0.4 GPa was obtained at 3%LBPA after 90days exposure to natural weather. Similarly, from Figure 4.8, the flexural strength of the polymer composite decreased with increased LBPA addition. The percentage reduction was 65% after exposure to soil at 0%LBPA, with flexural strength value of 62.13 MPa (after 30days) and dropped to 8.73 MPa (after 90days) at 12%LBPA, with modulus value of 1.2 GPa to 1.1 GPa, respectively. The lowest flexural strength value of the composite samples, exposed to soil, was observed to be 3.42 MPa at 9%LBPA after 30days; on the contrary, the lowest flexural modulus was observed to be at 6%LBPA after 90days (see Table A.17). The decrease in the flexural strength of the composites can be explained on the basis of agglomerate formation; the presence of these agglomerates

increased the flaws in the composite. The flaws became larger in size and wetting of the filler by the matrix phase occurred, thus forming the voids between the filler and the matrix polymer; these accelerated the rates of water absorption and caused more damage to the composite samples (AbdulKhalil *et al.*, 2010; Ana *et al.*, 2004 and Ismail *et al.*, 2003). A significant increase in flexural strength values was observed for composite samples exposed to natural weather for 30days at 9%LBPA which increase from 11.36MPa to 26.02 MPa at 12%LBPA; 60days at 9%LBPA which increase from 14.24 MPa to 23.00 MPa at 12%LBPA and finally for 90days at 6%LBPA which increase from 9.60 MPa to 10.37 MPa at 9%LBPA. Their modulus value was observed to be 0.8 GPa to 1.2 GPa; 0.5 GPa to 0.6 GPa and 0.5 GPa to 0.7 GPa respectively (see Table A.16). Equally, increase in flexural strength value was observed for test samples exposed to soil for 30days (at 9%LBPA) which increase sharply from 3.42 MPa to 24.71 MPa (at 12%LBPA); with rise in flexural modulus from 0.5 GPa to 1.1 GPa; similarly, after exposure for 60days at 6%LBPA, there was an increase from 17.71 MPa to 20.24 MPa at 9%LBPA with approximately 13% increase in modulus value (see Table A.17) before falling back at 12%LBPA (16.57 MPa). The results obtained show that pure polyester samples exhibit the highest flexural strength behaviour due to the matrix properties which displayed more ductility than the test composite samples. The addition of natural particulate filler to the polymer matrix has increased the degradation properties of the matrix and has also increased the stiffness of the polymer matrix composite, thus reducing the flexibility of the composite (see Table A.16 and A.17). The degradation can also be due to combined effect of microorganism and atmospheric pressure.. The flexural strength and flexural modulus of non-degraded samples exhibit an increase in value from 10.75 MPa at 0%LBPA to 14.17 MPa at 12%LBPA and 1.1 GPa at 0% to 1.4 GPa at 12%LBPA. Similar result had been reported earlier (Oladele and Adewole, 2013). The lowest values were observed to be at 6%LBPA for both strength and

flexural modulus. It is known that good bonding increases the stiffness of a material but, at the same time, decreases the impact strength or toughness of the materials. This is in accordance with the report elsewhere (AbdulKhalil *et al.*, 2010).

4.5 Hardness

Figures 4.11 and 4.12 show the hardness profile of the nano-LBPA – polyester matrix composite at different LBPA addition after exposure to natural weather and soil for 30, 60 and 90days.

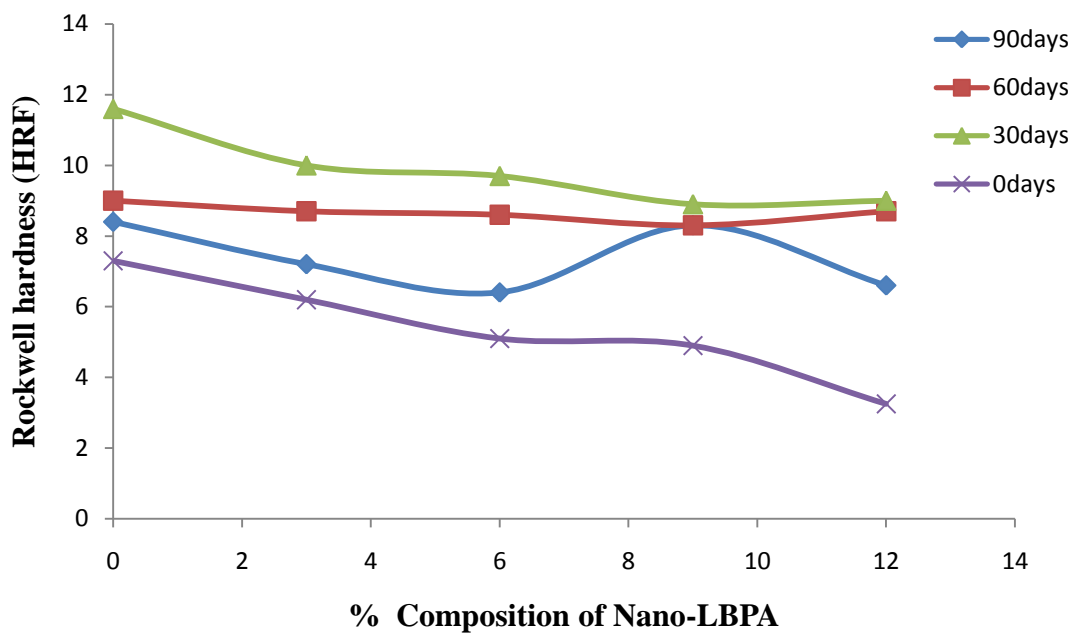


Figure 4.11: Hardness profile of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

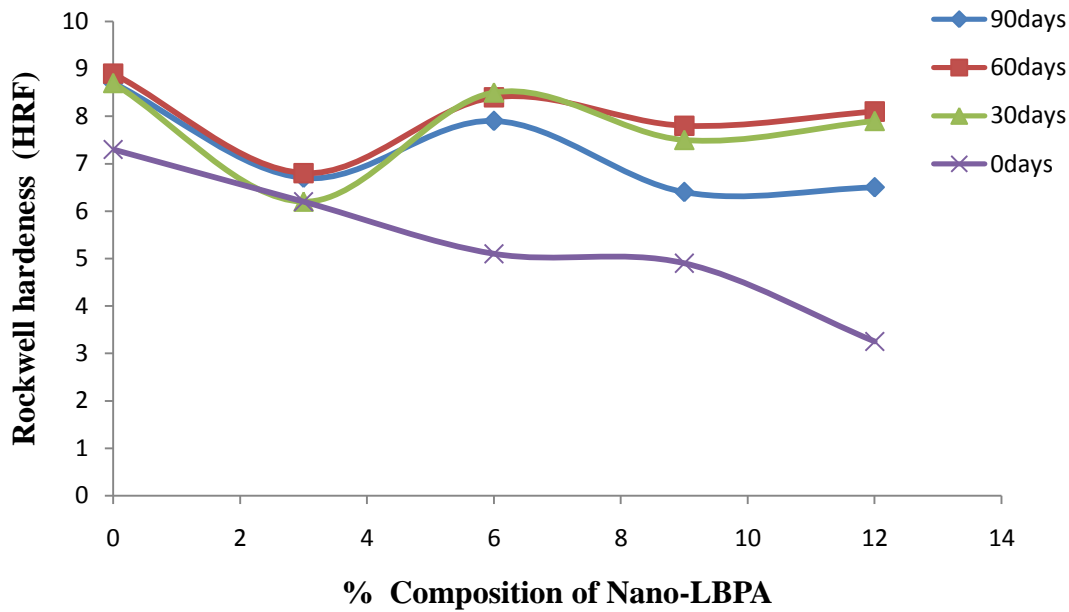


Figure 4.12: Hardness profile of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.

In Figure 4.11, the minimum hardness value of 6.4HRF (at 6%LBPA for 90days) was obtained after exposure to natural weather, and a maximum value of 11.6 HRF (at 0%LBPA for 30days). It can also be seen that there is a fluctuation in the hardness values of the test samples. The pure polyester samples (see Appendix A) had the highest hardness values for the entire period of exposure to soil and weathering compared to the composite samples. This might be due to the degradation of the composite after been attacked by microorganism and atmospheric pressure. This is similar to earlier report (Facca *et al.*, 2006 and Kim *et al.*, 2006). Decrease in hardness value with increased percentage by weight of reinforcement was observed for non-degraded sample. This agrees with an earlier report (Shehu *et al.*, 2014). The general reduction in mechanical properties of the polyester/nano-LBPA composite can be attributed to the degradable nature of the filler used.

4.6

Water Absorption

The percent water absorption of the polyester/Nano-LBPA composite samples at volume fraction of 0, 3, 6, 9 and 12%LBPA was computed using equation 3.1.

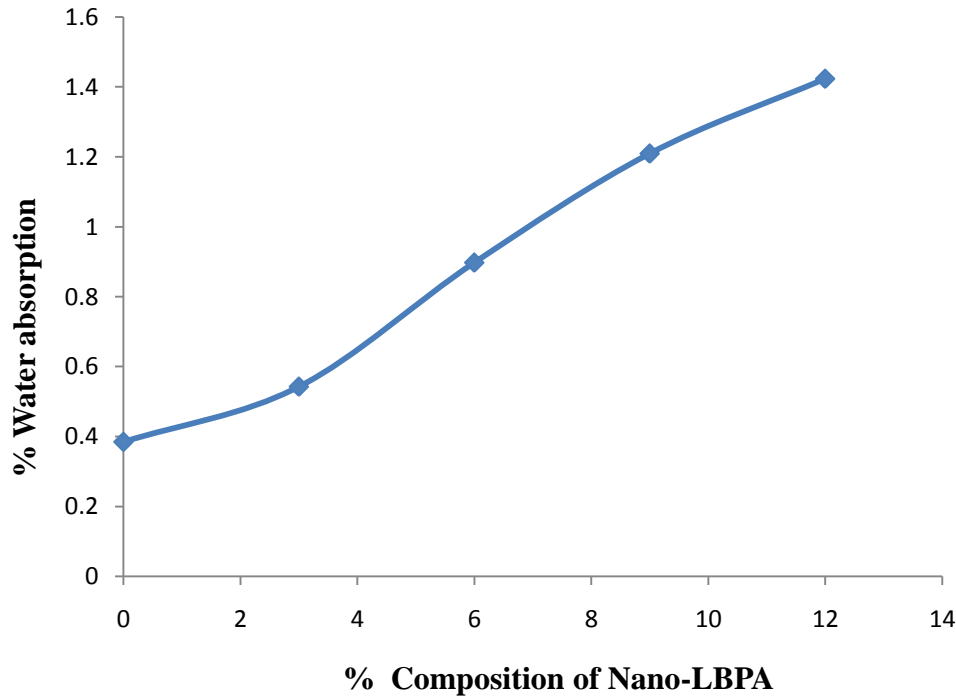


Figure 4.13: Water absorption profile of polyester/Nano-LBPA composite after 24hour

Figure 4.13 shows the percentage of weight gained as a function of time for these test samples. From the curve, it could be deduced that the water absorption increased as the volume fraction of LBPA increase for all test composite samples. This phenomenon can be explained by considering the water absorption characteristics of natural fillers, when the composite is exposed to moisture, the hydrophilic nature of the reinforcement makes it swell. As a result, weight gain in the composite samples was observed. The attack of the composite by water molecules resulted in debonding the matrix from the reinforcement. This is in accordance with earlier research (Dhakal *et al.*, 2007) showing an increased weight and micro-cracking of the composite as a result of sorption characteristics of the reinforcement.

4.7

Weight Loss

The percentage weight losses of different test samples (composite) were computed using equation 3.2. Figures 4.14 – 4.17 showed the trends in the weight losses of the samples.

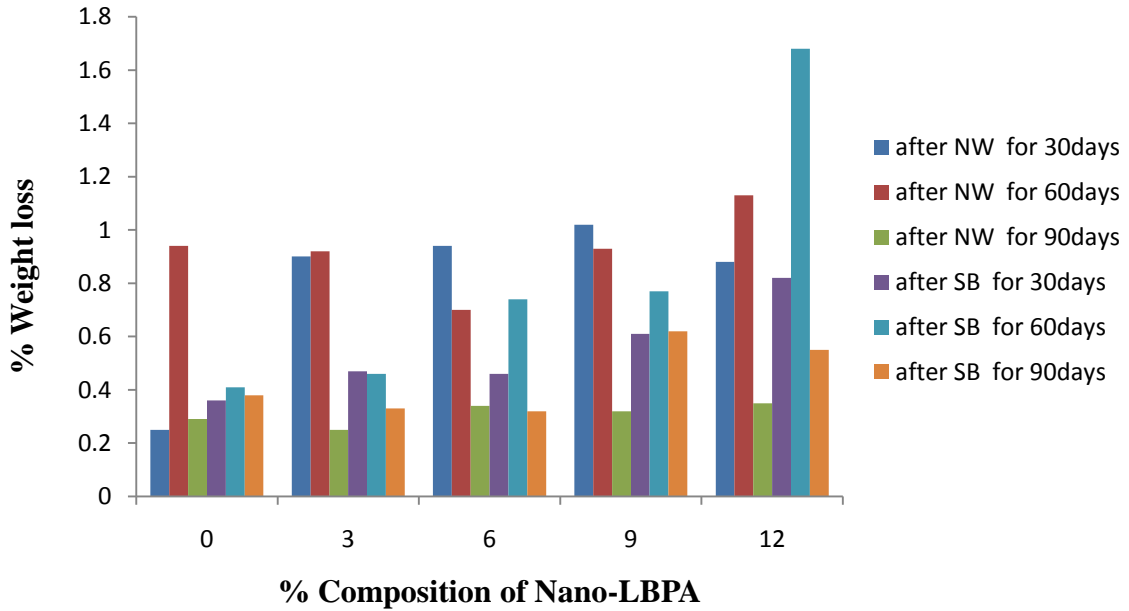


Figure 4.14: Weight loss profile of impact test samples after degradation.

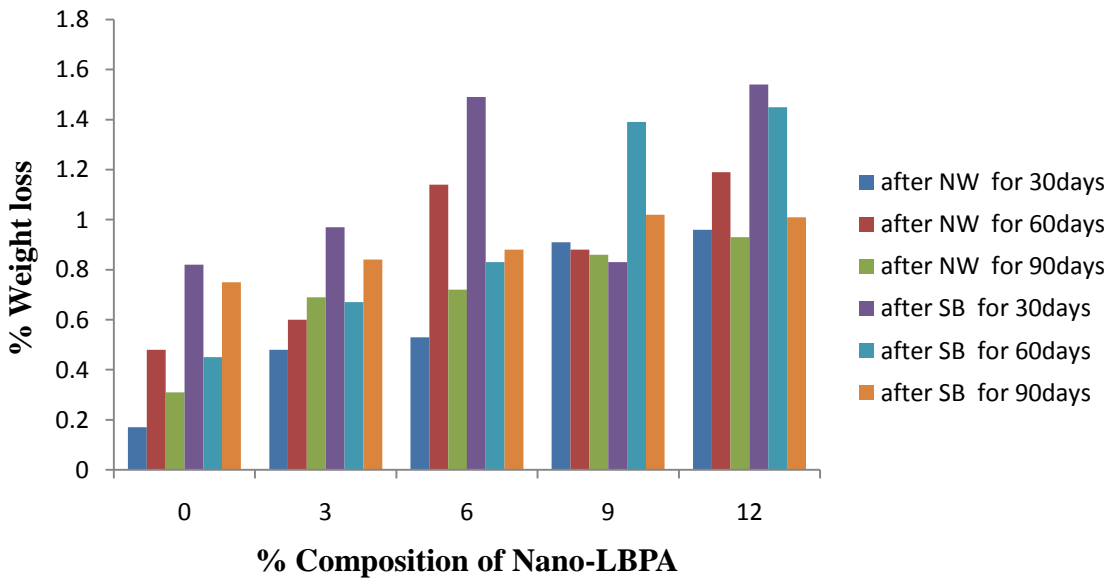


Figure 4.15: Weight loss profile of tensile test samples after degradation.

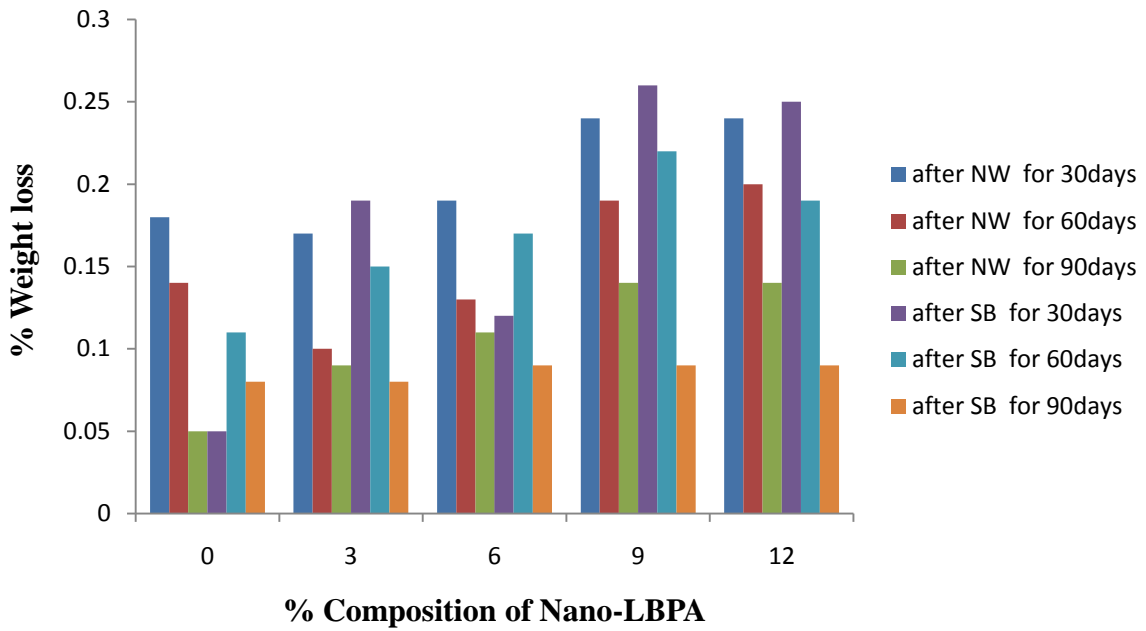


Figure 4.16: Weight loss profile of flexural test samples after degradation.

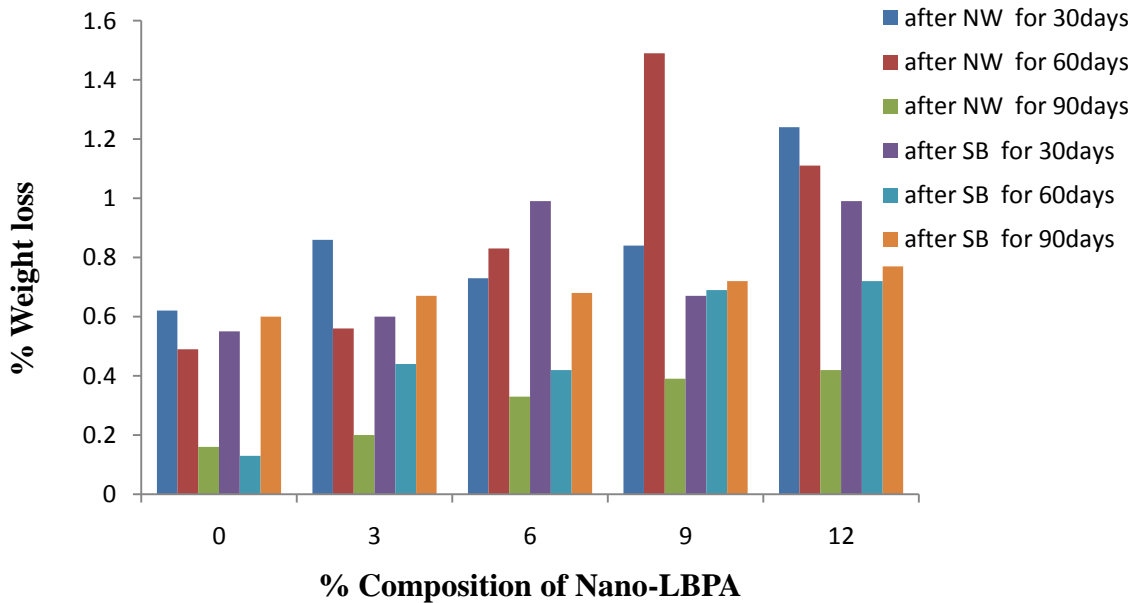


Figure 4.17: Weight loss profile of hardness test samples after degradation.

It was generally observed that the samples showed progressive weight losses with increase in LPBA reinforcements. For tests samples exposed to soil for 30 – 90days (at 0%LBPA –

12%LBPA), the percentage increase in weight loss of 0.36% - 0.55% for impact tests samples, 0.82% -1.01% for tensile test samples, 0.05% - 0.09% for flexural test samples and 0.55% - 0.77% for hardness test samples were attained. Similarly, the percentage weight losses were observed to increase from 0.25% - 0.35% and 0.17% - 0.93% for impact and tensile tests samples exposed to natural weather for 30 – 90days. For the flexural and hardness test samples, their percentage weight loss were found to decrease from 0.18% - 0.14% and 0.62% - 0.42% after weathering at 0%LBPA – 12%LBPA for 30 – 90days. The lowest percentage weight loss values was observed to be 0.25% after exposure period of 30days at 0%LBPA and 90days at 3%LBPAfor impact test samples, 0.17%after exposure period of 30days at 0%LBPAfor tensile test samples, 0.05% after 90days exposure at 0%LBPAfor flexural test samples and 0.20%for exposure period of 90days at 3%LBPAfor hardness test samples exposed to natural weather.

The tests samples buried in soil displayed a reduced percentage weight loss values after exposure period of 30 – 90days; 0.32% was obtained at 6%LBPAafter 90days for impact test samples, 0.45% at 0%LBPAafter 60days for tensile test samples, 0.05% at 0%LBPAafter 30days for flexural test samples and 0.13% at 0%LBPAfor 60days exposure to soil. It was also observed,however, that the percentage weight loss was prominent for 12%LBPA samples. This might be attributed to the increase in water uptake of the composite samples which could likely cause swelling and deterioration of the composite. The activities of microorganisms in the soil and the hydrophilic nature of LBPA that has the tendency to undergo swelling and shrinkage during weathering could have contributed to the reduced samples masses and lowered mechanical properties as reported (AbdulKhalil *et al.*, 2010).

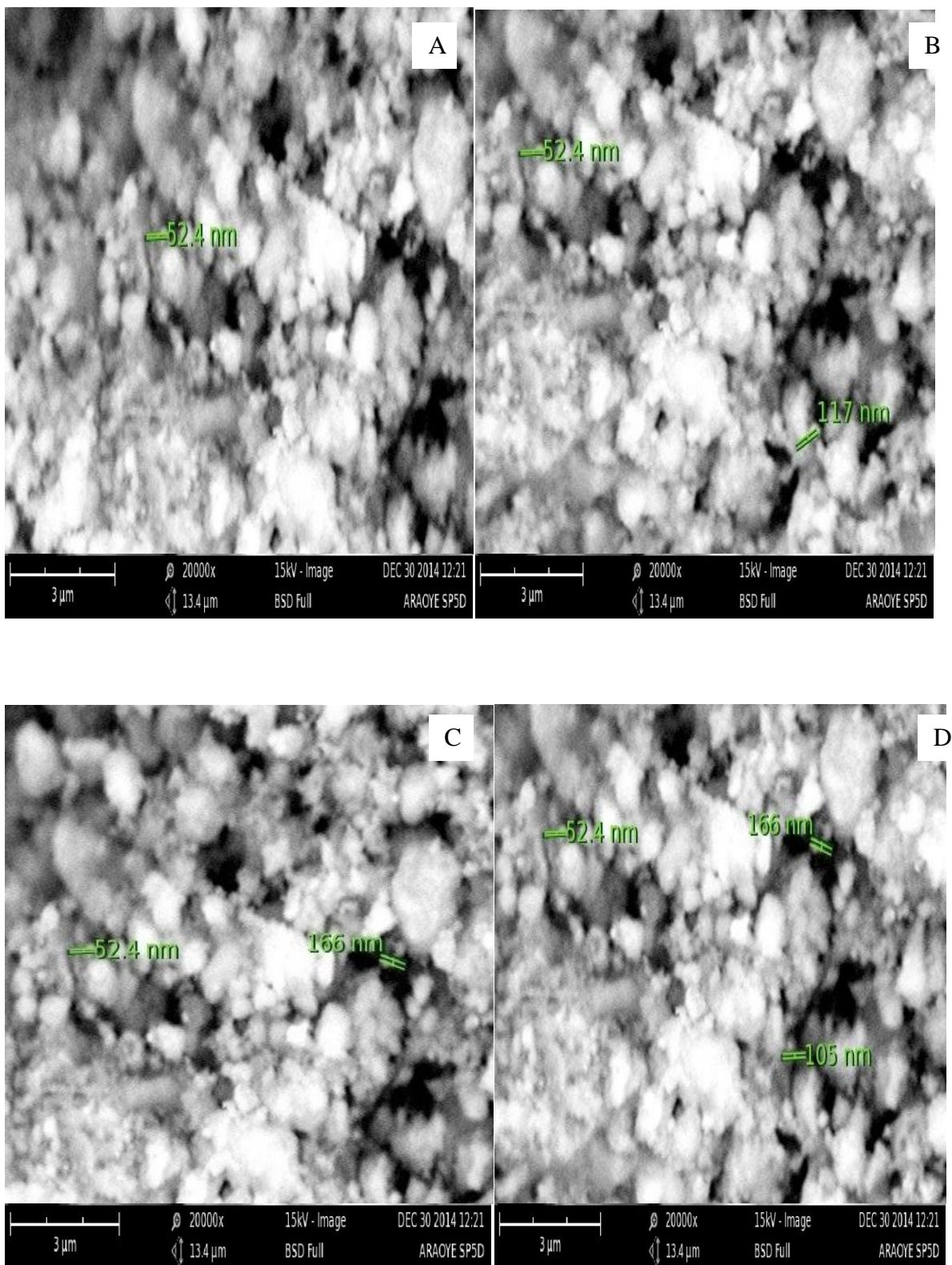


Plate I: SEM micrographs of the Nanoparticles developed from LBPA particle. A, B, C and D shows the particle size at different agglomerate formed.

The structural morphology and size of the particle were analyzed by Scanning Electron Microscope (SEM). In Plate I, SEM micrograph at 20000x magnifications shows a shaped particle of 52.4nm minimum diameter indicating that a nanoparticle sized LBPA was achieved in this study. Although these nano-sized particles were noticed to be irregular in shape; this irregularity in shape of the particles might be attributed to the formation of agglomerates by the particles which could have poorly affected the properties of the polyester composite samples. Equally, it has been stated that nanoparticles in an agglomerate state, might behave as larger particles, depending on the size of the agglomerate (Cristina *et al.*, 2007).

4.9 Correlation between Properties and Microstructure of the Produced Nano-Composite

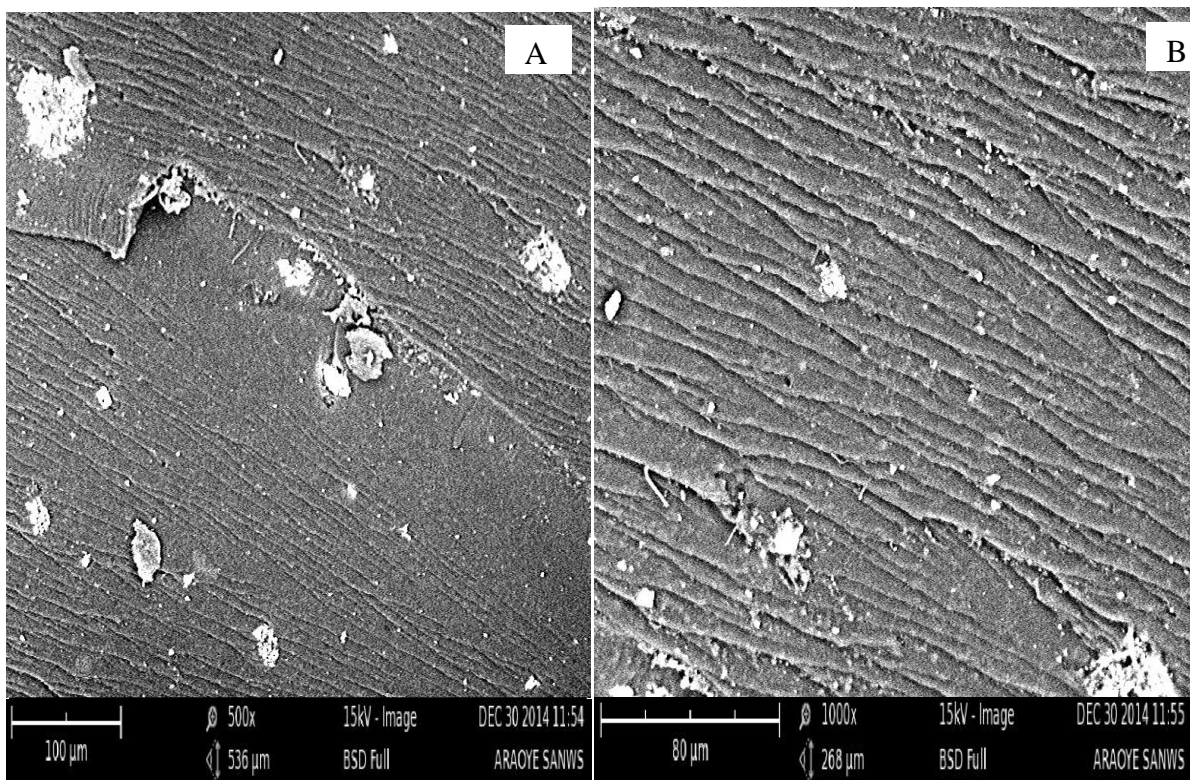


Plate II: SEM micrographs of the polyester/Nano-LBPA composite exposed to natural weather for 90 days (at 3% LBPA), showing a rough surface, (A) 500x (B) 1000x.

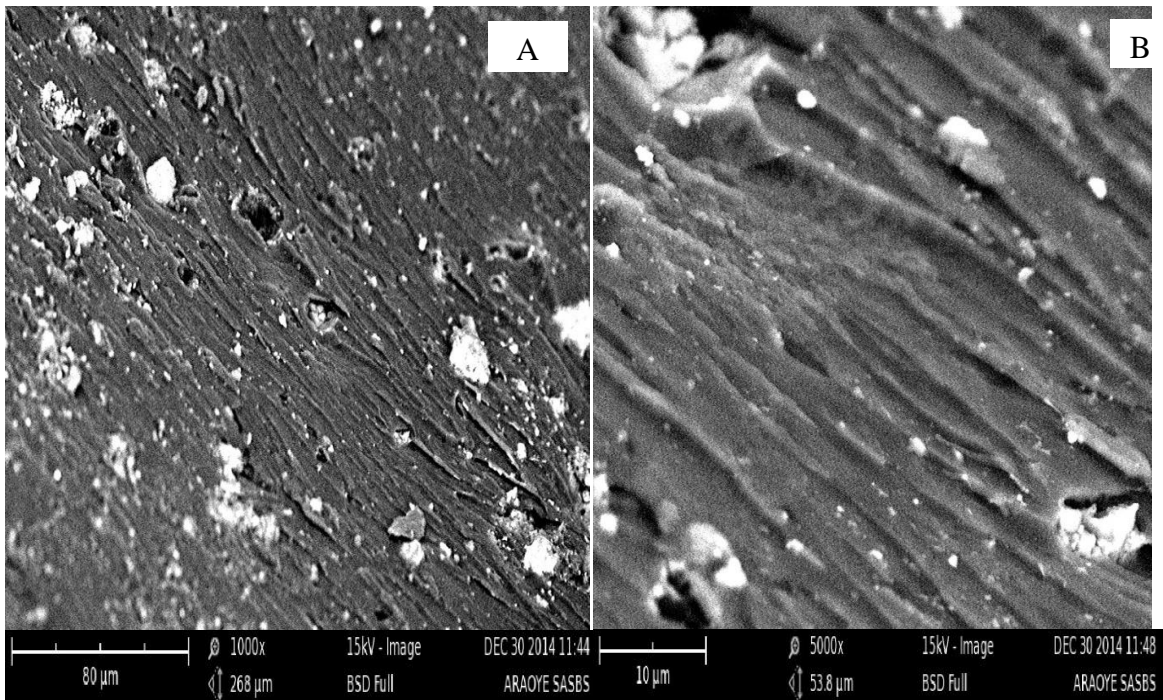


Plate III: SEM micrographs of the polyester/Nano-LBPA composite exposed to soil for 90days (at 9%LBPA), showing a rougher surface compared to Plate II, (A) 1000x (B) 5000x.

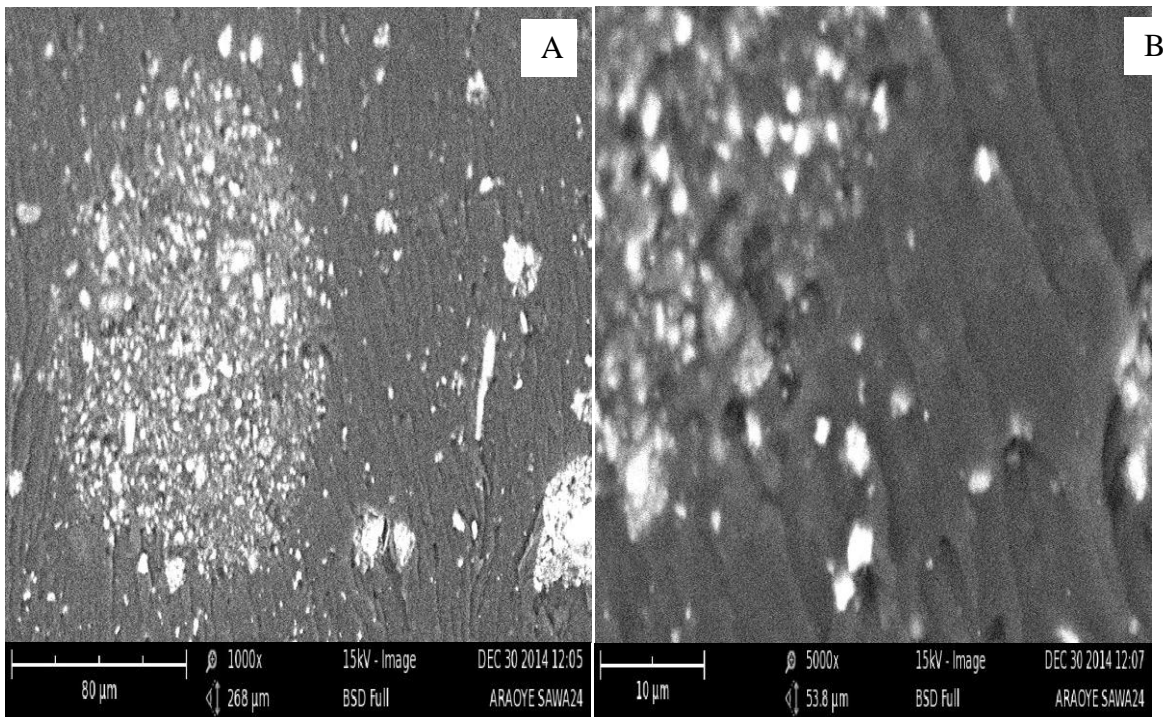


Plate IV: SEM micrographs of the polyester/Nano-LBPA composite after water absorption test for 24hours, showing agglomerate of particles within the matrix phases (A) 1000x (B) 5000x

The SEM micrographs in Plates II – IV can be used to interpret the impact, tensile, flexural, hardness, water absorption and wet losses of the composite samples.

PlateIV shows the micrograph of the composite after testing for water absorption (at 12%LBPA for 24hours). There were agglomerate of particles as observed from the microstructure; similar observation was noted in the micrograph of the composite samples exposed to soil and natural weather. This might be due to poor dispersion of particles in the matrix phases, leading to the formation of agglomerates. The presence of these agglomerates might have facilitated the high rate of water/moisture absorption by the composite; thus swelling pressures of the swelled particles would consequently cause micro-cracking particularly in the surrounding brittle polyester matrix as established elsewhere (Mat-Taibet *al.*, 2010).

The microstructure of the polyester/nano-LBPA composite fractured surface after degradation displayed a roughed surface (see Plate II andIII). The sample exposed to soil degradation (at 9%LBPA after 30days) – PlateIII, shows a rougher surface than that exposed to natural weather condition (at 3%LBPA after 90days); their pore sizes were noted to be an average of $760.29\mu\text{m}^2$ and $83.87\mu\text{m}^2$ respectively. The high pore size observed for the composite sample exposed to soil could be due to the removal of cellulose by the activities of microorganism in the soil as could be seen in PlateIII. The Presence of voids indicated the rate of biodegradation and the area attacked by microorganisms. LBPA is a hydrophilic material and has the tendency to undergo swelling and shrinkage due to absorption and de-sorption of moisture during weathering period. The LBPA particles that are not encapsulated by the polyester matrix could easily absorb moisture from the environment and from the rainfall – swelling pressures of the swelled LBPA particles occur. This might simultaneously cause micro-cracks particularly in the surrounding brittle polyester matrix, eventually leading to reduction in weight of the composite samples; thus lowered mechanical properties observed (Sapuan *et al.*, 2013; Mat-Taib *et al.*, 2010; Mehdi *et al.*, 2010). This corroborate with the results presented in section 5.1 – 5.6.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

In summary, the research work a study of the development, characterisation and degradability of polyester/nano-locust bean pod ash (LBPA)composite. Sol-gel technique was used to synthesize nanoparticles from LBPA; mechanical properties (impact, tensile, hardness and flexural strength) and physical (water absorption and weight loss) of the composite samples were evaluated. The composite samples were also subjected to degradation due to soil and natural weather to see the effect of these two conditions on the composite samples, after which the aforementioned mechanical tests as well as percentage weight loss of the samples were evaluated. Scanning Electron Microscope (SEM) was used to characterize the synthesized Nanosized LBPA particulates and test composites.The minimum average Particle size of the synthesized LBPA Nanoparticles was 52.4nm, which falls within the range of 1 – 100nm, the recommended particle size required for a material to be classified as Nanomaterial.

The mechanical properties of the control samples increased as the reinforcement was increased from 0%LBPA – 12%LBPA; the impact, tensile and flexural strengths increased from 0.03 – 0.37J/m, 4.30 – 6.84MPa and 10.75 – 14.17MPa respectively. The mechanical properties of buried and weathered samples decreased with increase in reinforcement (from 0%LBPA – 12%LBPA) and exposure time (90days). The impact, tensile, flexural and hardness values of the buried samples decreased from 0.04 – 0.023J/m, 32 – 10MPa, 47.27 – 16.47MPa and 8.7 – 6.5HRF indicating 43, 69, 65 and 25%,respectively. Similarly, there was a reduction in the impact, tensile, flexural and hardness values of the weathered samples from 0.05 – 0.023J/m, 28 – 12MPa, 62.13 – 8.73MPa and 11.6 – 6.6HRF indicating 54, 57, 86 and 43%,respectively. It was noted that the composite became more susceptible to degradation with increase in

reinforcement. The swelling and shrinking of natural filler when exposed to natural weather and activities of microorganisms in the soil might have been responsible for the decrease in their properties. The rate of moisture absorption of the composite samples increased with increase in reinforcement; the highest value of 1.42% was obtained at 12%LBPA. The percentage weight losses for the impact, tensile, flexural and hardness tests samples after soil burial and weathering were respectively 0.55, 1.01, 0.09, 0.77% and 0.35, 0.93, 0.14, 0.42% after 90days of exposure. SEM examinations of the weathered and buried samples showed roughened surfaces with some voids and pits observed on the soil buried samples.

5.2

Conclusions

Based on the results obtained from this research, the following conclusions were drawn:

The study has successfully synthesized polyester/nano-locust bean pods ash composite with the particulate reinforcement having an average size of 52.4nm as revealed by scanning electron microscopy.

In addition, the nano-locust bean pods ash reinforcement has been able to increase the impact, tensile, flexural and hardness properties of the polyester composite with an optimal content of 6% by weight of LBPA. The study has also confirm that the develop composite is biodegradable and eco-friendly.

5.3

Recommendations

Based on the research carried out, the following recommendations are offered:

- i. LBPA could be utilized as biodegradable/ecofriendly filler in polymeric materials. The composite developed in this work could be used for structural applications where high loading requirement is not of paramount importance.
- ii. The effect of dispersing agents on the particles distribution should be investigated. The study period for degradation of the test composite should be increased to 12 – 18 months to see the effect of prolonged exposure. Suitability of other agricultural wastes by-products as reinforcement should also be investigated.
- iii. High resolution characterization tools such as Transmission Electron Microscope (TEM) should be used to further characterize the composite samples. Also, the thermal properties of the composite should be investigated.

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APPENDIX A

Table A.1: Impact strength (J/m) of polyester/Nano-LPBA composite subjected to weathered condition for 30, 60 and 90 days.

% composition of nano-LBPA	Impact strength, J/m		
	30days	60days	90days
0	50	40	35
3	40	30	25
6	23	30	23
9	25	35	22
12	22	25	23

Table A.2: Impact strength (J/m) of polyester/Nano-LBPA composite subjected to soil burial condition for 30, 60 and 90 days.

% composition of nano-LBPA	Impact Energy, J/m		
	30days	60days	90days
0	40	45	65
3	25	22	25
6	35	25	37
9	25	25	25
12	23	23	23

Table A.3: Impact strength values of non-degraded polyester/Nano-LBPA composite.

% composition of nano-LBPA	0	3	6	9	12
Impact (J/m)	30	35	45	37	37

Table A.4: Tensile strength values of polyester/Nano-LBPA composite subjected to weathered condition for 30 days.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	180	9.6	28
3	1250	9.2	14
6	275	8.4	12
9	600	8.4	14
12	600	6.6	11

Table A.5: Tensile strength values of polyester/Nano-LBPA composite subjected to weathered condition for 60 days.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	1210	27.3	26
3	682	22.5	16
6	616	20.6	13
9	627	18	12
12	704	15.8	14

Table A.6: Tensile strength values of polyester/Nano-LBPA composite subjected to weathered condition for 90 days.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	1250	12.8	25
3	688	16.5	14
6	275	9.3	6
9	475	8.9	10
12	525	12.8	12

Table A.7: Tensile strength values of polyester/Nano-LBPA composite subjected to soil burial for 30 days.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	1130	12.7	32
3	600	6.9	24
6	750	11.1	27
9	350	9	18
12	650	8.4	13

Table A.8: Tensile strength values of polyester/Nano-LBPA composite subjected to soil burial for 60 days.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	1110	25.6	25
3	920	23.7	15
6	858	31.5	16
9	418	21.9	12
12	682	33	9

Table A.9: Tensile strength values of polyester/Nano-LBPA composite subjected to soil burial for 90 days.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	975	14.6	21
3	940	12.1	13
6	725	11.8	17
9	688	9.2	14
12	450	12.2	10

Table A.10: Tensile modulus values of polyester/Nano-LBPA composite subjected to weathered for 30, 60, 90 days.

% composition of nano-LBPA	Tensile modulus (GPa)		
	30days	60days	90days
0	0.29	0.09	0.19
3	0.15	0.07	0.08
6	0.14	0.06	0.06
9	0.16	0.05	0.11
12	0.16	0.09	0.14

Table A.11: Tensile modulus values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60, 90 days.

% composition of nano-LBPA	Tensile modulus (GPa)		
	30days	60days	90days
0	0.35	0.09	0.15
3	0.23	0.06	0.11
6	0.25	0.05	0.14
9	0.20	0.05	0.10
12	0.15	0.03	0.08

Table A.12: Tensile strength values of non-degraded polyester/Nano-LBPA composite.

% composition of nano-LBPA	Maximum load (N)	%Elongation	Tensile strength (MPa)
0	198	6	4.30
3	54	6	1.29
6	216	12	4.84
9	204	14.7	4.17
12	306	13.8	6.84

Table A.13: Tensile modulus values of non-degraded polyester/Nano-LBPA composite.

% composition of nano-LBPA	0	3	6	9	12
Tensile modulus (GPa)	0.02	0.03	0.05	0.04	0.07

Table A.14: Flexural strength values of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

% composition of nano-LBPA	Flexural strength (MPa)		
	30days	60days	90days
0	62.13	43.33	10.75
3	31.14	19.09	4.92
6	23.68	16.49	9.60
9	11.36	14.24	10.37
12	26.02	23.00	8.73

Table A.15: Flexural strength values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.

% composition of nano-LBPA	Flexural strength (MPa)		
	30days	60days	90days
0	47.27	42.56	27.71
3	20.96	11.96	18.94
6	13.47	17.71	12.75
9	3.42	20.24	13.77
12	24.71	16.57	16.47

Table A.16: Flexural modulus values of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

% composition of nano-LBPA	Flexural modulus (GPa)		
	30days	60days	90days
0	1.2	1.1	0.8
3	0.9	0.6	0.4
6	1.1	0.6	0.5
9	0.8	0.5	0.7
12	1.2	0.6	1.1

Table A.17: Flexural modulus values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.

% composition of nano-LBPA	Flexural modulus (GPa)		
	30days	60days	90days
0	1.2	2.0	0.9
3	1.0	0.5	0.8
6	0.9	0.8	0.4
9	0.5	0.9	0.5
12	1.1	0.6	0.7

Table A.18: Flexural strength values of non-degraded polyester/Nano-LBPA composite.

% composition of nano-LBPA	0	3	6	9	12
Flexural strength (MPa)	10.75	18.13	6.86	17.95	14.17

Table A.19: Flexural modulus values of non-degraded polyester/Nano-LBPA composite.

% composition of nano-LBPA	0	3	6	9	12
Flexural strength (GPa)	1.1	1.1	0.8	1.6	1.4

Table A.20: Hardness values of polyester/Nano-LBPA composite subjected to weathered condition for 30, 60 and 90 days.

% composition of nano-LBPA	Average Hardness values, HRF		
	30days	60days	90days
0	11.6	9	8.4
3	10	8.7	7.2
6	9.7	8.6	6.4
9	8.9	8.3	8.3
12	9	8.7	6.6

Table A.21: Hardness values of polyester/Nano-LBPA composite subjected to soil burial for 30, 60 and 90 days.

% composition of nano-LBPA	Average Hardness values, HRF		
	30days	60days	90days
0	8.7	8.9	8.7
3	6.2	6.8	6.7
6	8.5	8.4	7.9
9	7.5	7.8	6.4
12	7.9	8.1	6.5

Table A.22: Hardness values of non-degraded polyester/Nano-LBPA composite.

% composition of nano-LBPA	0	3	6	9	12
Hardness(HRF)	7.3	6.2	5.1	4.9	3.25

Table A.23: Water absorption Values of polyester/Nano-LBPA Composite after 24hours.

% composition of nano-LBPA	Initial Weight, W_1 (g)	Final Weight, W_2 (g)	% Water absorption
0	7.273	7.301	0.385
3	7.368	7.408	0.543
6	7.795	7.865	0.898
9	8.014	8.111	1.210
12	8.497	8.618	1.424

Table A.24: Percentage weight loss values of impact test samples after degradation.

% composition of nano-LBPA	After NW for 30days	After NW for 60days	After NW for 90days	After SB for 30days	After SB for 60days	After SB for 90days
0	0.25	0.99	0.29	0.36	0.41	0.38
3	0.90	0.92	0.25	0.47	0.46	0.33
6	0.94	0.30	0.34	0.46	0.74	0.32
9	1.02	0.93	0.32	0.61	0.77	0.62
12	0.88	1.13	0.35	0.82	1.68	0.55

NW = natural weather, SB = soil burial

Table A.25: Percentage weight loss values of tensile test samples after degradation.

% composition of nano-LBPA	After NW for 30days	After NW for 60days	After NW for 90days	After SB for 30days	After SB for 60days	After SB for 90days
0	0.17	0.48	0.31	0.82	0.45	0.75
3	0.48	0.60	0.69	0.97	0.67	0.84
6	0.53	1.14	0.72	1.49	0.83	0.88
9	0.91	0.88	0.86	0.83	1.39	1.02
12	0.96	1.19	0.93	1.54	1.45	1.01

NW = natural weather, SB = soil burial

Table A.26: Percentage weight loss values of flexural test samples after degradation.

% composition of nano-LBPA	After NW for 30days	After NW for 60days	After NW for 90days	After SB for 30days	After SB for 60days	After SB for 90days
0	0.18	0.14	0.05	0.05	0.11	0.08
3	0.17	0.10	0.09	0.19	0.15	0.08
6	0.19	0.13	0.11	0.12	0.17	0.09
9	0.24	0.19	0.14	0.26	0.22	0.09
12	0.24	0.20	0.14	0.25	0.19	0.09

NW = natural weather, SB = soil burial

Table A.27: Percentage weight loss values of hardness test samples after degradation.

% composition of nano-LBPA	After NW for 30days	After NW for 60days	After NW for 90days	After SB for 30days	After SB for 60days	After SB for 90days
0	0.62	0.49	0.16	0.55	0.13	0.60
3	0.86	0.56	0.20	0.60	0.44	0.67
6	0.73	0.83	0.33	0.99	0.42	0.68
9	0.84	1.49	0.39	0.67	0.69	0.72
12	1.24	1.11	0.42	0.99	0.72	0.77

NW = natural weather, SB = soil burial