



Biofillers in Natural Rubber Biotechnology Approach to Rubber Degradation

Dr. Raymond Dominic Uzoh

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Exceller Open



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Declaration

I hereby declare that this thesis was written by me and it is a record of my own research work. It has not been presented before in any previous application for a higher degree. All references cited have been duly acknowledged.

Dedication

I dedicate this research work to God the Father almighty, the creator with whom nothing is impossible, the God of all flesh, to the Lord Jesus Christ, the great high priest, shepherd of my soul and the Holy Spirit, my comforter, helper and advocate.

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Abstract

The observation of the International Agency for Research on Cancer (IARC) by rating carbon black as IARC classification 2B – possibly carcinogenic to humans and definitely carcinogenic to animals and the high costs of carbon black filler being derived from crude oil and natural gas has necessitated a search for alternative reinforcing fillers for the rubber industry that are cheap, renewable, non-toxic and abundant in nature. Moreover, the reckless burning of used automobile tyres and their disposal at refuse dumps without any means of biodegradation pose serious environmental disposal problems in recent times. In view of the above development, starch fillers were extracted from five plant sources, namely: Polynesian arrow root (amora), cassava, cocoyam, sweet potato and yam and their particle size, pH, amylose and amylopectin percentage composition were determined. The starch/ natural rubber composite was prepared by directly mixing and co-coagulating rubber latex and starch paste (gelatinized starch) with an aqueous electrolyte, Calcium Chloride and thereafter compounded in a two-roll mill according to American Society of Testing and Materials (ASTM) standard method, D3184-80. The starch/natural rubber blend was cured by Sulphur vulcanization and accelerators system according to ASTM standard. The trial batch starch fillers revealed that the best volume percentage for filler addition ranges from 20phr to 30phr. The formulated starch/natural rubber composite was characterized by Instron Universal testing machine (UTM) for tensile properties, x-ray diffraction analysis for crystallinity property, Fourier transform infra-red (FTIR) for associated functional groups, swelling test for degree of crosslink density (Vc) and differential scanning calorimetry (DSC) for glass transition temperature (Tg). X-ray diffraction revealed that the formulated biopolymer is a semi-crystalline material, while FTIR analysis showed the presence of the carbon-carbon double bond of cis-1, 4-polyisoprene at stretching band, 1644.5cm⁻¹, O-H stretches for free hydroxyl and O-H bonded at 3865cm⁻¹ – 3701cm⁻¹ and 3476 – 3426cm⁻¹, indicating the presence of starch molecule in the biopolymer. The DSC analyzer revealed that the glass transition temperatures of the rubber composites shifted to higher temperatures in the range of 85°C – 98°C. Swelling tests gave a set of increasing values of degree of crosslink density (Vc) as evidence of interfacial adhesion between starch filler and rubber matrix. The formulated starch/natural rubber composite was subjected to microbial degradation by isolated Bacillus megaterium, Bacillus sp. and Pseudomonas aeruginosa in a mixed culture. Biodegradation activity is maximum with the Fo rubber specimen (cured rubber without starch). The Schiff's reagent test indicated the presence of aldehyde groups in the residue of the inoculated starch/rubber specimens. Amongst the studied fillers, amora starch (extracted from a wild root crop) can partially replace carbon black as a natural rubber filler with reduced production cost and health risk, hence providing an alternative source of starch filler currently being sourced from maize and cassava in the rubber industry. This research has also introduced biotechnological process as a tool for rubber waste control and management.

Keywords: Natural rubber, gelatinized starch, fillers, degradation, compounding, latex, coagulation

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List of Acronyms and Abbreviations

ASTM - American Society of Testing and Materials
FTIR - Fourier Transform Infra-red
UTM - Universal Testing Machine
IARC - International Agency for Research on Cancer
DSC - Differential Scanning Calorimeter
MSM - Mineral Salt Medium
PDA - Potato Dextrose Agar
SEM - Scanning Electron Microscopy
XRD - X-Ray Diffraction
PFRR - Polymers from Renewable Resources
CFU - Colony Forming Unit
MPa - Megapascals
PLA - Polylactic Acid
NRL - Natural Rubber Latex
PBSA - Polybutylene Succinate Adipate
HCA - Hydroxy Carboxylic Acid
PBS - Polybutylene Succinate
PCL - Polycaprolactone
PBAT - Polybutylene Adipate Coterephthalate
PVA - Polyvinyl Alcohol
PGA - Polyglycolic Acid
USP - United States Patent
IRHD - International Rubber Hardness Degree
NRC - Natural Rubber/Cassava Starch
NRCO - Natural Rubber/Cocoyam Starch
NRP - Natural Rubber/Potato Starch
NRY - Natural Rubber/Yam Starch
NRCB - Natural Rubber/Carbon Black

1 | Introduction

1.1. Background of the Study

Although in the past, synthetic polymers were extensively used for multipurpose applications because of their satisfactory mechanical and thermal properties, their lack of biodegradability has recently complicated and discouraged their use (Albertsson & Karlsson, 1994; Wool, 1995). On the other hand, natural polymers (cellulose, starch, protein, natural rubber) though usually endowed with inherent biodegradability, have inferior mechanical properties and present processability problems that hold them back from widespread use (Krochta *et al.*, 1994; Andrady, 1994).

To overcome these drawbacks, various methods such as copolymerization, compositing (composite formation) and blending are commonly used (Hamad *et al.*, 2014). The attempts to resort to blending natural polymers or synthetic polymers with other natural polymers, like fibres, starch, cellulose, etc., have become more widespread (Arvanitoyannis *et al.*, 1997). Polymer blending is a well-used technique whenever modification of properties is required because it has an easy and straightforward procedure and is a low-cost operation (Tadmor & Gogos, 1979). The usual target for preparing a novel blend of two or more polymers is not to change the properties of the components drastically but to capitalize on the maximum possible performance of the composite. On several occasions, the initial dispersion of the blend components is further promoted by cross-linking, creation of interpenetrating networks, mechanical interlocking of components and use of ‘compatibilizing agents’ to ensure that no demixing will occur at a later stage (Tadmor & Gogos, 1979; Griffin, 1994). In some situations, the fabrication of materials containing both biodegradable and non-biodegradable polymers can be an effective method to reduce the total amount of polymer waste that cannot be degraded in nature (Hamad *et al.*, 2014).

Nowadays, using biodegradable materials has become necessary to maintain global environmental and ecological balance. ‘Green’ composites offered a major solution to waste disposal problems associated with traditional petroleum-derived plastics (Kumar *et al.*, 2012). Conventionally, such plastics are manufactured from petroleum derivatives that are not degradable and persist in the environment long after their useful life. As a result, interest in the use of naturally degradable and/or biodegradable polymers for plastics manufacturing, particularly for use in agriculture, has grown considerably in recent years (Fukuda, 1992; Briassoulis, 2004). The development of biocomposites started in the late 1980s and most of the biodegradable polymers which are now available in the market do not yet satisfy each of the requirements for biocomposites (Kumar *et al.*, 2012).

An essential number of biodegradable polymers are derived from both synthetic and natural sources, but most of them are quite costly (Amass *et al.*, 1998; Averous *et al.*, 2000). Examples of some commercial biodegradable polymers include the following:

- Polybutylene succinate adipate (PBSA),
- Hydroxycarboxylic acid (HCA),
- Polylactic acid (PLA),
- Polybutylene succinate (PBS),
- Polybutylene adipate coterephthalate (PBAT),
- Polycaprolactone (PCL),
- Thermoplastic starch (TPS),
- Polyhydroxybutyric acid (PHBA),
- Poly-3-oxybutyrate (P-3-OB),
- Polyglycolic acid (PGA),
- Polyvinyl alcohol (PVA)

Others are amylopectin, starch, amylose, chitin and chitosan, with wide applications in packaging material, agriculture, medical and pharmaceuticals.

According to John (2017) of Zion market research, Deerfield Beach, FL, global biodegradable polymer market was valued at around USD \$1.68 billion in 2014 and is expected to reach approximately

USD \$5.18 billion by 2020. Rising demand for biodegradable and bio-based products due to sustainable development policies and growing concern for the use of environmentally friendly products are the main drivers for the biodegradable polymer market. The escalating price of crude oil, which is the raw material for producing petroleum polymer, also helps drive the demand for biodegradable polymers (John, 2017). Moreso, rising end-user applications and economical raw material prices for biodegradable polymers are offering potential market opportunities in the years to come (John, 2017). World consumption of biodegradable polymers as of 2018 stood at USD \$1.1 billion, according to the specialty chemical research unit at HIS Markit Ltd, a London-based global information provider that was formed in 2016 when HIS Inc. and Markit Ltd merged. Consumption by region in 2018 is as follows:

- Western Europe, USD \$605 million (55%),
- Asia and Oceania, USD \$275 million (25%),
- North America USD \$209 million (19%) and
- Others USD \$11 million (1%) (Fortuna, 2018)

Growing environmental concerns have created an urgent need to develop new biodegradable materials that have comparable properties with today's polymeric materials at an equivalent cost. Using agricultural products in polymer applications is considered an interesting way to reduce surplus farm products and develop non-food applications (Averous *et al.*, 2000). Recently, attention has been increasingly devoted to biodegradable and plant-derived composites, which are now designated as 'green' composites (Takagi & Ichihara, 2004; Takagi, 2005) because of the strong demand for creating a resource-circulating society that poses no resource-shortage-related problems (Kumar *et al.*, 2012). One of the most commonly used approaches to create such degradable composites is to incorporate starch into degradable synthetic or natural polymers (Kim, 2012). Starch, a semi-crystalline polymer stored in granules as a reserve in most plants, is renewable, non-toxic and completely biodegradable with overwhelming abundance (Kim, 2012; Long *et al.*, 2006). It has received increased attention as a filler for composites (or as a component of polymer blends) because of its cost-effectiveness and high-volume availability (Kim, 2012). However, by itself, pure starch is not a good choice to replace petrochemical-based plastics because it is mostly water soluble, difficult to process and brittle when used without the addition of a plasticizer and its mechanical properties are very sensitive to moisture content (Long *et al.*, 2006). Blending two or more chemically and physically dissimilar polymers has shown the potential to overcome these difficulties (Ismail & Gamal, 2010; Ma *et al.*, 2008).

As a suitable polymer for use in blending with starch to ensure structural property modification, natural rubber latex (NRL) has many attractions (Rouilly *et al.*, 2004). It is a latex, which facilitates blending with starch and, indeed, with any particulate substance. Secondly, it is a renewable resource, can be biodegraded Linos and Steinbuechel (2001) and contains natural stabilizers (proteins and lipids), which should help compatibilization with starch. The polymer is essentially 100% cis-1, 4-polyisoprene and this conformation leads to a number of useful mechanical properties, such as improved mechanical strength on stretching (Rouilly *et al.*, 2004). It is also inexpensive and supplied as the natural latex with a broad particle size distribution of less than 100nm and can also be stabilized with ammonia (Rouilly *et al.*, 2004).

The above unique properties of natural rubber latex and previous research successes in incorporating starch as filler in natural rubbers, as reported by Stelescu *et al.* (2017) and Wang *et al.* (2018), have necessitated the choice of starch as filler for natural rubber in this research work. Moreso, starch is a renewable, cheap and environmentally friendly alternative to carbon black and silica and has been creatively used as a filler in tyre products to lower rolling resistance and reduce the use of carbon black made from natural gas or crude oil resources (Zhang *et al.*, 2006). Based on the above background, starch will be extracted from five local plants sources: *Taca leontopetaloides* (Polynesian arrowroot - amora), *Manihot esculenta* (cassava), *Colosia esculenta* (cocoyam), *Ipomoea batatas* (sweet potato), *Dioscorea rotundata* (yam) without chemical modification and will be gelatinized blended with natural rubber latex in aqueous phase by co-coagulation and latex compounding method designed by Novel polymers laboratory, Beijing, China, in addition to other processes leading to starch/rubber biopolymer composites with expected good physical and mechanical properties as well as being subjected to biodegradation activities of soil microorganisms. Most of the reported incorporation of

starch into natural rubber in previous research efforts was done with one or more chemical modifications of starch and natural rubber in addition to using coupling agents and compatibilizers. However, in this research, there will be no chemical modification of starch or natural rubber. This will be effected to investigate the role of particle size and reactive compatibilization, especially at the interfacial levels between the starch fillers and rubber matrix.

1.2. Statement of the Problem

Although synthetic polymers and composites have satisfactory mechanical properties, their lack of biodegradability has recently complicated and hindered their use in light of the current environment-friendly technologies (Albertsson & Karsson, 1994; Wool, 1995). Most rubber products, such as automobile tyres, conveyor belts, sporting goods, rainboots, shoe soles and most automobile car parts after their service life, are usually disposed of in the environment with reckless abandon and being non-biodegradable can stay on the land surface for many years posing environmental disposal problems. Most people have resorted to burning these rubber products, thereby indiscriminately introducing some toxic hydrocarbons, carbon monoxide smoke and soot into the atmosphere, which can provoke asthma attacks in patients and also affect the ozone layer in the long run.

Secondly, for many years, carbon black and silica have been the most widely used reinforcing fillers in the rubber industry. However, carbon black is originated from petroleum and natural gas, and due to the escalating crude oil prices, it is very costly. Moreover, its use in rubber products not only consumes much energy but also is harmful to our environment (Stelescu *et al.*, 2017). In addition, the fine particles of carbon black and silica causes easy lung damage and occupational illnesses such as cancer, kidney diseases, silicosis, etc., for rubber compounding operators and employees in the rubber processing industries (Li & Ryong Cho, 2012; Stelescu *et al.*, 2017). Silica is also known to have adverse effects on health, such as: silicosis, cancer (Group 1 according to IARC-the International Agency for Research on Cancer), autoimmune diseases, tuberculosis, etc. In 1995, the IARC rated carbon black as IARC classification 2B-possibly carcinogenic to humans and definitely carcinogenic to animals (Stelescu *et al.*, 2017). Moreso, the energy crisis of the 1970s and 1980s and the escalating high prices of crude oil and natural gas in recent times was an incentive to seek naturally occurring substitutes (as fillers) in rubbers and plastics in general (Long *et al.*, 2006; John, 2019). According to Easychemtrade, United Kingdom, an international market organization, carbon black (grade, N330, N220) is sold for USD \$700-950 per ton, finely divided Silica (grade, LM333), \$900 per ton, while cassava starch (food grade) is sold for USD \$250 per ton respectively.

Therefore, it is essential and expedient to develop a new cheap, clean, renewable, biodegradable and environmentally friendly reinforcing filler for rubber Products (Li & Ryong Cho, 2012).

Consequently, in the patent literature (USP, 2002, 2003), starch has been creatively used to partially replace conventional carbon black and silica as fillers in tyre products to lower the rolling resistance, reduce tyre weight, fuel consumption, and decrease CO₂ emission thereby reducing the use of carbon black made from natural gas or oil resource. Therefore, this research tries to incorporate starch fillers from less popular plants (non-economic crops) into natural rubber to reduce cost and risk to human health (Li & Ryong Cho, 2012; Stelescu *et al.*, 2017). Amora (polynesian arrow root) starch extracted from wild root crops is being studied with the expectation that it will replace cassava and maize, currently serving as the main source of starch fillers in the rubber industry. Besides, cassava and maize are economic crops, while amora is not.

Moreso, the findings from previous research show that microorganisms have the capacity to biodegrade both synthetic rubber poly (cis-1,4-isoprene) and natural rubber biopolymers (Basaiah & Nayanashree, 2015). Sudesh and Jayaram (2016) have opened a new application area for utilizing biotechnological processes in dealing with rubber waste disposal and environmental management problems since the devulcanization and recycling of used rubber tyres has proved non-economical and has little to offer in terms of mechanical properties. This research attempts to find a partial or full replacement for carbon black and Silica as fillers in natural rubber to reduce cost, protect our environment and reduce risks to human health, in addition to utilizing the latex compounding method (co-coagulation in aqueous media) in achieving good dispersion of starch fillers in natural rubber matrix thereby enhancing interfacial adhesion and improving physical and mechanical properties.

1.3. Aims and Objectives

This research is aimed at developing biodegradable starch/rubber biocomposites with good mechanical and performance properties, such as utilizing natural rubber latex in its natural form (due to the presence of protein and lipids as natural stabilizers) and local varieties of starchy crops (amora, cocoyam, and yam) in addition to potato and cassava, and applying them as filler without any chemical modification.

The objectives of this research study are as follows:

- To extract starch from *Tacca leontopetaloides* (amora), *Manihot esculenta* (cassava), *Ipomoea batatas* (sweet potato), *Colocasia esculenta* (cocoyam), *Dioscorea rotundata* (yam), characterization in terms of particle size and pH and determine amylose and amylopectin percentage composition.
- To prepare gelatinized starch from the isolated starch samples to reduce the particle size of starch to about 1 μ m to facilitate blending with natural rubber latex.
- To prepare biopolymer composite through co-coagulation of the rubber latex/gelatinized starch mixture with an aqueous electrolyte (Calcium Chloride), followed by curing the coagulum by Sulphur vulcanization and curing accelerators. This vulcanization process occurs by ionic mechanism and leads to the formation of Sulphur bridges (C-Sx-C) between macromolecules or by the cyclic combination of Sulphur. Rubber samples containing C-Sx-C cross-linking bridges exhibit better tensile strength values than those containing C-C bonds from peroxide cross-linking; hence, Sulphur vulcanization is chosen.
- To determine swelling properties of the biopolymer composites in aqueous and organic solvents (water and toluene). This is to determine the solvent permeability of the polymer and the degree of cross-link density (V_c) which gives an idea of the level of dispersion of the starch fillers in the rubber and the interfacial adhesion between the filler and the rubber.
- To characterize the biopolymer composites using Fourier transforms infra-red spectroscopy (FTIR) to investigate the nature of interaction between starch and rubber polymer. Scanning electron microscopy (SEM) gives the morphology of the polymer composite, while x-ray diffraction analysis gives the crystalline or the amorphous nature of the rubber composite.
- Instron universal testing machine (UTM) will give the tensile strength values against applied forces and elongation at break. Type A durometer will determine the hardness of the rubber polymers.
- Differential scanning calorimetry (DSC) will give the value of glass transition temperate (T_g) for the starch/rubber composites against a reference material at a determined heat flow rate. The glass transition temperature (T_g) is the transition between the elastic state (robbery state) and the glassy state, which is a unique property of any polymer.
- Weight loss/aging test will be carried out as preliminary signs of biodegradation activities. Biodegradation assessment of the biopolymer composites using soil microorganisms will also be carried out to find out the biodegradation property of the test microorganisms extracted from soils.

These tests listed above will assist in characterizing the formulated starch/rubber polymer and determining its usefulness and applications.

1.4. Scope of the Study

The scope of the present study is limited to:

- The formulation of biodegradable starch/ natural rubber composite using natural rubber latex and gelatinized starch.
- The characterization of the starch/natural rubber biopolymer composite by determining the physical, chemical and mechanical properties.

In this study, conventional fillers such as carbon black and silica are known to confer reinforcing properties on natural rubber and its products in terms of tensile strength, modulus, hardness, elongation at break, glass transition temperature (T_g), degree of cross-link density (V_c) (Surya & Siregar, 2014; Stelescu *et al.*, 2017; Wang *et al.*, 2018; Jong, 2018). To reduce high production costs due to the high costs of conventional fillers and to remove the risk posed to human health, an alternative

filler, such as starch, a renewable, cheap and non-toxic filler in gelatinized form, was dispersed into natural rubber applying latex compounding method and aqueous electrolyte coagulant to formulate an environmental friendly biopolymer capable of being biodegraded by soil microorganisms.

1.5. Significance of the Study

This research into alternative fillers for natural rubbers that are non-toxic, cheap, renewable and eco-friendly will be of great importance to the rubber industry, especially the automobile industry, which is by far the largest single sector among the users of natural rubber with tyres and tyre products accounting alone for over 50% of natural rubber (NR) consumption (UNCTAD, 2011).

The study will provide an alternative filler as a partial replacement for the conventional carbon black and silica which are expensive and pose some health risks to compounding operators in the rubber industry (Li & Ryong Cho, 2012; Stelescu *et al.*, 2017).

Moreso, a new approach of dispersing starch fillers into natural rubber via the latex compounding method without chemical modification of filler and natural rubber or the use of coupling agents and compatibilizers will become available for application in the rubber compounding industry, leading to good interfacial adhesion between filler and rubber matrix and hence good mechanical properties in the end product.

In addition to the foregoing, biotechnological processes will be adopted as one of the major solutions to rubber waste (automobile tyres and rubber products) disposal problems as devulcanization of used tyres is very expensive and recycling of used tyres has little to offer in terms of mechanical properties in the end product.

1.6. Justification of the Study

The introduction of natural starch filler into natural rubber and determining its biodegradable tendencies and tensile and mechanical properties could open the door to the research for the production of complete biodegradable automobile tyres, conveyor belts and other rubber goods in the future. The proposed starch/rubber biopolymer composites will find application in the formulation of 'green' tread for car tyres leading to lower tyre rolling resistance, low carbon (iv) oxide emission and low fuel consumption in automobiles. Starch filler as a reinforcing agent has the potential to partially replace the conventional carbon black and silica, thereby reducing cost, tyre weight and health risk. Starch/rubber biopolymer composites are eco-friendly and biocompatible and are necessary to maintain global environmental and ecological balance.

In addition, it will also enhance the sustainable exploitation of natural resources. Starch, being a cheap, natural and renewable resource, will reduce production costs drastically and lead to new uses for starch as a tyre additive in the rubber processing industry. Biodegradable starch/rubber biocomposites through biotechnology will offer the possible solution to waste disposal problems associated with traditional petroleum-derived polymers and rubber products. The proposed starch/rubber biocomposites will add economic value to starchy crops leading to increased cultivation and export, thereby increasing the income of farming populations in Nigeria. The use of rubber latex in its natural form is an advantage that enhances latex stability due to the presence of natural stabilizers (proteins and lipids), which promote coN_m2tibilization with gelatinized starch.

1.7. Operational Definitions

- Compounding: The art of mixing the additives with the natural rubber in a two-roll mill or in any other mixer to achieve a homogenous mixture.
- Filler: An inert material added to a polymer composition to improve its properties and/or to reduce its cost. When mixed with the resin (polymer), it forms a heterogenous mixture that can be moulded under the influence of heat, pressure or both.
- Coagulation: The coming together or aggregation of rubber particles to form lumps inside the rubber latex. This is brought about by either a chemical agent or using a device called a centrifugation device.

- Co-coagulation: The coming together or aggregation of rubber particles and starch fillers in a liquid medium to form a solid lump or coagulum inside the rubber latex/starch paste mixture brought about by a chemical agent called an electrolyte, e.g., Calcium Chloride solution.
- Filler loading: The introduction of filler into the polymer (rubber, plastic, resin, etc.) by any special skill or technique for proper dispersion in the rubber or the polymer.
- Vulcanization: The art of bridging the rubber macromolecular chains with Sulphur atom(s) at a particular temperature under some reaction conditions utilizing accelerators and activators. Carbon chains are linked with sulphur near the double bonds in the chain, C – Sx – C.
- Cure: Alternative word used interchangeably with vulcanization since they mean the same thing.
- Hardness: The resistance of a rubber material to a small rigid object pressed onto the surface at a certain force. Type A durometer gauge is used to measure hardness in international rubber hardness degree. Type A durometer measures indentation hardness which is the material resistance to indentation by an indenter.
- Tensile strength: It is the maximum tensile stress reached in stretching a test piece (either an O-ring or dumbbell) and it is measured in Megapascals (Nm⁻²), a metric unit.
- Elongation at break: It is the maximum stretching of a rubber material at the point where it breaks. It is determined with Universal testing machine (UTM) together with tensile strength.
- Composites: A composite is a material system composed of a mixture of two or more constituents that differ in form and/or composition and are insoluble in one another. This includes all filled polymers, laminates and reinforced plastics.
- Blend: This is the art of combining two or more polymers in a physical mixture to give a hybrid polymer with a better property than the original individual components. It is a physical modification process for a polymer.
- Swelling: This is the absorption of a solvent by a polymer (e.g., rubber), but it is not dissolved in the process due to the structural arrangement of the chains but rather swells and later reverses to its former position after some time, especially if the solvent is a volatile solvent, e.g., toluene, gasoline, etc.
- Accelerators: They are catalysts that promote vulcanization by sulphur in rubbers. They create a conducive environment for the sulphur to be able to attach to the carbon in the chains inside the rubber, e.g., Mercaptobenzothiazole (MBT).
- Latex: A white milky liquid that contains rubber particles in addition to other contents inside the latex. It is gotten from the rubber tree, *Hevea brasiliensis*.
- Biopolymer: Natural polymers gotten from either animals, or humans or plants and can also be prepared outside the living bodies of plants or animals. e.g., protein, starch, cellulose, natural rubber, etc.
- Additives: They are chemical agents or natural ingredients added to polymers during processing, compounding or vulcanization to aid the process, enhance a property in the polymer, or prevent degradation by air, ozone or solvent.
- Biodegradation: The breaking down of macromolecules in polymers, e.g. rubber, plastics, and resin, by microorganisms into smaller micromolecules through the action of enzymes. When it is a complete biodegradation, water and carbon (iv) oxide is the final product. Bacteria and fungi are known to be able to biodegrade polymers in recent times, although it is a very slow process.
- Biotechnology: The art of using microorganisms in fermentation, biodegradation, production of chemical agents, and production of enzymes by manipulation or exploitation of the behaviour of a given bacteria or fungi under some controlled conditions.
- Interfacial adhesion: This is the bond that exists between fillers and rubber particles in a polymer matrix. This is also a force of attraction that holds the fillers and the polymers together. It could be physical, chemical or semi-chemical bonding in nature.
- Gelatinization: This is the hydrolysis of starch with water under a moderate temperature. It takes place in the liquid phase and helps reduce the bulky size of the starch molecule by eliminating most of the hydrogen bonds holding the starch macromolecular chains together.

Introduction

- **Amora:** This is a wild root crop known as Polynesian arrow root, whose botanical name is *Tacca leontopetaloides*. It grows under cassava farms or other root crops or tubers, especially in the middle belt region of Nigeria, Plateau, Nassarawa, Taraba, Benue and Kogi States.
- **Amylose:** A linear chain molecule contained in starch in about 20% compositions. It is soluble in water and contains α 1, 4 glycoside linkage.
- **Amylopectin:** A branched-chain, network-chain molecule contained in starch in about 80% compositions. It is insoluble in water and contains α 1, 6 glycoside linkage.
- **Lag phase:** This is the time interval known as “tooling up” prior to the active multiplication of bacteria cells. During this time, the bacteria synthesize macromolecules required for multiplication, including enzymes, ribosomes, and nucleic acids, and they generate energy in the form of ATP.
- **Exponential phase:** During this time, cells divide at a constant rate and their numbers increase by the same percentage during each time interval. It is a time of active multiplication.
- **Stationary phase:** Cells enter the stationary phase when they have exhausted their supply of energy and nutrients. The total number of viable cells in the overall population remains relatively constant, but some cells are dying while others are multiplying. Cells that die release peptides and nucleic acid, providing a source of nutrients and energy to fuel the growth of other cells.
- **Death phase:** This is the period when the total number of viable cells in the population decreases as cells die off at a constant rate.
- **Phase of prolonged decline:** This phase is marked by a very gradual decrease in the number of viable cells in the population, lasting for months and, sometimes, for years.

2 | Literature Review

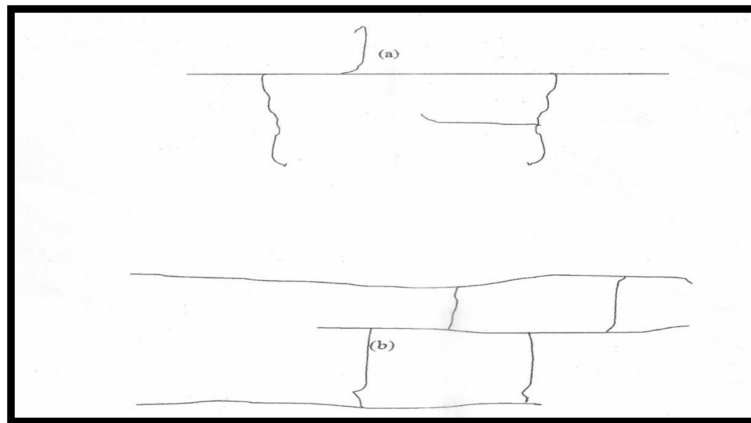
2.1. Polymers

From the lowly throwaway candy wrapper to the artificial heart, polymers touch our lives like no other class of materials, with no end to new uses and improved products in sight (Billmeyer, 2007). A polymer is a large molecule built up by repeating small, simple chemical units called monomers. In some cases, the repetition is linear, much as a chain is built up from its links. In other cases, the chains are branched or interconnected to form three-dimensional networks (Billmeyer, 2007). The science of macromolecules (Polymers) is divided between biological and non-biological materials and each is of great importance. Biological polymers form the very foundation of life and intelligence and provide much of the food on which man and other animals exist. Examples of biological polymers include protein, starch, cellulose and the genetic material deoxyribonucleic acid (DNA). Other natural polymeric materials are natural rubber, wool, lignocellulose, shellac, amber, resins, gums, asphalt, gum mastic, etc. Natural polymers have been utilized throughout the ages for sustenance, shelter, warmth and other requirements. Non-biological polymers include the synthetic materials used for plastics, fibres and elastomers. Today these substances are truly indispensable to mankind, being essential to clothing, shelter, packaging, transportation and communication, as well as to the other conveniences of modern living (Billmeyer, 2007). Typical examples of synthetic polymers are synthetic rubbers, bakelite, neoprene, styrene, butadiene rubber (SBR), nylon, polyvinyl chloride (PVC), Polypropylene (PP), silicone polymers, polystyrene, polyethylene, Poly(methylmethacrylate), etc.

The process of making polymers (macromolecules) from small, simple chemical units known as monomers is called polymerization. The repeat unit of the polymer is usually equivalent or nearly equivalent to the monomer starting material from which the polymer is formed (Billmeyer, 2007). Thus, the repeat unit of poly (vinyl chloride) is- $\text{CH}_2\text{CH-Cl}$. Hence, its monomer is vinyl chloride, $\text{CH}_2 = \text{CHCl}$. The length of the polymer chain is specified by the number of repeat units in the chain which is called the degree of polymerization (DP). The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the DP. The processes of polymerization are divided into two groups known as condensation and addition polymerization or, in more precise terminology, step-reaction and chain reaction polymerizations. Polycondensation or step reaction is entirely analogous to condensation in low-molecular-weight compounds. In polymer formation, condensation takes place between two polyfunctional molecules to produce one larger Polyfunctional molecule, with the possible elimination of a small molecule such as water. Addition or chain reaction involves a chain reaction in which the chain carrier may be an ion or a reactive substance with one unpaired electron called a free radical. A free radical is usually formed by the decomposition of a relatively unstable material called an initiator. The free radical is capable of reacting to open the double bond of a vinyl monomer and add to it, with an electron remaining unpaired (Billmeyer, 2007). In a very short time, usually, a few seconds or less, many more monomers add successively to the growing chain. Finally, two free radicals react to annihilate each other's growth activity and form one or more polymer molecules. With some exceptions, polymers made in chain reactions often contain only carbon atoms in the main chain (homochain polymers), whereas polymers made in step reactions may have other atoms, originating in the monomer functional groups, as part of the chain (heterochain polymers) (Billmeyer, 2007).

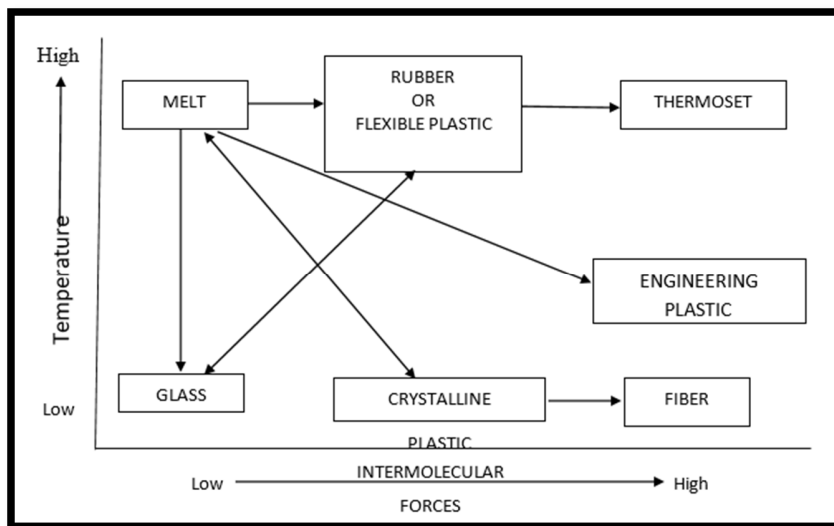
In contrast to the linear-chain molecules discussed above, some polymers have branched chains, often as a result of side reactions during polymerization. The term 'branching' implies that the individual molecules are still discrete. Still, in other cases, cross-linked or network structures are formed, as in using monomers containing more than two reactive groups in stepwise polymerization. Most linear or branched polymers can be made to soften and take on new shapes by the application of heat or pressure. Hence, they are said to be thermoplastic (Billmeyer, 2007).

Literature Review



Scheme 2.1: (A, B) Schematic Representation of (A) Branched and (B) Network Polymers (Billmeyer, 2007)

In the molten state, polymer chains move freely, though often with enormous viscosity, past one another if a force is applied. This is the principle utilized in the fabrication of most polymeric articles and is the chief example of the plasticity from which the very name ‘plastics’ is derived. If the irreversible flow characteristic of the molten state is inhibited by the introduction of a tenuous network of primary chemical bond cross-links in a process commonly called ‘vulcanization,’ the local freedom of motion of the polymer chains is not restricted and the product shows elastic properties associated with typical rubbers. If, however, the inter-chain forces result from secondary bonds, such as the interaction of polar groups, rather than primary chemical bonds, the rubber is not one of high elasticity but has the properties of limpness and flexibility. Secondary bond forces are capable of forming and breaking reversibly as the temperature is changed, as indicated by the arrows in scheme 2.



Scheme 2.2: The Inter-Relation of the States of Bulk Polymers (Billmeyer, 2007)

Continued primary bond cross-linking in the post-polymerization step of vulcanization converts rubber into hard rubber or ebonite, whereas cross-linking concurrent with polymerization produces a wide variety of thermosetting materials. Common examples are the phenol-formaldehyde and amine-formaldehyde families, widely used as plastics (Billmeyer, 2007). As the temperature of a polymer melt or rubber is lowered, a point known as the glass-transition temperature (T_g) is reached, where polymer materials undergo a marked change in properties associated with the virtual cessation of local molecular

motion. Thermal energy is required for segments of a polymer chain to move with respect to one another and if the temperature is low enough, the required amount of energy is not available. Below their glass-transition temperature, amorphous polymers have many of the properties associated with ordinary inorganic glasses, including hardness, stiffness, brittleness, and transparency. In addition to undergoing a glass transition as the temperature is lowered, some polymers can crystallize at temperatures below that designated as their crystalline melting point. However, not all polymers are capable of crystallizing. The properties of crystalline polymers are highly desirable; they are strong, tough, stiff, and generally more resistant to solvents and chemicals than their non-crystalline counterpart (Billmeyer, 2007; Seymour, 1982). In applications, polymers are used in the forms of plastics, fibres, rubbers or elastomers, liquid foams and solutions.

Natural polymers (e.g., Natural resins and gums) have been utilized throughout the ages for thousands of years. Asphalt was utilized in pre-biblical times; amber was known to the ancient Greeks, and gum mastic was used by the Romans (Billmeyer, 2007). The modern plastics industry began with the utilization of natural rubber for erasers and in rubberized fabrics a few years before Goodyear's discovery of vulcanization in 1839 (Billmeyer, 2007). In 1851, hard rubber (ebonite) was patented and commercialized and by 1870, cellulose nitrate (nitrocellulose), discovered in 1838, was successfully commercialized by Hyatt. Today, Hyatt's product, celluloid, has been superseded in almost all uses by more stable and more suitable polymers. This was subsequently followed by cellulose acetate, acetate rayon and cellophane. The oldest of the purely synthetic plastics is the family of phenol-formaldehyde resins, of which Baekeland's Bakelite was the first commercial product. Moreso, the first commercial use of styrene was in synthetic rubbers made by copolymerization with dienes in the early 1900s as in the product (SBR) styrene-butadiene rubber (Billmeyer, 2007).

Mechanically, Polymers exhibit bulk properties that are most often suitable for the end use and these properties indicate how polymers actually behave on a microscopic scale. These include the tensile strength of a material which quantifies how much stress the material will endure before suffering permanent deformation. Others are hardness, stress at 100%, elongation at break, permanent set, tear strength, etc. (Zhang *et al.*, 2004). Various methods have been adopted in manufacturing and modifying polymer and its properties. Polymer modifications can be achieved by blending two or more polymer materials to arrive at some desirable properties. These include various forms of blending discussed as follows:

2.2. Blending

The blending of polymers offers a method of modifying and extending polymer properties to satisfy commercial interest. A polymer blend has been defined as any physical mixture of two or more different polymers or copolymers that are linked by covalent bonds (Malcolm, 1990). When two or more existing polymers are blended successfully, a novel material is often formed. Advances in producing high-performance polymer-based compositions are highly favoured to result from the utilization of new mixtures of polymers and mixtures of polymers with reinforcing components rather than from new polymer composition (Billmeyer, 2007). It is a known fact that mixtures of two or more polymers do not generally form miscible systems (Alfrey & Schrenk, 1980). All but a small minority form two-phase systems, the mechanical properties of which are very poor except in special circumstances. Alfrey and Schrenk (1980) suggested that the circumstance leading to good, indeed often superior, properties in immiscible systems is the development of strong interfacial adhesion between the two phases. If this does not occur naturally, it may be possible to bring it about by adding a third polymer that adheres well to both phases, or by using appropriate block or graft copolymers as discussed below.

2.3. Block Copolymers

Methods of synthesis of two polymers containing long sequences of monomers are of interest since they may lead to polymers with properties widely different from those of either homopolymers or random copolymers (Billmeyer, 2007). In block copolymers, the sequences follow one another along the main polymer chain, as shown below:

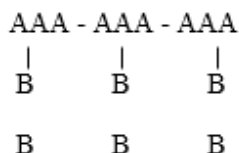
AABB - BBAA - AABBB --- Scheme

Scheme 2.3: Block copolymer

The ultimate aim in preparing block copolymers or graft copolymers is to obtain the desired copolymer free from a homopolymer or other unwanted species on a scale that allows evaluation of physical properties. In main block copolymers, polymers with labile end groups are utilized. The usual method of preparing block copolymers utilizes a polymer with end groups that can be made to react under different conditions. In stepwise polymerization, the method is trivially simple: two polyesters, for example, of different types, are separately prepared, mixed, and allowed to polymerize further. Ring-scission polymerization can be used effectively. Other techniques for making block copolymers are free-radical and unteminated anionic polymerization. Several commercial block copolymers are produced in this way (Billmeyer, 2007).

2.4. Graft Copolymers

In graft copolymers, sequences of one monomer are 'grafted' onto a 'backbone' of the second monomer type, as shown below:

*Scheme 2.4: Graft copolymer*

Graft copolymerization results from the formulation of an active site at a point on a polymer molecule other than its end and exposure to a second monomer. Most graft copolymers are formed by radical polymerization. The major activation reaction is chain transfer to polymer. In many instances, the transfer reaction involves the abstraction of a hydrogen atom. An important commercial application is the grafting of polystyrene or styrene-acrylonitrile copolymer onto butadiene or acrylonitrile-butadiene copolymer rubber in the production of acrylonitrile-butadiene-styrene (ABS) resins. Ultraviolet or ionizing radiation, or redox initiation, among other methods, can also be used to produce the polymer radicals leading to graft copolymers (Billmeyer, 2007). Grafting may result in the development of polymers that are miscible and with some improvements in mechanical properties. However, materials produced suffer some degree of immiscibility and phase separation; hence, the development of interpenetrating networks (IPN) was adopted to remove or minimize the problems of phase separation.

2.5. Interpenetrating Polymer Networks (IPNs)

A new class of multi-polymer systems has recently been synthesized in the form of two independent interpenetrating polymer networks. Interpenetrating Polymer Networks (IPNs) are a broad class of polymer blends/mixtures defined as a combination of two polymers in network form, with at least one of them synthesized and/or cross-linked in the immediate presence of the other (Lin *et al.*, 2011). Semi-interpenetrating polymer networks (Semi-IPNs) refer to a class of IPNs where only one of the polymers is cross-linked. One can, for example, take a lightly cross-linked polymer A, swell it with a second monomer B, plus a cross-linking agent and polymerize B or one can select the A and B systems to polymerize together by different mechanisms. For example, a styrene-divinylbenzene mixture polymerizes by a radical chain mechanism together with a polyurethane network forming by a step-reaction mechanism. Phase separation will, in general, take place, but the structure greatly restricts the sizes of the domains of each phase (Lin *et al.*, 2011). Individual constituents in IPNs are generically polymer resins and fibres, which serve as the matrix phase and the reinforcing phase, respectively. The procedure to synthesize IPNs can be generally classified into two categories, i.e., simultaneous and sequential approaches. Simultaneous synthetic methods start with a mixture of both monomers to form

two polymer networks simultaneously through different reaction routes. Sequential synthetic methods control different network reactions by sequentially adding different monomers. Currently, many commercial materials are produced as sequential IPNs, due to their flexibility and relative ease of processability (Lin *et al.*, 2011).

Moreover, semi-IPNs (S-IPNs) with semi-I and semi-II types refer to having the first or second polymers cross-linked, respectively. Novel synergistic properties have been observed in some cases of interpenetrating polymer networks (Billmeyer, 2007; Sperling, 1981) and have attracted considerable interest and continue to be of interest in both fundamental and applied research and development investigations. They have been utilized in widespread commercial applications and are considered promising in novel materials development. IPN's capability of forming tough but flexible materials enables its utilization for sound and vibration damping, biomedical applications, natural products and renewable resources, tough and impact-resistant materials, etc. (Sperling, 1981; Lin *et al.*, 2011). Other methods employed in modifying polymer properties include using additives and compounding.

2.6. Additives

Additives are added to modify properties, assist in processing and introduce new properties to a material. Additives can be added as solids, liquids, or gases. They are usually added mechanically (with or without subsequent chemical reaction), during formulation, or as the material is in the fluid state. Many additives have become parts of general formulations developed more as an art than science.

The following are the various types of additives:

- Antiblocking agents,
- Antifoaming agents,
- Antimicrobial agents,
- Lubricants,
- Mold release agents,
- Antioxidants,
- Plasticizers,
- Blowing agents,
- Coupling agents,
- Curing agents,
- Flame retardants,
- Reinforcements,
- Stabilizers,
- Viscosity modifiers

Many plastics or polymeric materials are virtually useless alone but are converted into highly serviceable products by combining them with particulate or fibrous solids (Billmeyer, 2007). These materials greatly enhance dimensional stability, impact resistance, tensile and compressive strength, abrasion resistance and thermal stability. An extremely important example of the beneficial effect of fillers is the reinforcement of rubber. Particulate fillers used in polymers are:

- Silica materials, including sand, quartz, and diatomaceous earth, silicates, including clay, mica, talc, asbestos, and some synthetic silicates,
- Glass, including granules, flakes, and solid and hollow spheres, Inorganic compounds, including chalk, limestone, alumina, magnesia and zinc oxides, barytes, silicon carbide and others,
- Metal powders and
- Finely divided cellulosic (Wood flour), etc

2.7. Plasticizers

According to the ASTM D - 883 definitions, a plasticizer is a material incorporated in a plastic to increase its workability and flexibility or dispersibility. The addition of a plasticizer may lower the melt viscosity, elastic modulus, and glass transition temperature (T_g) of a plastic. Plasticizers should be relatively non-volatile, non-mobile, inert, inexpensive, non-toxic and compatible with the system to be plasticized. They can be divided based on their solvating power and compatibility. Primary plasticizers

are used as either the sole plasticizer or the major plasticizer with the effect of being compatible with some solvating nature. Secondary plasticizers are materials that are generally blended with a primary plasticizer to improve some performance, such as flame resistance and mildew resistance, or to reduce cost. The following types of plasticizers are in common use: phthalate esters, accounting for over half of the total volume of plasticizers used. Di (2-ethylhexyl) phthalate (dioctyl phthalate, DOP) is the dominant plasticizer for polyvinyl chloride. Others include phosphate esters, adipates, epoxy plasticizers, fatty acid esters, glycol derivatives and hydrocarbon derivatives serving as secondary plasticizers (Billmeyer, 2007).

2.8. Compounding

The term 'compounding' is applied both to the selection of additives to modify the properties of a polymer and to their incorporation with the polymer to give a homogenous mixture in a form suitable for efficient use in the subsequent processing or fabrication step. The traditional compounding device in the rubber plastics industry is the two-roll mill. By proper selection of temperatures and speeds of rotation, the polymer is made to adhere to the front roll, except as it is cut off by the operator (Billmeyer, 2007). The compounding ingredients are added to the polymer mass as it passes between the rolls. Other compounding device includes compound or mixer extruder, with many advantages over the rolling mill. The contaminant is reduced, an inert atmosphere or vacuum may be utilized and continuous processes are more readily achieved, etc. Other compounding devices in common use are internal mixers such as kneaders, masticators, paddle blenders, tumblers and blenders (Billmeyer, 2007).

However, with all of the above methods of formulation, modification, blending and compounding of polymers leading to the production of polymeric materials with good mechanical properties and with wider applications, there appears to be the absence of biodegradability in all the forms of polymers discussed above. Biodegradable polymers have attracted an increasing amount of attention over the last two decades, predominantly due to environmental concerns (environmental responsibility) and the realization that our petroleum resources are finite. In another development with a view to producing environmentally friendly polymers and easing the incompatibility of most polymer blends, numerous natural biopolymers (starch) with various polyolefins were developed in the 1970s and 1980s. However, these blends were not biodegradable, and thus the advantage of using a biodegradable polysaccharide was lost (Long *et al.*, 2006). Another drawback of the blend involving petrochemical feedstock, e.g., polyolefins, is the fact that they are not eco-friendly and non-biodegradable.

Interestingly, the idea of developing biodegradable composite came at the right time to address the problems of degradation in polymers. Several studies by Jacob *et al.* (2007), Reis *et al.* (1997), Kim (2012) and Arvanitoyannis *et al.* (1997) have shown the possibilities of utilizing biopolymers in composite formation through the formulation of heterogeneous multiphase components. These systems, when used as blends, present tolerable surface characteristics that can be adjusted to favour surface adhesion. This is due to the fact that the main disadvantages of biodegradable polymers obtained from renewable sources are their dominant hydrophilic character, fast degradation rate, and, in some cases, unsatisfactory mechanical properties, particularly under wet environments (Long *et al.*, 2006). In principle, the properties of natural polymers like starch, cellulose, natural rubber, etc., can be significantly improved by blending or composite formation with other kinds of polymers or reinforcing fibres from renewable sources (Long *et al.*, 2006). In this case, blends of polymer from renewable resources can be used to develop new low-cost materials with improved performance. This will be highlighted in the following areas discussed below.

2.9. Composites

A composite is defined as a material system composed of a mixture or combination of two or more distinct constituents that differ in form and/ or composition and are insoluble in one another. This includes copolymers, filled polymers (reinforced plastics, carbon black/silica-filled rubber), laminates, etc. (Bhatnagar, 2010). Moreso, a composite material is a multiphase material with chemically dissimilar phases separated by a distinct inter-phase (Callister, 1999). The term 'composites' also

includes fibre-reinforced engineering structural materials, in which the fibres are continuous or long enough to be oriented to produce enhanced strength properties in one direction (Billmeyer, 2007). Varying the composition of the reinforcement matrix phase, through synchronization of properties, results in improved properties (Williams & Pool, 2000).

Biocomposites are materials derived from biological sources in which the reinforcement consists mainly of plant fibres such as cotton, flax, jute, sisal, regenerated cellulose, etc., in a polymer matrix. Biocomposites are broadly classified as materials made from natural fibre and petroleum-derived non-biodegradable polymers: Polypropylene (PP), Polystyrene (PS) or biodegradable polymers, Polylactic acid (PLA), polyhydroxy alkanooates (PHA), polyhydroxy butyrate (PHB) (Long *et al.*, 2006). Composite materials offer significant advantages over metal alloys and ceramics in terms of reduced corrosiveness, reduced release of allergic metal items such as nickel and chromium, and higher resistance to fatigue failure. More recently, much effort has been made to develop biodegradable polymer composites because of the worldwide environmental concerns and resource problems associated with the use of petroleum-derived plastics. Also, the non-compostable nature of most polymer packaging materials and composites products and their turning into a nuisance after the end use, in addition to the resultant waste disposal problems, has led to a new trend to develop completely biopolymer/biopolymer composites capable of biodegradability with good performance properties (Long *et al.*, 2006). Some natural constituents of biocomposites include protein, cellulose and natural starch. Interest in incorporating starch into polymers has become widespread and interesting (Carvalho *et al.*, 2003; Zhang *et al.*, 2006); hence, it is discussed below.

2.10. Starch

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance, annual renewal and cheap resource (Zhang *et al.*, 2004; Long *et al.*, 2006). However, by itself, pure starch is not a good choice to replace petrochemical-based plastics (Long *et al.*, 2006). It is mostly water soluble, difficult to process and brittle when used without the addition of a plasticizer. In addition, its mechanical properties are very sensitive to moisture content. Blending two or more chemically and physically dissimilar biopolymers has shown the potential to overcome these difficulties (Long *et al.*, 2006). During the past years, the effects of different types of fillers on natural rubber compounds have been studied in search of improvements in their physical and mechanical properties (Ichazo, Pena, Albano, *et al.*, 2007). Amongst these notable and important fillers are carbon black, silica and calcium carbonate.

Recently the application of fillers of organic origin has attracted a wider interest among scientists due to their low cost, renewable and environment-friendly nature (Ichazo, Pena Albano *et al.*, 2007). Several cellulosic and polysaccharide biopolymers, such as ground wood waste, nutshells, bamboo, white rice husk, cereal straw and starch, have been used as fillers for plastics and elastomers (Ichazo, Hernandez, Albano *et al.*, 2006).

Moreso, degradable polymer composites have long been considered part of the solution to the environmental and waste management problems posed by the extensive use of non-degradable polymeric material (Kim, 2012). One of the most commonly used approaches to create such degradable composites is to incorporate starch into degradable polymers, e.g., Guttapercha, 1, 4 trans-polyisoprene TPIP (Arvanitoyannis, Kolokuris *et al.*, 1997). Starch, a semi-crystalline biopolymer stored in granules as a reserve in most plants, is renewable, non-toxic and completely biodegradable (Robyt, 1987; Kim, 2012). It is also one of the substances more widely distributed in nature and consists of amylose and amylopectin (Chang *et al.*, 2008; Ismail & Gamal, 2010).

The thermoplastic properties of starch have been extensively studied and are directly related to its water content; in its dry state, the glass transition temperature (T_g) of starch is above its degradation temperature (Rouilly *et al.*, 2004). Composite materials are made from two or more constituent materials that are significantly different from each other in physical or chemical properties (Kim, 2012). There are some investigations concerning the reinforcement of elastomers with cassava starch (Nakason, Kaesman *et al.*, 2001). However, only a few reported the effect of this material on the physical properties of the resultant elastomer blend (Ichazo, Pena, Albano *et al.*, 2007).

Rubber composites (containing starch as filler), used as tread in 'green' tires, have attracted interest in a bid to reduce energy consumption and carbon dioxide emissions from automobiles (Wu, Ji, Zhang *et al.*, 2004). Goodyear Tyre Company, for example, uses a new starch-based material called BIOTRED to partially replace the conventional carbon black and silica to reduce tyre weight and rolling resistance (Wu, Ji, Zhang *et al.*, 2004). The Mechanical properties of starch-filled rubbers actually depend on many factors, among which are the dispersion level, the interfacial strength and the type of starch. In general, it is found that the reinforcing action of a filler depends upon its nature (chemical composition), particle size, type of elastomer and the amount of filler present (optimum loading) (Billmeyer, 2007). The report also found that the amylose content of starch can affect mechanical properties in starch/rubber blends (Rouilly *et al.*, 2004). Differences in amylose content have been reported to result in differences in starch physiochemical properties (Jane *et al.*, 1999). Amylose plays a big role in the pasting properties of starch, thus affecting the starch viscoelastic properties (Charles *et al.*, 2004; Novelo-Cen & Bentancur-Ancona, 2005). Furthermore, an increase in the amylose content of starch has also been found to lower the swelling power and solubility of starches (Sasaki & Matsuki, 1998), an important characteristic to be looked out for in any starch-filled rubber composites.

2.11. Biocomposites

Biocomposites are materials comprising one or more phase(s) derived from a biological origin. Biocomposites consist of biodegradable polymers as the matrix material and biodegradable fillers, usually biofibres (e.g., lignocellulose fibres). Since both components are biodegradable, the composite, as an integral part, is also expected to be biodegradable (Mohanty *et al.*, 2000). The history of composites from biological origin can be traced to biblical times from the book of Exodus. Moses' mother built the ark from rushes, pitch and slime, a kind of fibre-reinforced composite, according to the modern classification of materials (Long *et al.*, 2006). Fibres are widely used in polymeric materials to improve mechanical properties. Vegetable fibres (e.g., cotton, flax, hemp, jute, etc.) can generally be classified as bast, leaf or seed hair fibres (Long *et al.*, 2006). Cellulose is the major substance obtained from vegetable fibres and applications for cellulose fibre-reinforced polymers have again come to the forefront with a focus on renewable raw materials. Also, the reinforcement of polymers using fillers (Particulate or fibrous solids) is common in the production and processing of polymeric materials (Billmeyer, 2007; Long *et al.*, 2006).

Following the exceptional period of growth, the use of synthetic fibres (e.g., viscose, rayon, polyester, glass fibre) in fibre-reinforced synthetic resin (epoxy resins) matrices during the 1980s in applications such as in aerospace, automobile and thermal insulation, brought a resurgence of interest in their traditional forerunners and has been influenced by a number of factors, including increased environmental and health concerns, more sustainable methods of manufacture and reduced energy consumption. This trend supports the desire for lightweight structures (Hermann *et al.*, 1998). Materials from renewable sources are being sought to replace not only the reinforcement element but also the matrix phase of composite materials (Mohanty *et al.*, 2000). In terms of reinforcement, this could include plant fibres such as cotton flax, and hemp, fibres from recycled wood or waste paper, or even by-products from food crops and regenerated cellulose fibres (Mohanty *et al.*, 2000).

In 1996, shipments from the Canadian plastic industry increased by 10.6% from 1995 (Charron, 2001) to \$9.1 billion. Fomin (2001) reported that the end of the 20th century saw the worldwide production of synthetic plastics reach 130 million tons per year. European countries have reported an estimated average usage of 100 Kg of plastic per person each year (Mulder, 1998). Synthetic plastics are resistant to degradation and consequently, their disposal is fuelling an international drive for the development of biodegradable polymers (Kolybaba *et al.*, 2003). In recent years, there has been a marked increase in interest in biodegradable materials for use in packaging, agriculture, medicine, and other areas (Kolybaba *et al.*, 2003). In particular, biodegradable polymer materials known as biocomposites are of interest. Polymers form the backbones of plastic materials and are continually being employed in an expanding range of areas. As a result, many researchers are investing time into modifying traditional materials to make them more user-friendly and designing more polymer composites out of naturally occurring materials like starch, natural rubber, protein and cellulose (Kolybaba *et al.*, 2003). A number of biological materials may be incorporated into biodegradable

polymer materials, with the most common being starch and fibre extracted from various types of plants. The belief is that biodegradable polymer materials will reduce the need for synthetic polymer production, thus reducing pollution at a low cost, thereby producing a positive effect both environmentally and economically (Kolybaba *et al.*, 2003).

2.12. *Polymers from Renewable Resources (PFRR)*

Polymers from renewable resources (PFRR) have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons:

- Firstly, environmental concerns and
- Secondly, the realization that our petroleum resources are finite (Long *et al.*, 2006).

Generally, PFRR can be classified into three groups:

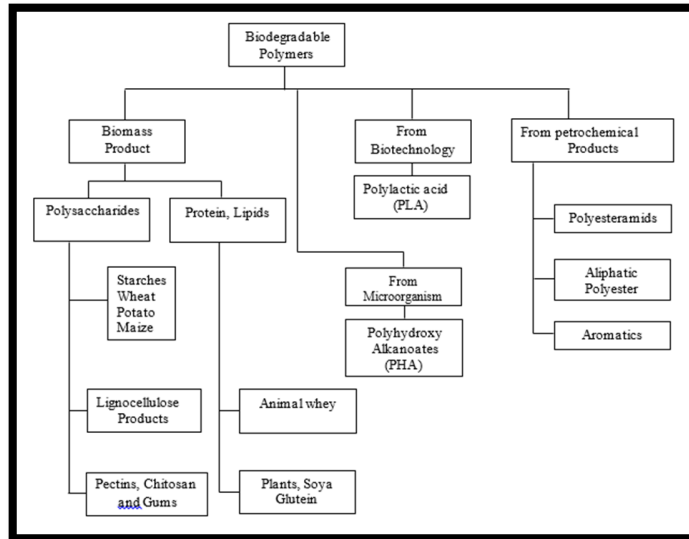
- Natural polymers, such as starch, natural rubber, protein and cellulose,
- Synthetic polymers from natural monomers, such as polylactic acid (PLA) and
- Polymers from microbial fermentation, such as poly hydroxybutyrate (PHB) (Long *et al.*, 2006)

More so, the availability of petroleum at a lower cost and the biochemical inertness of petroleum-based polymers have proven disastrous for the natural polymers market. It is only after a lapse of almost 50 years that the significance of eco-friendly materials has been realized once again due to environmental concerns, shortages and the high cost of crude oil. The inherent biodegradability of natural polymers also means that it is important to control the environment in which the polymers are used to prevent premature degradation (Long *et al.*, 2006).

However, like numerous other petroleum-based polymers, many properties of PFRR can also be improved through blending and composite formation. Blends and multi-layers of natural polymers with other kinds of PFRR can be used to improve the performance properties of natural polymers. These new blends and composites are extending the utilization of polymers from renewable resources (PFRR) into new value-added and low-cost products (Long *et al.*, 2006).

2.13. *Classification of Biocomposites*

Based on the biodegradability of the different matrices that can be used in composite formation, the classification of biodegradable polymers is given below, according to Averous and Boquillon (2004).



Scheme 2.5: *Classification of Biodegradable Polymers*
Source: Averous and Boquillon, 2004

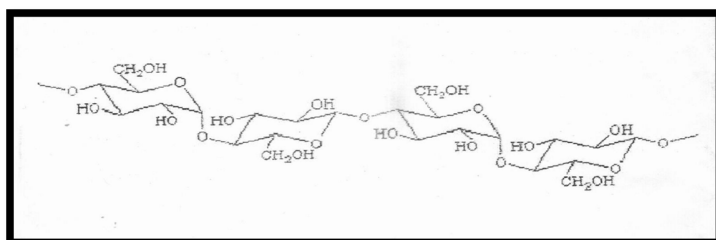
Scheme 2.5 shows a classification of biodegradable polymers in four-families. Except for the fourth family, which is of fossil origin, most polymers (family 1-3) are obtained from renewable

resources (biomass). The first family is agro polymers (e.g., polysaccharides) obtained from biomass by fraction. The second and third families are polyesters, obtained respectively by fermentation from biomass or from genetically modified plants (e.g., Polyhydroxyalkanoate, PHA) and by synthesis from monomers obtained from biomass (e.g., Polylactic acid, PLA). The fourth family is polyesters totally synthesized by the petrochemical process (e.g., Polycaprolactone (PCL), Polyesteramide (PEA), aliphatic or aromatic copolyesters). A large number of these biodegradable polymers (biopolymers) are commercially available. They show a large range of properties and they can compete with non-biodegradable polymers in different industrial fields (e.g., Packaging). Various studies done on composites from natural polymers/ biofibre, biopolymer/synthetic resin and biopolymer/biopolymer composite are discussed below: Naturally occurring biopolymers are derived from four broad feedstock areas (Tharanathan, 2003).

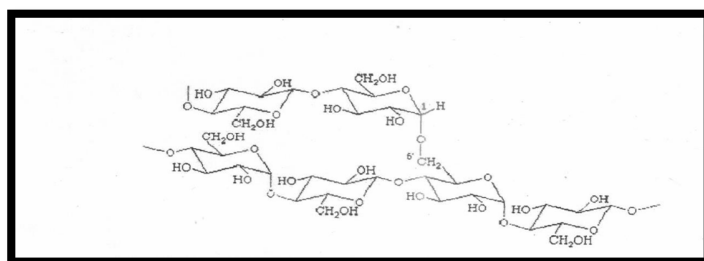
Animal sources provide collagen and gelatin, while marine sources provide chitin which is processed into chitosan. Microbial biopolymer feedstocks are able to produce Polylactic acid (PLA) and polyhydroxyalkanoates (PHA), while agricultural feedstocks provide starch, protein, cellulose, natural rubber, etc. (Kolybaba *et al.*, 2003).

2.14. Starch-Based Polymer Composites

Starch is an agricultural feedstock, hydrocolloid biopolymer found in various plants, including but not limited to wheat, corn, rice, beans and potatoes (Salmoral *et al.*, 2000; Martin *et al.*, 2001). Starch is usually utilized in the form of granules and is actually formed by one branched polymer, amylopectin and one linear polymer, amylose (Chandra & Rustgi, 1998). Amylose, the linear polymer, comprises approximately 20% w/w of starch, while amylopectin, the branched polymer, constitutes the remainder (Kolybaba *et al.*, 2003). Natural filler materials may be incorporated into synthetic plastic matrices as a rapidly biodegradable component. Often granular starch is added to polyethylenes to increase the plastic material's degradation rate (Kolybaba *et al.*, 2003). Starch can also be used in its gelatinized form (Verhooght *et al.*, 1995) or in its plasticized form (Martin *et al.*, 2001). Plastic materials that are formed from starch-based blends may be injection molded, extruded, blown or compression molded (Kolybaba *et al.*, 2003).



Scheme 2.6: Amylose Structure
Averous and Boquillon, 2004



Scheme 2.7: Amylopectin Structure and Cluster Model
Averous and Boquillon, 2004

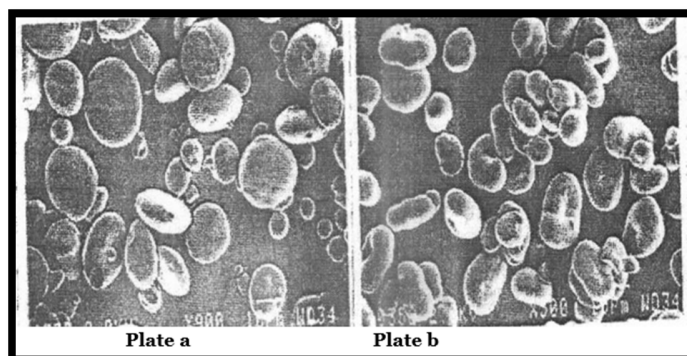


Plate 2.1 (A, B): Micrographs of Native Starch (SEM Observations): Wheat Starch (A) and Pea Starch (B). Scale = 10 Microns (Averous and Boquillon, 2004)

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance and its annual renewal (Long *et al.*, 2006). However, by itself, pure starch is not a good choice to replace petrochemical-based plastics. It is mostly water soluble, difficult to process and brittle when used without the addition of a plasticizer. In addition, its mechanical properties are very sensitive to moisture content (Long *et al.*, 2006). Blending two or more chemically and physically dissimilar natural polymers has shown the potential to overcome these difficulties (Long *et al.*, 2006).

In the 1970s and 1980s, numerous blends of starch and various polyolefins were developed. However, these blends were not biodegradable, and thus the advantage of using a biodegradable polysaccharide was lost (Long *et al.*, 2006). A great variety of materials derived from natural sources have been studied and proposed for different biomedical uses, namely polysaccharides (starch, alginate, chitin/chitosan) or protein (Soy, collagen, fibrin gel) and as reinforcement in the form of biofibres such as lignocellulosic natural fibres (Seal *et al.*, 2001; Mohanty *et al.*, 2000). Starch-based thermoplastic hydrogels for use as bone cement or drug-delivery carriers have been developed (Pereira *et al.*, 1998; Espigares *et al.*, 2002; Arvanitoyannis & Biliaderis, 1999) by blending starch with cellulose acetate. Pereira *et al.* (1998) reported on biodegradable hydrogels based on cornstarch/cellulose acetate blends produced by free-radical polymerization with methyl methacrylate and/or an acrylic acid monomer. The polymerization was initiated by a redox system consisting of benzoyl peroxide and 4-dimethylamino benzyl alcohol at low temperatures. Utilizing the biodegradable characters of starch-based blends with the biostability of the acrylic polymers, polymethylacrylate and polyacrylic acid used as the matrix of these systems and the incorporation of the well-known ceramic compound hydroxylapatite (Espigares *et al.*, 2002) produced partially biodegradable acrylic bone cement based on corn starch/ cellulose acetate blends. Varying amounts of a biocompatible, osteoconductive and osteophilic mineral component such as hydroxylapatite were incorporated to confer a bone-bonding character to the bone cement in this type of application (Espigares *et al.*, 2002).

In another related interesting research effort, Arvanitoyannis and Biliaderis (1999) reported on aqueous blends of methylcellulose and soluble starch, plasticized with glycerol or sugars, prepared by casting, extrusion and hot pressing. The observed glass transition temperature (T_g) depression for these polymer blends was proportional to the plasticizer content (water, glycerol and sugars). Although glycerol had a greater depressing effect on T_g than sorbitol, the latter had a greater impact as a plasticizer on the mechanical properties of the soluble starch/methyl cellulose blends. Generally, the tensile strength and flexural moduli of these blends were shown to decrease drastically with an increase in the total plasticizer content (Arvanitoyannis & Biliaderis, 1999).

In an effort to solve the problem observed in previous starch/cellulose acetate blends, Demirgoz *et al.* (2002) developed a method to control the moisture sensitivity of starch/cellulose acetate blends through chemical modifications. In their work, starch-based blends with cellulose acetate were chemically modified by chain cross-linking. This modification was based on the reaction between the starch hydroxyl groups and tri-sodium tri-metaphosphate. The resulting compounds were characterized by Fourier transform infrared (FTIR) and the respective properties were assessed and compared to the

original materials by means of the hydration degree, the degradation behaviour, contact angle measurements and mechanical testing. The results showed that the water uptake of these blends could be reduced by up to 15% and that, simultaneously, stiffer materials with a less pronounced degradation rate could be obtained (Demirgoz *et al.*, 2002).

2.15. Polymer Nanocomposites

Since the pioneering work by the Toyota group in the early 1990s, Oriakhi and Lerner (2002), on nylon-clay-based nanocomposites, polymer nanocomposites have attracted an increasing amount of attention (Long *et al.*, 2006). Polymer nanocomposites, such as polymer/silicate nanocomposites, have been shown to exhibit significant improvements in properties compared with pure polymers or conventional composites (Long *et al.*, 2006). The inclusion of well-dispersed nanosilicates in polymers has led to a vast array of changes in properties, including increased storage modulus, increased tensile and flexural properties, and decreased permeability and flammability (Long *et al.*, 2006; Oriakhi & Lerner, 2002).

A number of researchers have presented work in the field of starch nanocomposites. Park *et al.* (2001) reported on the preparation and properties of gelatinized starch/montmorillonite (MMT) clay nanocomposites using both naturally occurring sodium MMT and a number of alkyl ammonium-modified clays. X-ray diffraction studies (XRD) and transmission electron microscopy (TEM) showed an intercalated structure for the starch/sodium MMT.

However, the modified clays appeared either unchanged or agglomerated in structure (Park *et al.*, 2001). Park *et al.* (2001) found that the unmodified sodium MMT/ starch nanocomposite also exhibited the greatest increase in modulus of all the clays used. They also investigated the effect of clay content on the barrier properties of the nanocomposites and found that increasing clay content led to an improvement in barrier properties (Park *et al.*, 2001).

Huang *et al.* (1990) similarly investigated the formation of MMT-reinforced glycerol/plasticized thermoplastic starch using melt extrusion. Scanning electron microscopy (SEM) showed well-dispersed MMT platelet. Fourier transform infrared (FTIR) spectroscopy indicated that cooperation existed between MMT, starch molecules and hydrogen bonds that formed between the reactive hydroxyl groups of MMT and hydroxyl groups of starch molecules. The mechanical and thermal properties of the starch nanocomposites formed showed significant improvements (Huang *et al.*, 1990).

Preparation of natural rubber/ silica nanocomposite using one-and two-dimensional dispersants by latex blending process was attempted by Peng *et al.* (2016). The dispersion behaviours of graphene oxide (GO) and Poly (sodium P-styrene sulfonate) (PSS) modified silica doped into natural rubber (NR) matrix were investigated. Both GO and PSS improved the dispersibility of silica in the NR composition, and the tensile and tear strength of the NC/GO/ SiO₂ and NR/PSS/SiO₂ were improved compared to those of the NR/SiO₂ composites. Their strategy of modifying silica with GO and PSS has proven an effective approach for the development of elastic nanocomposites with application in the tyre industry (Peng *et al.*, 2016).

In a similar development, Menon *et al.* (2017) used phosphorylated cashew nut shell liquid prepolymer (PCNSL) as an organomodifier for kaolin and studied the role of the PCNSL-modified kaolin as a reinforcing nanofiller in natural rubber (NR) and its blends with Polybutadiene rubber (BR). Their findings revealed that PCNSL could act as a coupling agent and compatibilizer between kaolin and rubber. Improved physico-mechanical properties were observed at a dosage of 6phr of the modified kaolin in NR. Blends of NR with BR containing precipitated silica/PCNSL-modified kaolin hybrid filler showed improved tensile properties, tear strength and flex fatigue resistance along with lower heat build-up, which could be beneficial for applications such as automobile tyre sidewalls (Menon *et al.*, 2017).

Cao *et al.* (2017) also investigated the high reinforcing filler effect of cellulose nanocrystals (CNCs) extracted from tunicates (marine biomass) on epoxidized natural rubber (ENR). It was observed that hydrogen bonding formed between ENR and CNCs led to the homogeneous dispersion of CNCs and enhanced interfacial adhesion between them. Moreover, t-CNCs (cellulose nanocrystals from tunicates) with longer lengths and larger aspect ratios facilitated filler entanglements which led to higher reinforcing efficiency. Consequently, both hydrogen bonding and filler entanglements contributed to the improved mechanical properties of ENR/tCNCs nanocomposites (Cao *et al.*, 2017).

Ma *et al.* (2018) further investigated the role of particle size and reactive coNm-2tibilization on polymer nanocomposites. Ethylene-co-vinyl acetate rubber (EVM) possesses a low tensile strength (2 Nm⁻²) which limits its application range. Therefore, nano-sized starch (NSt) was used to reinforce it. Nano-sized starch (NSt) was reported as a reactive filler to reinforce ethylene-co-vinyl acetate rubber (EVM) by using epoxy-functionalized EVM (GMA-EVM) as compatibilizer together with 3-(2-aminoethylmino) propyl dimethoxy methyl silane (KH6O₂). This resulted in EVM/GMA-EVM/NSt nanocomposites having significantly improved properties. The improvement is attributed to the small starch particle size and chemical coNm2tibilization. The tensile strength (Ts) was increased from 9.2 to 18.7Nm⁻² when 20phr (per hundred rubber by weight) of the GMA-EVM compatibilizer was incorporated. Compared to EVM/Nst, the EVM/GMA-EVM/Nst nanocomposites possess stronger interfacial interaction between the fillers and the matrix according to morphology and crosslink density analysis. Besides the crosslink of EVM and GMA-EVM-chains created by dicumyl peroxide (DCP), under the aid of KH6O₂, extra chemical bonding was generated between (a) GMA-EVM chains, (b) GMA-EVM and Nst. Thus, strong reinforcement of EVM was obtained (Ma *et al.*, 2018).

Furthermore, there was an improvement in the properties of natural rubber composites reinforced with a complex filler network of biobased nanoparticles (soy particles) and ionomer, and carboxylated styrene-butadiene was undertaken (CSB) by Jong (2018). It was discovered that the effect of carboxylated styrene-butadiene (CSB) in conjunction with soy nanoparticles caused young modulus and tensile stress at 100 – 300% elongation to increase significantly while maintaining good tensile strength. CSB also improves the cohesion within the composites. The increase of reinforcement factor with increasing CSB and filler concentration in the composites indicates that the effect of CSB increased the reinforcement of soy nanoparticles more significantly at higher than lower filler concentrations. The results indicate great potential for improving rolling resistance in tyre tread applications (Jong, 2018).

2.16. Starch/ Polylactic Acid Composites

Another application of starch in biopolymer composites is in polylactide polymers (PLA), with an advantage in cost reduction since starch is an abundant, renewable, cheap and biodegradable biopolymer (Long *et al.*, 2006). Polylactide polymers have gained enormous attention as a replacement for conventional synthetic packaging materials in the last decade (Long *et al.*, 2006). By being truly biodegradable, being derived from renewable resources and providing consumers with extra end-user benefits such as avoiding paying the “green tax” in Germany or meeting environmental regulations in Japan, Polylactic acid (PLA) polymers are a growing alternative for packaging materials in numerous demanding markets (Long *et al.*, 2006). PLA is a biodegradable polymer, but its applications are limited by its high cost. Blending starch with PLA is one of the most promising efforts because starch is an abundant and cheap biopolymer and PLA is biodegradable with good mechanical properties (Long *et al.*, 2006). Ke *et al.* (2003) characterized blends of starch and PLA in the presence of various water contents. It was found that the initial moisture content of the starch had no significant effect on its mechanical properties but had a significant effect on the water absorption of the blends. Also, the thermal and crystallization properties of PLA in the blend were not affected by moisture content. Ke *et al.* (2003) also reported that the blends prepared by compression moulding had higher crystallinities than those prepared by injection moulding. However, the blends prepared by injection moulding had higher tensile strengths and elongations and lower water absorption values than those made by compression moulding. The crystallinities of the blends increased greatly with annealing treatment at the PLA second crystallization temperature. The decomposition of PLA indicated that PLA degraded slightly in the presence of water under the processing temperatures used (Ke *et al.*, 2003).

In another related research, Park and Im (2000) reported blends of PLA with gelatinized starch mixed with various ratios of water/glycerol using a twin-screw mixer. Gelatinization of starch was found to lead to the destruction or diminution of hydrogen bonding in starch granules and a decrease in crystallinity. Calorimetry data showed that starch acted as a nucleating agent and glycerol as a plasticizer, contributing to an improvement in the crystallinity of the PLA blends. When the content of starch increased, the size of spherulites in PLA blends was smaller and less regular. In the case of PLA/pure starch blends, voids appeared that were formed by the separation of starch particles from the matrix. These voids were not observed in the PLA/gelatinized starch blend. Similar blends were also

reported by Martin and Averous (2004). The mechanical properties gave a strong indication that a low level of compatibility existed in these blends. The blends showed two distinct T_g values. However, the T_g due to the PLA phase shifted towards the T_g of thermoplastic starch (TPS) with the blend composition, indicating some degree of interaction. Microscopic observations revealed non-uniformly dispersed PLA inclusions in the TPS Matrix, confirming that phase separation has occurred (Park & Im, 2000; Long *et al.*, 2006; Martin & Averous, 2001). However, the low level of compatibility in most biopolymer/biopolymer composites is being addressed by the incorporation of biofibres into natural polymers such as protein, starch, natural rubber, PLA, etc., in order to improve mechanical properties and compatibility (Long *et al.*, 2006).

2.17. Biofibre/ Biopolymer Composites

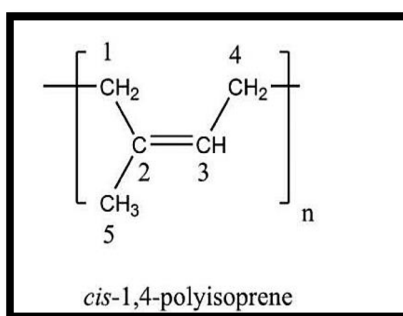
Fibre-reinforced plastics have successfully proven their value in various applications because of their excellent specific properties, e.g., high strength and stiffness and low weight (Long *et al.*, 2006). In this respect, natural fibres are of basic interest since they not only have the functional capability to substitute the widely used glass fibres but also have advantages from the point of view of weight and fibre-matrix adhesion, specifically with polar matrix materials. They have good potential for use in waste management due to their biodegradability and their much lower production of ash during incineration (Long *et al.*, 2006).

Alvarez *et al.* (2004) reported on biodegradable polymers based on starch reinforced by short sisal fibres with a range of fibre content of 5-15wt%. Curvelo *et al.* (2001) used cellulosic fibres from Eucalyptus urograndis pulp as reinforcement for thermoplastic starch to improve its mechanical properties. The composites were prepared with regular cornstarch plasticized with glycerol and reinforced with short cellulosic fibres (16% w/w) from the bleached pulp. The fibres were added to the thermoplasticized starch directly in an intensive batch mixer at 170°C. The mixture was hot pressed to 2-3mm thick plates and then cut to prepare the specimens for mechanical test. The composite showed an increase of 100% in tensile strength and more than 50% in modulus with respect to the non-reinforced thermoplastic starch. Scanning electron microscopy (SEM) of fractured surfaces revealed very good adhesion between the fibres and the matrix (Curvelo *et al.*, 2001). The results obtained clearly showed the advantages of using thermoplastic starch reinforced with cellulosic fibre, a natural, cheap and abundant material.

In a related research effort, Carvalho *et al.* (2003) characterized compounds of conventional cornstarch and glycerol reinforced with cellulose fibres by high-performance size exclusion chromatography. The compounds and composites were prepared in an intensive batch mixer at 150-160°C, with glycerol and fibre contents in the range of 30-50wt% and 1-15wt%, respectively. The results showed that an increase in glycerol content reduced starch degradation, whereas an increase in fibre content led to increased degradation. The change in the chromatographic profiles was more pronounced in the higher molecular weight fraction, corresponding to amylopectin.

2.18. Biofibre/ Natural Rubber Composites

Natural rubber is a high molecular weight polymeric substance with viscoelastic properties in which essentially all the isoprenes have the cis 1, 4-configuration, thus structurally, it is cis 1,4 -polyisoprene (Billmeyer, 2007; Rubber Board, 2002). Isoprene is a diene and 1,4 addition leaves a double bond in each of the isoprene units in the polymer, and because of this, natural rubber shows all the reactions of an unsaturated polymer. It gives additional compounds with halogens, ozone, hydrogen chloride and several other reactants that react with olefins (Rubber Board, 2002).



Scheme 2.8: Repeat Unit of Isoprene

The natural rubber polymer has a number average degree of polymerization of about 5000 and a broad distribution of molecular weights (Billmeyer, 2007). An interesting reaction of natural rubber is its combination with Sulphur, a reaction known as vulcanization which converts the plastic and viscous nature of raw rubber into an elastic mass with high tensile strength and comparatively low elongation (Rubber Board, 2002). It should be noted that the properties of elastomers like natural rubber depend, to a very large extent, on the details of vulcanization, reinforcement and compounding. It has also been discovered that the tensile strength of natural rubber can be increased to about 40% by reinforcement (Billmeyer, (2007).

As a result of its elasticity, resilience and toughness, natural rubber (NR) is the basic constituent of many products used in the transportation, industrial consumer, hygienic and medical sectors. Of the major end-use markets for rubber, transportation is by far the largest single sector, with tyres and tyre products accounting alone for over 50% of NR consumption (UNCTAD, 2002). Non-tyre rubber items include industrial products like transmission and elevator belts, hoses and tubes, industrial lining and bridge bearings, consumer products like golf balls, footballs, sports goods, erasers, footwear, and articles for use in the medical and health sector (condoms, catheters, surgical gloves, etc.) (UNCTAD, 2011; Rubber Board, 2002).

The primary advantage and effects of biofibre reinforcement on the mechanical properties of natural rubber composites include increased modulus, increased strength with good bonding at high fibre concentrations, decreased elongation at failure, greatly improved creep, increased and substantial improvement in cut, tear, and puncture resistance. The reinforcement by *Cocos nucifera*, a fruit fibre in natural rubber, has been extensively studied (Geethamma & Thomas, 1995). Research has also been directed towards the understanding of the effects of leaf fibre sisal in natural rubber (Varghese *et al.*, 1995). Results indicated improvements in mechanical properties.

The effects of concentration on the mechanical properties of oil palm-reinforced natural rubber composites were also investigated by Ismail *et al.* (1997) and they observed a general trend of reduction in tensile and tear strength with increasing fibre concentration. The above phenomena suggest the need for alignment of fibres to achieve the desired reinforcement leading to a more improved modulus.

Pineapple fibre and jute fibre have been found to be potential reinforcements in natural rubber (Bhattacharya *et al.*, 1986; Arumugan *et al.*, 1989). Researchers have utilized a novel fibre, isora (*Helicteres isora*), a stem fibre in natural rubber, to produce biocomposites (Lovely *et al.*, 2004). The fibres are separated by the process of retting. Isora resembles jute in appearance but surpasses it in terms of strength, durability and lustre. This is manifested in the properties of the reinforced phase (Lovely *et al.*, 2004). The effects of different chemical treatments like mercerization, acetylation, benzoylation and silane coupling agents on isora fibre properties were also investigated. They found out that isora fibre has immense potential as reinforcement in natural rubber. In a similar study, a unique combination of sisal and oil palm fibres in natural rubber has been utilized to design hybrid composites (Jacob *et al.*, 2004). It was seen that the incorporation of the fibres resulted in increased modulus. Also, chemical modification of both sisal and oil palm fibres was imperative for increased interfacial adhesion properties (Jacob *et al.*, 2004). The viscoelasticity, water absorption, dielectric and stress relaxation were also investigated. These properties were all enhanced by chemical modification (Jacob *et al.*, 2004).

However, most natural rubber products like footwear, gloves, automobile tyres, tubes, etc., are not biodegradable or compostable and, at the end of their service life, are usually disposed resulting in environmental degradation problems and when they are burned in incinerators, produce noxious fumes, carbon monoxide, carbon (iv) oxide and other dangerous hydrocarbon gases which are harmful to man and the ozone layer (Kolybaba *et al.*, 2003). Biodegradation of vulcanized rubber material is possible, although it is difficult due to the inter-linkages of the poly (cis-1,4,- isoprene) chains which result in reduced water absorption and gas permeability of the polymer (Jacob *et al.*, 2007). Certain streptomyces strains were reported in the degradation of rubber samples after twelve (12) months of incubation (Jacob *et al.*, 2007).

A major hurdle to the commercialization of green composites is the high cost of biodegradable matrix materials. Most biodegradable resins cost significantly more than the commonly used resins. Starch, being a cheap, natural resource and one of the most promising natural polymers from renewable resources (PFRR) owing to its inherent biodegradability and overwhelming abundance, has found application in natural rubber composites formation (Long *et al.*, 2006); (Zhang *et al.*, 2004).

2.19. Starch/ Rubber Composites

Natural rubber has been blended with starch for a number of different applications (Long *et al.*, 2006). Arvanitoyannis *et al.* (1997) reported on biodegradable blends based on gelatinized starch and 1,4-transpoly isoprene (gutta percha) for food packaging and biomedical applications. Components are mixed to an adequate degree of dispersion by thermal pressing.

A series of blends of gutta-percha with gelatinized starch, with and without plasticizers or compatibilizers, was prepared in an attempt to preserve the excellent biocompatibility of gutta-percha. A lower percentage concentration of plasticizer was incorporated into the blends to improve mechanical properties. The gas and water permeability values of the blends were found to be intermediate values between the two components (Arvanitoyannis *et al.*, 1997). The plasticizers considerably increased the percentage elongation but decreased the tensile strength, glass transition temperature and melting points of the composite matrix (Arvanitoyannis *et al.*, 1997).

The mechanical properties of starch-filled rubbers actually depend on many factors, among which the most important ones are the dispersion level, the interfacial strength, and the type of starch. However, the polar surface, high melting point, and large particle size of starch make it difficult to finely disperse starch in a rubber matrix (Zhang *et al.*, 2004). Therefore, the incorporation of starch into natural rubber by direct blending results in a micro-composite with large, dispersed particles, which causes significant deterioration of the mechanical properties of the vulcanizates, especially the resistance to abrasion and the tear properties (Zhang *et al.*, 2004). In order to finely disperse starch in a rubber matrix, Buchanan *et al.* (1971) and Buchanan *et al.* (1975) prepared cross-linked starch xanthide-rubber masterbatches by coprecipitating mixtures of soluble starch xanthide and elastomer lattices, during which starch xanthide was cross-linked. In the prepared curds, starch worked as the continuous phase and the latex particles as the disperse phase. The starch-elastomer crumb was further extruded to produce a phase inversion. As a consequence, it was demonstrated that cross-linked starch xanthide could be used as an effective rubber-reinforcing agent, especially in improving the fatigue life and abrasion resistance, when used to partially replace carbon black in a premium tread (Zhang *et al.*, 2004).

Similarly, a composite of starch/plasticizer with a lower softening point than that of starch was used to blend with rubber at a processing temperature high enough to cause the starch to melt, for example, in the range of about 150°C to 170°C, to generate a fine dispersion of starch in the rubber matrix (Zhang *et al.*, 2004). However, if this method is applied, it must be carried out at quite a high temperature and may cause the unsaturated elastomers to degrade. Additionally, some kinds of plasticizers, such as ethylene vinyl copolymer or poly (vinylalcohol), which are incompatible with non-polar rubber molecules, are inevitably introduced into the rubber matrix.

Another disadvantage of this method is that it is too complex (Zhang *et al.*, 2004).

Similarly, Carvalho *et al.* (2003) prepared thermoplastic starch/natural rubber blends, where rubber was the dispersed phase, by mixing a small amount of natural rubber latex with glycerolplasticized cornstarch in a Haake mixer without a co-coagulation process. The results revealed a

reduction in modulus and tensile strength, making the blends less brittle than thermoplastic starch alone. Phase separation was observed in some compositions, which was dependent on rubber and plasticizer content (glycerol). Increasing the plasticizer content made the addition of higher amounts of rubber possible. The addition of rubber was, however, limited by phase separation, the appearance of which depended on the glycerol content. Scanning Electron Microscopy (SEM) showed good dispersion of the natural rubber in the continuous phase of the thermoplastic starch matrix (Carvalho *et al.*, 2003). Moreover, the presence of non-rubber constituents of the latex was not only responsible for insuring the latex stability but also for improving the compatibility between the thermoplastic starch and the natural rubber phases (Long *et al.*, 2006).

Furthermore, another type of polymeric composite based on natural rubber and plasticized starch as a filler was prepared, characterized and cross-linked using peroxide in the presence of a polyfunctional monomer-trimethylolpropane trimethacrylate as a vulcanization co-agent (Stelescu *et al.*, 2017). They investigated the influence of plasticized starch amount on the physical-mechanical properties and behaviour in aqueous and toluene environments. The results revealed that the composites prepared have good physical-mechanical characteristics. There was a non-uniform increase in hardness, tensile strength and elongation at break and a non-uniform decrease in elasticity and tear strength. Moreover, natural rubber is resistant to water (variation of mass and volume in water has very low values) but not resistant to toluene (variation of mass and volume in toluene has high values). Starch is hydrophilic in nature – it absorbs water, and with an increased amount of starch in the blend, there is also an increase of mass and volume variation in water, although below 8%, which is moderately good.

These properties indicate that plasticized starch may successfully replace inorganic fillers in rubber mixtures, which are harmful and may cause occupational illnesses to employees in the rubber processing industry (Stelescu *et al.*, 2017). In another recent development, porous starch was efficiently esterified by dodecyl succinic anhydride (DDSA) in an attempt to modify starch to enhance better reinforcement (Wang *et al.*, 2018). In this study, the substitution degree of starch – dodecylsuccinate was optimized via single-factor experiments. Compared with the properties of composites containing carbon black as a unique reinforcing filler, the composites supplemented by DDSA-PS instead of partial carbon black exhibited relatively lower mechanical properties due to the probability of aggregation of modified porous starch under an increasing ratio of DDSA-PS/CB. However, the DDSAPS/CB/NR composites demonstrated the relieved Payne effect and, more significantly, the improvement of rolling resistance, hysteretic properties and generation of heat built-up. Therefore, DDSA-PS developed in this research will be a promising candidate as a novel filler in the nearest future in the rubber processing industry (Wang *et al.*, 2018).

Currently, there is an environmental pollution problem generated in part by packaging materials produced from non-biodegradable synthetic polymers made from petroleum. In an effort to solve this problem, Riyajan and Patisat (2018) have developed a novel packaging film from cassava starch (CS) and natural rubber (NR). The novel biopolymer film was obtained from the CS and NR using glycerol (GE) as a plasticizer in a water-based system. Having studied the physical properties of a 95/5 CS/NR blend film with varying glycerol (GE) contents based on their swelling ratio, moisture content, moisture absorption, mechanical properties and biodegradability in soil, it was found that the moisture content and moisture absorption tended to be directly proportional to the GE content, while the moisture content and moisture absorption of the sample decreased as a function of the NR content. The swelling ratio of the 95/5 CS/NR blend slightly decreased as a function of the NR and GE content. The elongation at the break of the CS/NR blend was also improved by the addition of GE. Moreover, the film showed good decomposition after 8 weeks in natural soil. Therefore, blending CS with NR in an appropriate amount helps to enhance the tensile strength, elongation at break and moisture resistance of CS films and also provides environmentally compatible solutions for waste disposal (Riyajan & Patisat, 2018).

2.20. Application of Biocomposites

Research and development is only a portion of the work done to introduce the use of biodegradable polymer materials (Kolybaba *et al.*, 2003). The design of such materials usually begins with a conceptual application. It may be expected to replace an existing material or a complementary one. Sectors where

applications for biopolymers have been introduced include (but are not limited to) medicine, packaging, agriculture, and the automotive industry (Kolybaba *et al.*, 2003). Biopolymers that may be employed in packaging continue to receive more attention than those designated for any other application. All levels of government, particularly in China (Chau & Yu, 1999) and Germany (Bastioli, 1998), are endorsing the widespread application of biodegradable packaging materials to reduce the volume of inert materials currently being disposed of in landfills occupying scarce available space. It is estimated that 41% of plastics are used in packaging and that almost half of that volume is used for packaging food products (Kolybaba *et al.*, 2003).

BASF, a world leader in the chemical and plastic industry, is working on further development of biodegradable plastics based on polyester and starch (Fomin, 2001). Ecoflex is a fully biodegradable plastic material that was introduced to consumers by BASF in 2001. The material is resistant to water and grease, making it appropriate for use as a hygienic disposable wrapping, and fit to decompose in normal composting systems. Not all biopolymer applications in the field of medicine are as involved as artificial organs. The umbrella classification of bioactive materials includes all biopolymers used for medical applications. One example is artificial bone material which adheres and integrates into the bone in the human body. The most commonly employed substance in this area is called bioglass (Kokubo *et al.*, 2003).

The automotive sector is responding to societal and governmental demands for environmental responsibility. Biobased cars are lighter, making them a more economical choice for consumers as fuel costs are reduced. Natural fibres are substituted for glass fibres as reinforcement materials in plastic parts of automobiles and commercial vehicles (Lammers & Kromer, 2002). Starch-filled rubbers (starch/rubber composites) will also find application in footwear, handgloves, sportsgoods, tyre tubes, etc., with partial or full biodegradability and with good performance properties (Kolybaba *et al.*, 2003; Zhang *et al.*, (2004). The attraction of biocomposites in all these areas is their derivation from renewable resources, slowing the depletion of limited fossil fuel reserves (Kolybaba *et al.*, 2003).

2.21. Swelling of Rubber Biocomposites

Generally, polymer-based materials are not soluble in water, but they are capable of absorbing various amounts of water depending on their chemical nature, formulation and on the humidity and temperature of the environment to which they are exposed (Paiva Jr *et al.*, 2004). Liquid swelling experiments of composites are essential for the following reasons:

- As a method to analyze their service performance in a liquid environment and
- To study the characteristics of the matrix-fibre interface (Geethamama & Thomas, 2005).

Articles made from composites come in contact with different liquids during their service performance. They come in contact with liquids or vapours, either aqueous or organic, affecting the immediate and long-term performance of the material. This can happen either as a part of the service requirement, like in the case of oil seals, marine articles, etc., or by the accidental splashing of oil greases that occurs with automobile components (Kumar *et al.*, 2012). Moreso, solvent swelling experiments of rubbery composites are also important as a method of analyzing their service performance when in contact with solvents (Lovely *et al.*, 2006). Swelling of rubber vulcanizates in a number of solvents has been studied (Khinavar & Aminabhavi, 1991). An important difference between vulcanized and raw rubber is that vulcanized rubber possesses a structure that cannot be broken down completely by any solvent. The materials, therefore, swells and cannot be dispersed (Lovely *et al.*, 2006). The contact of rubbers with organic solvents can be well explained by absorption and diffusion phenomena. Equilibrium swelling is another technique that has been used to assess fibre/rubber adhesion (Lovely *et al.*, 2006; Jacob *et al.*, 2004). Swelling parameters are used to evaluate the swelling behaviour of rubber biocomposites, namely: swelling index percentage and swelling coefficient (α). This swelling study (parameters) provides information on the interface strength, degree of dispersion of fibres and their alignment in the elastomer matrix. The swelling behaviour of rubber biocomposites can also be defined as an index of the ability with which the sample swells (Lovely *et al.*, 2006).

2.22. Biodegradability of Rubber Composites

Synthetic polymers were extensively used for multi-purpose applications in the past because of their satisfactory mechanical and thermal properties. However, their lack of biodegradability has recently complicated and discouraged their use (Albertsson & Karlsson, 1994; Wool, 1995). According to Albertsson and Karlsson (1994), biodegradation is defined as an event that takes place through the action of enzymes and/or chemical decomposition associated with living organisms such as bacteria or fungi. Natural rubber (NR) is a macromolecular isoprenoid, poly (cis-1,4-isoprene) and is synthesized by more than 2000 plant species, mostly belonging to the Euphorbiaceae, and by some fungi (Jendrossek *et al.*, 1997). Despite the development of chemosynthetic rubbers, NR is still produced in large amounts (107 tons/year) from the rubber tree *Hevea brasiliensis* and is used to produce tyres, latex gloves, condoms, etc.

Degradable polymer composites such as rubber composites have long been considered part of the solution to the environmental and waste management problems posed by the extensive use of non-degradable polymeric materials (Kim, 2012). One of the most commonly used approaches to create such degradable rubber composites is to incorporate starch and natural fibres (hydrophilic biodegradable components) into the rubber elastomer to enhance its biodegradability (Kim, 2012; Kolybaba *et al.*, 2003).

Rubber composites used for the tread of 'green' tyres have attracted increasing interest in recent years (Zhang *et al.*, 2004). This is mainly due to the fact that energy consumption and carbon (iv) oxide emission from automobiles has become a serious threat to the environment. Starch, which is a natural, cheap, and easily biodegradable polymer, has the potential to be tentatively used as a biodegradability-enhancing material in rubber products (Zhang *et al.*, 2004). The degradation of natural rubber was first studied by Sohngen and Fol, cited in Jendrossek *et al.* (1997), who used solution-cast films of NR as the carbon source for the isolation of natural rubber (NR) – degrading microorganisms. The isolated natural-rubber degrading microorganisms can then be used to degrade rubber composites of various compositions and formations (Jendrossek *et al.*, 1997). Recently, there has been an increasing surge of interest in the field of plant fibre-reinforced rubber composites. Biofibre-reinforced rubber composites are used in various fields ranging from the automotive industry to the construction industry due to their lightness and partial degradation properties (Jacob *et al.*, 2007). Jacob *et al.* (2007) investigated the biodegradability and aging characteristics of hybrid biofibre-reinforced natural rubber biocomposites. In their research, natural rubber was reinforced with sisal and oil palm fibres and composites were fabricated based on different fibres loading. Chemically modified fibres, namely mercerized and silanized fibres, were also used to prepare composites. Biodegradation tests were carried out under soil burial conditions. It was seen from their findings that the durability of the composites was greatly dependent on chemical treatment and fibre content. Aging experiments were performed using a scanning electron microscope to evaluate the degree of degradation after 12 months of exposure to soil. Results revealed that rubber composites containing chemically functionalized biofibres were found to be less prone to degradation (Jacob *et al.*, 2007). The losses in mechanical properties were found to increase with fibre content, indicating that biodegradation was more dependent on the presence of lignocellulosic fibres than on natural rubber matrix (Jacob *et al.*, 2007).

2.23. Natural Rubber Degrading Bacteria

The degradation of natural rubber (NR) was first studied by Sohngen and Fol (1914), cited in Jendrossek *et al.* (1997), who used solution-cast films of natural rubber as the carbon source for the isolation of NR-degrading microorganisms. Spence & Van Niel (1936), cited in Jendrossek *et al.* (1997), developed a more sensitive clear zone technique by emulsifying NR latex in mineral agar resulting in an opaque medium. Growing on those media, NR – degrading microorganisms form translucent halos around the colonies. This technique was used to isolate a few NR-degrading fungi and bacteria (Borel *et al.*, 1982).

Evidence for the presence of an extracellular polyisoprenoid oxygenase, which specifically cleaves NR, was shown for a xanthomonas strain, and acetonyl-diprenyl-acetaldehyde was identified as low molecular mass degradation products (Tsuchii & Takeda, 1990).

Besides natural rubber, chemically cross-linked (e.g., vulcanized) rubber can also be biodegraded slowly by microorganisms (Heisey & Papadatos, 1995; Tsuchii *et al.*, 1996).

Biodegradation of vulcanized rubber material is possible, although it is difficult and very slow due to the interlinkages of the poly (cis -1,4- isoprene) chains (Jacob *et al.*, 2007). However, Jacob *et al.* (2007) reported that certain *Streptomyces* strains were seen to degrade rubber samples after 12 months of incubation. In their study above, tensile specimens were exposed to soil for a period of 6 and 12 months and the tensile strengths were coNm-2red before and after burial. Results revealed significant weight loss of the tensile samples on exposure to soil. There was also substantial decay in the mechanical performance of the rubber composites (Jacob *et al.*, 2007).

Jendrossek *et al.* (1997) reported on the biological mechanism of polyisoprene degradation even as they screened various culture collections and isolated and characterized a large number of natural rubber-degrading bacteria from various ecosystems in Singapore, Malaysia, Germany and Italy. In a similar research on bacterial degradation, Jendrossek *et al.* (1997) also reported using natural rubber latex as the sole source of carbon and energy and isolated 50 rubber-degrading bacteria. Out of these 50 isolates, 33 were identified as *Streptomyces* species and 8 as *Micromonospora* species. Jendrossek *et al.* (1997) reported screening of 1220 bacteria obtained from different culture collections and obtained 46 additional rubber-degrading bacteria as follows:

- *Streptomyces* 31 strains,
- *Micromonospora* 5,
- *Actinoplanes* 3,
- *Nocardia* 2,
- *Dactylosporangium* 1,
- *Actinomadura* 1,
- Unidentified 3.

Morphological characterization of aerial mycelium and spore chains in combination with fatty acid pattern justified the classification of 5 strains as the species *S. coelicolor*, 9 strains as *S. griseus*, 4 strains as *S. halstedii*, 6 strains as *S. rochei* and 1 strain as *S. violaceo* (Jendrossek *et al.*, 1997).

All the rubber-degrading isolates were identified as members of the *Actinomycetes*, a large group of mycelium-forming Gram-positive bacteria. Interestingly, no Gram-negative bacterium was isolated during the experimentation (Jendrossek *et al.*, 1997). Growth of selected strains in liquid mineral medium with solution-cast films of NR (0.2%) as a carbon source resulted in significant weight loss (10-30%) and reduction of the weight average molecular mass of the residual polymer from 640,000 to 25,000 as determined by gel permeation chromatography (Jendrossek *et al.*, 1997). This significant reduction of the average molecular mass of solution-cast films of natural rubber from 640,000 to 25,000 in liquid culture upon bacterial growth indicates the participation of an endo-cleavage mechanism of degradation (Jendrossek *et al.*, 1997).

2.24. Biodegradation Process

Biodegradation, according to Albertsson and Karlsson (1994), is defined as an event that takes place through the action of enzymes and/or chemical decomposition associated with living organisms, such as bacteria or fungi. Just as important as how a material is formed is how it is degraded (Albertsson & Karlsson, 1994). A general statement regarding the breakdown of polymer material is that it may occur by microbial action, photodegradation, or chemical degradation (Kolybaba *et al.*, 2003). All three methods are classified under biodegradation, as the end products are stable and found in nature (Kolybaba *et al.*, 2003).

Several methods are usually applied to assess the biodegradability of novel materials. Some of the classical methods are: burial in soil, exposure to seawater, enzymatic hydrolysis, simple water hydrolysis (exposure to water at pH 7.0) and accelerated alkali hydrolysis (Arvanitoyannis *et al.*, 1997). The soil burial method is well-known to be a slow process mainly because of the low percolation rate (Peanasky *et al.*, 1991; Gopheen & Wool, 1991). However, it is noteworthy that the burial soil test reflects more than any other test on real-life conditions, though soil composition usually varies from place to place (Arvanitoyannis *et al.*, 1997). Normal soil bacteria and water are generally all that is required

(Sain, 2002). Polymers which are based on naturally grown materials (such as starch or flax fibre) are susceptible to degradation by microorganisms (Kolybaba *et al.*, 2003).

In the case of materials where starch is used as an additive to a conventional polymer matrix, the polymer in contact with the soil and/or water is attacked by the microbes. The microbes digest the starch, leaving behind a porous, sponge-like structure with a high interfacial area and low structural strength. When the starch component has been depleted by an enzymatic attack, each reduction results in the scission of a molecule, slowly reducing the weight of the matrix until the entire material has been digested (Shetty *et al.*, 1990).

Photodegradable polymers undergo degradation from the action of sunlight (ASTM 883-96). In many cases, polymers are attacked photochemically and broken into small pieces. Further microbial degradation must then occur for biodegradation to be achieved (Kolababa *et al.*, 2003). Some biodegradable polymer materials experience a rapid dissolution when exposed to particular (chemically based) aqueous solutions. For example, environmental polymer product is soluble in hot water. Once the polymer dissolves, the remaining solution consists of polyvinyl alcohol and glycerol (Kolybaba *et al.*, 2003). Similar to many photodegradable plastics, full biodegradation of the aqueous solution occurs later through microbial digestion (Blanco, 2002).

3|Materials and Methods

3.1. Materials

Local varieties of starchy crops, *Manihot esculenta* Crantz (cassava), *Dioscorea rotundata* Poir (yam), *Ipomoea batatas* (L) Lam (sweet potato), and *Colocasia esculenta* (L) Schott (cocoyam) were purchased from agricultural food market in Mubi, Adamawa State, Nigeria, while *Tacca leontopetaloides*, polynesian arrow root (amora) was obtained from a farmland in Paiko village, Gwagwalada area council FCT, Nigeria. Natural rubber latex, dry rubber content (DRC) 30% was obtained from Rubber Research Institute of Nigeria, (RRIN) Iyanomo, Benin City, Edo State, Nigeria. Calcium Chloride (coagulating agent) supplied by BDA (laboratory grade) was purchased from a laboratory/ diagnostic material store in Benin, while toluene (swelling solvent) supplied by BDA (laboratory grade) was purchased from a chemical store at Gwagwalada, Abuja. Compounding chemicals and additives (Zinc oxide, Stearic acid, Mercaptobenzothiazole, Tetramethylquinoline, Sulphur and Carbon black) (industrial grades) supplied by Parchem fine and specialty chemicals were purchased from the industrial chemical store at Benin City, Edo State.

3.2. Methodology

3.2.1. Extraction of Starch

The method of Vasanthan (2001) was adopted to extract starch from plant sources. The healthy cassava and yam tubers, as well as the root crops, sweet potatoes, cocoyam and amora, were peeled, washed and cut into smaller pieces and then grated using a manual metallic grater. The grated particles of the above starchy crops were poured into an electric blender, Lexus Usha, to obtain a paste and then mixed with clean water about ten times the weight of the ground starchy paste to form a suspension. The suspension was filtered with a very fine sieve. The filtrate was allowed to stand for twenty-four hours in the presence of 1% sodium thiosulphate solution to prevent fermentation. After the twenty-four-hour period of sedimentation, the supernatant was decanted to get the starchy cake. The starchy cake was washed with clean water to get the white starchy wet cake which was then dried at 45°C in a Raj Scientific Hot air oven for 48 hours. The dry starchy cake was then milled using a ceramic pestle and mortar to obtain the starchy powdered granules. The dried powdered starch granules were transferred into five plastic containers and properly labeled accordingly.

3.3. Particle Size and pH Determination

The particle size of the starch granules was determined according to AOAC (2010). In the determination, 1g of starch granule was dissolved in 25cm³ of distilled water and transferred to a glass slide and viewed under Olympus electric binocular microscope at four objective lens magnification. The pH of the starch granules was also determined using a Medfield digital pH meter at which 1g of starch granule in 25cm³ of distilled water. The probe of the pH meter was placed inside a beaker containing 25cm³ of the starch suspension to read the pH of the sample digitally (AOAC, 2010).

3.4. Determination of Amylose and Amylopectin in Starch Samples

3.4.1. Mobile Phase and Sample Preparation

The amylose and amylopectin percentages in the five starch samples were determined using the high-performance liquid chromatography (HPLC) buck Scientific BLC 10/11 model according to the standard methods of Association of Official Analytical Chemist (AOAC, 2000). The mobile phase was prepared by dissolving methanol in water in a ratio of 95:5. They were mixed appropriately and filtered using a filtration gadget and HPLC membrane filter paper and sonicated for 20 minutes. 2g of starch sample was placed inside a 25cm³ standard volumetric flask and made up with mobile phase. It was refluxed, centrifuged, decanted and then filtered using HPLC-grade filter paper. Analysis was performed by injecting 20µl of the prepared sample into the HPLC equipped with a UV 205nm

detector. A C-18, 4.5 x 150mm, 5 columns and a mobile phase of 95:5 (methanol: water) were used at a flow rate of 1.00ml/minute at room temperature. A 0.1mg of mixed standards (amylose/ amylopectin) was analyzed for identification. Peak identification was conducted by correlating the retention times of authentic standards and those obtained from the prepared starch samples. The concentrations were obtained using a four-point (0.1ppm, 0.2ppm, 0.3ppm and 0.4ppm) calibration curve. The area values were then fed into a computer-programmed analyzer/device to read the concentrations of the amylose and amylopectin in the starch samples.

3.5. Preparation of Gelatinized Starch Based on 0 – 90phr Filler Addition

The gelatinized starch was prepared according to the method of Zhang *et al.* (2004). The equivalent weight in grams of 10 parts per hundred rubber (phr), 20 phr, 30 phr and up to 90 phr of the trial batch starch samples: amora and yam, was weighed out using Shimadzu laboratory weighing balance. Each of the starch fillers was transferred into distilled water in a stainless-steel bowl to form an aqueous suspension of the starch. The stainless-steel bowl containing the starch aqueous suspension was placed in a water bath at 90°C and stirred for 30 minutes until the aqueous suspension became transparent. The transparent gelatinized starch (starch paste) was allowed to cool to room temperature. The procedure was later repeated for the remaining starch samples - cocoyam, cassava and sweet potato. After this, the volume percentage for filler addition was determined from the trial batch starch fillers.

3.6. Preparation of Starch/Natural Rubber Composite Based on 0–90 phr Filler Addition

Two of the starch fillers under investigation (amora and yam starch) were selected at random as a trial batch to test run the addition of starch fillers into natural rubber in place of carbon black. The physical and mechanical properties of the starch/rubber composite were determined at 0 – 90 phr filler additions in comparison with carbon black filled natural rubber to determine the best volume percentage addition for the starch fillers. The formulation of the trial batch starch rubber composite based on the 0 – 90 phr filler addition and compounding ingredients is displayed in table 3.1, while the second batch composites based on 0 – 30 phr is shown in table 3.2.

3.6.1. Preparation of Starch/ Natural Rubber Coagulum

The method of Zhang *et al.* (2004) was adopted to prepare rubber coagulum. The gelatinized starch was poured with stirring into a four-litre capacity plastic container containing one litre of natural rubber latex (dry rubber content (DRC), 30%). The mixture was thoroughly mixed and vigorously stirred with a wood stirrer for proper homogenization for 30 minutes. After being homogenized, between 100 – 150 cm³ of 10% Calcium Chloride aqueous solution (coagulant) was then added to co-coagulate the rubber latex/starch mixture. The resultant rubber latex/starch blend was immediately poured into a round-shaped plastic tray pan and left overnight to form a coagulum. The coagulum was then washed with water and transferred to an Indian-made Lohashilpi Sheeting machine LB15X model with contra-rotating rollers, where it was compressed into thin sheets with embossed ribbed patterns. The compressed sheets, having been washed with water, were then placed on a hanger to drain off the water droplets. The ribbed sheet of the coagulum was cut into short strands with scissors, poured into tray pans, labeled and kept in a dry oven at 80°C for 18 hours to be ready for the next stage of compounding. Also

“Control A,” or the first reference sample, was prepared without any starch filler (NRCB30) and was compounded with carbon black filler, whereas all the other samples containing starch/natural rubber were compounded without carbon black. The second reference sample, “Control B,” was prepared without any filler but just cured natural rubber (NRo).

Composition (phr)	Starch										
Starch	0	5	10	20	30	40	50	60	70	80	90
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Mercaptobenzothiazole (MBT)	3	3	3	3	3	3	3	3	3	3	3
Tetramethylquinoline (TMQ)	1	1	1	1	1	1	1	1	1	1	1
Sulphur	3	3	3	3	3	3	3	3	3	3	3
Carbon black											

Table 3.1: Formulation for the First Trial Batch of Starch/ Natural Rubber Composites Using Amora and Yam Starch Filler
Key: Phr = Part per Hundred Rubber

Composite (phr)	NR ₀	NR -10	NR - 20	NR - 30	NRCB ₃₀
Starch	0	10	20	30	0
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Mercaptobenzothiazole	3	3	3	3	3
Tetramethylquinoline	1	1	1	1	1
Sulphur	3	3	3	3	3
Carbon black					30

Table 3.2: Formulation for the Second Batch Starch/ Natural Rubber Composites in Part per Hundred Rubber (phr)

Key: NR - 10
NR - 20
NR - 30
NRCB₃₀

Starch -filled natural rubber

= Carbon black filled natural rubber (Control)

NR₀ = Natural rubber without starch/ carbon black

3.7. Compounding/ Vulcanization Procedure

Compounding/vulcanization was done using conventional low-temperature Sulphur curing and accelerator systems in accordance with the American Society for Testing and Material (ASTM)-designation D3184-80. The recipe for the formulation of starch/ natural rubber composite is given in tables 3.1 and 3.2. The starch-filled natural rubber blend was thoroughly masticated in a two-roll mill which already has been preheated to 80oC for about five minutes. The nip of the two-roll mill was adjusted to enable the natural rubber blend to form a band on the front roll. The activating agents (activator) - zinc oxide and stearic acid were then added in quick succession and mixed for about two minutes. The filler (carbon black for NRCB₃₀ only) was added, and then the accelerator(s) (MBT) and anti-oxidant (TMQ) were loaded and mixed for about three minutes. The curing agent, Sulphur, was introduced last. The rubber mixture was then mixed thoroughly for three minutes, blended and released from the two-roll mill and was kept for 24 hours to allow for proper maturation. Thereafter, it was taken to the hydraulic press for vulcanization at 140oC for about five minutes. After the trial batch, starch/rubber composites were formulated based on 0 – 90 phr filler additions of amora and yam starch. The best volume percentage for filler addition was found out to be between 20 phr – 30 phr filler addition, and based on this, the second batch starch/rubber composite from cassava, cocoyam and sweet potato starch was formulated and characterized. Tests sample of dumbbell shape were punched out from the vulcanized rubber sheets for mechanical testing on the Instron Universal Testing Machine (UTM).

3.8. Characterization of the Starch/ Natural Rubber Composites

3.8.1. Physical and Mechanical Property Testing

Tensile properties of the vulcanized composites were determined by the method described under ASTM D412 using a Lloyd Instruments machine, Instron Universal Testing Machine (UTM), Model EZ20. Standardized dumbbell-shaped specimens (ISO 527-2) with 13 mm long and 3.3 mm wide rectangular working sections cut from the vulcanized sheet were used for the test. The specimen was mounted between a fixed and a movable grip at a rate of 500 mm/min and a steadily increasing load was applied to the specimen until failure occurred. An average of 3 measurements was taken for each specimen.

3.8.2. Hardness Test

Hardness test measures the resistance of the rubber material to a small rigid object pressed onto the surface at a certain force. Type A durometer gauge from Polymer Laboratory, Rubber Research Institute of Nigeria (RRIN), Benin City, was used to measure hardness in international rubber hardness degree (IRHD) of the starch/rubber vulcanizates by the method described under ASTM D2240. Type A durometer measures indentation hardness which is the resistance of the material to indentation by an indenter.

3.8.3. X-ray Diffraction (XRD) Analysis

X-ray diffraction analysis was carried out according to the method described by Zhang *et al.* (2004). Diffraction patterns of the samples were obtained by the use of an X-ray diffractometer Shimadzu 6000 model using a Cu target at 40Kv, 30mA run between 00 to 1200 theta (θ) Bragg angle (Scan range) at a rate of between 2 and 10 degrees per minute. The rubber composites, being a mixture of semi-crystalline and amorphous material, will produce both diffraction peaks and ridges on the diffractogram. The diffraction patterns of the starch/rubber samples are presented in figures 4.3, 4.4, 4.5, 4.6, 4.7 & 4.8 in chapter four.

3.8.4. Swelling Test

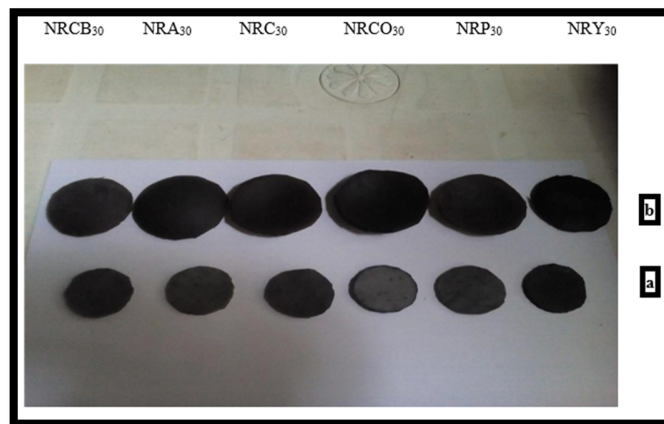


Plate 3.1: Picture of Rubber Specimens before Swelling (a) and (b) After Swelling

Key:	NRCB ₃₀	=	Control with 30 phr carbon black
	NRA ₃₀	=	Amora starch at 30 phr loading
	NRC ₃₀	=	Cassava starch at 30 phr loading
	NRCO ₃₀	=	Cocoyam starch at 30 phr loading
	NRP ₃₀	=	Potato starch at 30 phr loading
	NRY ₃₀	=	Yam starch at 30 phr loading

Swelling tests were carried out according to the method described by Lovely *et al.* (2006) and Surya & Siragar (2004). Circular specimens of diameter 24 mm were cut out from the vulcanized rubber sheets. The thickness and diameter of the specimens were measured by means of a screw gauge and vernier calipers, respectively. Specimens of known weight in grams were immersed in the solvents, toluene and water, respectively, in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper and weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. The weight in grams of the specimen after equilibrium swelling (at 72 hours) was also measured. The samples were then dried in a Carbolite oven CB/E20 model at 600C until constant weights were obtained. Swelling parameters were calculated as given in sections 3.7.4.1, 3.7.4.2, 3.7.4.3 & 3.7.4.4.

3.8.4.1. Swelling Data Analysis

The swelling test results were used to calculate the molecular weight between two crosslinks (M_c) by applying the Flory-Rehner equation.

$$M_c = \frac{-\rho p V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2} \quad (1)$$

$$V_r = \frac{1}{1 + Q_m} \quad (2)$$

The following constants from the literature were used where:

- p is the rubber density (p of NR = 0.92g/cm²)
- V_s is the molar volume of toluene ($V_s = 106.4\text{cm}^3/\text{mol}$)
- V_r is the volume fraction of the polymer in the swollen specimen
- Q_m is the weight increase of the blends in toluene and
- χ is the interaction parameter of the rubber network solvent (χ of N.R = 0.393).

The degree of the crosslink density is given by:

$$V_c = \frac{1}{2M_c} \quad (3)$$

3.8.4.2. Calculation of Q_t (Molar Percentage Uptake of the Solvent)

The molar percentage uptake of the solvent, Q_t , for the composite samples was determined using the equation.

$$Q_t = \frac{(W_2 - W_1/M_s)}{W_1} \times 100 \quad (1)$$

Where:

- W_2 and W_1 are the weights of the specimen before and after swelling and
- M_s is the molar mass of the solvent.

3.8.4.3. Swelling Index

Swelling Index is calculated and expressed as a percentage using equation (2)

$$\text{Swelling index \%} = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (2)$$

Where:

W_1 and W_2 are the initial and final (swollen) weights of the sample.

3.8.4.4. Swelling Coefficient (α)

The swelling behaviour of the composites can also be assessed from the swelling coefficient values. It is an index of the ability with which the sample swells and is determined by the equation,

$$\text{Swelling coefficient, } \alpha = \{A_s/m\} \times [1/d] \quad (3)$$

Where:

- A_s is the weight of the solvent sorbed at equilibrium swelling,
- m the mass of the sample before swelling and
- d is the density of the solvent used.

3.8.5. Fourier Transform Infra-Red (FTIR) Spectrometric Analysis

FTIR analysis was carried out by the method described by Mostafa *et al.* (2015). FTIR was used to detect the absorption bands of associated functional groups and the nature of the interaction between the various components of the bio-composites (starch, rubber). Perkin Elmer, spectrum BX, an England instrument with KBr discs, was employed for the analysis. FTIR spectroscopy measurements were made and the peaks were indicated in the chart. The wavelength cm^{-1} ranges between 4000 and 400 cm^{-1} . The infrared spectra absorption bands of the various rubber samples plus the reference samples pure starch and pure rubber were shown in tables 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, 4.5 & 4.16 in chapter four.

3.8.6. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was carried out by the method described by Kurian *et al.* (1989). The fracture surface of the rubber material was carefully cut out from the rubber flat disk and stored in a desiccator to avoid contamination and then sputter-coated with gold within 24 hours of producing the fracture surface. Scanning electron microscopy (SEM) observations were made from the rubber specimens using EVO/MA10 SEM equipment at a heating voltage of 10Kv and a space difference (WD) of 13.5mm. The morphology of the rubber specimens is displayed on the SEM micrographs, as shown in plates 4.1, 4.2, 4.3, 4.4, 4.5 & 4.6 in chapter four.

3.8.7. Thermal Analysis with Differential Scanning Calorimetry (DSC)

The thermal transition properties of the starch/rubber composites were studied according to the method described by Rao & Johns (2008) using a Mettler Toledo DSC 822 thermal analyzer with application HB4000. The samples ranging from 4.7 mg to 6.7 mg were inserted into the apparatus and the DSC scan was made from -1000C to 3000C at a heating rate of 100C min^{-1} . The pan for sample preparation is made of aluminum, 40 μl . Flat disks ranging from 4.7 mg to 6.7 mg were cut from the starting material (rubber composite). The sample was cooled at room temperature from -1000C to 100C min^{-1} . Atmosphere: Nitrogen, 50ml/min. The glass transition temperature (T_g) of each sample was taken as the initial change in the slope of the heat capacity of the DSC curve, as shown in Appendices XV, XVI, XVII, XVIII, XIX & XX.

3.8.8. Weight Loss / Aging Test

Weight loss/ aging test was conducted according to the method described by Musa *et al.* (2011) and Jacob *et al.* (2007). Polymer specimens were cut out from the vulcanized sheet for hardness, tensile strength and elongation at the break test. The rubber composite was then buried under a domestic refuse dump at the Federal Polytechnic staff quarters, Mubi, at a 50 cm depth below the soil surface for six months. At the end of the test period, the specimens were dug out of the refuse dump, washed and rinsed with distilled water and then dried at 600C for 3 hours to stop any microbial action before the final physical and mechanical properties measurement to determine any variation in properties due to weight loss/aging activities.

3.8.9. Microbial Degradation Test

Microbial degradation test was conducted according to the method described by Jendrossek *et al.* (2000) and Tsuchii & Takeda (1990). Based on the experience of previous rubber degradation bioassays, rubber degrading microorganisms are usually isolated from soils under rubber tree plantations, wastewater lakes where rubber latex wastes are usually disposed of, and/or inside pool of water gathered in rubber tyres where there is a source of carbon from natural rubber as a nutrient (Jendrossek *et al.*, 2000; Tsuchii & Takeda, 1990). Soil samples were collected from under the soil of the Eucalyptus tree garden behind Science Laboratory Complex, Federal Polytechnic, Mubi, Adamawa

State as a control and also from *Hevea brasiliensis* rubber tree plantation at Rubber Research Institute of Nigeria (RRIN), Iyanomo, Edo State with reference number, RRIN/NG 900 series 0001. These soil samples were used to isolate microorganisms from the soil, which are then used to assay for biodegradation activities. The starch/rubber composites made from amora filler at 5 phr, 30 phr and 90 phr plus an unfilled rubber were used as test specimens for the biodegradation test and are identified as F5, F30, F90 and Fo, respectively.

3.8.9.1. Preparation of Nutrient Agar Plate for Bacteria Culture

Nutrient agar was prepared according to the manufacturer's instructions (Fluka Biochemika, Germany). 28 g of nutrient agar was suspended in 1000 cm³ of distilled water. It was brought to a boil to dissolve completely. It was then sterilized by autoclaving (autoclave is a stainless steel pressure cooker) at 121°C for 15 minutes. It was allowed to cool to room temperature and then poured into a sterilized petri dish and allowed to solidify.

3.8.9.2. Preparation of Potato Dextrose Agar (PDA) for Fungi Culture

Potato dextrose agar (PDA) was prepared according to the manufacturer's instructions (Tulip Diagnostics (p) Ltd, India). 39g of the PDA was suspended in 1000 cm³ of distilled water. The mixture was mixed thoroughly and warmed slightly above room temperature to dissolve the PDA completely. It was then sterilized by autoclaving at 121°C for 15 minutes and allowed to cool to room temperature and poured into a sterilized petri dish and allowed to solidify.

3.8.9.3. Inoculation of Agar Plates

1g of soil sample was suspended in 10 cm³ of distilled water with proper shaking. By using the streak method of the wire loop, the nutrient agar plate and the potato dextrose agar plate were inoculated with the soil inoculum for bacteria and fungi isolation. The inoculated media plates were then incubated for 24 and 72 hours and observed for bacteria and fungi growth. After the expiration of the incubation period, both bacteria colonies and moulds (fungi) were identified on the agar plates. These were sub-cultured into other sterilized agar petri dish plates to obtain pure cultures of the bacteria and fungi. Unfortunately, no visible colonies of bacteria were seen on the plates inoculated with soil suspension from Federal Polytechnic, Mubi (the control), but only green and black mould. The bacteria colonies were only observed in the plates inoculated with rubber tree plantation soil suspension-spherical colonies and filamentous colonies. The reasons are as follows: the environment was not favourable for bacterial growth under the Eucalyptus tree soil in Federal Polytechnic Mubi, while the environment favoured the bacterial growth under rubber tree plantation soil. According to previous research on natural rubber (NR) degrading bacteria, the greatest numbers (up to approximately 10⁵ NR - degrading bacteria per gram) were obtained from soil samples of *Hevea brasiliensis* plantations and from waste ponds of a rubber-producing coNm-2ny in Malaysia (Jendrossek *et al.*, 1997). Some have been isolated from pools of water gathered in used rubber tyres in Germany, where natural rubber served as a carbon source and energy from isolated microorganisms, especially bacteria (Jendrossek *et al.*, 2000; Jayaram & Sudesh, 2016).

3.8.9.4. Preparation of Mineral Salt Media (MSM)

Mineral salt media was prepared according to Schlegal (1995) and Jendrossek *et al.* (1997).

The composition is as follows: KH₂PO₄-1.0 g, K₂HPO₄-1.0 g, NH₄NO₃-1.0 g, MgSO₄.7H₂O-0.2 g, FeCl₃- 0.05 g, CaCl₂.2H₂O- 0.02 g.

Each of the salt was weighed out accordingly using a Metlar balance and dissolved in 100ml distilled water separately, then mixed together in a 1000 cm³ volumetric flask and then made up to 1000 cm³ mark with distilled water. 250 cm³ of the mineral salt media (MSM) was sterilized by autoclaving at 121°C for 15 minutes. Also, 1% of the particulate rubber material was prepared, weighed and sterilized at 121°C for 15 minutes to be used as a source of carbon and energy for the bacteria (Jendressek *et al.*, 1997 and Jendressek *et al.*, 2000). 9 cm³ of the sterilized mineral salt media (MSM) was poured into 8 test tubes and then 1% of the carbon source (rubber specimens) was introduced into the tubes with MSM. Finally, the bacteria strains were introduced into the tubes containing the MSM

and the carbon source (rubber specimens). Four different types of rubber materials from amora starch/rubber composites plus an unfilled rubber were used and designated as F5, F30, F90 and Fo. The 8 test tubes of the MSM/ carbon source media were incubated at 37°C for 24 hours. Then 1 ml of the above media (MSM)/ carbon source was used to inoculate agar plates, four for each set of the two bacteria strains and four types of rubber composites giving 8 plates. They were incubated at 37°C for 24 hours and observed for colony formation.

A control, a test tube with a 9 cm³ of MSM, was set up without any carbon source (rubber specimens) but inoculated with the bacterial strains and incubated for 24 hours and then was used to inoculate an agar-agar plate (neutral agar) and incubated at 37°C for 24 hours and observed for colony formation.

3.8.9.5. Serial Dilution Procedures

Serial dilution procedures were employed according to Schlegel (1995) and ISO 4833 (1991). 9ml of distilled water was poured into nine test tubes and then 1 cm³ of inoculum (from the MSM/ Carbon source/ bacteria media) was introduced into the first test tube and then subsequently 1 ml was transferred into the next test tube in sequence until the 9th test tube. Then 1 cm³ of the medium was taken out from the last tube (9th) to give 9ml medium in each tube. 10⁻³ and 10⁻⁴ dilution tube was used to inoculate nutrient agar plates using a spread glass tube (a device for spreading bacteria) for each bacteria strain totaling 16 agar plates. They were incubated at 37°C for 24 hours and observed for colony formation. The serial dilution was carried out at two consecutive dilutions according to ISO 4833 (1991). The plates containing fewer than 300 colonies at two consecutive dilutions were used to calculate the results from a weighted mean. The number (N) of colony-forming units per ml (Cfu/ cm³) of test samples is calculated as follows:

$$N = \frac{c}{v} (n_1 + 0.1n_2) d.$$

Where:

- C is the sum of colonies on all plates counted
- V is the volume of inoculum (bacteria strain) applied to each plate
- n₁ is the number of plates counted at the first dilution
- n₂ is the number of plates counted at the second dilution
- d is the dilution from which the first count was obtained

The number (N) gives the viable number of cells in the colonies (ISO 4833, 1991).

3.8.9.6. Gram-Stain Differential Technique

Gram-stain differential technique was employed according to Nester *et al.* (2004) to differentiate the bacteria into Gram-positive and Gram-negative bacteria. A smear of the bacteria from pure culture was made on a sterilized glass slide, allowed to dry and then heatfixed by passing over a Bunsen burner flame 3 times. The slides were placed on a staining rack and then flooded with crystal violet (primary stain) and allowed to stay for 1 minute. It was further washed with water and flooded with neutral red (staining solution) for 1 minute before washing with water. The slides were flooded with lugol iodine for 1 minute and washed with water, after which it was decolorized with acetone for 1 second and washed with water immediately and allowed to dry. The slide was finally observed in an oil immersion objective microscope (Olympus) at 100x magnification.

3.8.9.7. Aldehyde Group Test

Schiff's reagent test for aldehyde, according to Shah *et al.* (2012), was conducted on the residue of inoculated biodegraded rubber vulcanizate specimens. The Schiff's reagent was stained on the rubber particulates (specimens) in a test tube and a purple colour was obtained, which indicates the presence of an aldehyde group. This is a qualitative test for the presence of aldehyde groups. It is not confirmed if the aldehyde is from the biodegradation residue from the rubber specimens since FTTR analysis indicated the presence of carbonyl/ketones/aldehyde groups in amora starch/rubber composite at 30 phr (F30) and unfilled cured natural rubber (Fo) before the biodegradation test. This test is not confirmatory but qualitative.

4|Results and Discussion

4.1. Physicochemical Characteristics of the Starch Fillers

The results of the measurements and test described earlier are given in sections 4.1 – 4.15.

4.1.1. Particle Size, pH, Amylose and Amylopectin Percentage of the Starch Samples

The particle size and pH values of the five starch samples (amora, cassava, sweet potato, cocoyam and yam) are displayed in table 4.1. The particle size analysis revealed that cocoyam starch has the smallest particle size, followed by a cassava starch sample. However, the potato starch sample has the largest particle size, followed by yam starch. These results are considerable to those previously reported by Vasiljevic (2009) and Zaidul *et al.* (2007) for yam, sweet potato, cocoyam and cassava but without any suggested relationship with material property. According to table 4.1, amora starch and yam starch have pH approximately close to neutral pH 7 with values of 6.9 and 6.8, respectively, while the others (cassava, cocoyam and sweet potato) have acidic pH values of 4.9, 4.1 and 5.2, respectively. The amylose and amylopectin percentage composition of the starch samples is shown in table 4.2. Yam starch has the highest value (29.68), while amora starch has the lowest value for amylose (14.86). Other values of amylose are 16.45, 18.89, and 22.34 for cocoyam, cassava and potato in ascending order. The results above are also consistent with those reported by Vasiljevic *et al.* (2009) on the amylose composition of yam, sweet potato and cocoyam, with values as follows: 31.33 for yam, 28.69 for sweet potato and 14.45 for cocoyam, respectively. The report of Baguma *et al.* (2011) is consistent with the values obtained for amylose in cassava starch, with values ranging from 18.95 – 24.67 in percentage composition. The remaining balance in percentage composition is amylopectin, as displayed in table 4.2, with 84.97% for amora and 70.29% for yam starch, while the others are 77.64%, 80.98%, and 83.50% in ascending order for potato, cassava and cocoyam, respectively.

According to the observation of Buchanan *et al.* (1971), as reported by Rouilly *et al.* (2004), it was observed that the amylose content of starch can affect mechanical properties in starch/rubber blends. In this regard, the various plant starches were screened to determine the amylose/ amylopectin percentage composition.

Table 4.3 shows the percentage of amylose along with corresponding tensile strength, hardness and elongations at break at 30 phr filler loading. The above observation of Buchanan *et al.* (1971) is partially correct because the amylose molecule in starch is a linear chain molecule and the linear chain in starch polymer contributes to the crystallinity of the semi-crystalline molecule. Moreso, crystallinity in polymer structure enhances mechanical properties (tensile strength) in most polymer materials (Billimeyer, 2007; Bhatnagar, 2010). However, the results from table 4.3 show that the increased percentage of amylose in starch fillers studied did not produce a corresponding effect in terms of tensile strength in all the rubber composites investigated. Instead, a variation occurred (also indicated in a histogram in Appendix I). This variation was seen in the discrepancy observed in amora and yam starch filler, where amora with the lowest amylose percentage (14.86) produced the highest tensile strength of 57.43 Nm⁻² at 30 phr filler addition and yam starch with 29.68% amylose (the highest among the fillers) produced a tensile strength value of 32.36 Nm⁻² at 30 phr filler addition. However, other factors, such as hydrodynamic particle effect and filler-filler interaction (particle network formation), are the major determining phenomena responsible for the mechanism of modulus enhancement (mechanical property) in reinforced rubbers (Roland, 2016). Hydrodynamic effect states that particulate fillers increase both the viscosity and the elastic modulus (mechanical property) of a polymer or rubber compound at a higher concentration of the filler above the threshold for percolation or wetting. Filler-filler interaction is the aligning of the filler particles within the rubber matrix to provide a framework of support at filler concentration above the threshold (Roland, 2016). These two phenomena above are the major mechanisms behind reinforcement in particulate-filled rubbers and not just amylose content.

Starch granule	Particle Size (μm)	pH
Amora	156 x 47	6.90
Cassava	158 x 44	4.90
Cocoyam	159 x 42	4.10
Sweet Potato	153 x 46	5.20
Yam	155 x 40	6.80

Table 4.1: Particle Size and pH of Starch Samples

Source of Starch	(%)Amylose	(%) Amylopectin
Amora	14.86	84.97
Cassava	18.89	80.98
Cocoyam	16.45	83.50
Potato	22.34	77.64
Yam	29.68	70.29

Table 4.2: Amylose and Amylopectin Percentage Composition in Starch Samples

Composite NR/ % Amylose break (%)	% Amylose	Tensile Hardness	Elongation at starch break	strength (Nm^{-2}) (IRHD)
NRA ₃₀	14.86	57.43	47 – 48	10007
NRC ₃₀	18.89	9.40	55 – 56	2842
NRCO ₃₀	16.45	27.40	59 – 60	5495
NRP ₃₀	22.34	35.70	52 – 53	6654
NRY ₃₀	29.68	32.36	60 – 61	7588
NRCB ₃₀	–	87.63	66 – 88	6807

Table 4.3: Amylose Content of Starch and Mechanical Properties in Starch/ Rubber Composites at 30 Phr
 Key: IRHD = International Rubber Hardness Degree
 NRCB₃₀ = Carbon Black Filled Natural Rubber
 NR = Natural Rubber

4.2. Effect of Trial Batch Starch Fillers (Amora and Yam) at 0 – 90 Phr on the Physical and Mechanical Properties of Starch/ Rubber Composites

According to the established behavioural pattern for fillers in rubbers, at less than 50 volume percent in filler concentration, a material that behaves like rubber is produced in which the fillers are the dispersed phase and the rubber is the continuous phase. At well above 50 volume percent concentration, a material that behaves more like a plastic is produced in which the filler becomes the continuous phase and the rubber becomes the dispersed phase. This is called phase inversion. The table showing the effect of the trial batch starch fillers (amora and yam) at 0 – 90 phr is shown in Appendix XXI and XXII. According to Appendix XXI for amora starch filler, a high tensile strength (57.43 Nm^{-2}) was seen at 30phr filler addition, after which a decline occurred from 40 phr till 80 phr in which a maximum tensile strength (58.20 Nm^{-2}) occurred and then another decline at 90 phr in the tensile strength value is 20.60 Nm^{-2} . This decline in tensile property can be attributed to phase inversion that has occurred in which the starch filler has become the continuous phase while rubber is the dispersed phase. Although a maximum tensile strength occurred at 80 phr (58.20 Nm^{-2}), the material should be more plastic than rubber due to the high concentration of starch filler. The tensile strength at the two maximums (57.43 Nm^{-2} and 58.20 Nm^{-2}) is still below the tensile strength value (87.63 Nm^{-2}) for carbon black-filled rubber at 30 phr. According to the table in Appendix XXII for yam starch filler, a high tensile strength (76.17 Nm^{-2}) which happens to be the optimum, is seen at 20 phr filler addition,

after which a decline occurred from 30 phr – 90 phr filler addition due to phase inversion. The optimum tensile strength (76.17 Nm⁻²) of the yam starch-filled rubber before the decline is comparable to the tensile strength value (87.63 Nm⁻²) of carbon black-filled rubber at 30 phr. In consideration of the trial batch starch filler addition from 0 – 90 phr and the attendant tensile properties and the decline in tensile properties due to phase inversion, the best volume percentage filler concentration for the starch fillers would appear to be within the range of 20 phr to 30 phr. Based on the above findings, the rest starch fillers (potato, cocoyam and cassava) were added to the rubber in the range of 20 phr – 30 phr for maximum and optimum tensile properties (Tables 4.7 & 4.8).

4.3. Optimum Filler Limit and Optimum Tensile Strength in Yam and Amora Starch/ Rubber Composite

The first batch of starch filler screening was carried out on amora and yam starch filler selected at random as a trial batch from 0 to 90 phr filler loading.

The first screening results in Appendix XXI and XXII, as shown in figures 4.1 and 4.2, indicate that amora starch produced an optimum filler loading limit at 80 phr under phase inversion and maximum tensile strength of 58.20 Nm⁻², while yam starch filler produced an optimum filler loading limit at 20 phr before phase inversion and optimum tensile strength of 76.17 Nm⁻². In amora starch-filled rubber, at optimum filler limit (80 phr), a soft material with hardness 44.50 irhd and elongation at break of 14895 was recorded, while for yam starch at optimum filler limit (20 phr), a material with hardness 57.5 and elongation at break of 11273 was recorded.

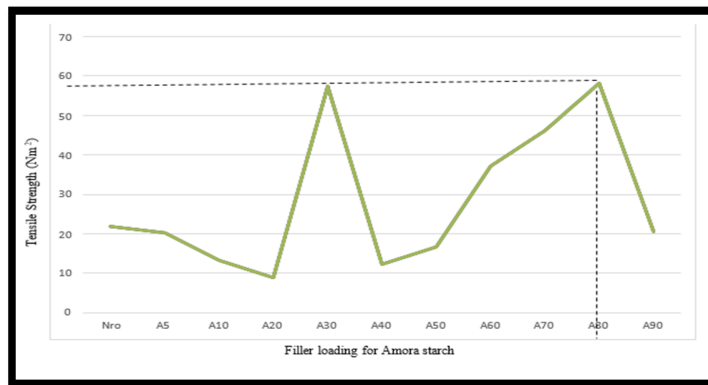


Figure 4.1: Plot of Filler Loading Against Tensile Strength for Amora Starch Optimum Limit
Key: Optimum Point (...)

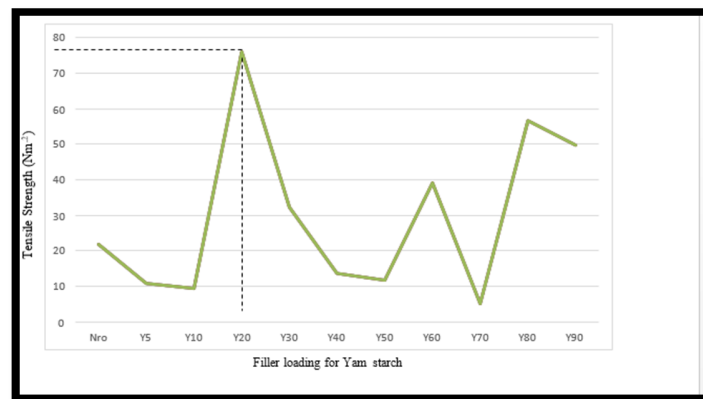


Figure 4.2: Plot of Filler Loading Against Tensile Strength for Yam Starch Optimum Limit
Key: Optimum point (...)

4.4. Effect of Amora and Cassava Starch Fillers on the Tensile Strength, Elongation at Break and Hardness of the Starch/ Rubber Composites

Table 4.4 shows the variation of percentage starch on the tensile strength, elongation at break and hardness of the starch rubber composites. According to table 4.4, filler loading from 10 phr to 20 phr did not improve the tensile strength (Ts) of the amora starch-filled rubber composites in comparison with the unfilled rubber and the control sample, Ro. However, their hardness values improved due to filler reinforcement (Stelescu *et al.*, 2017). Elongation at the break of the rubber decreased as well at 10 - 20 (phr) due to the increase of filler in the rubber. However, at 30 phr filler loading, the tensile strength (Ts) and hardness improved by 61.8% and 56.8%, respectively, above the value for the unfilled rubber, while elongation at break decreased by 41% due to increased filler content in the rubber. The control sample, Ro (carbon black filled rubber), still maintained a higher value in tensile strength (87.63) and hardness (66.80) and a moderate elongation at break (6807), indicating a better reinforcement of the rubber due to the hydrodynamic effect, reactive sites on the carbon black, nanometre particle size and better wetting property (Alan, 2017; Roland, 2016). The values are also represented in the histograms in Appendix II.

Table 4.5 shows the variation in the percentage of cassava starch on the tensile strength, elongation at break, and hardness of the rubber starch composite. According to table 4.5, the tensile strength of cassava starch-filled rubbers ranges from 7.10 to 9.40 Nm⁻² compared to 21.90 Nm⁻² of the unfilled rubber (Ro). In terms of hardness, there was an improvement from 51.50 average hardness to 55.50 average hardness, which is expected since the addition of fillers to rubber improves hardness (Stelescu *et al.*, 2017). Elongation at break also decreased severely by 85% from that of unfilled rubber, which is also expected since the introduction of fillers in rubber lowers elongation at break and elasticity (Stelescu *et al.*, 2017). According to data presented in table 4.5, in comparison to the control sample, Ro (carbon black-filled rubber), cassava starch-filled rubber performed poorly,

Cassava starch filler appears to be a poor reinforcing filler in terms of tensile strength when compared to amora starch filler (carbon black, potato, and yam starch filler). This finding is consistent with the work of Ichazo *et al.* (2007), which related that cassava starch filler at 10phr, 20 phr, 40 phr, 60 phr and even when functionalized with 20 phr malaeic anhydride as a coupling agent did not improve the tensile strength and tear strength of natural rubber. The effects of cassava starch filler discussed above are displayed on two histograms in Appendix III.

Natural Rubber	Tensile Strength	Elongation at Break	Hardness (IRHD)
Starch (phr)	(Nm ⁻²)	(%)	
NR	21.90	17069	20-21
NRA ₁₀	13.33	4850	56-57
NRA ₂₀	8.93	2883	52-53
NRA ₃₀ NRCB ₃₀	57.43	10007	47-48
	87.63	6807	66-68

Table 4.4: Physical and Mechanical Properties of Amora Starch Filled Natural Rubber

Key: NRCB₃₀ = Natural rubber with carbon black filler (Control A) at 30 phr
 phr = Part per hundred rubber
 NRo = Natural rubber without any filler (Control B)
 IRHD = International rubber hardness degree
 A₁₀ – A₃₀ = Amora starch at 10 – 30 phr filler loading

Natural Rubber/ Starch (phr)	Tensile Strength (Nm ⁻²)	Elongation at Break (%)	Hardness IRHD
NR ₀	21.90	17069	20-21
NRC ₁₀	7.10	2498	50-53
NRC ₂₀	9.00	2186	55-57
NRC ₃₀	9.40	2842	55-56
NRCB ₃₀	87.63	6807	66-68

Table 4.5: Physical and Mechanical Properties of Cassava Starch-Filled Natural Rubber

Key: NRCB₃₀ = Natural rubber with carbon black filler (Control A) at 30 phr
 phr = Part per hundred rubber
 NR₀ = Natural rubber without any filler (Control B)
 IRHD = International rubber hardness degree
 NR = Natural rubber
 C₁₀ – C₃₀ = Cassava starch at 10 – 30 filler loading

4.5. Effects of Cocoyam and Potato Starch Filler on the Tensile Strength, Elongation at Break and Hardness of the Starch/ Rubber Composites

Table 4.6 shows the variation in the percentage of cocoyam starch on the tensile strength, elongation at break and hardness of the starch/ rubber composites. Cocoyam starch filler addition at 10 phr and 20 phr did not yield tangible reinforcement in terms of tensile strength and elongation at break compared to unfilled rubber (Control B) and carbon black filled rubber (Control A). However, there was a significant improvement in average hardness from 49.50 to 59.50 due to the reinforcing action of fillers in improving hardness in rubbers (Stelescu *et al.*, 2017). Moreso, the increased filler content in the rubber decreased elongation at the break by an average margin of 77% which is expected as increased filler content in rubber decreases both percentage elongation at break and elasticity due to increased stiffness (Stelescu *et al.*, 2017). The values are also shown in two histograms in Appendix IV.

Table 4.7 shows the variation in the percentage of potato starch filler on starch/rubber composites. The addition of potato starch fillers into natural rubber at 10 phr and 20 phr did not produce good reinforcement, but at 30 phr, it yielded better reinforcement of 35.70 Nm⁻². Elongation at break and hardness improved moderately, according to table 4.7. The hydrodynamic effect and filler-filler interaction are responsible for this improvement (Roland, 2016). Lower reinforcement at 10 phr and 20 phr also means that the filler concentration has not surpassed the threshold concentration to allow for percolation and/or wetting (Roland, 2016). The discussed values above are displayed in two histograms in Appendix V.

Natural Rubber/ Starch (phr)	Tensile Strength (Nm ⁻²)	Elongation at Break (%)	Hardness (IRHD)
NR ₀	21.90	17069	20-21
NRCO ₁₀	12.31	2752	49-50
NRCO ₂₀	11.60	3434	51-52
NRCO ₃₀	27.40	5495	59-60
NRCB ₃₀	87.63	6807	66-68

Table 4.6: Physical and Mechanical Properties of Cocoyam Starch-Filled Natural Rubber

Key: NRCB₃₀ = Natural rubber with carbon black filler (Control A) at 30 phr
 phr = Part per hundred rubber
 NR₀ = Natural rubber without any filler (Control B)
 IRHD = International rubber hardness degree
 CO₁₀ – CO₃₀ = Cocoyam starch at 10 – 30 phr filler loading

Natural Rubber/ Starch (phr)	Tensile Strength (Nm ⁻²)	Elongation at Break (%)	Hardness (IRHD)
NR ₀	21.90	17069	20-21
NRP ₁₀	11.50	3137	54-55
NRP ₂₀	12.90	3490	58-59
NRP ₃₀	35.70	6654	52-53
NRCB ₃₀	87.63	6807	66-68

Table 4.7: Physical and Mechanical Properties of Potato Starch-Filled Natural Rubber

: NRCB₃₀=Natural rubber with carbon black filler (Control A) at 30 phr
 phr =Part per hundred rubber
 NR₀ = Natural rubber without any starch filler (Control B)
 IRHD = International rubber hardness degree
 P10 – P30= Potato starch at 10 – 30 phr filler loading

4.6. Effect of Yam Starch Filler on the Tensile Strength, Elongation at Break and Hardness of Starch/ Rubber Composite

Table 4.8 shows the results/variation in the percentage of yam starch filler on the starch/rubber composite. According to table 4.8, the reinforcing behaviour of yam starch filler started at 20 phr and decreased at 30 phr. This high reinforcing behaviour of yam starch filler at 20 phr can be attributed to the following:

- Surpassing its threshold filler concentration, hydrodynamic effect (Roland, 2016)
- High amylose content (29.68) (Rouilly *et al.*, 2004).

This reinforcing behaviour of yam starch filler is also displayed in two histograms in Appendix VI.

Natural Rubber/ Starch (phr)	Tensile Strength (Nm ⁻²)	Elongation at Break (%)	Hardness (IRHD)
NR ₀	21.90	17069	20-21
NR _{Y10}	9.53	2544	54-55
NR _{Y20}	76.17	11273	57-58
NR _{Y30}	32.36	7588	60-61
NRCB ₃₀	87.63	6807	66-68

Table 4.8: Physical and Mechanical Properties of Yam Starch-Filled Natural Rubber

Key: NRCB₃₀=Natural Rubber with Carbon Black Filler (Control A) at 30 Phr

Phr=Part per Hundred Rubber

Nr₀=Natural Rubber without Any Filler (Control B)

IRHD=International Rubber Hardness Degree

Y₁₀ – Y₃₀=Yam Starch at 10 – 30 Filler Loading

4.7. X-ray Diffraction Analysis

The x-ray diffraction patterns for the starch/rubber composites are shown in figures 4.3, 4.4, 4.5, 4.6, 4.7 & 4.8.

From the x-ray diffractogram in figure 4.4, the diffraction pattern of the control sample (NRCB₃₀) shows that the control sample (NRCB₃₀) was not completely in the amorphous state but had some crystalline region which was indicated by the diffuse diffraction peaks at 170, 210 and 340 with the 170 (Shoulder Peak) and 340 being the strong peak, and weak peak appearing around 800 intensity (counts). The 210 peak was displayed at around 990 intensity (counts), indicating a higher concentration of the crystalline region. Since most natural polymers like starch, cellulose and gutta percha (1, 4-trans-polyisoprene) all exhibit diffraction peaks showing crystalline regions in their x-ray diffractograms,

natural rubber (1, 4-cis-polyisoprene) is not an exception (Zhang *et al.*, 2004; Mostafa *et al.*, 2015; Arvanitoyannis *et al.*, 1997).

According to figure 4.4, the diffraction pattern of sample NRA₃₀ (amora starch-filled natural rubber) displayed a broad diffraction peak at 21°, at about 1450 intensity (counts) and a shoulder peak at 26° with an intensity of about 750. From this diffractogram, the broad peak of intensity 1450 at 21° was recorded coNm-2red to 990 intensity, of 21° peak in the NRCB₃₀ (the control), showing that the presence of the starch filler (semi-crystalline polymer) in the natural rubber matrix has increased the region of crystallinity in the rubber matrix and also in concentration (30 part per hundred rubber (phr) loading) as indicated by the higher intensity of 1450. The presence of the diffraction peaks in pronounced dimensions is evidence that a strong crystalline region exists in the rubber blend studied. Crystallinity also contributes to a good tensile strength of polymers hence good tensile properties of amora starch-filled rubber composites at 30 phr.

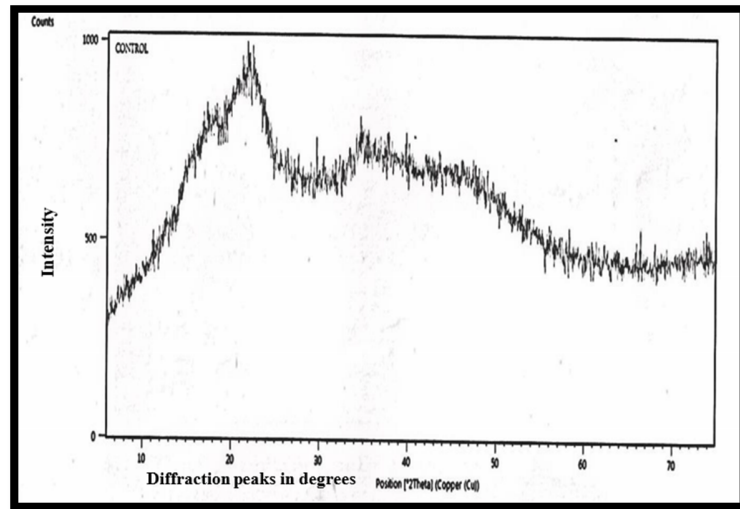


Figure 4.3: X-ray Diffractogram of the Control Sample NRCB₃₀

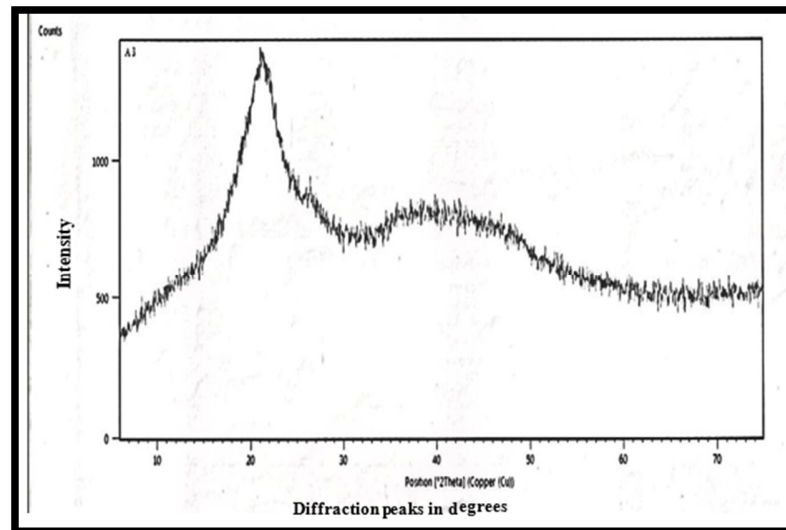


Figure 4.4: X-Ray Diffractogram of Sample NRA₃₀ Diffraction Pattern of Sample Ca₃ (Cassava Starch Filled Rubber) in Figure 4.4 Exhibited A Broad Diffraction Peak of 21° With Intensity of 1250 and a Shoulder Peak of 26° with 750 Intensity Somewhat Similar to the Diffraction Pattern of Sample NRA₃₀ In Figure 4.4 and Both Indicating Strong Crystalline Region in the Rubber Composites

From the diffractogram of sample NRCO30 (Cocoyam starch-filled rubber), as shown in figure 4.6, the diffraction pattern showed a diffuse broad peak at 22° and 34° with the intensity of 900 and 750, respectively, indicating lower concentrations of the semi-crystalline region in the rubber composite. This is in contrast to the diffraction patterns of sample NRA30 and sample NRC30 discussed previously and very similar to the diffraction pattern of the control sample (NRCB30) displayed in figure 4.3. Also, a lower count of 900 at the maximum broad diffuse peak of 22° suggests that the starch filler in the composite contributed poorly to the crystalline region of the rubber composite. Fortunately, cocoyam starch had the smallest particle size among the starch samples and hence, it became very easy for the starch granules crystallites to disappear completely during the gelatinization process at a temperature of 90° and did not recrystallize during and after compounding in the two-roll mill.

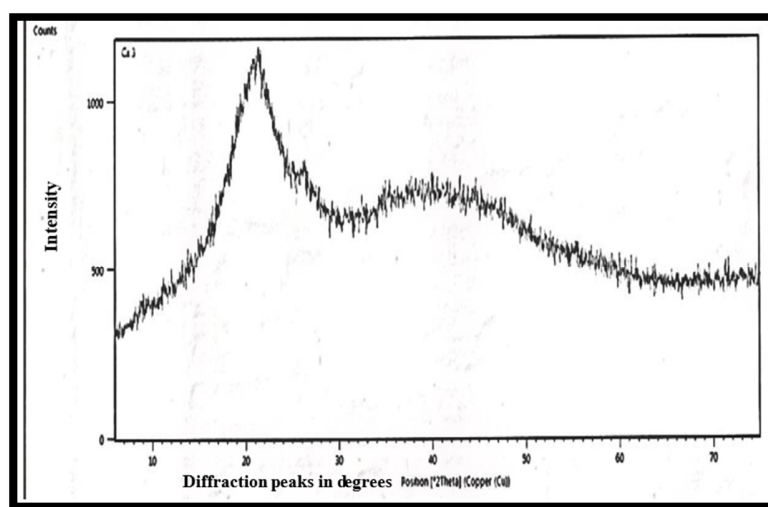


Figure 4.5: X-ray Diffractogram of Sample NRC₃₀

From the diffraction pattern of sample NRP30 (Potato starch/ natural rubber composite) in figure 4.7, it is seen that four sharp diffraction peaks at 15°, 17°, 18° and 23° with intensities at 1000, 1400 and 1450 were observed and two diffuse peaks at 33° and 38° with 800 counts/ intensity were observed. These four sharp peaks exhibited by the diffraction pattern of sample NRP30 are very similar to the diffraction pattern exhibited by starch x-ray diffractogram report by Zhang *et al.* (2004) and also correspond to four out of the five crystalline regions of A-type starch (Campas-Baypoli *et al.*, 2002). This behaviour suggests that gelatinization did not completely destroy the crystalline part of starch. The peaks also appeared at higher intensities of 1000, 1400 and 1450, indicating higher concentrations at the crystalline region of the natural rubber composite. Crystallinity also enhances tensile modulus and tensile strength in elastomers.

According to figure 4.8, the diffraction pattern of sample NRY30 (yam starch/ natural rubber) displayed four diffraction peaks at 15°, 17°, 18° and 23° at intensities of 600, 700 and 800, a shoulder peak of 27° at 500 intensity and two sharp and narrow diffraction peaks of 50° and 60° with intensities of 1450 and 1400, respectively. Fortunately, three out of four diffraction peaks corresponded to the crystalline region of A-type starch (Campas-Baypoli *et al.*, 2002). Moreover, the diffraction peaks at 50° and 60° in the diffraction pattern of yam starch/ natural rubber composites are sharper and narrower with higher intensities showing an increase in the degree of crystallinity and a tendency to higher tensile strength (Montane *et al.*, 1998; Mostafa *et al.*, 2015). This strong crystalline region in yam starch/natural rubber composite partly accounts for the higher tensile strength property of the composite since crystallinity enhances the good tensile property.

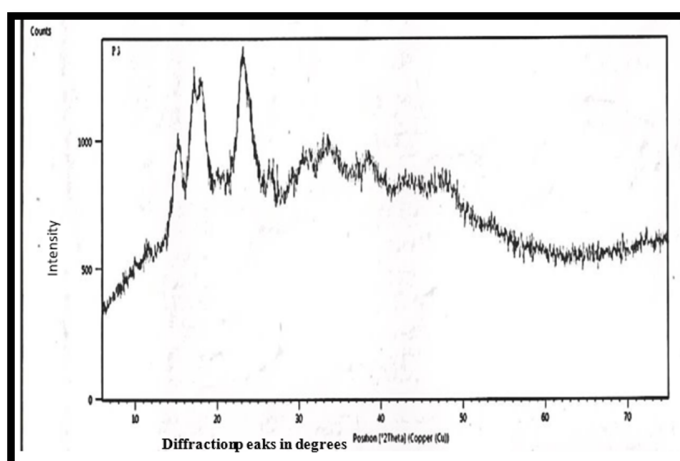


Figure 4.5: X-ray Diffractogram of Sample NRC₃₀

4.8. The Swelling Properties in Solvents

Appendices XXIII – XXIX show the calculated values of swelling properties of the starch-filled natural rubber composites in toluene and water: molar (mol) percentage uptake of the solvent, Q_t , swelling index percentage, swelling coefficient (α), molecular weight between two crosslinks (M_c), the degree of crosslink density (V_c) and the effect of starch fillers on swelling properties, respectively.

The swelling test of polymers shows the behaviour of polymers in designated solvents. Toluene was used in this test, being an organic solvent with known constants, molar volume, and interaction parameters of rubber network-solvent values (0.393). An important difference between vulcanized and raw rubber is that the former possesses a structure that cannot be broken down completely by any solvent. The material, therefore, swells and cannot be dispersed (Lovely *et al.*, 2006). The swelling test also assesses the filler-rubber adhesion. According to Appendices XXIII to XXIX, the molar volume % uptake, swelling index % and swelling coefficient (α) decreases steadily as the filler addition increases from 10 phr to 30 phr. Fillers, if bonded effectively, are supposed to restrict the swelling of elastomers. On the other hand, the degree of crosslink density (V_c) values increase as the filler addition moves from 10 phr to 30 phr in all the starch/rubber composites. Results obtained are consistent with those reported by Lovely *et al.* (2006) and Surya & Siregar (2014), with a degree of crosslink density in the range of 42.6×10^{-5} mol/cm³ to 46.1×10^{-5} mol/cm³ and molar volume % uptake in the range 1.9 – 2.6. It was also observed that the higher the molecular weight between two crosslinks, the lesser the degree of crosslink density and vice-versa. In other words, the degree of crosslink density (V_c) in mol cm⁻³ is inversely proportional to the molecular weight between two crosslinks, M_c , i.e., $V_c \propto 1/M_c$ by a constant 0.5 which was applicable to all the samples at 30 phr starch filler loading in toluene solvent irrespective of the type of starch so that $V_c = 0.5/M_c$ gives the value of the degree of crosslink density without using the Flory/ Rehner equation, $V_c = 1/2M_c$.

According to Appendix XXIV, among the swelling properties in the water, there was strong resistance in the water and being an inorganic solvent, it yielded negligible molar (mol) % uptake and swelling coefficient, with the control sample NRCB₃₀ having the lowest value of 0.06 and 0.012, respectively. Water is used because of the presence of starch (hydrophilic filler) and also to test the service performance of the final product (tyre) when in contact with water (Lovely *et al.*, 2006).

The reduction in mol % uptake, swelling index % and swelling coefficient (α) in the starch/rubber composites as the filler loading increased from 10phr to 30phr were caused by restrictions on elastomer swelling by the fillers in the rubber matrix as a result of good filler-rubber interaction and adhesion in the composites (Lovely *et al.*, 2006). The reduction was further supported by the increased hindrance exerted at higher filler loadings. The work of Riyajan and Riyapan (2013) reported that the % swelling ratio of starch/natural rubber composite decreased as the concentration of cassava starch moved from 10 phr to 40 phr filler loading. This behaviour applied to all the different starch-filled rubber under investigation. This supports the principle that a higher value of crosslink

density is evidence of good interfacial adhesion between the filler and the rubber and then filler-filler interactions (Cao *et al.*, 2017; Roland, 2016).

4.9. Fourier Transform Infra-Red (FTIR) Spectral Analysis

When two or more substances are mixed, physical blend versus chemical interactions is reflected by the changes/appearances in absorption bands. Therefore, the analysis of FTIR spectra is expected to indicate whether or not changes have occurred and the formation of new chemical bonds. Table 4.9 shows the absorption band for control A (Carbon black-filled rubber composite). According to table 4.1, O-H stretch and free hydroxyl are prominent at 3865 – 3751 cm⁻¹, while C–O stretching band is prominent at 1028 cm⁻¹. The tentative functional group is the alcohol group belonging preferably to a starch molecule. C–H stretching absorption, C–H bend, and CH₃C–H bend are indicative of the presence of alkane or alkyl functional groups. C=O stretching band is also located as indicative of a saturated aliphatic group (Coates, 1996; Mcmurry, 1996).

Table 4.10 shows the FTIR spectra bands for samples NRP30 (Potato starch/rubber composite) O–H stretching band and free hydroxyl of the range between 3778.51 – 3700.00 are present. O–H stretch,

H–bonded are located at 3472 cm⁻¹. These are suggestive of the alcohol functional group. C–H stretching band (2920 cm⁻¹), H–C=O: C–H stretch, (2276 cm⁻¹), CH₃C–H bend (1375.78 cm⁻¹) are suggestive of the alkanes/alkyl group, aldehydes groups and alkyl groups, respectively, while C–C (in-ring) is suggestive of the aromatics.

Absorption cm ⁻¹	Assignment	Tentative Functional Group
3865.00	O-H stretch, Free hydroxyl	Alcohol
3751.33	O-H, stretch free hydroxyl	Alcohol
2919.80	C-H stretch,	Alkane, Alkyl
2854.47	C-H stretch	Alkyl, Alkane
2366.33	Nil	Nil
1741.68	C=O, stretch	Ester, saturated aliphatic
1541.33	N-O, asymmetric stretch	Nitro group
1458.53	C-H, bend	Alkanes
1385.00	CH ₃ C-H bend,	Alkanes, Alkyl
1028.36	C-O stretch	Alcohol

Table 4.9: FTIR Spectral Analysis of Carbon Black Filled Rubber Composite at 30 Phr

Absorption cm ⁻¹	Assignment	Tentative Functional Group
3778.31	O-H stretch, Free hydroxyl	Alcohol
3700.00	O-H, stretch free hydroxyl	Alcohol
3472.00	O-H stretch, H-bonded	Alcohol
2920.00	C-H stretch	Alkyl group, Alkane
2276.00	H-C=O: C-H stretch	Aldehyde
1597.00	C-C stretch (in-ring)	Aromatics
1375.78	CH ₃ C-H bend	Alkyl, Alkane groups

Table 4.10: FTIR Spectral Analysis of Potato Starch/ Rubber Composite at 30 Phr

Table 4.11 shows the absorption band for sample NRC30 (Cassava starch/rubber composite).

O–H stretching band, free hydroxyl (3854 cm⁻¹), and O–H stretching, H–bonded (3426 cm⁻¹) are suggestive of alcohol functional groups belonging preferably to the starch molecules. The C–H stretching band (2922 – 2856 cm⁻¹) is suggestive of the alkane backbone of the cis-1, 4polyisoprene structure (Coates, 1996).

–C=C– stretching bond (1644.54 cm⁻¹) of the alkene group is suggestive of carbon-carbon double bond of cis-1, 4- polyisoprene in rubber, which is consistent with the report of Riyajan and Patisat (2018) and Riyajan *et al.*, (2012). C–O stretch (1054 cm⁻¹) is also indicative of alcohols and carboxylic acids present.

Table 4.13 shows the absorption band recorded for sample NRCO₃ (Cocoyam starch/ rubber composite). O–H stretch (3779 cm⁻¹ – 3476 cm⁻¹) is present. C–H stretch (2919 cm⁻¹ and 2853 cm⁻¹) are also present. They are suggestive of the alcohols group and alkane/alkyl groups, respectively.

H–C=O: C–H stretch (2278 cm⁻¹) is suggestive of the aldehydes. C=O stretch (1743 cm⁻¹) of the esters and saturated aliphatic are present (Coates, 1996). C–C stretch (in-rings), indicative of the aromatics and CH₃C–H band (1377.52 cm⁻¹) of alkanes/alkyl groups, are present.

Absorption cm ⁻¹	Assignment	Tentative Functional Group
3854.00	O-H stretch, Free hydroxyl	Alcohol
3744.80	O-H, stretch free hydroxyl	Alcohol
3426.00	O-H stretch, H-bonded	Alcohol
2922.37	C-H stretch	Alkyl group, Alkane
2856.61	C-H stretch	Alkyl, Alkane
2358.87	Nil	Nil
1644.54	-C=C-, stretch	Alkenes
1539.00	N-O, asymmetric stretch	Nitro compound
1045.00	C-O, stretch	Alcohol, Carboxylic acid

Table 4.11: FTIR Spectral Analysis of Cassava Starch/ Rubber Composite at 30 phr

Absorption cm ⁻¹	Assignment	Tentative Functional Group
3779.00	O-H stretch, Free hydroxyl	Alcohol
3701.00	O-H, stretch free hydroxyl	Alcohol
3476.00	O-H stretch, H-bonded	Alcohol
2919.50	C-H stretch	Alkyl, Alkane
2853.56	C-H stretch	Alkyl, Alkane
2278.00	H-C=O: C-H, stretch	Aldehyde
1743.00	C=O, stretch	Esters, saturated aliphatic
1593.00	C-C, stretch (in-ring)	Aromatics
1544.19	N-O, asymmetric stretch	Nitro compound
1450.55	C-H, bend	Alkyl, Alkane
1377.52	CH ₃ C-H, bend	Alkyl, Alkane
1024.61	=C-O-C, sym.-stretch	Ethers

Table 4.12: FTIR Spectral Analysis of Cocoyam Starch/ Rubber Composite at 30 phr

Tables 4.13 and 4.14 show the absorption bands for samples NRA₃₀ and NRY₃₀ (Amora starch/rubber composite and Yam starch/rubber composite.) C–H bend (1459 cm⁻¹) and O–H stretch (3777 – 3466 cm⁻¹) are both common in both absorptions and are suggestive of the alcohol group. C–H stretch (2919 2855 cm⁻¹) is both present and indicative of alkyl group/alkanes. C–O stretch (1029 cm⁻¹), suggestive of carboxylic acid, is present.

All the starch/rubber samples contained hydroxyl group absorption bands. It was supported by the work of Riyajan and Patisat (2018), where it occurred at 3227 cm⁻¹ for the H-bonded type. The C–H out-of-plane bending of the cis-1, 4 addition was recorded in the range of 1459 cm⁻¹ – 1377 cm⁻¹ in the rubber blends, according to Coates (1996) and Peng *et al.* (2016).

Almost all the spectral bands (absorptions) found in the starch/rubber samples are similar to those observed in the unfilled rubber and the pure starch.

Absorption cm^{-1}	Assignment	Tentative Functional Group
3777.00	O-H stretch	Alcohol
3466.00	O-H, stretch	Alcohol
2920.70	C-H stretch	Alkyl, Alkane
2855.41	C-H stretch	Alkyl, Alkane
2279.00	Nil	Nil
1735.00	C=O, stretch	Saturated aliphatic
1597.00	C-C, stretch (in-ring)	Aromatics
1544.61	N-O, asymmetric stretch	Nitro compound
1450.29	C-H, bend	Alkanes
1377.52	-CH ₃ C-H, bend	Alkyl, Alkane
1248.00	C-N, stretch	Aliphatic amines
1089.00	C-N, stretch	Aliphatic amines
1024.66	=C-O-C, symmetric stretch	Ethers

Table 4.13: FTIR Spectral Analysis of Amora Starch/ Rubber Composite at 30 Phr

Absorption cm^{-1}	Assignment	Tentative Functional Group
3755.73	O-H stretch, free hydroxyl	Alcohol
2919.37	C-H, stretch	Alkanes
2855.00	C-H stretch	Alkanes
2373.00	Nil	Nil
1739.78	C=O, stretch	Carbonyl compound
1542.53	N-O, asymmetric stretch	Nitro compound
1459.00	C-H, bend	Alkanes
1029.00	C-O, stretch	Alcohol, carboxylic acid

Table 4.14: FTIR Spectral Analysis of Yam Starch/ Rubber Composite at 30 Phr

Absorption cm^{-1}	Assignment	Tentative Functional Group
2916.57	C-H, stretch	Alkanes & alkyl
2849.77	C-H, stretch	Alkanes & Alkyls
2326.13	Nil	Nil
2114.98	C≡O, stretch	Alkynes
1991.97	=C-H, bend	Alkenes
1701.15	C=O, stretch	α , β -unsaturated aldehydes, ketones
1432.64	C-C, stretch (in-ring)	Aromatics
1375.40	CH ₃ C-H, bend	Alkanes & alkyls
1312.36	C-O, stretch	Carboxylic acids, esters, ethers
1013.96	C-O stretch	Carboxylic acids, esters, ethers
832.17	C-Cl stretch	Alkyl halides

Table 4.15: FTIR Spectral Analysis of Unfilled Vulcanized Rubber Nro (Reference Sample)

Results and Discussion

Absorption cm ⁻¹	Assignment	Tentative Functional Group
3290.55	O-H, stretch, H- bonded	Alcohols
2917.53	C-H, stretch	Alkanes
2850.14	C-H stretch	Alkanes
2114.22	-C≡O-, stretch	Alkynes
1641.79	C=C, stretch	Alkenes
1339.06	N-O, symmetric stretch	Nitro compounds
1148.68	C-N, stretch	Aliphatic amines
1076.30	C-N, stretch	Aliphatic amines
994.31	=C-H, bend	Alkenes
926.95	=C-H bend	Alkenes
859.85	=C-H bend	Alkenes
761.12	C-CL stretch	Alkyl halides
508.32	C-Br stretch	Alkyl halides

Table 4.16: FTIR Spectral Analysis of Starch (Reference Sample)

4.10. Thermal Analysis with Differential Scanning Calorimetry (DSC)

The temperature plot of differential scanning calorimetry showing the thermal transitions of the polymer samples is shown in Appendices XV – XX.

Appendices XV-XX show the thermal transitions of rubber samples studied. The polymer sample has both amorphous and crystalline regions, even as supported by the X-ray diffractograms previously. The glass transition temperature (T_g) of the rubber samples ranges from 85oC to 98oC and has been displayed in table 4.17. The glass transition temperature (T_g) is the middle line of the temperature gradient taken when the heat capacity of this rubber polymer starts to change or increase gradually when it is heated. Usually, polymers have higher heat capacity above the glass transition temperature than they have below it and this gradual change takes place over a temperature range. All the rubber samples studied showed a high glass transition temperature above uncured rubber (-70oC) since they all contain fillers, either starch or carbon black filler. It has been established that good dispersion of fillers in rubber and good interfacial adhesion between the filler and the rubber matrix increases glass transition temperature (T_g) and crosslink density properties in rubber (Cao *et al.*, 2017; Wang *et al.*, 2018). This is because interactions between the fillers and the polymer (rubber) molecules reduce molecular movement and flexibility of the polymer chains at the interfaces. A polymer chain that can move around fairly easily will have a very low (T_g), while one that does not move so well will have a high (T_g). The more easily a polymer can move, the less heat it takes for the chains to commence wiggling and break out of the rigid glassy state and into the soft rubbery state (Jang, 1994; Droste & Dibenedatto, 2017). This is the reason why all the rubber composites have higher glass transition temperature (T_g) values above that of uncured natural rubber (T_g – 70oC). Finally, the carbon black-filled rubber has the highest (T_g) value (153oC), indicating better reinforcement, strong interfacial adhesion and good dispersion in rubber and hence, good mechanical properties above the starch-filled rubbers. Table 4.17 is shown below.

Glass Transition Temperature (T_g) °C				
Natural	rubber/	Amora	starch	Composite 85
Natural	rubber/	Cassava	starch	composite 98
Natural	rubber/	Potato	starch	composite 91
Natural	rubber/	Cocoyam	starch	composite 92
Natural	rubber/	Yam	starch	composite 92
Natural	rubber/	Carbon	black	composite 153

Table 4.17: Glass Transition Temperature (T_g) of the Starch/ Rubber Composite

Key: Phr

= Part per Hundred Rubber

*Natural Rubber = -70°C

*Starch = 60°C

* = Glass Transition Values of Natural Rubber and Starch
Obtained from Standard Data in Literature

4.11. Scanning Electron Microscopy (SEM) Morphology Analysis

The Scanning electron microscopy (SEM) micrographs of the control sample, NRCB30, starch-filled natural rubber composites, NRA30 and NRY20 at 500x and 1000x magnification are shown in plates 4.1, 4.2, 4.3, 4.4, 4.5 & 4.6 from pages 92 – 100.

From information on the SEM image of sample NRCB30, as shown in figure 4.9 in page 94, the particle size of the majority of the particles is in the range of 1.37 µm – 4.24 µm. Moreover, the carbon black filler particles embedded in the matrix of the rubber composite and other supporting evidence of good interfacial interaction of carbon black filler and rubber is given by the high tensile strength of 87.63 Nm⁻² and a high degree of crosslink density value of 51.9 x 10⁻⁵ cm⁻³, previously shown in table 4.4 and Appendix XXIII. The particle size of the particles in sample NRCB30 is the smallest among the samples screened, suggesting that the smaller the particle size, the better the reinforcement and the better interfacial adhesion between the two phases (Cao et al., 2017; Stelescu et al., 2017).

From information on the SEM image of sample NRA30, as shown in figure 4.10 in page 97, the particle size of the majority of the particles is in the range of 1.42 µm – 7.95 µm. Moreover, the amora starch particles are embedded in the matrix of the rubber composite. The topography displayed in the SEM image is evidence of good dispersion of filler and interfacial interaction between filler and the rubber matrix. Other supporting evidence is the higher value of tensile strength of 57.43 Nm⁻² and the higher value of the degree of crosslink density of 44 x 10⁻⁵ cm⁻³, previously shown in table 4.4 and Appendix XXV, respectively.

According to the 500x and 1000x magnification image of the SEM micrograph in plates 4.5 and 4.6 showing the morphology of sample NRY20 and information from figure 4.11, the particles in the starch/ rubber composites are completely embedded in the matrix. This is consistent with good compatibility between the fillers and the rubber matrix induced by the latex compounding method and introducing starch filler in gelatinized form, thereby reducing the bulky size of the starch molecules. According to the information in figure 4.11, the particle size of the majority of the particles in the starch/rubber composite is in the range of 2.66 µm – 10.19 µm. Other supporting evidence of strong interfacial interaction and good dispersion of filler in the rubber matrix is a good tensile strength value of 76.17 Nm⁻² at optimum filler loading and a high value of degree of crosslink density of 37.90 x 10⁻⁵ cm⁻³ for sample NRY20, previously shown in table 4.8 and Appendix XXVII, respectively.

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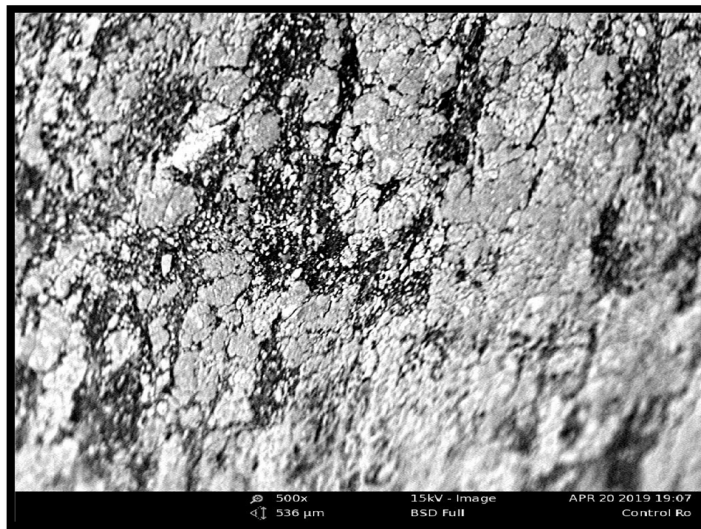


Plate 4.1: SEM Micrograph of Control Sample, NRCB₃₀

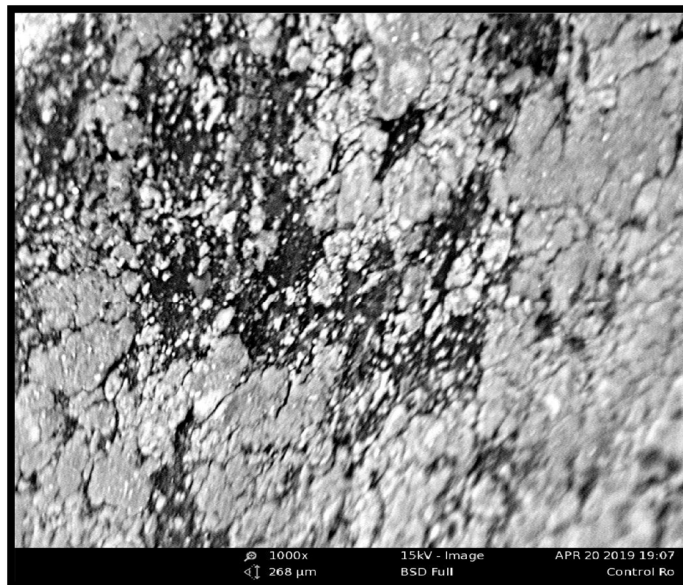


Plate 4.2: SEM Micrograph of Control Sample, NRCB₃₀

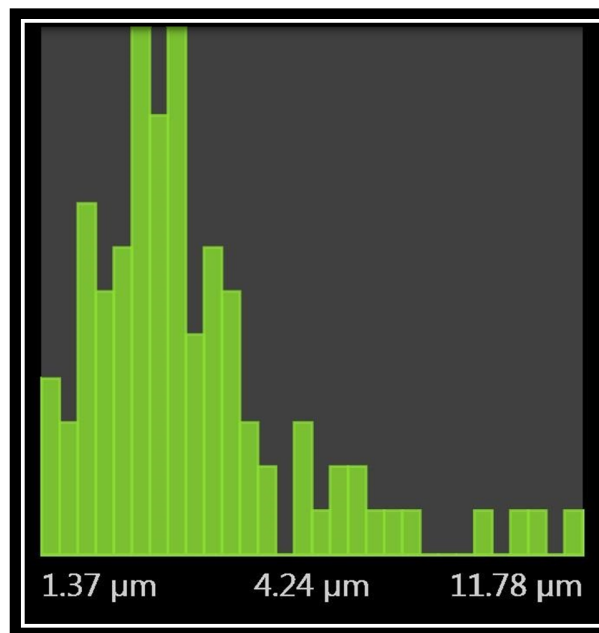


Figure 4.9: SEM Fibre Histogram of Control Sample, NRCB30

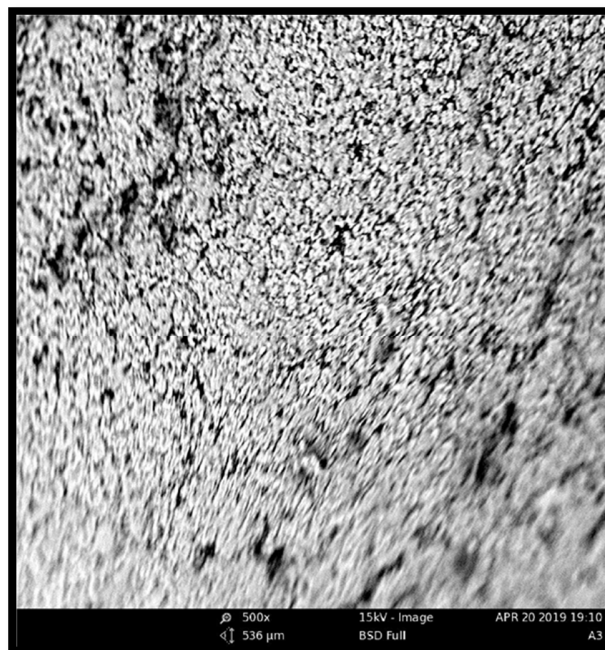


Plate 4.3: SEM Micrograph of Sample, NRA30

Results and Discussion

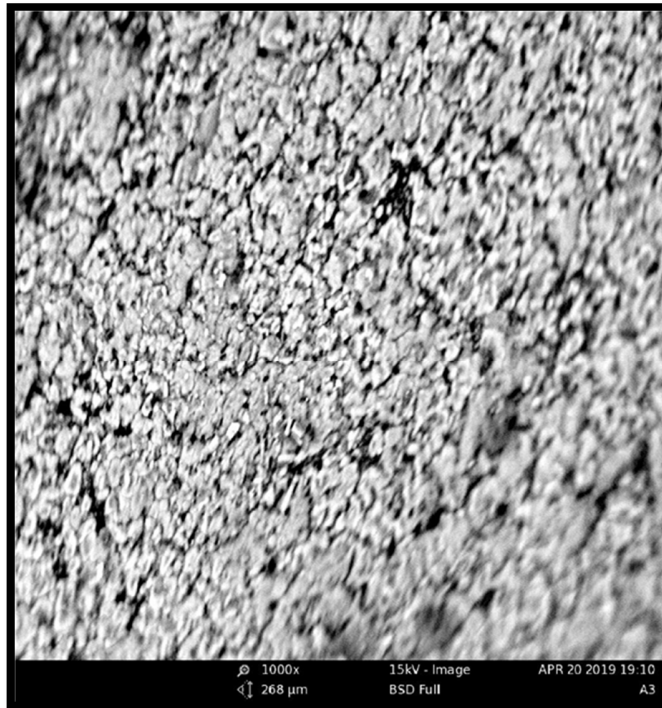


Plate 4.4: SEM Micrograph of Sample, NRA30

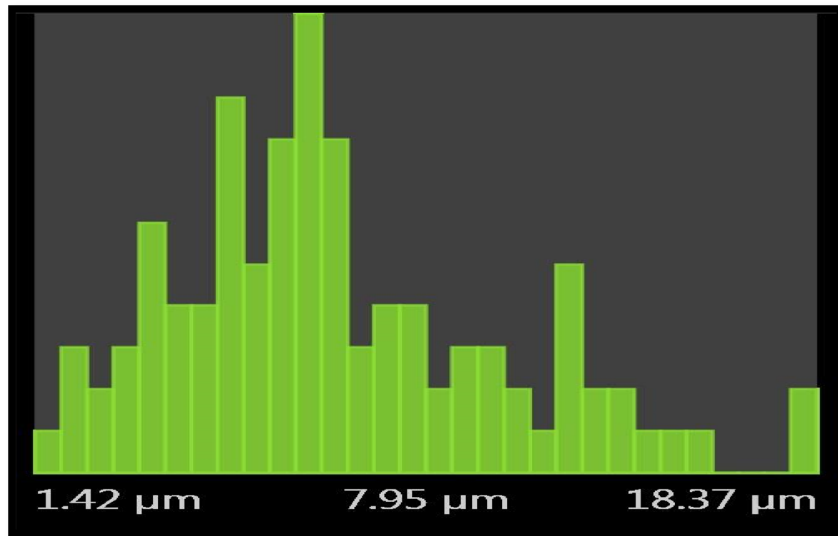


Figure 4.10: SEM Fibre Histogram of Sample, NRA30

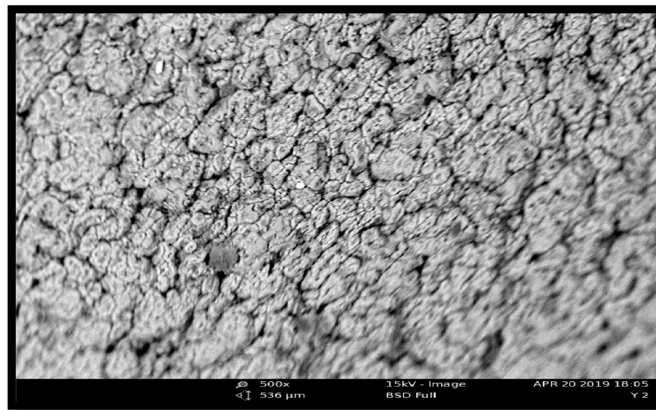


Plate 4.5: SEM Micrograph of Sample, NRY20

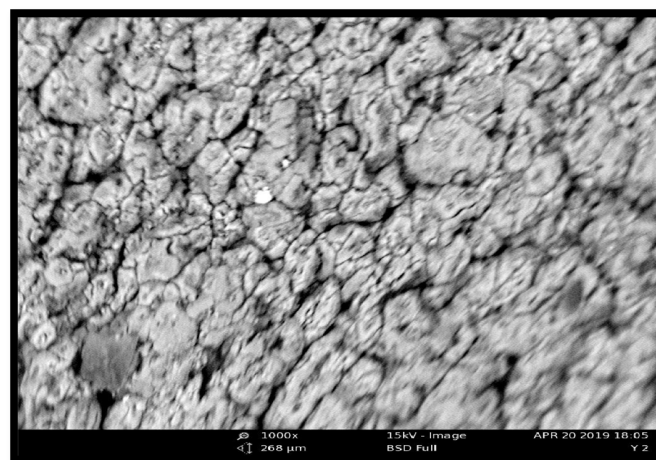


Plate 4.6: SEM Micrograph of Sample, NRY20

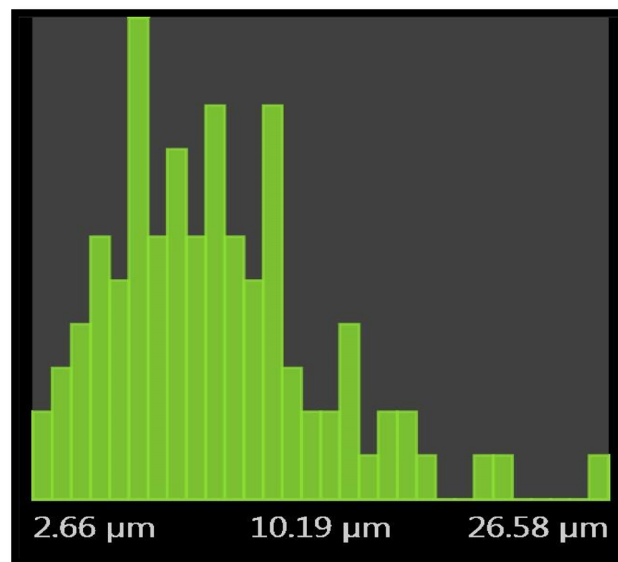


Figure 4.11: SEM Fibre Histogram of Sample, NRY₂₀

4.12. Weight Loss/ Aging Test Results

According to table 4.18, no loss in weight occurred in tensile strength (57.43 Nm⁻²) and elongation at break (10007), but it retained its properties after the weight loss/aging test. The rest of the rubber composites dropped in their values in tensile strength in various percentages, such as NRC₃₀ (19%), NRCO₃₀ (30%), NRP₃₀ (30%), NRY₃₀ (21%), and NRCB₃₀ (22%). In elongation at break property, sample NRA₃₀ also retained its elongation at break value at 10007, while the other rubber composites lost value in various percentages except for sample NRC₃₀ which increased its value by 22%. In terms of hardness, only sample NRA₃₀ increased in hardness by 6%, while the rest rubber composites dropped their values in terms of hardness in various percentages, such as NRC₃₀ (25%), NRCO₃₀ (15%), NRP₃₀ (11%), NRY₃₀ (16%), NRCB₃₀ (2.2%). This observation suggests that sample NRA₃₀ is more resistant to weight loss/aging conditions than the rest rubber composites, including the control, NRCB₃₀.

Composite Tensile Percentage Elongation Percentage Average Percentage at 30 phr strength Reduction/ at break Reduction/ Hardness Reduction/ Filler (Nm⁻²) Increase loading									
NRA₃₀	57.43	-0	Nil	10007	0	0	50.50	Nil	+6.00
NRC ₃₀	7.80	-19	Nil	3469	Nil	+22	41.50	-25.00	Nil
NRCO ₃₀	19.20	-30	Nil	5231	-4.80	Nil	50.50	-15.00	Nil
NRP ₃₀	24.90	-30	Nil	6336	-4.80	Nil	46.50	-11.00	Nil
NRY ₃₀	25.50	-21	Nil	6981	-8.00	Nil	59.50	-1.60	Nil
NRCB ₃₀	68.50	-22	Nil	6262	-8.00	Nil	65.50	-2.20	Nil

Table 4.18: Physical and Mechanical Properties after Weight Loss/ Aging Test

Key: NRA₃₀ =Natural rubber/ Amora starch composite
 NRC₃₀ =Natural rubber/ Cassava starch composite
 NRCO₃₀ =Natural rubber/ Cocoyam starch composite
 NRP₃₀ =Natural rubber/ Potato starch composite
 NRY₃₀ =Natural rubber/ Yam starch composite
 NRCB₃₀ =Natural rubber/ Carbon black composite
 + = % increase
 - = % reduction

4.13. Results of Microbial Degradation by Soil Microorganisms

The two mixed cultures: spherical colony bacteria and filamentous colony bacteria, were introduced to the starch-filled rubber (F5, F30, F90 and unfilled rubber, Fo) in a mineral salt medium as a sole source of carbon and energy. Direct inoculation and serial dilution with 0.1ml inoculum on agar plates produced bacteria colonies by both mixed cultures. The spherical colony bacteria type produced colonies above 300 at 24 hours after incubation (too numerous to count, TNTC) and therefore, its growth pattern could not be monitored and was not used. Instead, a filamentous colony type with less than 100 colony counts at 24 hours of inoculation was used to monitor the colony growth pattern, Heterotrophic Plate Count (HPC) (ISO 4833, 1991). Table 4.19 shows the colony counts calculations for the bacteria growth. Unfilled rubber composite (without starch filler), Fo and amora starch/natural rubber composite at 5phr (F5), 30 phr (F30) and 90 phr (F90) filler addition were used as test starch/rubber specimens for biodegradation test. According to Heterotrophic plate count (HPC) ISO 4833 (1991), unfilled rubber, Fo (cured rubber without starch), yielded a viable number of cells (N), which increased steadily from 320 at the lag phase to 427,272.7 after 72 hours under serial dilution. The presence of protein and lipids in the unfilled cured rubber sample Fo served as a nutrient source for the bacteria in addition to the rubber molecule. Since there was no starch in this specimen, the microorganism would likely exhaust the protein and lipids before feeding on the rubber, which is a much heavier molecule of high molecular mass, hence the observed cell multiplication. Moreso, the bacteria are still in their exponential phase in the closed system after 72 hours under serial dilution. Specimen F5 (rubber filled with 5phr starch) yielded growth of cells from 340 at lag phase to 454,545.5 after 48 hours and then declined after 72 hrs to 380,000. This decline is probably because the bacteria have entered its stationary phase, having

exhausted the available nutrients in the medium, probably from lipids, protein and starch in the rubber composite. Specimen F30 (rubber filled with 30 phr starch) yielded growth of cells from 300 at lag phase to 453,636.4 after 48hrs and then declined to 340,909 after 72hrs. This decline after the exponential phase indicates that the bacteria has entered its stationary phase, having exhausted the available nutrients, starch, lipids, and protein in the rubber composite or that the presence of waste product generated has made growth conditions unfavourable. Specimen F90 (rubber filled with 90 phr starch) yielded growth of cells 150 at lag phase and increased to 274,545.5 after 48hrs and then continued to increase up to 418,181.8 till 72hrs. Here, starch is in the continuous phase and rubber is in the dispersed phase. The bacteria is still in the exponential phase of growth, having enough nutrients to feed on, like starch, protein and lipids, which are easier to digest than high molecular mass rubber molecules.

According to the graph in figure 4.12, there was an increase in the growth of the microorganism, according to colony count, from the lag phase, after 48 hours and then after 72 hours, respectively, for F0 and F90 and then with a decline after 72 hours for F5 and F30. The control setup containing the inoculum inside the mineral salt medium (MSM) only without any carbon source (rubber vulcanizates) did not produce any bacteria colony on the agar plate showing that rubber vulcanizates are the only source of carbon and energy in the test experimental setup (ISO 4833,1991).

Duration	24 hours (Lag phase)	48 hours	72 hours
F ₀	320	280,909	427,272.7
F ₅	340	454,545.5	380,000
F ₃₀	300	453,636.4	340,909
F ₉₀	150	274,545.5	418,181.8

Table 4.19: Viable Number of Cells (N) CFU/ML
Key: CFU = Colony Forming Unit

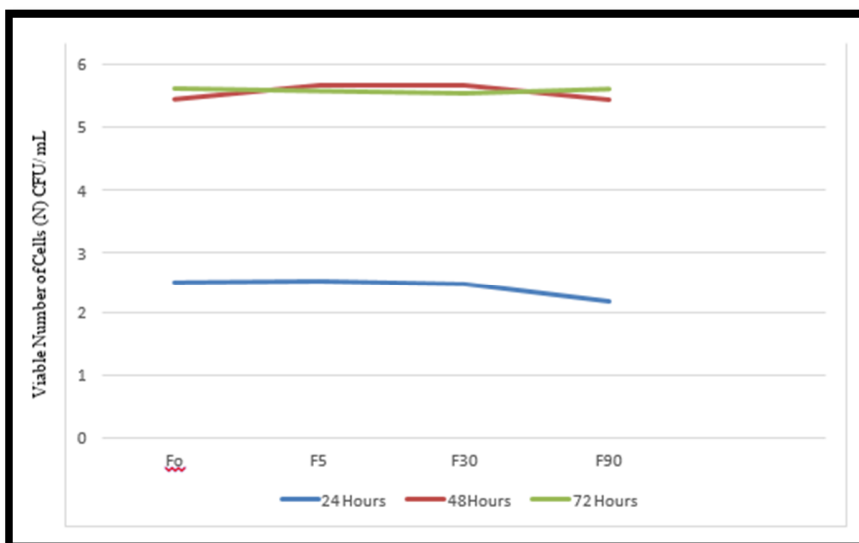


Figure 4.12: Plot of Viable Number of Cells (N) CFU/mL against No. of Hours

Duration	24 hours (Lag phase)	48 hours	72 hours
F ₀	2.51	5.45	5.63
F ₅	2.53	5.66	5.58
F ₃₀	2.48	5.66	5.53
F ₉₀	2.18	5.44	5.62

Table 4.20: Viable Number of Cells (N) in Logarithm Value

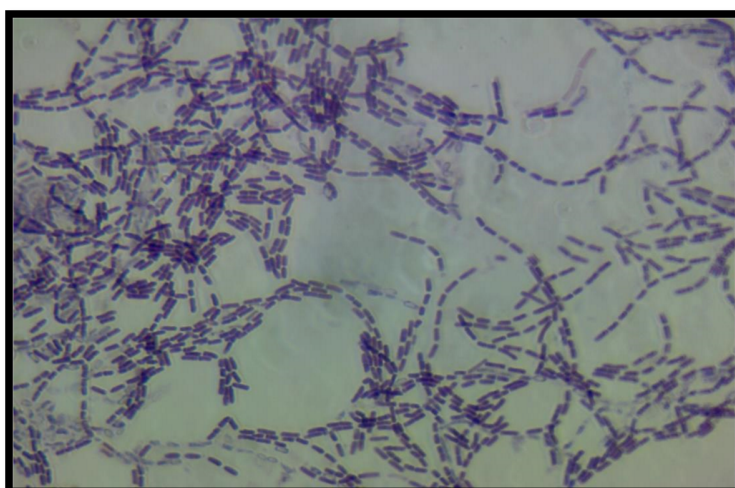


Plate 4.7: A Slide of Gram Stain Reaction Showing Two Gram Positive Bacteria in a Mixed Culture, *Bacillus species* (+), *Bacillus megaterium* (+)

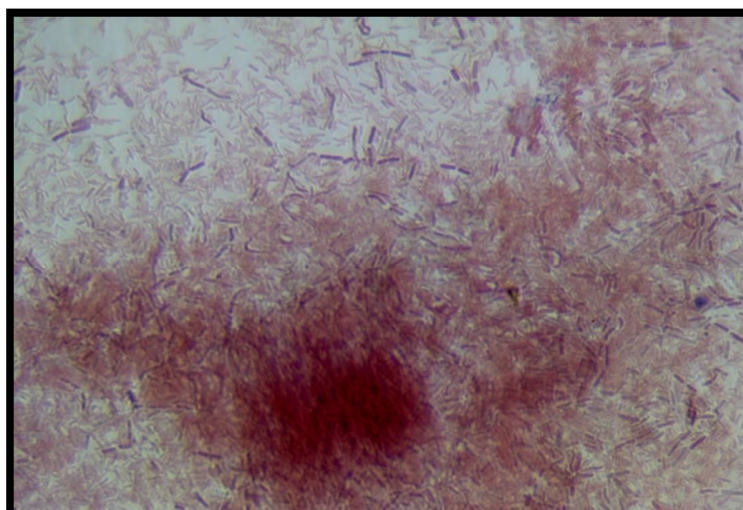


Plate 4.8: A Slide of Gram Stain Reaction Showing Two Bacteria in a Mixed Culture, *Pseudomonas Aeruginosa* (-), *Bacillus Megaterium* (+)

4.14. Bacteria Degradation/ Identification Tests

The test bacterium was identified to be in mixed culture in both plates 4.7 and 4.8 and was identified by biochemical tests, as indicated in table 4.21. The organisms are as follows:

- *Pseudomonas aeruginosa* (-), Gram-negative bacterium
- *Bacillus megaterium* (+), Gram-positive bacterium
- *Bacillus spp.* (+), Gram-positive bacterium

The bacteria worked together in a mixed culture to feed on the starch/ rubber composites, as indicated by the colony growth calculations that showed the viable number of cells (N) (ISO 4833, 1991) in table 4.19. In plate 4.8, *Pseudomonas aeruginosa*, a Gram-negative rod and *Bacillus megaterium*, a Gram-positive rod, worked in a mixed culture to feed the starch/rubber composite, while *Bacillus megaterium* and *Bacillus sp* in plate 4.7 worked together in a mixed culture to feed on the starch/ rubber composite in the mineral salt medium as indicated by the colony growth calculations showing the viable number of cells (N) in the colonies. This observation is supported by the work of Jendrossek *et al.* (2000), where *Pseudomonas aeruginosa* produced holes in polymer films when used as the sole source of carbon and energy on a solid mineral salt medium.

Steinbuchel *et al.* (2000) also discovered that the strain AL 98, *Pseudomonas aeruginosa*, was able to considerably disintegrate natural rubber (NR), either in the raw state as NR latex concentrate or in the vulcanized state as NR latex glove as well as raw synthetic cis-1, 4polyisoprene. Moreso, *Bacillus sp* SBS25, a Gram-positive bacteria isolated from soil, was found to be effective in the biodegradation of natural rubber latex (Cherian & Jayachandran, 2009).

The work of Shah *et al.* (2012) also reported that the strain AF-666, *Bacillus sp*, isolated from a soil sample, was found to degrade polyisoprene rubber both on basal agar plates (Latex overlay) and in a higher medium.

Tajuddin and Azura (2012) posited that *Bacillus megaterium* has large potential in the degradation process for biodegradable natural rubber latex film. The bacteria proved to be a useful and viable accelerating media for the biodegradation of natural rubber films.

Moreso, the Government of Canada's (2018) science-based evaluation of *Bacillus megaterium* strain, ATCC 14581, revealed that the organism is not hazardous to human health or the environment and that the characteristics of *Bacillus megaterium* strain, ATCC 14581, make it suitable for use in various applications, including wastewater treatment, bioremediation and biodegradation, cleaning and deodourizing as well as enzyme and chemical production.

Bacterial Isolates			
TESTS	Bacillus megaterium	Bacillus spp.	Pseudomonas aeruginosa
Gram reaction	+	+	
Motility	Motile	Motile	Motile
Spore shape	Oval	Oval	NA
Spore position	Central spore	Central spore	NA
Swelling of bacillary body	-	-	NA
Growth at 45°C	-	++	
Growth in 7 % NaCl	++	-	
Utilization of Citrate	++	-	++
Glucose	++	++	++
Arabinose	-	-	
Mannitol	-	-	++
Xylose	-	-	++
Indole	-	-	-
Urease	++	-	++
Gelatin hydrolysis	++	-	++
Oxidase			++
Pigment			++
Growth at 5° C			-
Growth at 42° C			++
Growth on MacConkey			++
Lactose			-
Maltose			-
Salicin			-
Sucrose			-

Table 4.21: Biochemical Characterization of Isolates from Nutrient Agar Slants

Key: (+) Gram Positive Bacteria

(-) Gram Negative Bacteria

++ Positive Growth

-- No Growth

4.15. Aldehyde Group Test on Degradation by-Product

Schiff's reagent test revealed the presence of aldehyde groups in the breakdown products of biodegradation of the starch/rubber vulcanizates by showing purple colour on the residue of starch/rubber vulcanizate particles. FTIR analysis on amora starch-filled rubber at 30 phr, F30, revealed the presence of carbonyl/ketones functional group, C=O stretch at 1735 cm⁻¹ absorption bend as well as in the unfilled cured rubber, Fo at 1702 cm⁻¹, before the biodegradation test was carried out. It is not ascertained whether the aldehyde groups found on the starch/rubber residue were from bacteria activity, the degradation product, or the starch/rubber composite. The only evidence of biodegradation activity in this study was from the multiplication of bacteria utilizing the starch/rubber specimens as a source of carbon and energy when the agar plate was inoculated with bacteria at 10⁻³ and 10⁻⁴ dilutions. The colony counts, as indicated by the calculated viable number of cells (N) of colony forming unit per mL (CFU/mL), are shown in table 4.19. Since the source of the aldehyde group is not confirmed, it is not tendered as evidence of biodegradation in this study but just a simple qualitative test. The aldehyde groups are actually found to be part of acetyl-diprenyl-acetaldehyde, a breakdown product of natural rubber (Tsuchii & Takeda, 1990). Jayaran and Sudesh (2016) reported a decrease in the number of cis-1,4 double bonds in the polyisoprene chain and the appearance of Ketone and aldehyde groups, indicating an oxidative attack at the double bond of rubber hydrocarbon. Their report clearly showed that *Streptomyces* sp, CFMR7 was able to cleave the carbon backbone of cis-1,4- polyisoprene.

Nayanashree and Basaiah (2015) also reported that the enzymes *Laccase* and *Manganese peroxidase* found in *Bacillus subtilis* are responsible for natural rubber degradation and that biodegradation of natural rubber by *Bacillus* species is purely an enzymatic reaction. This was further supported by Karsten and Steinbuchel (2005), who reported that the analysis of the division products of natural and synthetic rubbers isolated from various bacterial cultures indicated without exception that there was oxidative cleavage of the double bond in the rubber polymer backbone. They reported that aldehyde and/or carbonyl groups were detected in most of the analyzed degradation products isolated from cultures of various rubber degrading strains.

5|Summary, Conclusion and Recommendations

5.1. Summary

According to the trial batch starch filler (amora and yam) additions from 0 – 90 phr, the attendant tensile properties and the decline in tensile properties due to the phase inversion, and the best volume percentage filler addition for the starch fillers appear to be within the range of 20 phr to 30 phr. The other starch fillers (cocoyam, cassava and potato) were added to the rubber in the range of 20 to 30 phr filler addition. The rubber composites produced moderate tensile properties in 20–30 phr range.

X-ray diffraction analysis and differential scanning calorimeter revealed that the formulated biopolymer is a semi-crystalline polymer material with glass transition temperatures (T_g) higher than the value for uncured and unfilled natural rubber. Stronger interfacial adhesion was evidenced by higher values in the degree of crosslink density (V_c) as the filler loading increased from 10 phr to 30 phr, as revealed by the swelling text experiment in toluene. The characteristic carbon-carbon double bond of the cis-1, 4-polyisoprene was located at 1644.54 cm^{-1} stretching band by Fourier transforms infrared spectroscopy indicating the presence of rubber molecule in the formulated biopolymer while the presence of O-H stretches for free hydroxyl and O-H bonded are indicators that starch molecule is present in the biopolymer composite.

Degradation activity of the microorganisms shows maximum bacteria activities after 72 hours on the cured rubber without starch filler, followed by degradation activity on starch-filled rubber at 90 phr, which steadily increased from the lag phase to 72 hours under serial dilution.

Evidence of biodegradation activity was shown by the multiplication of the bacteria mixed culture at 10⁻³ and 10⁻⁴ dilution as indicated by the calculated viable number of cells (N) of colony forming unit per mL (CFU/mL) in the agar plates. There was evidence that the bacteria feed on the starch/rubber composite as a source of nutrients (carbon source) and energy because the rubber specimen contains other nutrients such as protein, lipids and starch, which are easier to digest than natural rubber and provide growth factor for the bacteria during the period.

5.2. Conclusion

From the investigations carried out in this study, the following conclusions can be drawn:

The results obtained indicated that starch fillers used as an alternative filler produced moderately good reinforcement in terms of physical and mechanical properties comparable to the conventional filler, and carbon black was used as a control. The best volume percentage for starch filler addition (optimum filler limit) is in the range of 20 phr–30 phr, pending further investigations. Moreso, amora starch has the potential to replace cassava and maize as a source of starch filler in the rubber industry and can also partially replace carbon black and silica as filler for natural rubber.

Applying the latex compounding method, aqueous electrolyte coagulant and gelatinization of starch filler before incorporating it into natural rubber has helped to reduce the bulky size of starch molecules. A medium of dispersing starch filler in the natural rubber matrix was created, thereby producing in the process strong interfacial adhesion between starch filler and natural rubber. Biodegradation activity in the mixed culture is highest on rubber cured rubber without starch and least on starch filled at 30 phr.

Biodegradation activity of the mixed culture of *Pseudomonas aeruginosa* and *Bacillus megaterium*, *Bacillus sp.* and *Bacillus megaterium* in the degraded residue product has opened a new application for utilizing biotechnological processes in rubber waste control. This will reduce the burning of used tyres and rubber products and prevent the introduction of obnoxious and toxic hydrocarbons into the atmosphere leading to ozone layer depletion. The starch/natural rubber composite developed can, with little fortification, be utilized as a tyre thread material in automobile tyres. This will reduce absolute dependence on carbon black or silica and reduce cost in the process.

5.3. Recommendations

- Having established that soil bacteria could feed on rubber material when introduced as a sole source of carbon and energy, future rubber degradation research should expose the rubber material (vulcanizates) in the soil under *Heavea Brasilienses* tree plantation having been found to dwell in those soil types and investigate their degradation property in their natural habitat.
- Transmission electron microscopy (TEM) and Atomic force microscopy (ATM) should be used in future studies on the morphological characterization of the blends to further understand the nature of the interaction between starch fillers and natural rubber.
- Dynamic mechanical, thermal analyzer, DMTA and thermogravimetric analyzer could also be used to collaborate with the results of differential screening calorimetric analysis in future research in this area.

5.4. Contribution to Knowledge

This research has introduced to the list of fillers, new starch fillers that have not been used in the rubber industry: Polynesian arrow root (amora) starch, yam starch (*Dioscorea rotundata*) and cocoyam starch (*Colocasia esculenta*). This research will introduce an opportunity for further investigation of the application of biotechnological processes as a tool for rubber waste control and management.

A new horizon of knowledge has been opened towards understanding the nature of the bonding interactions between starch filler and the rubber matrix in starch-filled rubbers with respect to reactive compatibilization and particle size reduction in fillers. The introduction of starch into natural rubber (without any chemical functionalization) by the use of the latex compounding method and aqueous electrolyte coagulant has reduced the bulky size of starch molecules and created a system of weak intermolecular attractions between starch filler and natural rubber.

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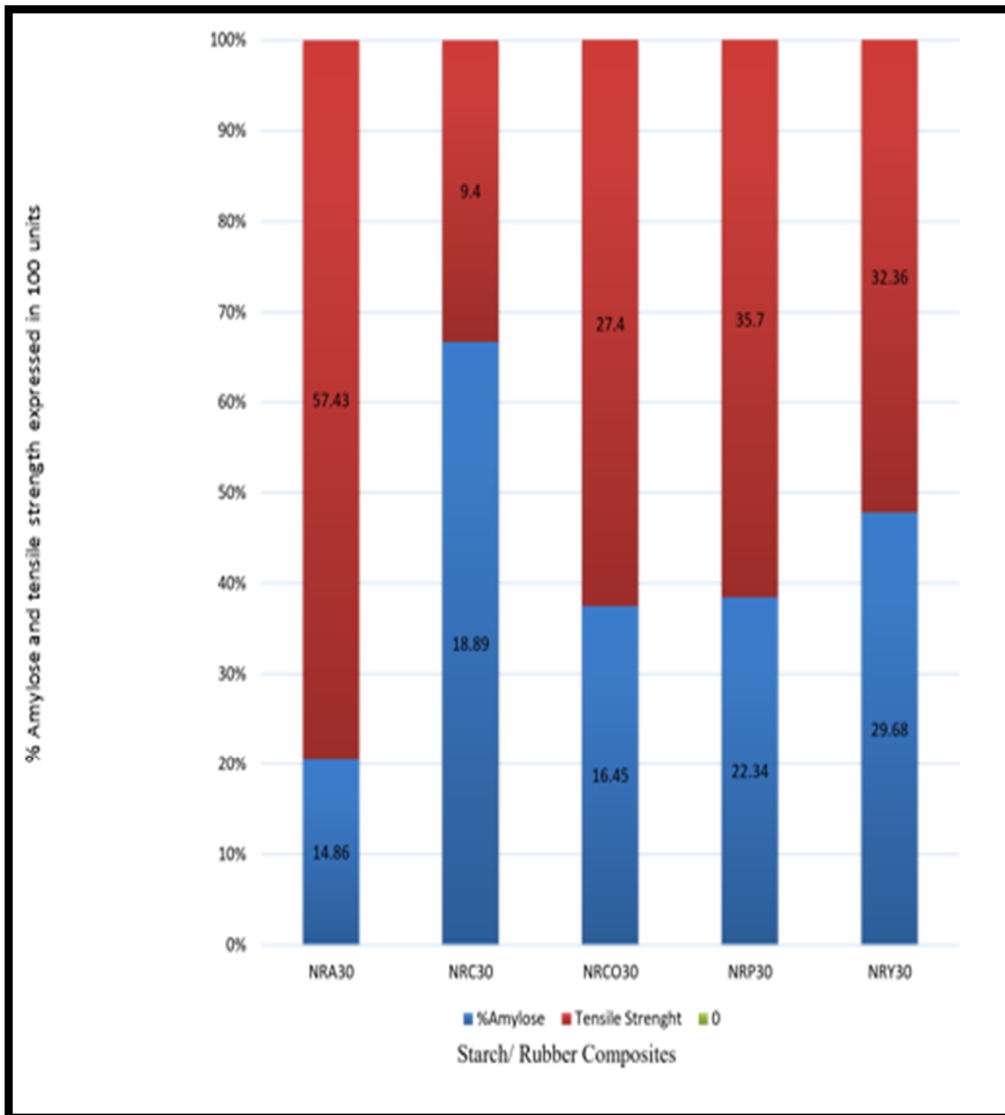
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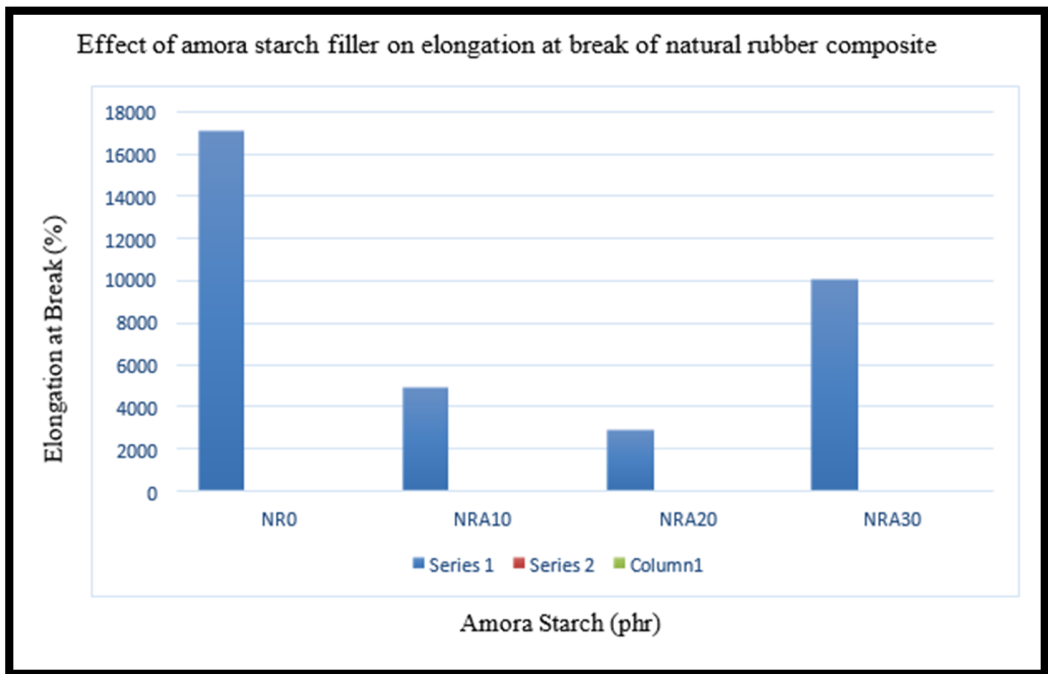
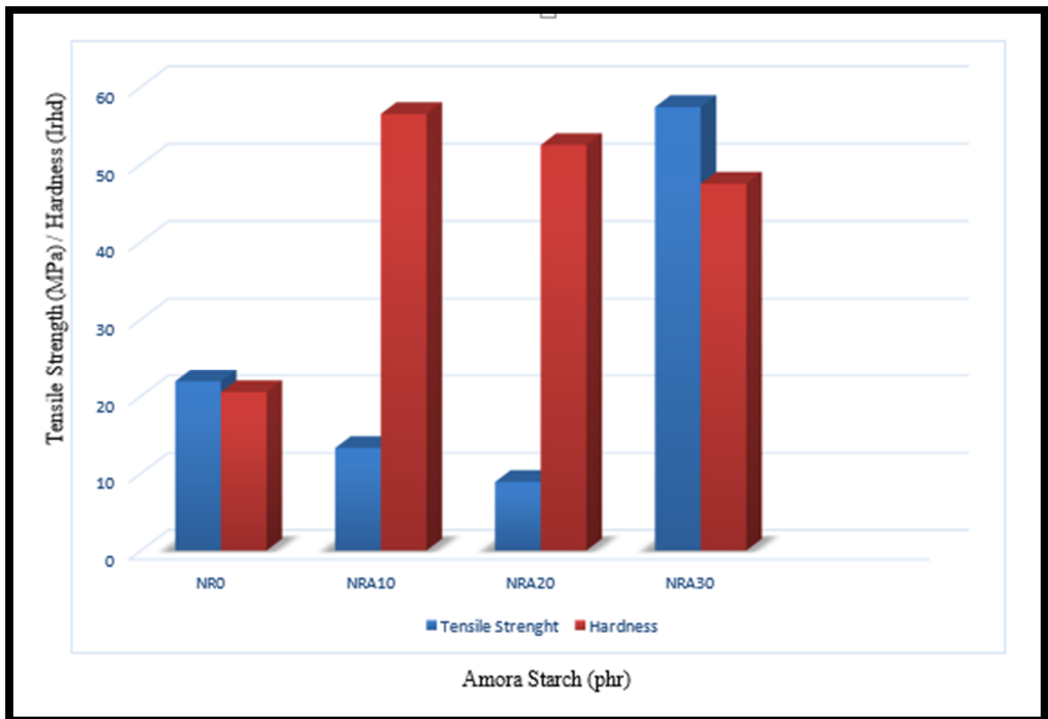
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Appendices

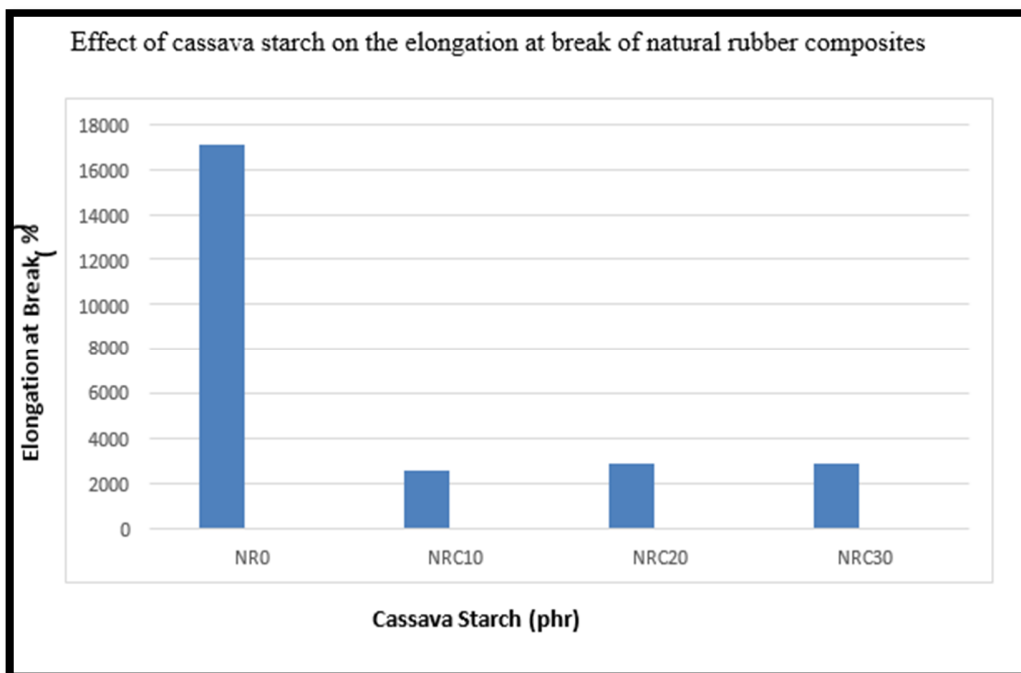
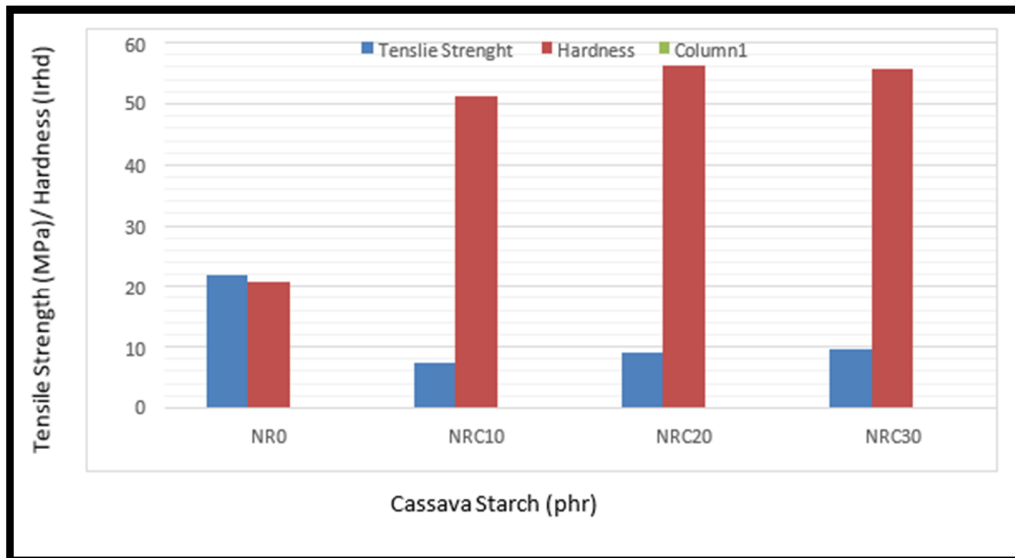
Appendix I: Histogram of Amylose Content and Tensile Strength of Starch/ Rubber Composite



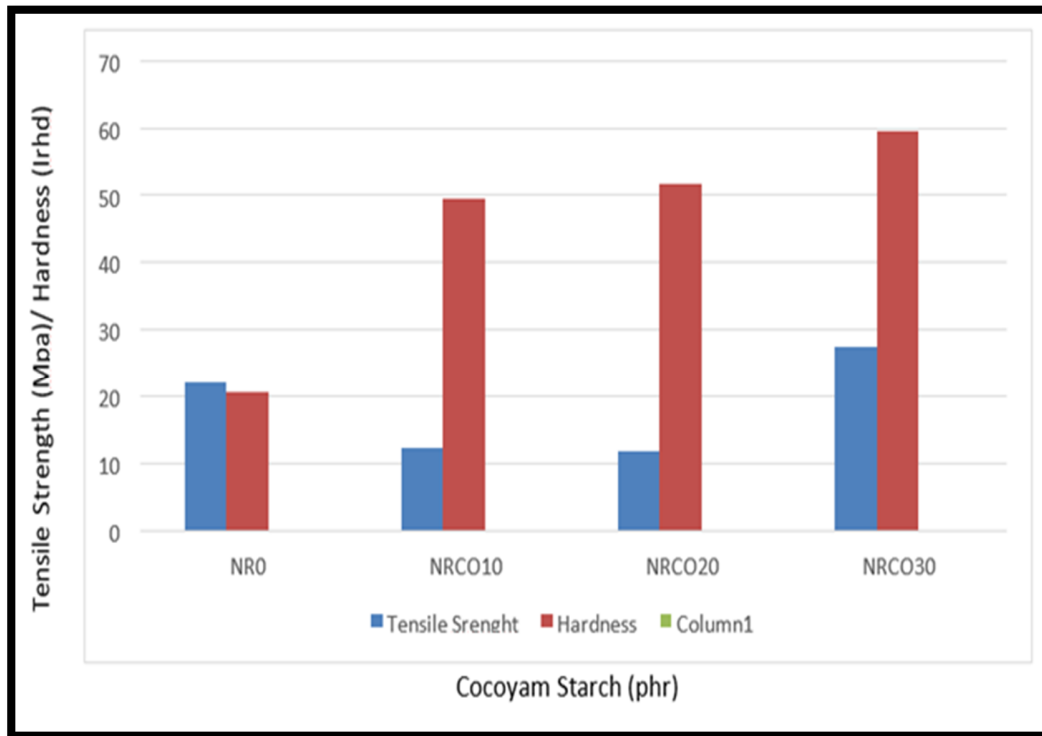
Appendix II: Effect of Amora Filler on the Tensile Strength/Hardness of Starch/Rubber

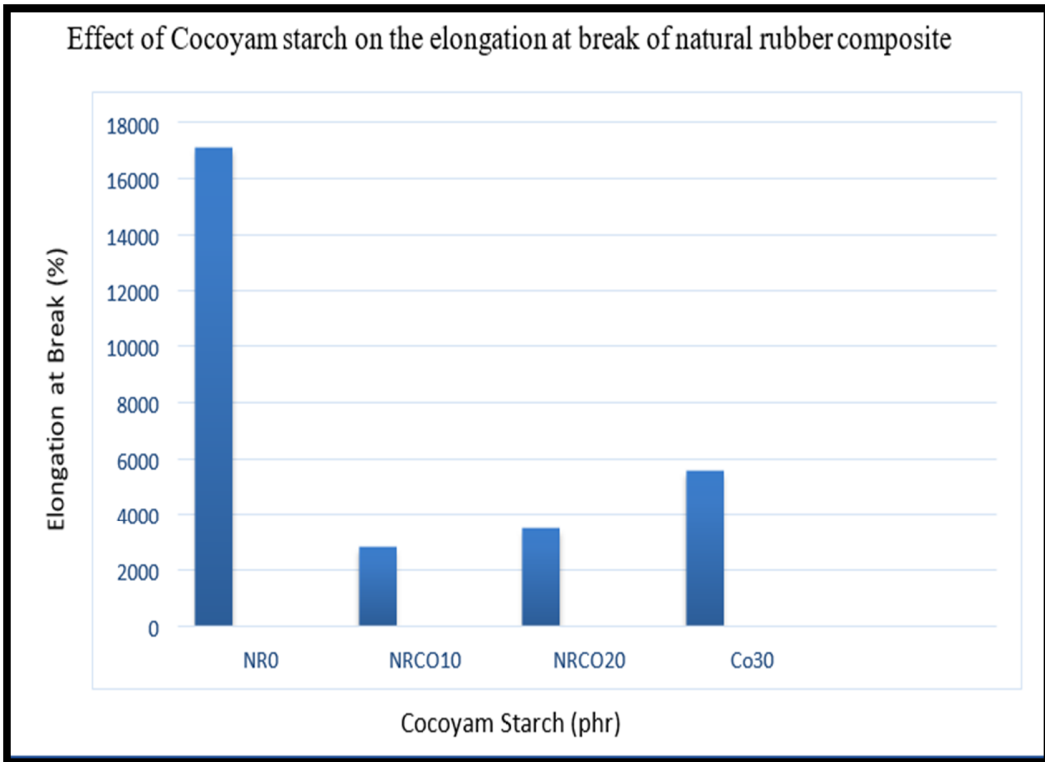


Appendix III: Effect of Cassava Starch Filler on Tensile Strength/ Hardness of Natural Rubber Composite

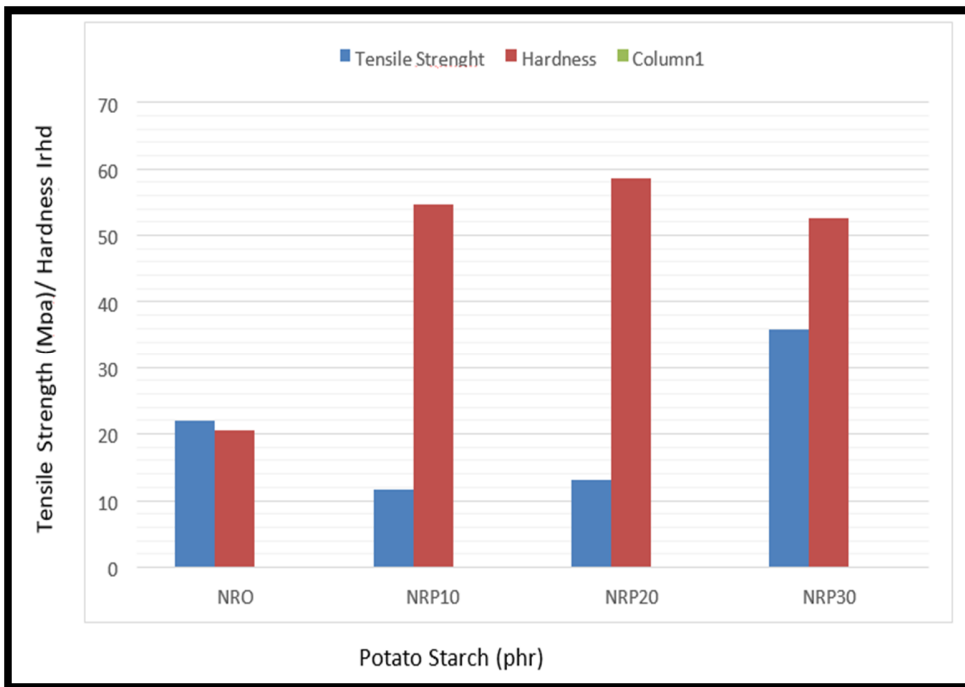


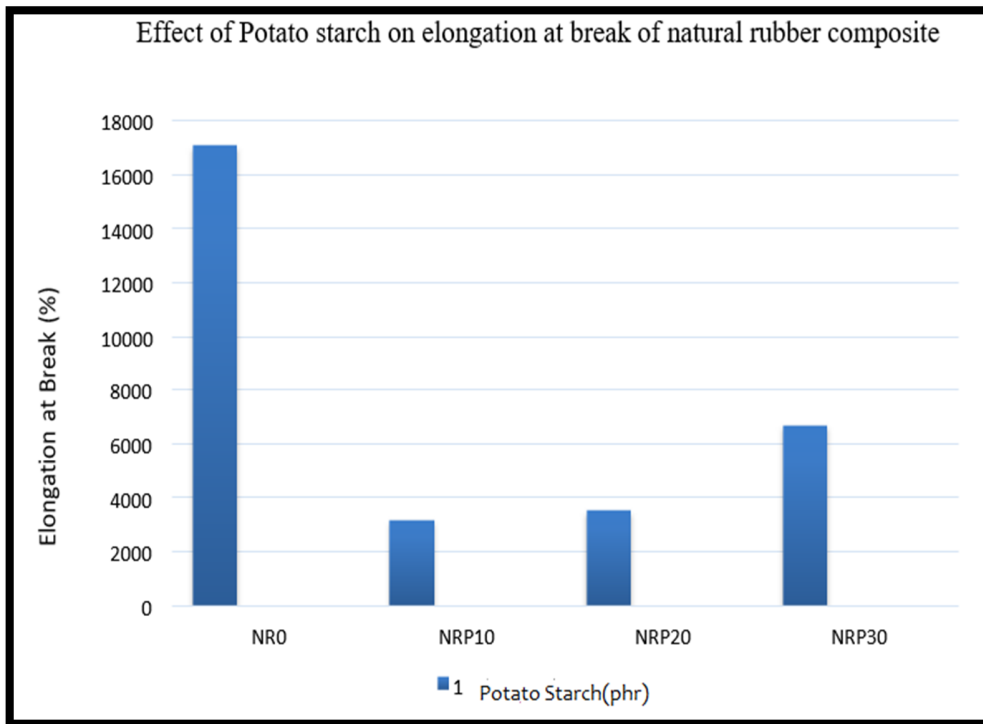
Appendix IV: Effect of Cocoyam Starch on the Tensile Strength/ Hardness of Natural Rubber Composites



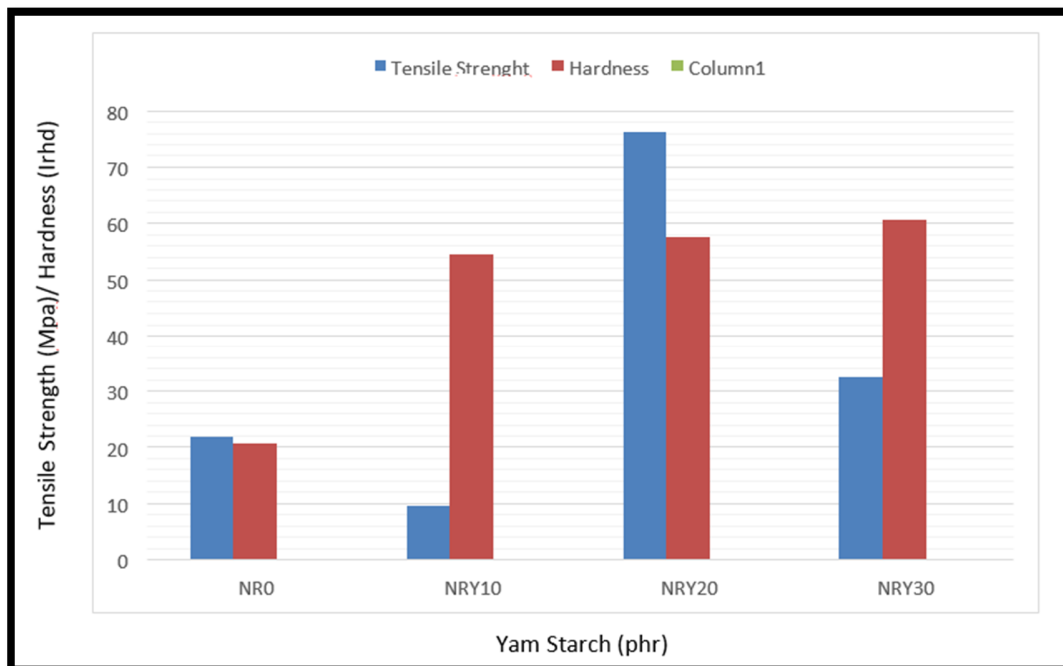


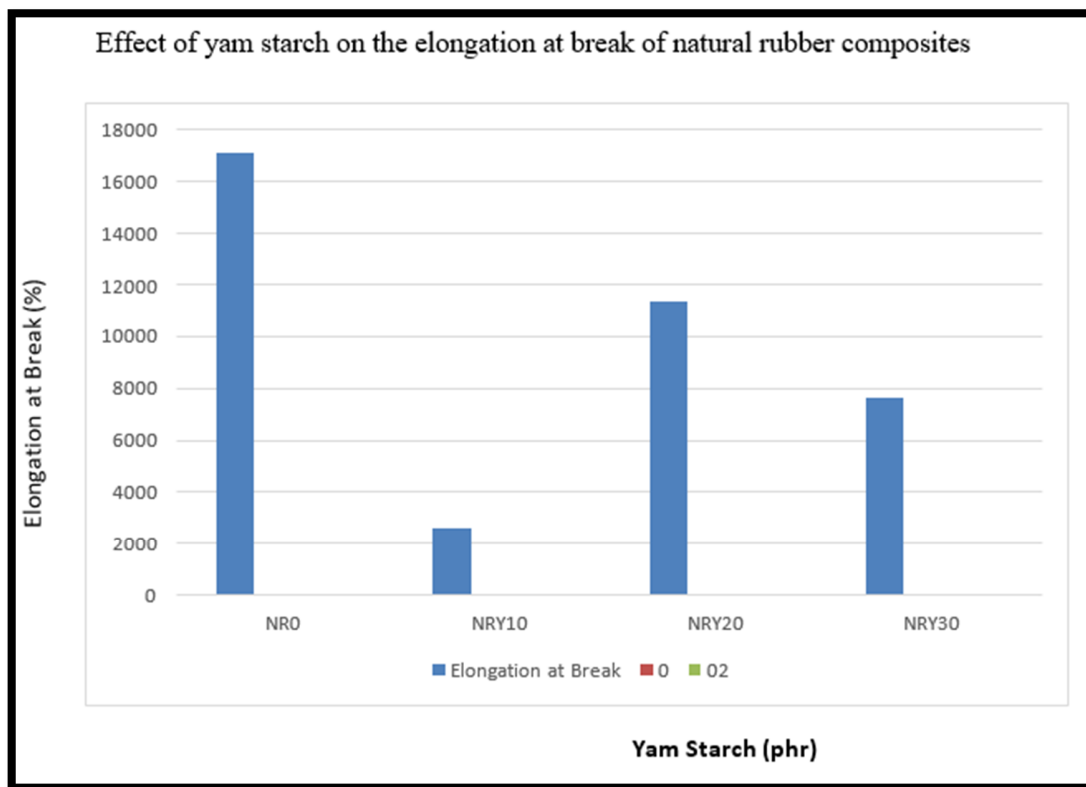
Appendix V: Effect of Potato Starch on Tensile Strength/Hardness of Natural Rubber Composites



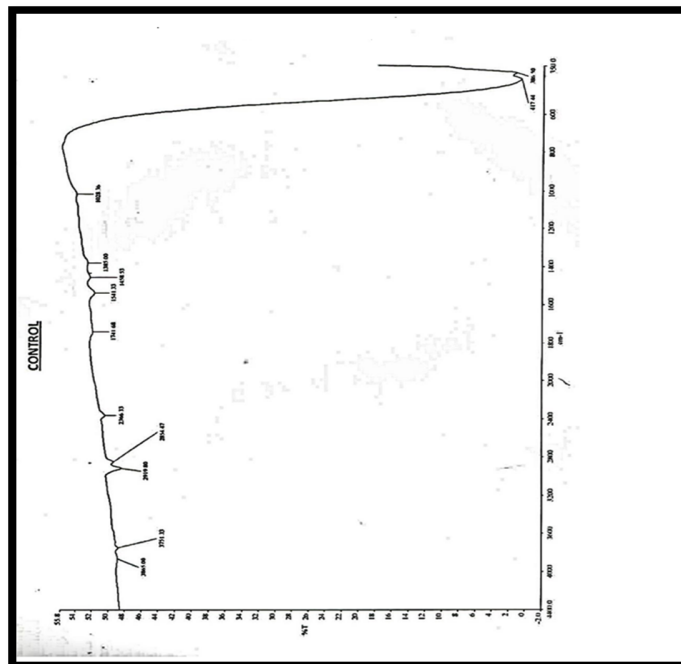


Appendix VI: Effect of Yam Starch on the Tensile Strength/ Hardness of Natural Rubber Composites

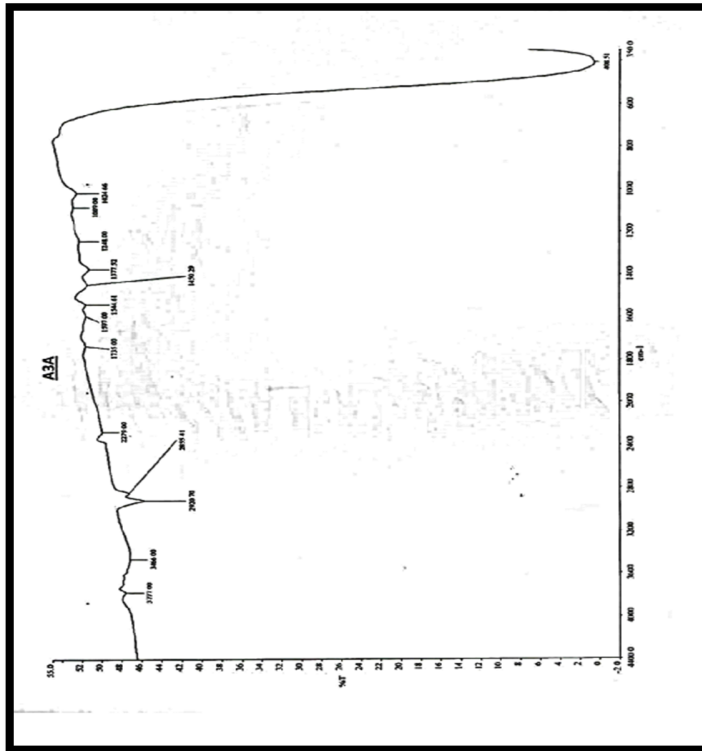




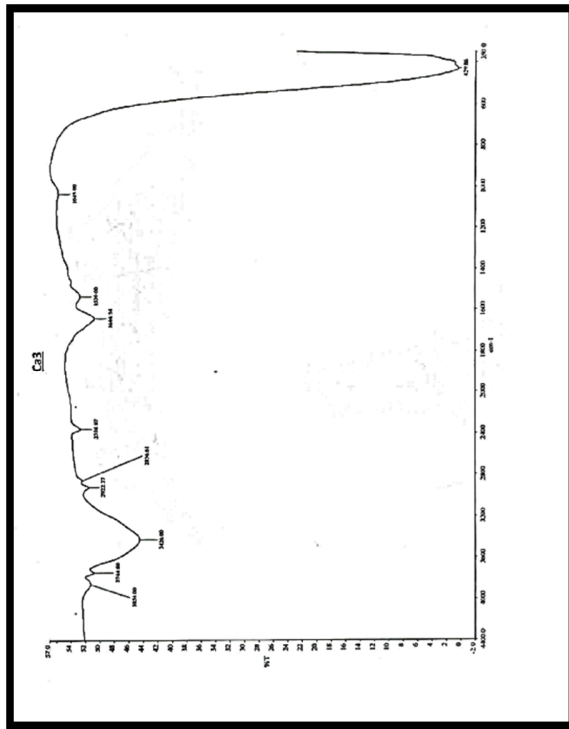
Appendix VII: FTIR Spectra of Control Sample NRCBA₃₀



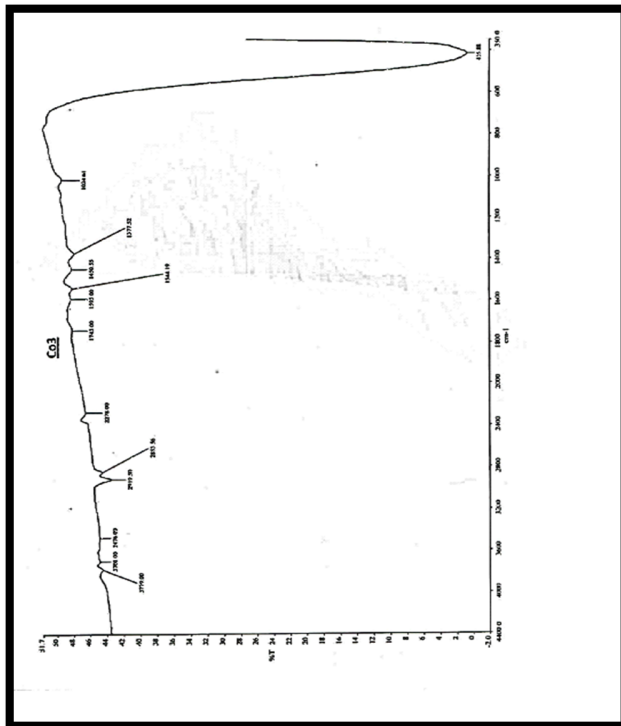
Appendix VIII: FTIR Spectra of Sample NRA₃₀



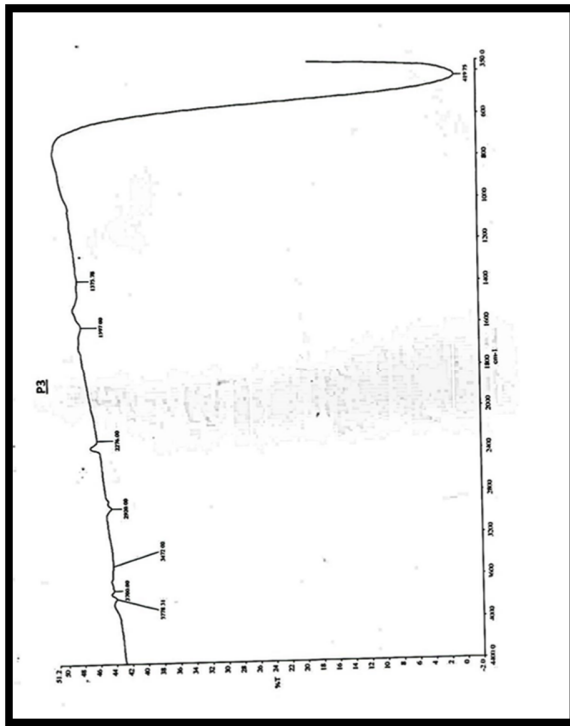
Appendix IX: FTIR Spectra of Sample NRC₃₀



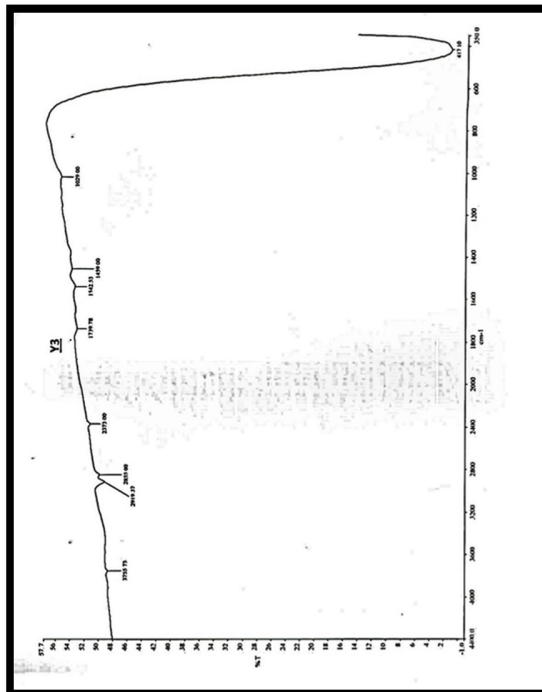
Appendix X: FTIR Spectra of Sample NRCO₃₀



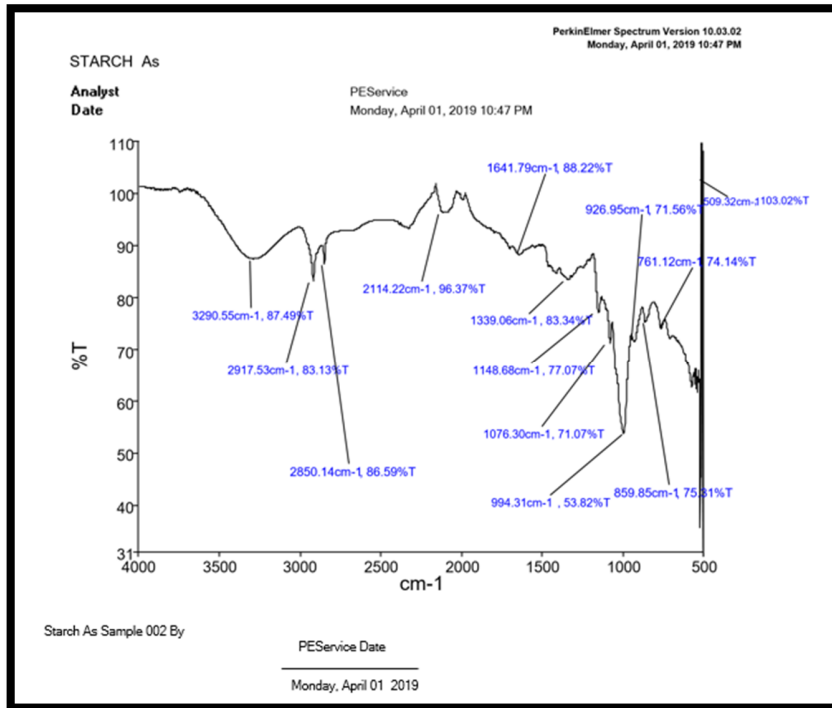
Appendix XI: FTIR Spectra of Sample NRP₃₀



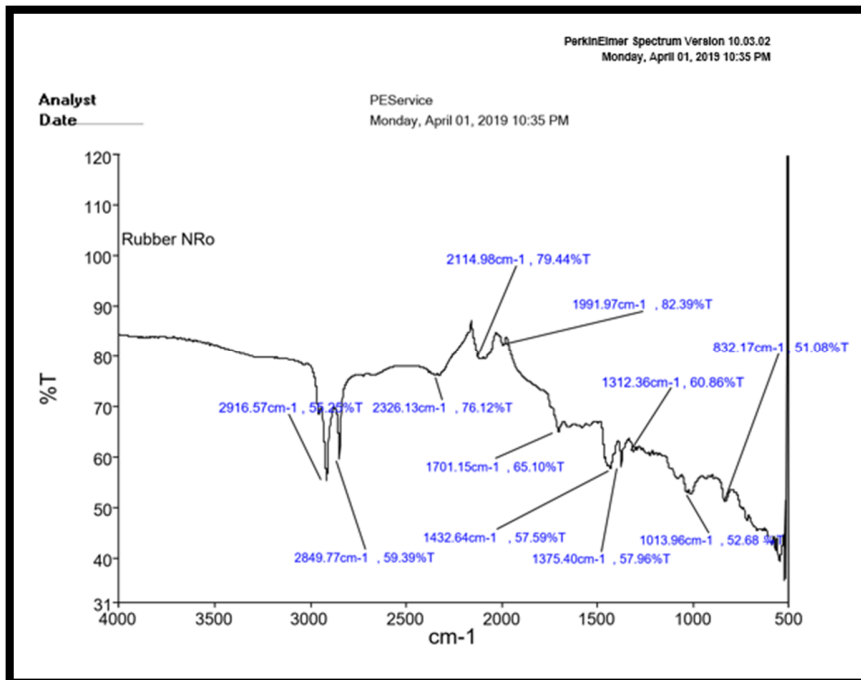
Appendix XII: FTIR Spectra of Sample NRY₃₀



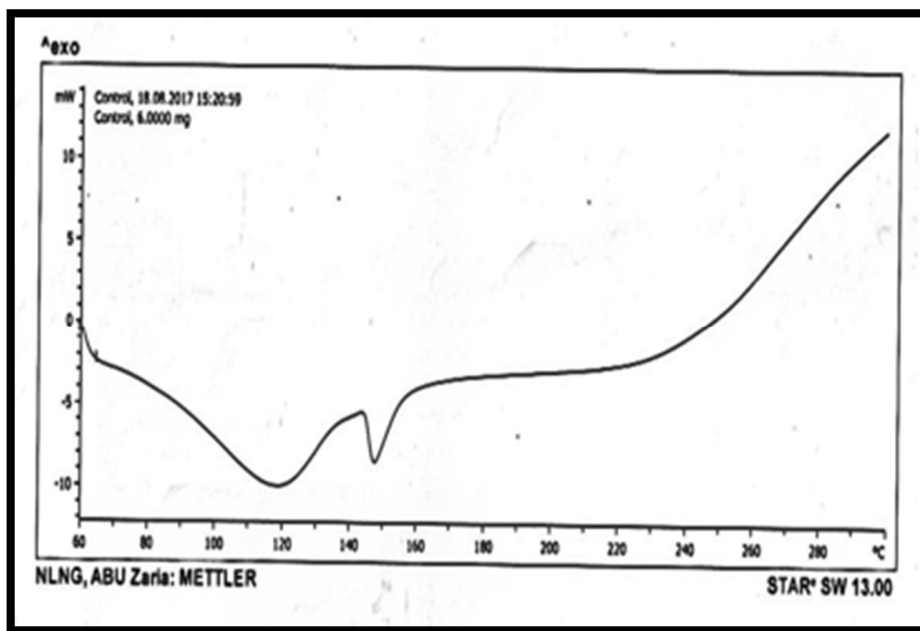
Appendix XIII: FTIR Spectra of Pure Starch



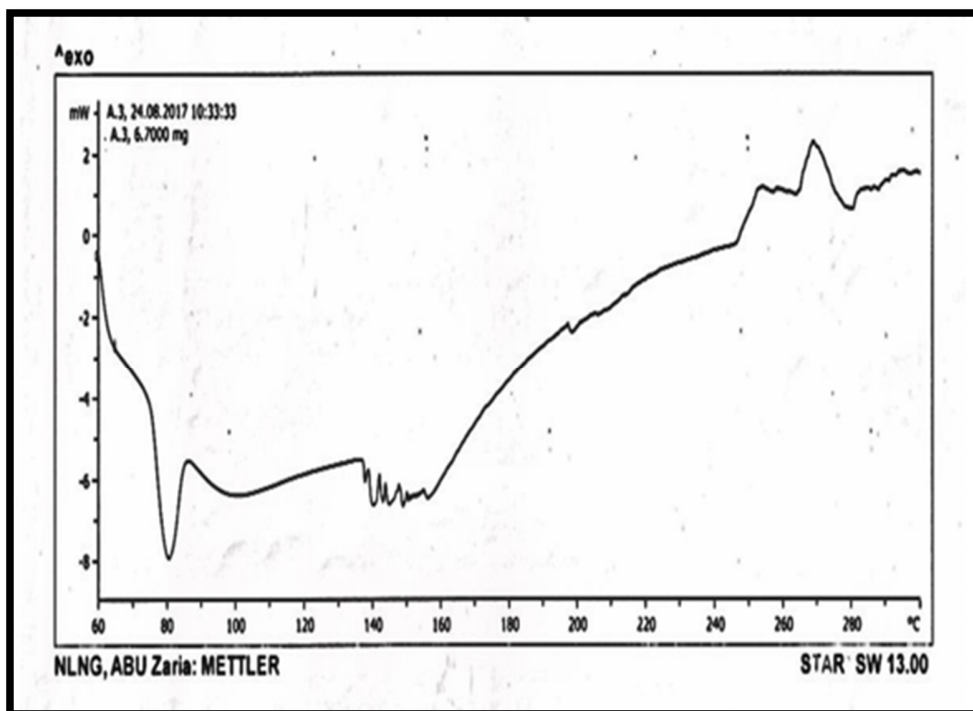
Appendix XIV: FTIR Spectra of Pure Rubber



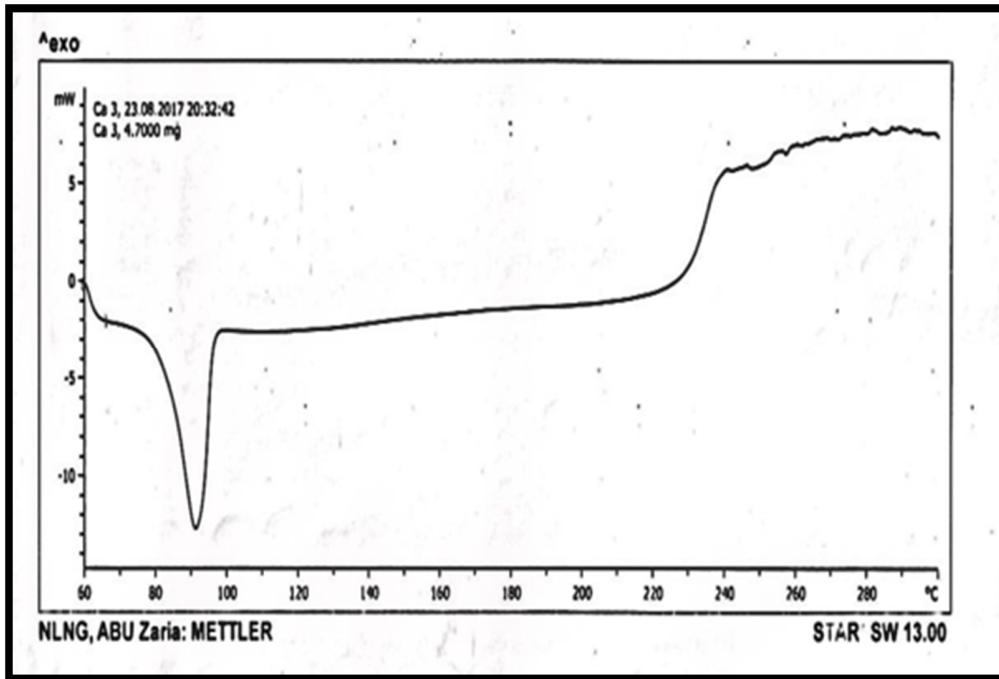
Appendix XV: DSC Temperature Plot of Sample NRCB₃₀ (Control Sample)



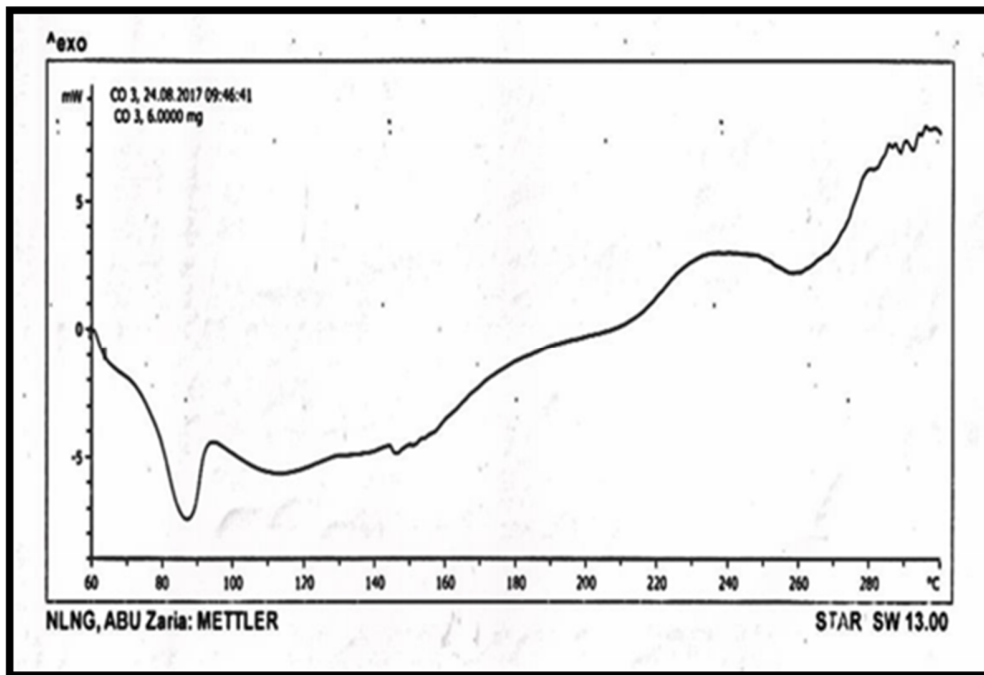
Appendix XVI: DSC Temperature Plot of Sample NRA₃₀



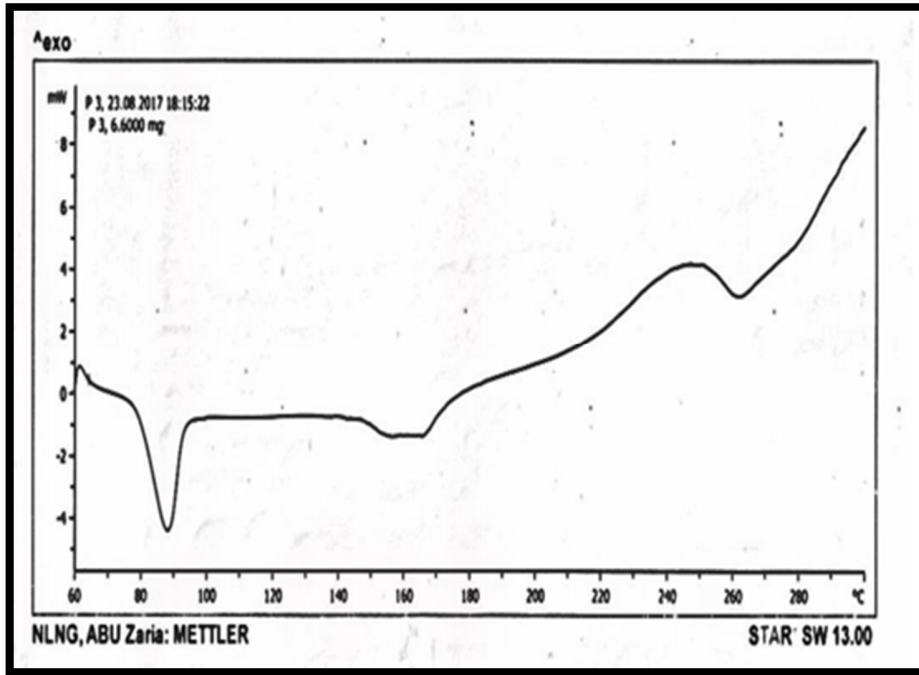
Appendix XVII: DSC Temperature Plot of Sample NRC₃₀



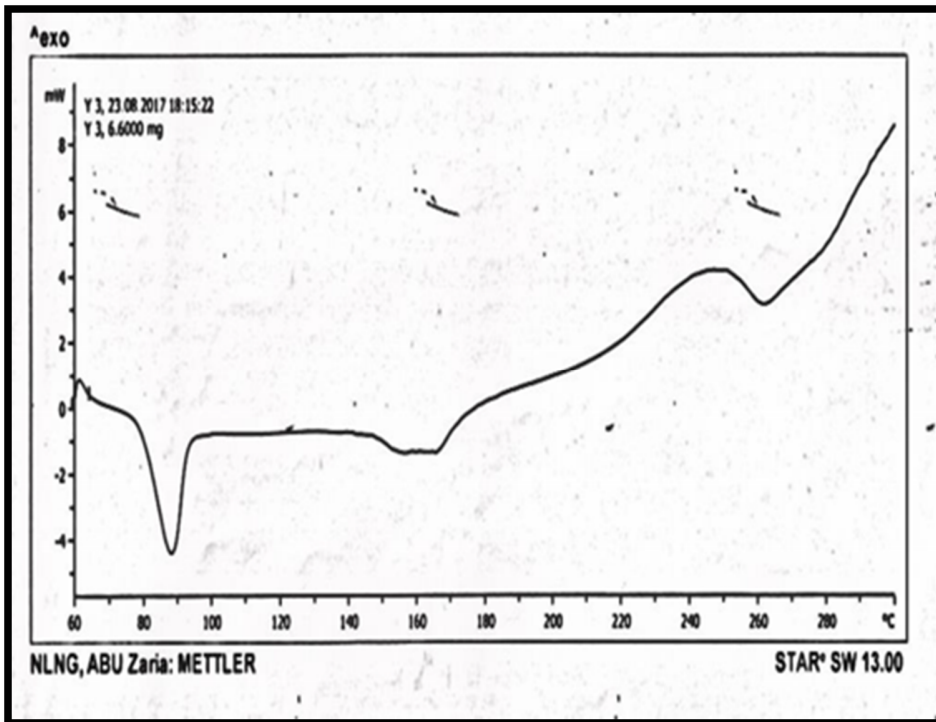
Appendix XVIII: DSC Temperature Plot of Sample NRCO₃₀



Appendix XIX: DSC Temperature Plot of Sample NRP₃₀



Appendix XX: DSC Temperature Plot of Sample NRY₃₀



Appendix XXI: Physical and Mechanical Properties of Amora Starch-Filled Natural Rubber at 0 – 90 Part Per Hundred Rubber (Phr)

Sample 0-90 (phr)	NRo	NRA5	NRA10	NRA20	NRA30	NRA40	NRA50	NRA60	NRA70	NRA80*	NRA90	NRCB30
Tensile Strength (Mpa)	21.9	20.3	13.3	8.9	57.4	12.3	16.7	37.2	46.2	58.2	20.6	87.6
Elongation at Break (%)	17069	13866	4850	2883	10007	2600	2666	5711	13567	14895	3112	6807
Hardness (IRHD)	20-21	52-53	56-57	52-53	47-48	44-45	51-51	54-55	59-60	44-45	59-60	66-68
Average hardness	20.5	52.5	56.5	52.5	47.5	44.5	51.5	54.5	59.5	44.5	59.5	67
Key: NRA	=	Amora starch-filled natural rubber composite										
0 – 90	=	Filler loading in part per hundred rubber										
NR ₀	=	Cured natural rubber without any filler										
NRCB ₃₀	=	Natural rubber filled with Carbon black at 30 phr										
(*)	=	Optimum filler loading at 80 phr										
IRHD	=	International rubber hardness degree										
MPa	=	Megapascals										

Appendix XXII: Physical and Mechanical Properties of Yam Starch-Filled Natural Rubber at 0 – 90 Part Per Hundred Rubber (Phr)

Sample 0-90 (phr)	NRo	NR5	NR10	NR20*	NR30	NR40	NR50	NR60	NR70	NR80	NR90	NRCB30
Tensile												
Strength (Mpa)	21.9	10.9	9.5	76.1	32.3	13.7	11.8	39.2	5.2	56.7	49.8	87.6
Elongation at Break (%)	17069	1792	2544	11273	7588	1804	1537	9839	5281	16544	14861	6807
Hardness (IRHD)	20-21	40-41	54-55	57-58	60-61	56-57	62-63	51-52	52-53	41-42	50-51	66-68
Average hardness	20.5	40.5	54.5	57.5	60.5	56.5	62.5	51.5	52.5	41.5	50.5	67
Key: NRY	=	Yam starch-filled natural rubber composite										
0 – 90	=	Filler loading in part per hundred rubber										
NR ₀	=	Cured natural rubber without any filler										
NRCB ₃₀	=	Natural rubber filled with Carbon black at 30 phr										
(*)	=	Optimum filler loading at 20 phr										
IRHD	=	International rubber hardness degree										
MPa	=	Megapascals										

**Appendix XXIII: Swelling Test Parameters in Toluene For
Natural Rubber Composite at 30 (Phr) Filler Loading**

S/N	Natural Rubber Composites	Initial Weight	Initial Swelling Weight	Weight of Solvent Sorbed at Equipment	Mol. % uptake of the	Swelling Index	Swelling Coefficient (α)	Degree of Crosslink Density	Molecular Weight btw two Crosslink
	(30 phr)	(g) (W1)	(g) (W2)	(W1 - W2)	solvent Qt	%		(Vc/mol cm ⁻³)	(Mc)
1	NRA ₃₀	1.658	5.3143	3.6563	2.4	221	2.55	44.0 x 10 ⁻⁵	113.62
2	NRC ₃₀	1.7963	6.8531	5.0568	3.06	282	3.25	36.1 x 10 ⁻⁵	118.67
3	NRCO ₃₀	1.7653	5.2504	3.4851	2.15	197	2.28	39.9 x 10 ⁻⁵	125.02
4	NRP ₃₀	1.8257	6.5722	4.7465	2.83	260	3	37.5 x 10 ⁻⁵	133.34
5	NRY ₃₀	1.7085	5.806	4.0975	2.61	240	2.77	41.1 x 10 ⁻⁵	121.78
6	NRCB ₃₀	2.0284	4.8023	2.7739	1.49	137	1.58	51.9 x 10 ⁻⁵	96.36
Key: phr	=	Part per hundred rubber,							
NRA ₃₀	=	Amora starch filled,							
NRC ₃₀	=	Cassava starch filled,							
NRP ₃₀	=	Potato starch filled rubber,							
NRY ₃₀	=	Yam starch filled rubber,							
NRCB ₃₀	=	Control sample, (carbon black filled rubber).							
NRCO ₃₀	=	Cocoyam starch filled rubber.							

**Appendix XXIV: Swelling Test Parameters in Water for Natural Rubber
Composites at 30 (Phr) Filler Loading**

S/N	Natural Rubber Composites at 30 (phr) filler loading	Initial Weight	Final Weight	Weight of Solvent at Equipment Swelling	Mol. % uptake Qt	Swelling Index %	Swelling Coefficient (α)	
		(g) (W1)	(g) (W1)	(W2 - W1)				
1	NRA ₃₀	1.7746	1.8316	0.057	0.18	3.2	0.032	
2	NRC ₃₀	1.7817	1.8763	0.0946	0.29	5.3	0.053	
3	NRCO ₃₀	1.6844	1.7315	0.0471	0.16	2.8	0.028	
4	NRP ₃₀	1.8662	1.9012	0.035	0.1	1.9	0.019	
5	NRY ₃₀	1.781	1.8533	0.0723	0.23	4.1	0.041	
6	NRCB ₃₀	2.1265	2.1512	0.0247	0.06	1.2	0.012	
Key: phr	=	Part per hundred rubber,						
NRA ₃₀	=	Amora starch filled,						
NRC ₃₀	=	Cassava starch filled,						
NRP ₃₀	=	Potato starch filled rubber,						
NRY ₃₀	=	Yam starch filled rubber,						
NRCB ₃₀	=	Control sample, (carbon black filled rubber).						
NRCO ₃₀	=	Cocoyam starch filled rubber.						

Appendix XXV: Effect of Amora Starch Filler on Swelling Parameters in Toluene

S/N	Amora/ Rubber Composites (phr)	Mol % uptake of solvent Qt	Swelling Index %	Swelling Coefficient (α)	Molecular Weight btw two Crosslink	Degree of Crosslink Density	V_c ($\times 10^{-5}$ Mol cm^{-3})
1	NRA ₁₀	3.44	316.7	3.66	149.41	0.00335	33.5 $\times 10^{-5}$
2	NRA ₂₀	3.32	305.3	3.52	151.1	0.00331	33.1 $\times 10^{-5}$
3	NRA ₃₀	2.4	221	2.55	113.62	0.0044	44.0 $\times 10^{-5}$
Key: NRA ₁₀	=	Natural rubber/ amora starch at 10					
NRA ₂₀	=	Natural rubber/ amora starch at 20					
NRA ₃₀	=	Natural rubber/ amora starch at 30					
phr	=	Part per hundred					

Appendix XXVI: Effect of Sweet Potato Starch on Swelling Properties of Natural Rubber Blends In Toluene

S/N	Filler quantity (phr)	Mol % uptake (Qt)	Swelling index (%)	Swelling Coefficient (α)	Degree of Crosslink density (V_c)	Molecular weight btw two crosslinks
1	NRP ₁₀	2.86	263	3.04	36.3 $\times 10^{-5}$	137.69
2	NRP ₂₀	3.06	282	3.25	35.5 $\times 10^{-5}$	140.82
3	NRP ₃₀	2.83	260	3	37.5 $\times 10^{-5}$	133.34
4	NRCB ₃₀	1.49	137	1.58	51.9 $\times 10^{-5}$	96.36
Key: NRP ₁₀	=	Natural rubber/ potato starch at 10 phr				
NRP ₂₀	=	Natural rubber/ potato starch at 20 phr				
NRP ₃₀	=	Natural rubber/ potato starch at 30 phr				
phr	=	Part per hundred rubber,				

Appendix XXVII Effect of Yam Starch on Swelling Properties of Natural Rubber Blends in Toluene

S/N	Filler quantity (phr)	Mol % uptake (Qt)	Swelling index (%)	Swelling Coefficient (α)	Degree of Crosslink density (V_c)	Molecular weight btw two crosslinks
1	NRY10	3.02	278	3.2	36.3 $\times 10^{-5}$	137.69
2	NRY20	2.76	254	2.93	37.9 $\times 10^{-5}$	131.71
3	NRY30	2.61	240	2.77	41.1 $\times 10^{-5}$	121.78
4	NRCB30	1.49	137	1.58	51.9 $\times 10^{-5}$	96.36
Key: NRY10	=	Natural rubber/ yam starch at 10 phr				
NRY20	=	Natural rubber/ yam starch at 20 phr				
NRY30	=	Natural rubber/ yam starch at 30 phr				
phr	=	Part per hundred rubber,				

Appendix XXVIII Effect of Cocoyam Starch on Swelling Properties of Natural Rubber Blends In Toluene

S/N	Cocoyam Rubber Composite sO(phr)	Mol % uptake of solvent Qt	Swelling Index %	Swelling Coefficient (α)	Molecular Weight btw two Crosslink (M_c)	Degree of Crosslink Density (V_c)	Vc ($\times 10^{-5}$ Mol cm^{-3})
1.	NRCO ₁₀	3.07	282.06	3.26	162.37	0.00308	30.8
2.	NRCO ₂₀	2.99	275.0	3.18	146.15	0.00342	34.2
3.	NRCO ₃₀	2.15	197.0	2.28	125.02	0.00399	39.9
Key: NRCO ₁₀ = Natural rubber/ cocoyam starch at 10 phr NRCO ₂₀ = Natural rubber/ cocoyam starch at 20 phr NRCO ₃₀ = Natural rubber/ cocoyam starch at 30 phr phr = Part per hundred rubber,							

Appendix XXIX: Effect of Cassava Starch on Swelling Properties of Natural Rubber Blends in Toluene

S/N	Filler quantity (phr)	Mol % uptake of solvent Qt	Swelling Index %	Swelling Coefficient (α)	Degree of Crosslink Density (V_c)	Molecular Weight btw two Crosslink (M_c)
1.	NRC ₁₀	3.26	300	3.46	34.6×10^{-5}	144.49
2.	NRC ₂₀	2.92	269	3.10	36.9×10^{-5}	135.32
3.	NRC ₃₀	3.06	282	2.25	36.1×10^{-5}	138.67
4.	NRCB ₃₀	1.49	137	1.58	51.9×10^{-5}	96.36
Key: NRC ₁₀ =Natural rubber/ cassava starch at 10 phr NRC ₂₀ =Natural rubber/ cassava starch at 20 phr NRC ₃₀ =Natural rubber/ cassava starch at 30 phr phr=Part per hundred rubber,						

The book titled "Biofillers in Natural Rubber and a Biotechnology Approach to Rubber Degradation" presents well-documented research on the utilization of starch bio-fillers derived from various plant sources and their characterization. The study explores the introduction of starch fillers into natural rubber through the process of latex compounding, following modification through gelatinization. Standard compounding techniques were employed to incorporate the starch-filled natural rubber composite, which was subsequently characterized using universal testing instruments (UTM) and other relevant properties.

To address the degradation of natural rubber composites, biotechnology methods utilizing micro-organisms were employed, resulting in positive outcomes. This book is highly recommended for undergraduate and postgraduate students in fields such as Polymer Science, Materials Science, Industrial Chemistry, Material Engineering, and Biotechnology. It is also beneficial for chemical engineering students at both undergraduate and postgraduate levels.

The research findings of this study highlight the practical applications of starch-filled natural rubber, including its potential use in tire thread production, rubber composite products, and insulation products for automobiles and industrial machinery. Furthermore, the incorporation of biotechnology and bio-fillers in rubber presents a viable solution to the problem of rubber waste disposal.



Dr. Raymond D. Uzoh is an accomplished individual in the field of industrial chemistry, having graduated with honors and an upper second-class division degree from Delta State University, Abraka, Nigeria. He furthered his education by obtaining a Master's Degree in the same discipline from the esteemed Abubakar Tafawa Balewa University, Bauchi, Nigeria.

Dr. Uzoh currently serves as a Principal Lecturer and Head of Department of Materials Science Technology at the Federal Polytechnic, Mubi, Adamawa state, Nigeria. He has also held the position of Editor for Journal of Applied Science and Management (JASM) at the Federal Polytechnic, Mubi, Adamawa State, Nigeria. In addition to his academic pursuits, he is a versatile freelance writer who has contributed articles to national newspapers and magazines.

With a deep involvement in scientific research, Dr. Uzoh has conducted extensive studies in various aspects of industrial chemistry, particularly in the field of material science, focusing on natural rubbers, their composites, and the application of biotechnology in the degradation of natural rubber. These research endeavors have resulted in valuable applications within the automobile industry and the wider polymer industry. His research interests also extend to pharmaceutical products and the design and formulation of new products. Dr. Uzoh's findings have been published in reputable national and international journals, solidifying his reputation as a prolific researcher.

Beyond his academic and research achievements, Dr. Uzoh is recognized as an esteemed conference speaker, a life coach, and an entrepreneur.



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