PRODUCTION AND CHARACTERISATION OF PLASTIC SHEETS FROM POLYETHYLENE WASTE BLENDED WITH HYDROLYSED CASSAVA STARCH

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ABSTRACT

This study focused on the production and characterisation of plastic sheets from polyethylene waste blended with hydrolysed cassava starch. Polyethylene waste was melt blended with hydrolysed starch in a twin screw extruder to form blends of various ratios in percentage weight: 100:0, 90:10, 80:20, 70:30, 60:40, and 50:50. The morphology and microstructures of the cassava starch and hydrolysed cassava starch obtained from the high-resolution scanning electron microscopy (HRSEM) study revealed that the particles in the cassava starch are spherical, smooth and clustered. While the features in the hydrolysed cassava starch are etched, rough and clogged, indicating the etching of the amorphous regions of the starch granule by dilute H_2SO_4. The elemental composition of the cassava starch and hydrolysed cassava starch using energy dispersion X-Ray spectroscopy (EDX) revealed the presence of C (60 %) and O (39.46 %) for cassava starch and C (55.23 %) and O (44.77 %) for hydrolysed cassava starch respectively. The thermal properties of the polyethylene waste and hydrolysed cassava starch blends using thermogravimetric analysis showed that as hydrolysed starch increased from 0 % to 50 %, the thermal stability of polyethylene decreased from 442.54 °C to 345.71 °C. Water absorption capacity of the polyethylene waste/hydrolysed cassava starch blend increased from 0.642 to 1.285 % as the amount of the hydrolysed starch in the blend increased. Hardness and impact strength results showed that increase in amount of hydrolysed cassava starch content in the blends led to a decrease from 1.981 to 0.376 J/m^2 and 98.667 to 96.333 Nmm^2 respectively. The plastic sheets produced from polyethylene waste and hydrolysed cassava starch blends were studied under compositing conditions for 22 weeks. The 100 % polyethylene waste did not lose weight while the highest percentage weight loss observed was 5.92 % for the 50 % hydrolysed cassava starch blend. The morphology and microstructures of polyethylene waste and polyethylene waste/hydrolysed cassava starch blend obtained from HRSEM study showed that the hydrolysed starch decomposed out of the polyethylene matrix leaving pores in the matrix, however the matrix did not decompose. The addition of hydrolysed starch to plastic may reduce the amount of plastics in circulation.

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CHAPTER ONE

1.0   INTRODUCTION

1.1   Background to the Study

Plastics are mainly hydrocarbons, they are synthetic in nature. They are easy to produce, cheap, and versatile in application. They also have high mechanical and thermal properties. However, they are non-biodegradable and so cause environmental pollution such as sewage blockage, clogging of water bodies, and release of fumes like CO_2 when burnt and are hazardous to life. The high demands in plastic usage in packaging industry is increasing and the production of synthetic plastics in line with the extensive growth of human populations has risen remarkably (Zhao *et al.,* 2020). Over 60 % have been improperly disposed and channelled to rivers and oceans via wind and rainfall, thus leaving an enormous amount of unrecyclable and untreated plastic wastes to pollute the environment (Kehinde *et al.,* 2020). These packaging materials such as polyethylene, polypropylene and polypropylene terephthalate are derived from non-renewable petroleum-based fuels which are either thermoplastic or thermosetting polymers of high molecular mass (Siracusa & Blanco, 2020).

The improper disposal of plastic wastes have a negative impact on public health like littering and choking of sewage system as a result of the extremely long periods required for natural decomposition. Plastic waste happens to be the most noticeable component in waste dumps and open landfills in most African countries like Nigeria (Kehinde *et al.,* 2020). Development of biobased materials which will be low-cost, and readily biodegradable will be of interest. Among these biodegradable materials is starch which is natural and cellulosic in nature, locally and widely available, biodegradable and environmentally friendly. However, it has low mechanical and thermal properties. Hydrolysed starch can be synthesized from starch by methods like chemical, enzymatic,

and physical treatments. These particles are safe for human health and are increasingly utilized in food and non-food industries which have attracted interest as a packaging material due to its better barrier properties. Hydrolysed starch are hydrophilic and characterized by presenting an OH-rich surface (Sandhu and Nain, 2017). This makes the hydrolysed starch more compatible with the plastics when used to create blends than ordinary starch. For example, the optimal blending ratio of plasticized starch and polybutylene adipate terephthalate (PBAT) on effect of cassava starch after plasticizing with glycerin and organic acids was investigated by Yi *et al.* (2020). They reported that the difference in surface polarity between starch and PBAT depends on their properties and compatibility. Furthermore, their work was supported by adding a compatibilizer to improve the compatibility of starch with PBAT in order to increase starch lipophilic property and improve material properties.

The biodegradation process for biobased polymers is composting that involved anaerobic process where microorganisms such as bacteria, archaea, and fungi use the organic material available for metabolic processes and growth (Bátori *et al.,* 2018). During this process, CO_2, water and biomass are main products which can be influenced by chemical structure and the environmental conditions. Microorganisms responsible for biodegradation possess optimal growth conditions that differ from each other. Non-enzymatic hydrolysis and enzyme-catalyzed hydrolysis results from the breakdown of high molecular weight chains by microorganisms, producing shorter chains which are small enough to pass semi-permeable outer bacterial membranes and be utilized as carbon and energy sources. Furthermore, microbial organisms present in soil or compost differ across geographical regions, influenced by environmental factors and inherent conditions of the media. According to literature, biodegradation of contaminated

plastics under composting conditions reduced plastic pollution and disposal of plastics in landfills (Siracusa, 2019).

However, to the best of the authors' knowledge, this is the first work reporting the production of plastic sheets from plastic waste blended with hydrolysed cassava starch. In this study, blends of polyethylene waste with hydrolysed starch were characterized for their morphology, thermal properties, mechanical properties, water absorption capacity and response to microbial attack.

1.2   Statement of the Research Problem

Effects of Plastic wastes, especially the polyethylene commonly used as sachet water and packaging materials, to the environment include blockage of sewages, clogging of water bodies resulting in the death of aquatic life and release of hazardous fumes and gases like CO_2 when burnt. They are not biodegradable and exhibit high processing temperature.

Problem of biodegradable starch sheet is that it is difficult to produce industrially because their thermal decomposition temperatures are lower than their melting temperatures (Tm) and glass transition temperature (Tg). Common biodegradable plastic sheets produced from biopolymers like starch have weaker mechanical and poor water barrier properties compared to synthetic plastics.

1.3   Justification for the Study

Blending polyethylene waste and hydrolysed cassava starch will result in a product with better thermal stability and improved mechanical properties than that of ordinary starch sheets. Due to the generally lower processing temperature characteristics of polyethylene and hydrolysed starch an idea of the degradation temperatures of the

polyethylene waste with hydrolysed cassava starch blends will help to determine the processing conditions of the blends. Biodegradability is a desirable property for any environmentally friendly product. Good response to microbial attack of the polyethylene waste/hydrolysed cassava starch blends will make them suitable for wider applications such as in packages and domestic uses. This will lead to a significant reduction in the amount of polyethylene wastes in circulation. Also, production of the polyethylene waste/hydrolysed cassava starch blends will ensure effective use of the cassava starch in commercial production of useful end-use plastic materials. For this reasons, blending of biodegradable materials derived from natural polymers with the plastics could help to tackle the aforementioned shortcomings.

1.4   Aim and Objectives of the Study

Aim:

The aim of this work is to produce and characterize plastic sheets from the blends of polyethylene wastes with hydrolysed cassava starch.

Objectives:

i.   Extraction of cassava starch from cassava tubers by wet method and preparation of hydrolysed cassava starch (HCS) using dilute H_2SO_4.

ii.   Characterisation of cassava starch and hydrolysed cassava starch respectively using High-Resolution Scanning Electron Microscope (HRSEM) and Energy Dispersive X-Ray Spectroscopy (EDX).

iii.   Production of polyethylene wastes and hydrolysed cassava starch blends

iv.   Characterisation of the polyethylene wastes/hydrolysed cassava starch blends using;

- thermo gravimetric analysis (TGA)

- water absorption capacity

- mechanical properties such as impact strength and hardness

- microbial degradation effect (Soil burial method)

- morphological examination of polyethylene waste, buried and unburied polyethylene waste/hydrolysed cassava starch blend samples using HRSEM.

1.5   Scope of the Study

This research focused on the preparation and characterisation of polyethylene waste/hydrolysed cassava starch blends and the effect of varying amounts of the hydrolysed cassava starch on the properties of the blends.

CHAPTER TWO

2.0 **LITERATURE REVIEW**

2.1 Applications of plastic

Plastics have become the key drivers of innovations and application development. The applications of plastic has increased in many folds from 4000 tones per annum in 1990 to 5 million tones per annum in 2005 and is expected to rise further (Justice *et al.,* 2021). This increased applications have resulted in the increase of plastic waste. Futhermore, plastic wastes have been attracting attention due to extensive litter on land. Its wide range of application includes packaging industry, wrapping materials, shopping and garbage bags, fluid containers, household clothing, toys, and industrial products, and construction material (Alabi *et al.,* 2019). It is a fact that plastics will not at all degrade and remains on landscape for numerous years. Furthermore, the strength of recycling a virgin plastic material is reduced due to thermal degradation (Schyns and Shaver, 2021).

2.2 Synthetic Plastics and Bio-plastics

Over the last decades, there has been increase in the use of polymers as food packaging materials because of their advantages which include cheapness, ease of production and versatility (Nilsen-Nygaard *et al.,* 2021). However, it is widely accepted that the use of long-lasting polymers for short-lived applications (packaging, catering, surgery, hygiene) is not entirely adequate (Guillard *et al.,* 2018).

Growing environmental awareness to enable sustainable environment and prevention of plastic waste disposal in the environment has encouraged the development of biodegradable materials from renewable resources which has replaced conventional

non-biodegradable materials in many industrial applications (Ncube *et al.,* 2021). Polysaccharides such as starches have several advantages that make it possible to replace synthetic polymers in plastics industries because of their low cost, non-toxicity, biodegradability and availability (Mendesa *et al.,* 2016 and Sagnelli *et al.,* 2017). As opposed to most conventional plastics, biodegradable plastics are metabolized by environmental microorganisms, and therefore plant-based bio-plastics represent one of the most interesting clean alternative to conventional plastics (Sagnelli *et al.,* 2017).

Starch-based films are however brittle and hydrophilic. These limit their processing and application but to overcome these drawbacks, starch can be mixed with various synthetic and natural polymers. These approaches are multilayer structures with aliphatic polyesters, blends with natural rubber and composites with fibres. Another widely used approach to improve mechanical properties of starch films is the addition of chitosan (Mendesa *et al.,* 2016).

2.3   Plastic Wastes

The extensive use of petroleum-derived polymers is responsible for the increasing concern about the environmental Impact strength of plastics due to both their origin and end-of-cycle, since most of them are not biodegradable. Worldwide polymer production was estimated to be 260 million metric tons per year in 2007 and it is considered that in 2020 each person will consume around 40 kg of plastic annually (Lamberti *et al.,* 2020).

Plate I: (A) Waste pure water sachet in a waste dump, Tunga, Minna, (B) Waste pure water sachet in Elim water factory, Minna

Types of plastic waste found in most refuse dumps are polyethylene used in sachet water (Plate I) packaging, trash bags, grain storage bags and shopping bags; poly(vinyl chloride) used in bottles, packaging and containers; poly(ethylene terephthalate) used predominantly in beverage bottles and similar containers; poly(styrene) a light spongy material used in meat, eggs and miscellaneous product trays and hot beverage cups; and poly(propylene) used in yogurt containers, straws, margarine tubs and special bags (Ogundairo *et al.,* 2021). Most of these plastics are discarded after single use and become garbage. The manufacturing of plastics involve various chemical processes and utilizes variety of chemical compounds and additives including phenols, amines and

esters, antioxidants, UV and light stability improvers, antistatic agents and heat stabilizers that impart the finished product specific characteristics for its intended use (Hahladakis *et al.,* 2018). However, the additives, their chemical reaction and degradation products incorporated into the polymeric material have the potential to be released into the environment and cause significant health and environmental concerns (Schyns and Shaver, 2021).

The byproducts of plastic combustion are airborne particulate emission and solid ash residue. Several studies have demonstrated that soot and solid ash residue possess a high potential of pollution causing significant health and environmental concerns (Velis and Cook, 2020). The soot when generated is accompanied with volatile organic compounds (VOCs), semi-VOCs, smoke (particulate matter), particulate bound heavy metals, polycyclic aromatic hydrocarbons (PAHCS), polychlorinated dibenzofurans (PCDFs) and dioxinsii and has the ability to travel thousands of kilometers, depending on prevailing atmospheric conditions, before it can drop back on earth and enter into the food chain (Velis and Cook, 2020). The composition of byproducts of plastic combustion as to their type and concentration depends on the combustion temperature and the flame residence time. The toxicity of combustion products generated from burning of plastic waste has been evaluated by various researches (Nanda and Berruti, 2020). A high concentration of persistent free radicals have been found both in the soot and the solid residual ash which are considered to be very important in the creation of adverse health effects especially to human lungs (Verma *et al.,* 2016). The combustion of PE (both low (LDPE) and high density (HDPE) polyethylene) at different operating conditions detected more than 230 VOCs and semi-VOCs especially olefins, paraffin, aldehydes and light hydrocarbons (Verma *et al.,* 2016). Amongst VOCs, benzene is a known carcinogen and has been observed to be released in significant quantity during

plastic waste combustion. Some of the toxic semi-VOCs including benzo(a)pyrene and 1,3,5 trimethylbenzene have also been observed in significant quantities in the emissions from plastic combustion. Heavy metals including lead, cadmium, chromium and copper have been measured in the smoke and the solid residue ash. DEHP is one of the compounds among the plasticizers used in plastic manufacturing that has been described by USEPA as a probable human carcinogen, a potential endocrine disruptor and is believed to be harmful by inhalation, generating possible health risks and irreversible effects. This compound is also released during the combustion of plastic waste.

2.4 Environmental Effect of Plastic Polymers

Plastic is one of the most foundational materials in today's world. In plastic industry, the continuous expanding of the plastic products utilization, the disposal of post-consumer plastic products has become a difficult issue and this has become a global hazard. Tones of plastic are discarded yearly and persist for hundreds of years due to lack of stringent laws and strict regulation in regards to the dumping of polyethylene bags which are non-biodegradable plastics. Various awareness programs have been staged to educate the growing ignorant population to reduce the usage and proper disposal of plastics. This ignorance has led to the continuous inappropriate disposal of waste (Agamuthu and Law, 2020). Despite the fact that they are inexpensive as well as light, they are harmful in the following ways:

2.4.1 Effect on soil

A vast amount of land is continuously lost when polyethylene bags enter into the soil; they clog passage of mineral salts and oxygen to the soil. When blocked, the soil is incapable of yielding crops appropriately, this can cause huge problems to farmers and

consumers like poor harvest and food scarcity. The presence of polyethylene bags in the soil changes the chemical composition of the soil with time (Agamuthu and Law, 2020).

2.4.2 Effect on health and hygiene

As plastics are non-biodegradable, they clog and choke on water that can act as procreation places for many of malady germs which sooner or later cause an endemic in the surrounding inhabitants. Waste materials serve as a procreation place for various disease carriers. Female Anopheles mosquito spreads malaria. There are also exceptional germs like the cholera germ that has led to the death of millions of inhabitants in the world (Agamuthu and Law, 2020).

2.4.3 Clogging of drains and sewage

Polyethlyene bags easily block sewage and supply of water which leads to disease and flood during rainy season. They can also cause water clogging since water cannot drip all the way through them, and this can be an excellent reproduction ground for a number of species that spread disease (Agamuthu and Law, 2020).

2.4.4 Effect on wildlife

About a million animals such as dolphins, turtles, whales are killed every year due to these bags. Many animals such as cow, goat and dogs mistaken plastic as food. Plastic bags, once ingested cannot be digested or conceded by an animal, so it stays in the gut. Plastic in animal's gut avert food digestion and can lead to a very slow and painful death (Agamuthu and Law, 2020).

2.5 Degradation and Biodegradation of Polymers

All polymers degrade to some extent on a certain time-scale depending on environmental conditions. Degradable polymers are those that degradation results in the

decrease of their molecular weight through chain scission. Degradation of such polymer is complete when low molecular weight compounds and biomass through mineralization and bioassimilation is obtained (Vohlídal, 2020). In biodegradable polymers on the other hand, chain scission is caused by cell (human, animal, fungi) activity, thus it is an enzymatic process that is usually accompanied and promoted by physicochemical phenomena as well. The two types of processes, physical and enzymatic have combined effect for degradation to be complete (Ojogbo, 2019).

Bio-degradable stands for the proficient of undergoing decay into methane, water, carbon dioxide, inorganic material, and biomas (Pathak, 2017). A principal technique is the enzymatic act of microbes that are able to be precise. There are diverse media to examine bio-degradability. Material compostability is the degradability using manure intermediate (Sani *et al.,* 2020). Bio-degradation is the dilapidation of an organic substance due to the microorganism's enzymatic act. The yields are CO_2, water and new biomass (in the presence of oxygen (Mondal, 2015). However, a different composting environment like temperature and humidity cycle must be realized to decide the compostability level (Folino *et al.,* 2020). The accretion of contaminants with poisonous wastes might slow down plant growth. The main concern is to decide the environmental toxicity intensity for these byproducts, named as eco-toxicity. A number of common regulations make certain the estimates of the biodegradability progression (Meereboer *et al.,* 2020).

2.6 Prospects of Biodegradable Plastics

For better sustainability, eco-efficiency, and green chemistry, a search for renewable and environmentally friendly resources is on. Among the natural polymers, starch takes prior attention (Joseph *et al.,* 2021). Starch is a biodegradable polysaccharide, high in

abundance, low in cost and exhibits thermoplastic characteristics. Thus, it has become a more promising alternative material to replace conventional plastics in individual market segments (Smith, 2019). Synthetic polymer has been greatly used in every field of human activity. These artificial macromolecular substances are usually generated from petroleum and most of them are regarded as non-degradable. However, the resources of petroleum are limited, and the flourishing use of nonbiodegradable polymers has caused serious environmental tribulations (Doppalapudi *et al.,* 2014). The advantages of synthetic polymers are distinct, and can tailor quickly. In spite of this, they are somewhat expensive. This reminds us to focus for an alternative natural polymer, which is naturally biodegradable and can meet different necessities (Reddy *et al.,* 2021).

Owing to its totally biodegradable, cheap and renewability, starch is showing potential to develop sustainable resources. In view of this, starch has been getting attention since 1970s. Efforts have been made to make starch-based polymers for conserving the petroleum resources, sinking environmental impact and probing more applications (Reichert *et al.,* 2020).

2.7   Cassava

Cassava (*Manihot esculenta Crantz*) is a staple food for over 800 million people in the tropics and it is cultivated over a wide variety of soils. Cassava ranks fourth among food staples which is mostly cultivated in West Africa, tropical South America, and South East Asia (Chisenga *et al.,* 2019). Among starch producing botanicals, including main cereal crops, cassava is the highest producer of carbohydrates per hectare and can be grown at considerably lower cost. Cassava is often viewed as 'inferior crop', 'poor people crop', and as 'dangerous toxic crop' (Farias *et al.,* 2020). These tags on cassava were due to some limitation of the crop including low quality and quantity of protein,

and the presence of anti-nutritional factor cyanogenic glucosides that undermine its nutritional value. Efforts to increase its commercial utilization recognize blending cassava flour with other high protein content flours/starches derived from other botanical sources. Breeding objectives for increase nutritional quality in cassava has focused on bio-fortification of cassava with beta-carotene. The bio-fortified cassava is yellow fleshed and is the most recent genotype purposely bred to supply pro-vitamin A carotenoids in human diet (Alamu *et al.,* 2020). Application of cassava flour and starch in product development and food formulations is guided by their end use properties such as composition, physicochemical and functional properties (Chisenga *et al.,* 2019).

Plate II: Cassava tubers from Gwari market, Minna, Niger state

The shelf life stability of fresh cassava is limited due to rapid postharvest quality deterioration which occur immediately after harvest (Zainuddin *et al.,* 2018). High cyanide content limits consumption of cassava. Chemical composition of cassava varies from specie to specie. The chemical composition is dependent on a number of factors

such as cultivar, the geographical location, maturity stage of the plant, and environmental conditions (Boakye *et al.,* 2020). Immediate processing of cassava roots after harvest leads to decreased cyanide content and improved shelf life stability (Parmar *et al.,* 2017). Cassava products are either fermented or unfermented and contribute to the growing industrial application of cassava. The unfermented cassava primary products include flour, starch and chips.

2.8   Starch

Starch is the main storage reserve of polysaccharide of plants and a biopolymer of considerable significance to humans. It is a renewable, cheap and biodegradable natural raw material used widely in the food industry, in many non-food applications and as a source of energy after conversion to bioethanol (Kumar and Thakur, 2017). Plant starch is synthesized inside plastids by coordinated interactions of multiple biosynthetic enzymes and deposited in storage organs, such as roots, tubers, fruits, grains and seeds, as well as in leaves and stems (Smith and Zeeman, 2020). Starch is obtained from plant parts like the tubers of cassavas, yams, potatoes or the seeds of rice, corn, wheat and tapioca. It is particularly abundant in cereal grains, vegetables, tubers and immature fruits (Wang and Guo, 2020). Tubers like cassava are the main sources of starch for consumption but cassavas and potatoes contribute 5 % to the global starch supply. Starch is one of the most bounteous natural biomass.

Native starch occurs naturally in the form of insoluble, semi-crystalline granules, which are made up of two glucose homopolymers: amylose and amylopectin (Meimoun *et al.,* 2018) and the relative amounts of each vary depending on the plant source. As an example, corn starch has about 28 wt. % amylose while cassava starch has 17 wt. % (Mendesa *et al.,* 2016 and Sagnelli *et al.,* 2017).

Besides consumption in food as a source of energy for plants and food for humans, it is a renewable and biodegradable polymer which has diversified usage in industries (Yazid *et al.,* 2018). Starch has been extensively used to produce biodegradable films (da Silva Pereira *et al.,* 2021). Films developed from starch are described as isotropic, odourless, tasteless, colourless, non-toxic and biologically degradable. Unfortunately, there are some strong limitations for developing starch based products, since they present poor tensile properties and high water vapor permeability when compared to conventional films derived from crude oil on account of their hydrophilic nature and their sensitivity to moisture content (Rangari *et al.,* 2019). Usually, the second major component of a starch based film is the plasticizer, which is used to overcome film brittleness caused by high intermolecular forces. Plasticizing agents commonly used for thermoplastic starch production include water and glycerol, polyethylene glycol and other polyols, such as sorbitol, mannitol and sugars (Liu *et al.,* 2020).

Plate III: Starch Powder

2.8.1   Composition of starch

The starch granule is a biopolymer of two major polysaccharides, namely amylose and amylopectin. These molecules consist of chains of α-(1-4)-linked D-glucose residues, which are interlinked with α-(1-6)-glycosidic linkages, thus creating branches in the polymers (Chisenga *et al.,* 2019). Amylose is the longer chains linear polymer composed of glucopyranose units, while amylopectin is the short chains branched polymer with significantly higher molecular weight (Yee *et al.,* 2021). The amylopectin chains form double-helices responsible for the crystallinity in starch. The semi-crystallinity in starch is due to the radially arranged linear and branched macromolecules (Ito and Lacerda, 2019).

As stated above, starch granule semi-crystalline nature contains crystalline and amorphous. The crystallinity is strongly associated with amylopectin molecule. Amylose is believed to be largely found in the amorphous lamellae and amylopectin forms crystalline lamellae (Yee *et al.,* 2021). The structural crystallinity were identified as type A, B and C using X-ray diffraction analysis. The A-type crystallinity are crystallites of double-helices of short chains, and are closely packed into a monoclinic unit cell containing 8 water molecules (Agama-Acevedo *et al.,* 2019). The B-type crystallinity associated with crystallites of double-helices, which are loosely packed in hexagonal unit cell containing 36 water molecules. Some starches contain a mixed pattern (A and B) designated C-type. The variation in double helices and packing pattern influences morphology and size of the starch granule. Cassava starches were reported to exhibit A- or C-type (Bastioli *et al.,* 2020).

2.8.2   Approaches to the modification of starch

The adjustment of the properties of biopolymers to the intended application has wide variety of approaches used for their modification like plasticization, the incorporation of fillers and reinforcements, blending and Impact modification (Rajeswari *et al.,* 2021).

2.8.2.1 *Plasticization*

Plasticization is often used for the modification of biopolymers to improve their processibility and other properties demanded by a specific application.

2.8.2.2 *Blending*

Physical blending is simply mixing of polymeric materials while in the melt state without any chemical reaction taking place. It is a convenient way to develop new materials with the desired properties combination (Zhang *et al.,* 2018). Blending can be done using conventional machinery that is not expensive. This approach can be used to achieve a very wide range of properties in the product to meet the requirements of the targeted application. Physical blending is aimed at improving the properties of the polymer product to meet certain targeted application as well as maximization of the performance of a material (Kaur *et al.,* 2018).

2.8.2.3   *Modification by acid hydrolysis*

Acid hydrolysis exposes starch to mineral acids such as H_2SO_4, HCl, HNO_3 and H_3PO_4 at temperatures below the gelatinization temperature. The degree of hydrolysis changes as a function of treatment time (Seligra *et al.,* 2016). In acid hydrolysis, the hydroxonium ion attacks the oxygen in the glycosidic bond and later hydrolyses the linkage (Krithika and Ratnamala, 2019). An acid works on the starch granule surface prior to entering the inner

region of starch. Acid modifications can alter physicochemical properties but maintain the granule structure intact. Acid hydrolysis is a common method to increase the amount of short linear chains like amylose. Acid hydrolysis in starch chemical modification has been widely applied to modify starch. The treatment forms crystalline structures that withstand enzymatic hydrolysis (Punia, 2020).

2.8.2.4   Modification by debranching

Debranching is an enzymatic starch modification that uses hydrolysis of amylopectin facilitated by certain debranching enzymes to form short linear starch molecules. Enzymatic debranching is a common method to produce linear chains, which contributes to a high content of resistant starch (Liu *et al.,* 2017). Pullulanase is one of the notable debranching enzymes that cleaves the α-1,6 linkages in pullulanase, amylopectin, and other polysaccharides. Debranching of amylopectin can generate more short linear molecules and further will realign a new crystalline structure when allowed to retrograde (Pratiwi *et al.,* 2018). Thus, debranching is commonly combined with autoclaving-cooling or heat moisture treatment which enables increase in the resistant starch yield (Arp *et al.,* 2020).

2.8.2.5   Modification by autoclaving-cooling cycles

A starch suspension will form a gel upon heating to constant temperature. When cooled, the gel will turn into a partially crystalline structure (Yang *et al.,* 2021). The autoclaving process involves heating starch in excess water. During the process, the starch will

gelatinize and undergo disruption of its granular structure. It is well-documented that the gelatinization temperature affects the yield of resistant starch (Pratiwi *et al.,* 2018). Upon starch solution cooling, the amylose molecules will recrystallize along with retrogradation. The starch molecules will re-aggregate during retrogradation to form a densely packed structure (Yang *et al.,* 2021).

2.8.2.6   Modification by heat moisture treatment (HMT)

Heat moisture treatment (HMT) is a physical modification of starch that uses controlled heat and moisture. The treatment does not involve gelatinization and thus does not cause any damage to the granular structure (Maniglia *et al.,* 2020). The method treats the starch granules at limited moisture levels (<35 % moisture w/w) for 15 min to 16 hours at temperatures above the gelatinization temperature (84-120 °C). The mechanism occurs by increasing interactions of starch chains (Pratiwi *et al.,* 2018). It initially disrupts the crystalline structure and dissociation of double helix structures followed by re-association of the disrupted crystals. Heat moisture treatment (HMT) also triggers perfection of the starch crystallites. It initially leads to incipient swelling and the resulting mobility of amorphous regions, which then favours ordering of the double helix (Maniglia *et al.,* 2020).

2.8.2.7   Combination of starch modification techniques to produce resistant starch

Many efforts have been conducted to optimize the yield of resistant starch. One of the most common methods is the application of a combination of modifications to obtain higher yields of resistant starch (BeMiller, 2020). For instance, a combination of acid hydrolysis and autoclaving-cooling cycles was applied to optimize the yield of resistant starches in pea starch and cassava starch. In other studies, enzymatic debranching was

conducted prior to retrogradation to obtain higher yields of resistant starch in pea starch, sago starch, high amylose corn starch, and rice starch (Pratiwi *et al.,* 2018).

2.9   Hydrolysed Starch

Hydrolysed starch originate from the disruption of the semi-crystalline structure of starch granules. The crystalline regions of starch granules can be isolated by mild acid hydrolysis using hydrochloric acid or sulphuric acid (*Gonçalves et al., 2014*).

Acid hydrolysis on starch involves an electrophilic attack on the oxygen atom of the α (1-4) glycosidic bond by the hydroxonium ion (H_3O^+). The electrons generated in one carbon-oxygen bonds move to the oxygen atom to generate an unstable, high energy carbocation intermediate. The carbocation intermediate is a lewis acid, which subsequently reacts with water (Figure 2.1), a lewis base, thereby regenerating a hydroxyl group (Hoover, 2000).
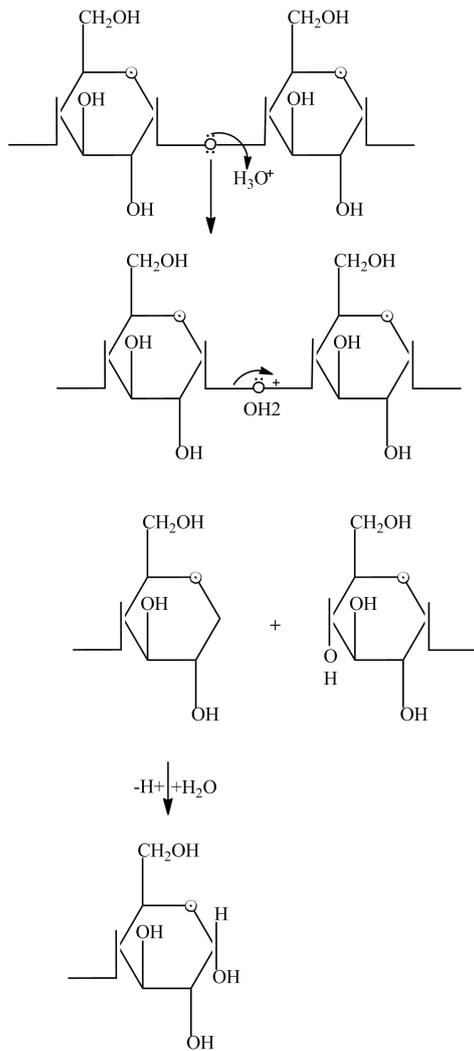
Figure 2.1 Acid hydrolysis of starch

Source: Hoover (2000)

The structure and some physicochemical properties of potato and cassava starch were obtained by mechanical treatment of native starch. With the help of scanning electron microscopy and the non-contact atomic force microscopy, Xie *et al.* (2014) discovered that the shape and dimensions of the obtained hydrolysed starch of both potato and cassava starch fit the basic structural features of native starch granules (*Cui and Zhu, 2020*). This observation was supported by aqueous solubility and swelling power of the particles as well as their iodine binding capacity which were similar to those for

amylopectin-type short branched polysaccharide species (Egharevba, 2019 and *Shirai*

et al. 2013). The results obtained indicated that glycosidic bonds of the branch

linkage points in the granule amorphous lamellae might be broken during the applied

mechanical treatment that released amylopectin clusters out of the granules. Guo *et al.*

(2019) concluded that Hydrolysed starch had their qualitative properties different from

those of native starch granules and could be utilized in new applications.

Hydrolysed starch has remarkable application as reinforcement fillers in polymeric

composites (Wang *et al.,* 2018). There are several applications of hydrolysed starch

ranging from packaging, emulsion stabilizer, fat or oil replacers, drug delivery, paper

making, paper coating, adsorbents for wastewater and many others (Sandhu and Nain,

2017 and Dong and Vasanthan, 2020). They are also useful in food packaging

technology because they increase the mechanical and water vapour resistance of the

matrix as well as hinder its recrystallization during storage in high humidity

atmospheres (Maniglia *et al.,* 2020). Synthetic polymers provide excellent physical

properties and chemical resistance in different industries. However, they are not

biodegradable but biodegradable hydrolysed starch can be incorporated into a variety of

matrices of both natural and synthetic polymers to improve their biodegradability

(Wang *et al.,* 2018). The application of biodegradable polymers is possible and

advantageous only in a few areas, mainly in packaging and agriculture, although

medical applications of certain types can be also important (Siracusa, 2019).

2.10   Characterisation Techniques

Several analytical techniques have been studied in the characterisation of plastic blends.

The characterisation techniques discussed here are thermogravimetric analysis, high

resolution scanning electron microscopy, energy dispersive X-ray spectroscopy among others.

2.10.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a thermo analytical method which determines the measurement of residual weight loss with respect to temperature in a controlled environment. The weight loss may be attributed to thermal degradation, loss of water and volatiles. TGA profile of the precursors defines the weight loss of the precursors with respect to temperature due to the volatile matter and surface bounded water release (Mishra and Mohanty, 2018). This analysis revealed the thermal stability and degradation temperatures for the different components of the blends produced. Ismail *et al*. (2017) studied the thermogravimetric behaviour of thermoplastic starch and plasticizers. The authors reported a thermogravimetric analysis at a temperature range of between 25 to 550 °C and a heating rate of 3 °C /minute in a nitrogen environment. They observed a first peak occurring between 37-156 °C and attributed it to evaporation of moisture. A second peak was observed between 228-393 °C that was termed as the thermal degradation of starch. Dubdub *et al*. (2020) reported a temperature of 471 °C (at a heating rate of 10 K/minute) as the degradation temperature for polyethylene when they studied the thermal decomposition of polyethylene at different heating rates of 5, 10, 20 and 40 K/minute in nitrogen environment.

2.10.2 High resolution scanning electron microscopy

High resolution scanning electron microscopy (HRSEM) is a characterisation method that creates high-resolution images of a sample surface. HRSEM gives information concerning the surface structure, morphology and the aggregation degree of micro and macro materials. The crystalline nature of the scanned material is also an information

provided by the HRSEM. The various multiple signals such as back scattered electrons and X-rays secondary electrons are obtained through the bombardment of atoms present in the material with beams of electrons (Kakubo *et al.,* 2020). Dolas *et al.* (2020) studied the effect of starch modification on physico-chemical, functional and structural characterisation of cassava starch. He observed that the starch granules were spherical and smooth while the hydrolysed starch particles were rough and reduced in particle size.

2.10.3 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDX) is a non-destructive significant characterisation utilized to determine the qualitative and semi quantitative elemental composition of the unknown samples. It involves beam of electrons (X-ray excitation) interaction with the atomic composition of the sample through a scanning microscopy to produce unique spectrum with peaks corresponding to particular elements in the sample. The elemental distribution pattern of materials in EDX is provided in a line scan form that relates to particular peaks formed through X-ray emission. EDX also separates the X-rays of the elements into an energy spectrum and characterizes the spectrum to determine the quantity of each element in the material. EDX is commonly connected with HRSEM through the scanning of the selected area in sufficient time to obtain the average weight of the elements (Pazzaglia *et al.,* 2019). Dolas *et al.* (2020) studied the effect of starch modification on physico-chemical, functional and structural characterisation of cassava starch. He observed that both the unmodified starch and the modified starch contained carbon and oxygen atoms however the percentage oxygen content of the modified starch was higher than that of the unmodified starch.

2.10.4 Mechanical properties

Mechanical properties describe the material's reaction to an applied force, such as tension, compression and impact. Justice *et al.* (2021) studied the innovative use of plastics for a cleaner environment observed that the mechanical properties of polymers play a particularly important role in applications where plastic components are designed to withstand stress. Mechanical properties of plastics are not constants and often change as a function of temperature, rate of loading, and other conditions. For example, temperatures below room temperature generally cause an increase in strength properties while ductility, fracture toughness, and elongation usually decrease as observed by Hale, (2016) who studied the mechanical properties of polyethylene and starch based blends. Temperatures above room temperature usually cause a decrease in the strength properties of metallic alloys. Ductility may increase or decrease with increasing temperature depending on the same variables. There is often significant variability in the values obtained when measuring mechanical properties. Seemingly identical test specimen from the same lot of material will often produce considerable different results. Therefore, multiple tests are commonly conducted to determine mechanical properties and values reported can be an average value or calculated statistical minimum value (Hammache *et al*., 2020). The fundamental mechanical material characteristics include:

- Impact strength is a measure of the resistance of a material to impulsive stress. It can be determined with a Charpy or Izod test. Impact tests is used as a quality control method to assess notch sensitivity and for comparing the relative toughness of engineering materials.
- Stiffness measures the resistance of a material to elastic deformation or deflection. A material which suffers light deformation under load has a high degree of stiffness.

- Hardness is the resistance to permanent indentation of the surface of a material. Large hardness means resistance to plastic deformation or cracking in compression and better wear properties

- Toughness is the ability of a polymer to deform plastically and to absorb energy in the process before fracture. The key to toughness is a good combination of strength and ductility. A material with high strength and high ductility will have more toughness than a material with low strength and high ductility. It has units of energy per volume. Material toughness equates to a slow absorption of energy by the material. (Alabi *et al.,* 2019).

CHAPTER THREE

3.0   MATERIALS AND METHODS

3.1   Materials

3.1.1   Reagent used in the study

The reagent used in this study are of analytical grade and used as received.

Table 3.1 represents the list of different equipment and reagents used for the characterisation and production of the polyethylene waste, hydrolysed cassava starch and polyethylene waste/hydrolysed cassava starch blends.

3.2   Sample Collection and Pre-treatment

Cassava tubers were obtained from Gwari Market, Minna, Niger State from which starch was prepared. Waste pure water sachet were obtained from Federal University of Technology, Bosso campus, Minna, Niger State as plastic waste.

3.2.1   Sample pretreatment

The fresh cassava tubers were peeled to remove the skin and defect portions. The peeled tubers were washed with distilled water and diced.

Waste pure water sachet were shredded, thoroughly washed to remove dirt and air-dried. They were weighed until constant weight was achieved and stored for further use.

3.3   Starch Extraction

Starch was extracted from peeled and diced cassava tubers according to the method described by Wu *et al.* (2019). The diced tubers were crushed with distilled water using a mortar and pestle. The mixture was stirred thoroughly and sieved with a cheese cloth.

Table 3.1: Reagent and Equipment Used

Instrument/Reagent	Model/Purity	Manufacturer
Sulphuric acid	99.5%	British Drug House
Beakers		
Conical flask		
Funnels		
Filter paper		
Measuring cylinder		
Mortar and Pestle		
Oven	MINO/50	Genlab, United kingdom
Incubator shaker	TC544	Lab world, China
Continuous mixer	XK-300	Yuntai,China
Extruder (Two-roll mill)	XK-160	Yuntai, China
Hydraulic press	XQ-1500	Yuntai, China
Shore A hardness tester	GW-079F	Guangdong, China
Impact strength tester	CY510B	Shandong, China
Muffle furnace	FSE-621-010L	Gallenkamp, England
Digital weighing balance	Scout Pro SPU	Ohaus Cooperation, China
Magnetic Stirrer	78HW-1	Gallenkamp, England
HRSEM (High Resolution Scanning Electron Microscope)	Zeiss Auriga	
Thermogravimetric analyser	Perkin Elmer	USA

The retained solids were rinsed with distilled water and discarded. The filtrate was allowed to stand overnight at room temperature. The starch settled down while the water was decanted. The sedimentation process was repeated until the white starch was obtained. The starch was dried at 50 °C in an oven until constant weight was obtained. The dried flour was grounded and sieved using 80 μm sieve. The obtained starch was kept in an air tight container for further use.

3.4   Preparation of Hydrolysed Cassava Starch

Hydrolysed Cassava starch was produced using H_2SO_4 according to the method described by Wu *et al.,* (2019) with slight modification in the concentration of H_2SO_4. In a 1000 cm^3 beaker, 115 g of extracted cassava starch powder was suspended in 800 cm^3 of 2.5 $moldm^{-3}$ of H_2SO_4 solution. The mixture was stirred and placed on a magnetic stirrer at 40 °C and further stirred for 3 hours at 500 rpm. It was then removed and placed in an incubator shaker for 10 days at 40 °C and 500 rpm after which polyethylene glycol was added to stop further reaction. The resultant solution was then filtered using Whatman filter paper and the hydrolysed starch was retained in the filter paper as the residue. The residue was washed severally with distilled water until it was neutral to litmus paper. Then the residue was dried at 60 °C to constant weight, grinded, sieved with an 80 μm and stored in an airtight container for further use.

3.5   Examination of morphology and microstructure of cassava starch and hydrolysed cassava starch Using High Resolution Scanning Electron Microscope (HRSEM)

The surface morphology and microstructure of cassava starch and hydrolysed cassava starch were characterized using HRSEM. The HRSEM equipped with EDX was further used to determine the elemental composition of cassava starch and hydrolysed cassava starch. The sample was sprinkled on a sample holder and sputter coated with Au-Pd using Quorum T15OT sputter coater for 5 minutes prior to analysis. The sputter coated samples were firmly attached to the carbon adhesive tape and analysed using HRSEM equipped with an in-lens standard detector at 30 kV. The microscope in the HRSEM equipment was operated with electron high tension (EHT) of 5 kV for imaging.

3.6   Blending and Extrusion of the Blend

The polyethylene water sachet waste were shredded and mixed with the hydrolysed cassava starch powder in a continuous mixer at 160 rpm in various ratios such as: 100:0, 90:10, 80:20, 70:30, 60:40 and 50:50, labeled sample A, B, C, D, E and F, respectively. Afterwards, the blend in the continuous mixer was fed into an extruder with 2 row mill compounding machine at a pressure of 3 MPa where they were melt blended at a temperature of 150 °C. The blend was then fed to a hydraulic press where the flat sheets of the blends were obtained at a pressure of 70 MPa and a temperature of 150 °C for 5 minutes. Afterwards, the blend was cooled gradually by passing it over water-cooled rolls.

3.7   Characterisation   of   Polyethylene   Waste   and   Polyethylene Waste/Hydrolysed Starch Blends

Polyethylene waste and the polyethylene waste/hydrolysed cassava blends were characterized for their thermal properties, water absorption capacity, mechanical properties, response to microbial attack and morphological properties,.

3.7.1 Determination of the thermal properties of polyethylene waste and polyethylene waste/hydrolysed starch blends

 The thermal stabilities of polyethylene waste and polyethylene waste/Hydrolysed starch blends were determined using thermo-gravimetric analysis (TGA). Polyethylene waste and polyethylene waste/hydrolysed starch blends were analysed in nitrogen environment at a flow rate of 20 ml/min and heating rate of 10 °C/min between 50 °C and 600 °C. To a zeroed thermal balance, sample weights of 10.657 mg, 15.617 mg, 12.226 mg, 18.83 mg, 19.294 mg and 11.433 mg for sample A, B, C, D, E and F respectively were loaded and recorded into the equipment using pyris manager software.

The analysis was then initiated after constant weight was noted using the created heating profile (temperature scan).

3.7.2 Water absorption analysis

A circular shape from the prepared sheet of the polyethylene waste with a radius of 2 cm was cut according to ASTM D570 with slight modifications in the duration used for soaking the samples. It was weighed, the weight was recorded as W_1. The sample was immersed into distilled water for 24 hours. It was then removed from the water and wiped with a towel to remove excess water from the surface. The sample was weighed again and recorded as W_2. The percentage water uptake/absorption was obtained using the formular:

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

where;

W_1 is the initial weight of the sample and W_2 is the final weight of sample after soaking in water for 24 hours. The procedure was repeated two more times and the average of the water absorption of the samples was taken. This procedure was repeated for all the samples.

3.7.3 Hardness test

A rectangular shaped sample from the prepared sheet of the polyethylene waste with dimensions 20 mm x 10 mm x 3 mm (length x breadth x width respectively) was machined cut and placed on the hardness tester ASTM D2240. Various weights ranging from 500 g to 1000 g was attached to the indentor and the handle pooled down to lift up the sample together with the plate towards the indentor and the indentor was released.

The sample came in contact with the indentor and the first hardness reading was taken. The process was repeated two more times at different positions and the average of the hardness readings was taken as the hardness of the test material. This procedure was repeated for all the samples.

3.7.4 Izod impact strength test

A rectangular shaped sample from the prepared sheet of the polyethylene waste with dimensions 20 mm x 10 mm x 3 mm (length x breadth x width respectively) was machined cut. The sample was then notched at a notch angle of 45° and a notch depth of 3.5 mm and placed in the izod impact strength tester specimen holder according to ASTM D3641. The scale indicator was adjusted to zero position and the striking hammer was released to break the sample and the first impact strength reading was taken. The process was repeated two more times and the average of the impact strength readings was taken as the impact strength of the test material. This procedure was repeated for all the samples.

3.7.5 Soil burial tests

The tests of the samples from the prepared sheet of the polyethylene waste and polyethylene waste/hydrolysed cassava starch blends were carried out according to the method described by Lv (2017) with slight modification in the duration and depth of burial. Two pots were filled to capacity with compost soil obtained from a flower garden in Tunga, Minna. Each sample was cut into a dimension of 3.5 cm x 6 cm and buried in the soil to a depth of 12 cm. The pots were placed in the laboratory and soil moisture was maintained by sprinkling water every 12 hour (twice a day). Excess water was drained through a hole at the bottom of the pot. The degradation of the samples was determined every week by carefully removing the sample from the soil and washing it

with distilled water to remove soil from the sample. The sample was dried with a cloth and kept in the desiccator until constant weight was obtained. Weight loss of the sample over time was used to indicate the microorganism degradation effect on the soil buried samples. The percentage weight loss was calculated using the equation below:

Effect of microorganism degradation (Wt loss (%))
$$= \frac{W_i - W_d}{W_i} \times 100 \qquad \text{Equation (3.2)}$$

where;

W_d is the dry weight of the sample after being buried, W_i is the initial weight of the samples before they were buried.

3.7.6 Examination of morphology and microstructure of polyethylene waste, polyethylene waste/Hydrolysed starch blend Using High Resolution Scanning Electron Microscope (HRSEM)

The surface morphology and microstructure of polyethylene waste, polyethylene waste/Hydrolysed starch blend and buried polyethylene waste/Hydrolysed starch blend were characterized using HRSEM. The HRSEM equipped with EDX was further used to determine the elemental composition of polyethylene waste, polyethylene waste/Hydrolysed starch blend and buried polyethylene waste/Hydrolysed starch blend. The sample was sprinkled on a sample holder and sputter coated with Au-Pd using Quorum T15OT sputter coater for 5 minutes prior to analysis. The sputter coated samples were firmly attached to the carbon adhesive tape and analysed using HRSEM equipped with an in-lens standard detector at 30 kV. The microscope in the HRSEM equipment was operated with electron high tension (EHT) of 5 kV for imaging.

CHAPTER FOUR

## 4.0   RESULTS AND DISCUSSION

4.1   HRSEM/EDX Analysis of unhydrolysed and hydrolysed cassava starch

4.1.1   HRSEM Analysis of unhydrolysed and hydrolysed cassava starch

The HRSEM micrographs showing the morphology and microstructure of the unhydrolysed and hydrolysed starch samples are shown in the Plates IV A and B below respectively.
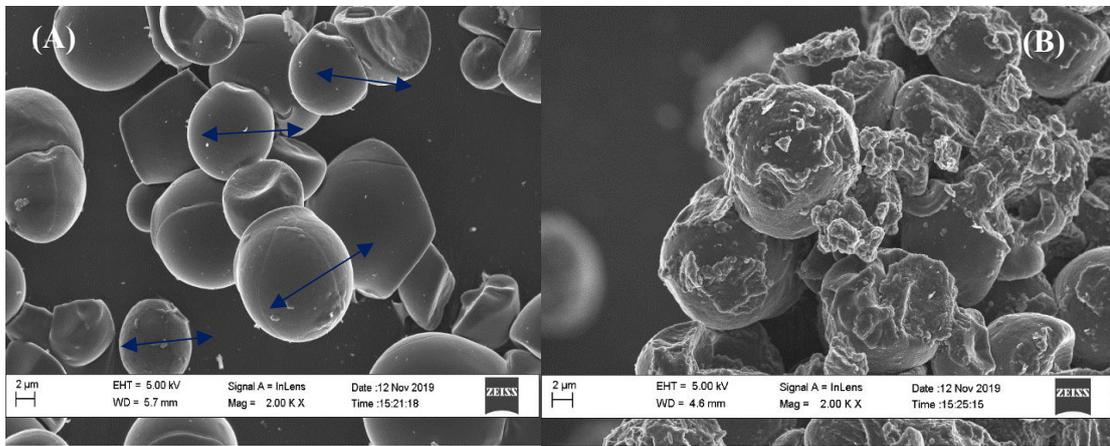
Plate IV: Morphology and microstructure of (A) Unhydrolysed starch (B) Hydrolysed starch

Plate IV (A) shows that unhydrolysed starch particles are spherical, smooth and clustered with open spaces in between the clusters. Whereas in plate IV B it is clear that the particles have been etched by the acid (H_2SO_4) and became rough due to the attack of the acid on the amorphous regions of the starch granules making the surface more exposed to reactions. This observation is similar to that by Dolas *et al.* (2020) who studied the effect of starch modification on physico-chemical, functional and structural characterisation of cassava starch. He observed that the starch granules were spherical and smooth while the hydrolysed starch particles were rough and reduced in particle size. Acid molecules preferentially attack the amorphous regions of the starch granule

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resulting in the rapid hydrolysis of these regions over the crystalline regions. Thus the surfaces of the hydrolysed starch appear eroded making them more exposed and reactive than the unhydrolysed starch particles.

4.1.2 EDX Analysis of unhydrolysed and hydrolysed cassava starch

The elemental composition of unhydrolsyed cassava starch and hydrolysed cassava starch are shown in table 4.1 below.

Table 4.1: Elemental Composition of the Cassava Starch and Hydrolysed Starch

	Element composition (%)	
Material description	Carbon	Oxygen
Unhydrolysed starch	60.54	39.46
Hydrolysed starch	55.23	44.77

The EDX analysis of the unhydrolysed and hydrolysed cassava starch samples showed the presence of C and O elements respectively. The amount of carbon is higher in the unhydrolysed cassava starch (60.54 %) than in hydrolysed cassava starch (55.23 %). Whereas the percentage composition of Oxygen increased from 39.46 % for unhydrolysed starch to 44.77 % for hydrolysed cassava starch (Table 4.1). The decrease in the carbon content and increase in amount of oxygen in the hydrolysed sample could be attributed to Hoover (2000) explanation of the acid hydrolysis of starch which involves an attack on the oxygen atom of the α (1-4) glycosidic C-O bond of the unhydrolysed starch by the hydroxonium ion (H_3O^+) (Figure 4.1), the electrons generated in one C-O bonds move onto the oxygen atom to generate an unstable, high energy
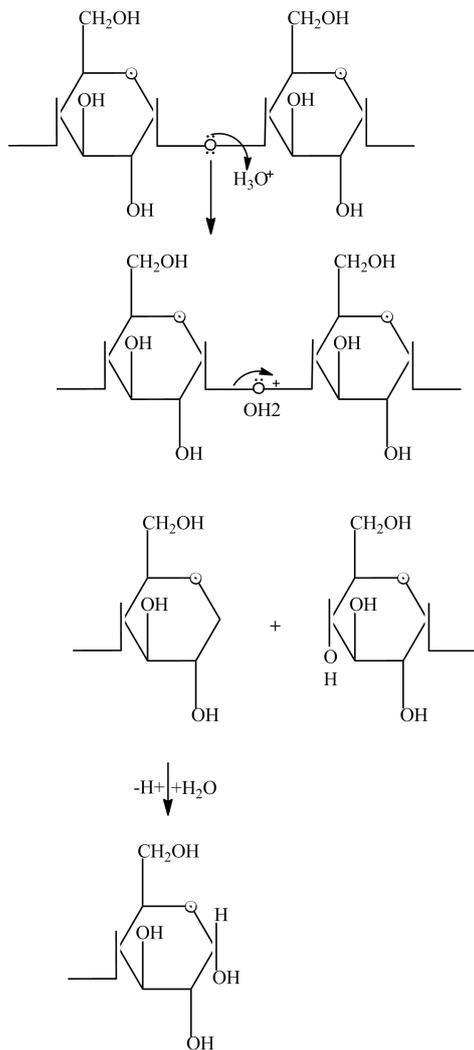
Figure 4.1 Acid hydrolysis of starch

Source: Hoover (2000).

Carbocation intermediate. The carbocation intermediate is a lewis acid, so it subsequently reacts with water, a lewis base, thereby regenerating an additional hydroxyl group (Hoover, 2000. In addition, the polysaccharide chain length reduces thereby increasing the surface area of the granule and its reactivity.

4.2 Thermo Gravimetric Analysis (TGA)

The onset, peak degradation and endset temperatures of the polyethylene

waste/hydrolysed cassava starch blends are shown in Table 4.2 below:

Table 4.2: Thermogravimetric Analysis Data

Sample (weight%)	Onset Temperature 1 (°C)	Onset Temperature 2 (°C)	Peak degradation temperature, T_p 1 (°C)	Peak degradation temperature, T_p 2 (°C)	End set temperature (°C)
Polyethylene (100)	316.24			442.54	508.87
Polyethylene/HCS (10:90)	315.9	401.21	349.88	421.23	434.49
Polyethylene/HCS (20:80)	314.24	397.49	336.11	414.62	493.83
Polyethylene/HCS (30:70)	311.57	396.75	336.48	409.29	485.19
Polyethylene/HCS (40:60)	303.44	341.49	324.55	406.15	405.17
Polyethylene/HCS (50:50)	271.54	391.31	316.99	403.71	524.98

The TGA curves (Appendices C and D) for the blends of polyethylene and hydrolysed cassava starch showed three mass loss peaks except for 100 % polyethylene waste which shows only one. The first peak which ranges between 80 °C and 150 °C corresponds to the loss of water and volatile compounds which gradually proceeded to the second peak.

The second mass loss peak which occurred between 316 °C and 350 °C is the thermal degradation of hydrolysed cassava starch. This thermal degradation can be associated with the breakage of long chains of starch and destruction of glucose rings. This observation is slightly different from that reported by Ismail *et al*. (2017) who studied the thermogravimetric behaviour of thermoplastic starch and plasticizers. The authors reported a thermogravimetric analysis at a temperature range of between 25 to 550 °C and a heating rate of 3 °C /minute in a nitrogen environment. They observed a first peak occurring between 37-156 °C and attributed it to evaporation of moisture. A second peak was observed between 228-393 °C that was termed as the thermal degradation of starch. The difference between their result and this study could be due the differences in temperature heating rate. It has been said that higher heating rates results in higher peak degradation temperatures (Dubdub *et al*., 2020).

The third mass loss peak occurred between 403 °C and 442 °C (Table 4.2) which is as a result of the thermal degradation of polyethylene waste. Dubdub *et al*. (2020) reported slightly higher figures of 471 °C (at a heating rate of 10 K/minute) when they studied the thermal decomposition of polyethylene at different heating rates of 5, 10, 20 and 40 K/minute in nitrogen environment. The difference could be due to the fact that polyethylene waste (pure water sachet) was used in this study while they used virgin polyethylene in their studies. The pure water sachets may have undergone heat deformation due to high processing temperatures during the manufacture of the

materials hence resulting in a less thermally stable material than the virgin polyethylene. Furthermore, Velis and Cook (2020) studied the toxic pollutants from plastic waste and revealed that the thermal degradation of polyethylene at different operating conditions released volatile organic compounds like olefins, paraffins, aldehydes and light hydrocarbons. Increasing the amount of hydrolysed starch in the blends led to decrease in the thermal stability of blends as starch are more thermally unstable than polyethylene.

4.3   Water Absorption, Hardness and Impact Strength Properties

The water absorption capacity (weight %), hardness and impact strength tests of unmodified polyethylene waste and modified polyethylene waste with hydrolysed cassava starch are shown in the Table 4.3 below:

Table 4.3: Water Absorption, Hardness and Impact Strength Properties

Sample	Water absorption (%)	Hardness (Nmm^2)	Impact strength (J/m^2)
PE/HCS 100:0	0.000±0.15	98.667±1.53	1.981±1.14
PE/HCS 90:10	0.642±0.23	97.333±2.08	0.987±0.58
PE/HCS 80:20	0.751±0.40	97.000±1.36	0.960±0.57
PE/HCS 70:30	0.951±1.02	96.667±1.16	0.702±0.41
PE/HCS 60:40	0.963±0.90	96.667±1.53	0.535±0.31
PE/HCS 50:50	1.285±0.80	96.333±0.58	0.376±0.22

Keys: PE= Polyethylene, HCS= Hydrolysed cassava starch

4.3.1 Water absorption

It was observed from Table 4.3 that blend F with 50 % HCS showed the highest water absorption value of 1.285 % while 100 % polyethylene waste did not absorb water. The

water absorption value of polyethylene with HCS may be due to the hydrophilic nature of the starch dispersed in the polyethylene matrix, which easily absorbs moisture from the environment (Yi *et al.,* 2020). Hydrolysed cassava starch has hydroxyl functional groups in its molecular structure which makes it hydrophilic as seen in Figure 4.3.

4.3.2 Hardness

100 % Polyethylene waste showed higher values of hardness 98.667 Nmm^2 compared to polyethylene waste/HCS blends (97.333 to 96.333 Nmm^2) as seen in Table 4.3. The lower hardness observed for polyethylene waste/HCS blends could be due to the weak interaction between the hydrophobic polyethylene and hydrophilic starch (Santos *et al.* 2018).

4.3.3 Impact strength

100 % Polyethylene waste showed higher values of impact strength 1.981 J/m^2 compared to polyethylene waste/HCS blends 0.987 to 0.376 J/m^2 respectively) as seen in Table 4.3. The lower impact strength values observed for polyethylene waste/HCS blends could be due to the weak interaction between hydrophobic polyethylene and hydrophilic starch (Santos *et al.* 2018). The presence of hydrolysed starch in the polyethylene waste matrix could act as stress concentration areas within the bulk of the polymer creating weak points for premature failure. The weakening effect of the starch increases with increase in its percentage content.

4.4   Soil Burial Properties

The mass of 100% polyethylene wastes and samples of polyethylene containing various percentage of hydrolysed starch recorded over 22 weeks of burial were plotted in Appendix E and the total percentage weight loss calculated are given in Table 4.4

Table 4.4: Total Percentage Weight Loss After 22 Weeks Burial

Polyethylene/HCS Ratios (wt %)	Total weight loss after 22 weeks (%)
100:0	0
90:10	0.25
80:20	0.98
70:30	2.8
60:40	3.9
50:50	5.92

The degradation of polyethylene waste/HCS blends was computed from the weight loss of the blends buried in flower pots in the laboratory at step B over a period of 22 weeks. It was seen from the figure that 100 % polyethylene did not lose weight within the period of study. The Polyethylene waste/hydrolysed cassava starch blends lost weight to different levels. Weight loss was an indication of the degradation of hydrolysed starch component of the blend. The maximum weight loss of 5.92 % was observed for the blend with the highest amount of HCS (50 % HCS), indicating that the weight loss is directly proportional to the amount of HCS present in the blends (Table 4.4).

Furthermore, the weight loss of polyethylene waste/ HCS blends may be as a result of effect of microorganisms. The nature and extent of degradation of polymer product depends on the microbial content of the environment, environmental factors such as temperature, pH, nutrition and humidity and the characteristic of the polymer. (Sintim *et al.,* 2020; Vasile *et al*., 2018). During the degradation process, microorganisms use oxygen to oxidize the carbon content from the hydrolysed starch to produce CO_2 in aerobic conditions and CO in anaerobic conditions as the major metabolic product as seen in the reaction scheme below:

Aerobic condition: (Starch) $\xrightarrow[\text{microorganism}]{H_2O}$ $CO_2 + H_2O + \text{Cells} + \text{Energy}$

Anaerobic condition: (Starch) $\xrightarrow[\text{Microorganism}]{H_2O}$ $CO + H_2O + \text{Cells} + \text{Energy}$
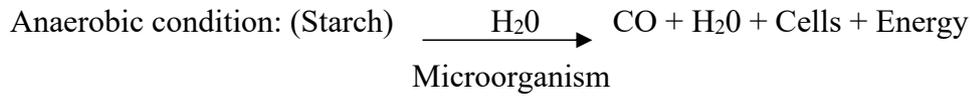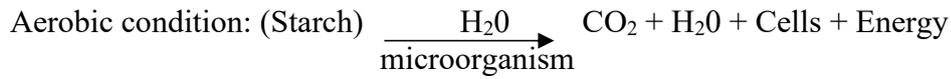
Source: Gautam and Kaur (2013)

4.4.1 Mechanism of degradation of Polyethylene waste/HCS Blend

Figure 4.2 shows the mechanism of degradation of Polyethylene waste/HCS blend by microorganisms
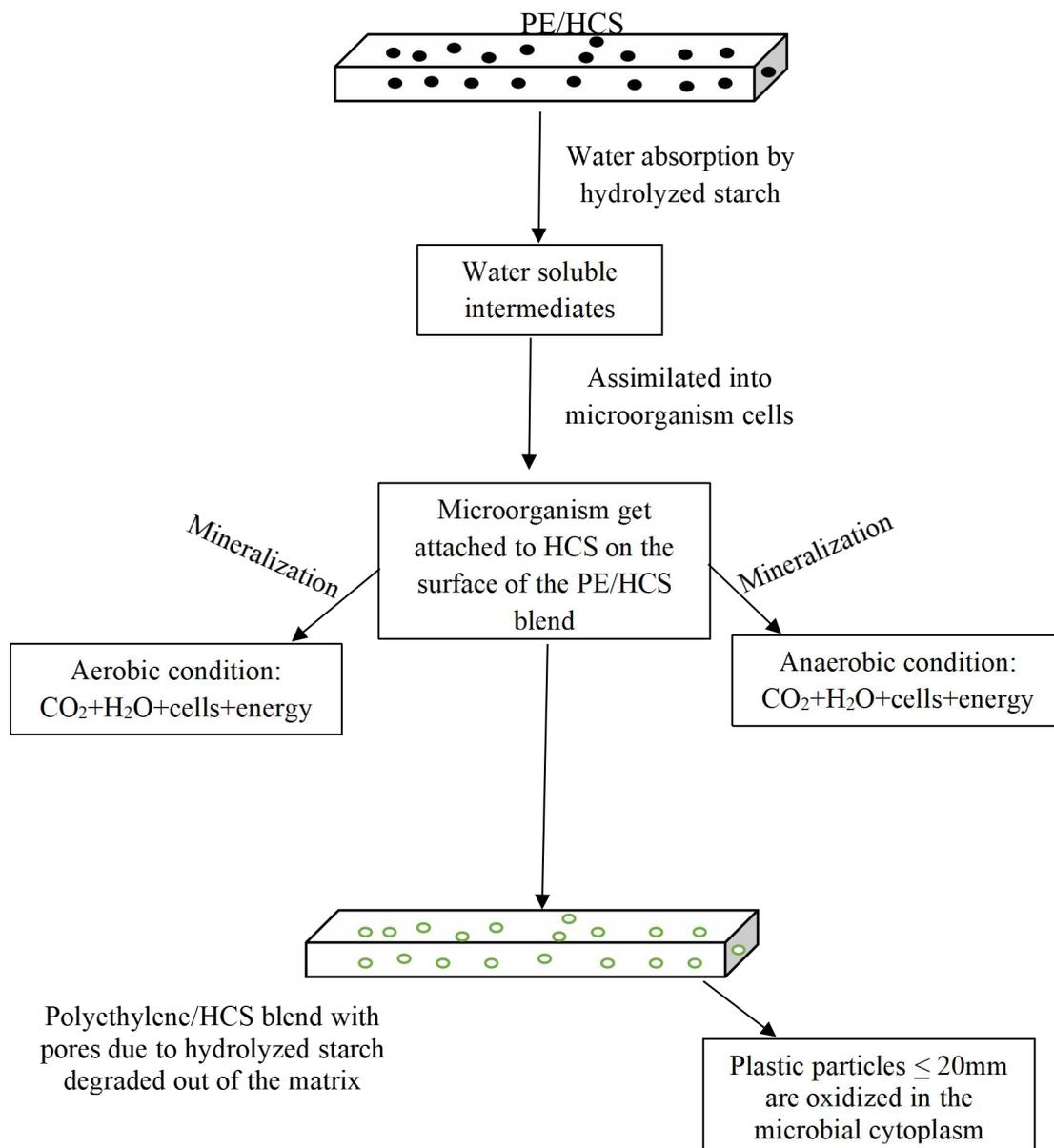
Figure 4.2: Mechanism of degradation of Polyethylene waste/HCS Blends

Source: Gautam and Kaur (2013))

The degradation of the blends buried in soil involves chemical hydrolysis and bacterial degradation followed by biological hydrolysis and oxidation. The degradation of starch in the Polyethylene waste/HCS composites involved the uptake of water by the samples which enhance the attachment of microorganisms on their surface. The degradation of starch samples by microorganisms yield carbon resulting in the hydrolysis of polymeric chains to produce water, carbon (IV) oxide and metabolic biomass (Tai *et al*., 2019). This depletes the amount of starch in the polyethylene matrix thereby reducing the amount of plastic waste in the environment.

4.5 HRSEM/EDX Analysis of Polyethylene Waste, Buried and Unburied Polyethylene waste/hydrolysed cassava starch Blends

4.5.1 HRSEM Analysis of Polyethylene Waste, Buried and Unburied Polyethylene waste/hydrolysed cassava starch Blends

The HRSEM micrographs showing the both the cross sectional and surface view of the morphology and microstructure of polyethylene waste, unburied and buried polyethylene waste/hydrolysed cassava starch blends are shown in the Plates V A, B, C, D, E and F below.
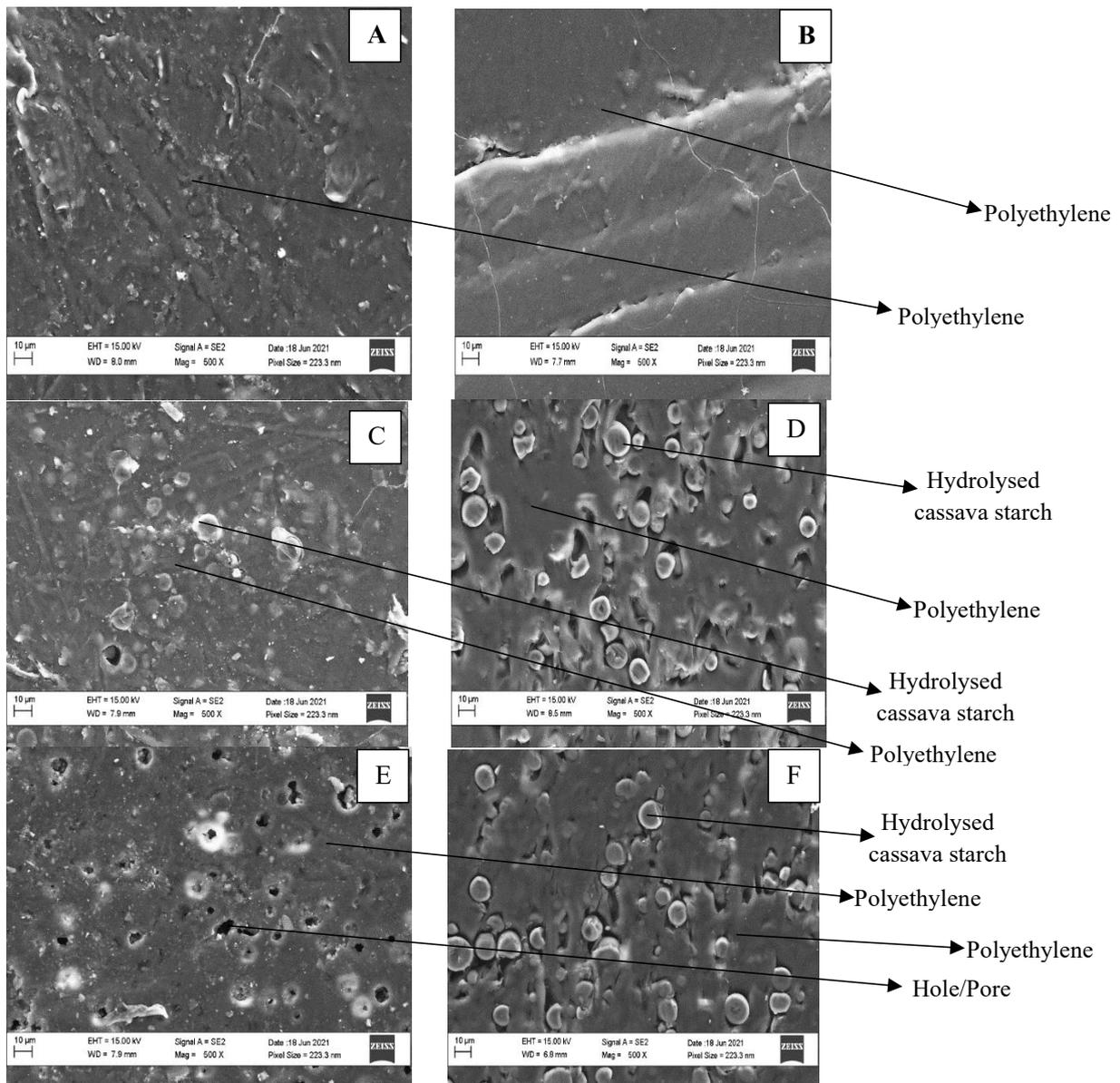
Plate V: Morphology and microstructure of 100 % polyethylene and polyethylene blends

Key: (A) surface view of polyethylene waste (B) cross sectional view of polyethylene waste (C) surface view of unburied polyethylene waste/hydrolysed cassava starch blend (D) cross sectional view of unburied polyethylene waste/hydrolysed cassava starch blend (E) surface view of buried polyethylene waste/hydrolysed cassava starch blend (F) cross sectional view of buried polyethylene waste/hydrolysed cassava starch blend

The polyethylene waste micrograph revealed a continuous microstructure without pores (holes) and particles of hydrolysed starch (Plate VA and B). Whereas, the unburied blend (Plate VC and D) revealed an even dispersion of the hydrolysed starch particles in the polyethylene matrix without pores (holes). Plate VF (cross sectional view of buried

blend) showed an even dispersion of hydrolysed starch particles while Plate VE (surface view of buried blend) showed pores (holes) within the matrix indicating partial degradation of the sheet. The pores (holes) were created when the hydrolysed starch was degraded out of the matrix. The polyethylene matrix remained smooth without any sign of degradation. The decomposition observed in the buried sample indicates that microbial activities affected only the hydrolysed starch thereby decreasing the weight of the blend depending on the amount of hydrolysed starch present in the blend samples.

4.5.2 EDX analysis of polyethylene waste, unburied and buried polyethylene waste/hydrolysed cassava starch blend

Table 4.5 shows the elemental composition of the polyethylene waste, unburied and buried polyethylene waste/hydrolysed cassava starch blends obtained from the micrographs of EDX results in Appendices F, G and H respectively.

Table 4.5: Elemental Composition of Polyethylene Waste, Unburied and Buried Polyethylene Waste/Hydrolysed Cassava Starch Blend

	Element composition (%)	
Material description	**Carbon**	**Oxygen**
Polyethylene waste	96.76	3.24
Unburied PE/HCS blend	87.81	12.19
Buried PE/HCS blend	89.98	10.02

Key: HCS = Hydrolysed cassava starch, PE = Polyethylene Waste

The EDX analysis of polyethylene waste, unburied and buried polyethylene waste/hydrolysed cassava starch blends showed the presence of C and O elements. The percentage composition of carbon is highest in the 100 % polyethylene waste sample with a value of 96.76 % and the oxygen content is a negligible value of 3.24 %. The

high value of carbon could be due to the molecular formula of polyethylene consisting mainly of carbon and hydrogen. The unburied polyethylene waste/hydrolysed cassava starch blend had the highest O content of 12.19 % and a C content of 87.81 % which could be due to the presence of hydrolysed starch in the polyethylene matrix since the molecular formula of starch contains oxygen and carbon. The buried polyethylene waste/hydrolysed cassava starch blend had a C content of 89.98 % and O content of 10.02 %. The difference in the C and O content of the unburied and buried polyethylene waste/hydrolysed cassava starch blend could be due to the degradation of hydrolysed starch from the polyethylene matrix of the buried blend (Folino 2020).

CHAPTER FIVE

5.0   CONCLUSION AND RECOMMENDATIONS

5.1   Conclusion

This study focused on the production and characterisation of plastic sheets from polyethylene waste and hydrolysed cassava starch blends. The following conclusions were drawn based on the results obtained from the study;

i.   Starch was extracted from cassava tubers by wet method and preparation of hydrolysed cassava starch by acid hydrolysis was achieved using 2.5 moldm^{-3} of H_2SO_4 at 500 rpm, at a temperature of 40 °C for 10 days.

ii. The HRSEM of the morphology and structure of the cassava starch granules revealed smooth and spherical particle sizes which significantly changed after acid hydrolysis to an etched and clogged particles.

iii. The EDX analysis of the Cassava starch and hydrolysed cassava starch revealed Cassava starch had 60.54 % C and 39.46 % O while HCS had 55.23 % C and 44.77 % O. The decrease in the C and increase in O contents can be associated with the scission of C-O bond in the starch by H_3O^+ and subsequent hydrolysis to produce additional hydroxyl groups.

iv. Production of plastic sheets by melt blending of polyethylene wastes and hydrolysed cassava starch using two roll mixer was achieved.

v.   The incorporation of hydrolysed cassava starch in the polyethylene waste blends decreased the thermal stability of the polyethylene waste/HCS blends as amount of hydrolysed cassava starch increased.

vi. Water absorption capacity of the 100 % polyethylene waste was 0 % while water absorption capacity of the polyethylene waste/hydrolysed starch blend increased from 0.642 to 1.285 % as the hydrolysed starch in the blends increased.

vii. Hardness decreased from 98.667 to 96.333 Nmm^2 as the amount of hydrolysed cassava starch in the blends increased.

viii. Impact strength decreased from 1.981 to 0.376 J/m^2 as the amount of hydrolysed cassava starch in the blends increased.

ix. 100 % polyethylene waste sample did not lose weight throughout the 22 weeks of the soil burial test. The maximum weight loss of 5.92 % was found in polyethylene waste/hydrolysed cassava starch blend (50:50). This indicates that the rate of degradation of polyethylene waste/HCS blends is directly proportional to the amount of hydrolysed cassava starch in the blend.

x. The HRSEM of the 100 % Polyethylene waste revealed a smooth and continuous morphology with no holes. The unburied polyethylene waste/hydrolysed cassava starch blend showed a homogeneous distribution of hydrolysed starch particles while the buried polyethylene waste/hydrolysed cassava starch blend showed homogeneous dispersion of pores. These pores were created when the hydrolysed starch was degraded out of the matrix. The matrix remained smooth without signs of degradation. This indicates that microbial activities affected only the hydrolysed starch decreasing the entire weight of the blend.

xi. The addition of hydrolysed cassava starch to plastics in general reduces the amount of synthetic plastic in the environment.

5.2   Recommendations

Based on the results of the analysis, the following recommendations are made;

i.   The implementation of sustainable practices will help minimize environmental pollution and conserve resources for future generations and the need to adopt environmental stewardship and sustainability.

ii.   Hydrolysed cassava starch is poised to establish an even stronger role in the manufacture of sustainable plastics and other bio-products largely because starch is abundant, renewable, and inexpensive. Strategies for improving the properties of hydrolysed cassava starch -based plastics such as blending hydrolysed cassava starch with other polymers and using hydrolysed cassava starch in composite materials to make biopolymers need to be implemented in developing viable replacements for petroleum based plastics

iii.   Further studies could be carried out to get an idea of the best percentage of hydrolysed cassava starch that can be added to polyethylene to produce blends that can be most useful for packaging and household items.

5.3   Contributions to Knowledge

This study employed the use of hydrolysed cassava starch as filler in polyethylene waste (pure water sachet) matrix to produce a blend of plastic sheet. The addition of hydrolysed cassava starch to polyethylene waste decreased mechanical properties and thermal stability, but increased water absorption capacity and response to microbial attack of the polyethylene waste hydrolysed cassava starch blend. The addition of hydrolysed cassava starch to polyethylene waste will result in the significant reduction in the amount or polyethylene waste in curriculum.

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APPENDICES

APPENDIX A

The EDX micrograph showing the elemental composition of the unhydrolysed cassava

starch is shown in Appendix A below.
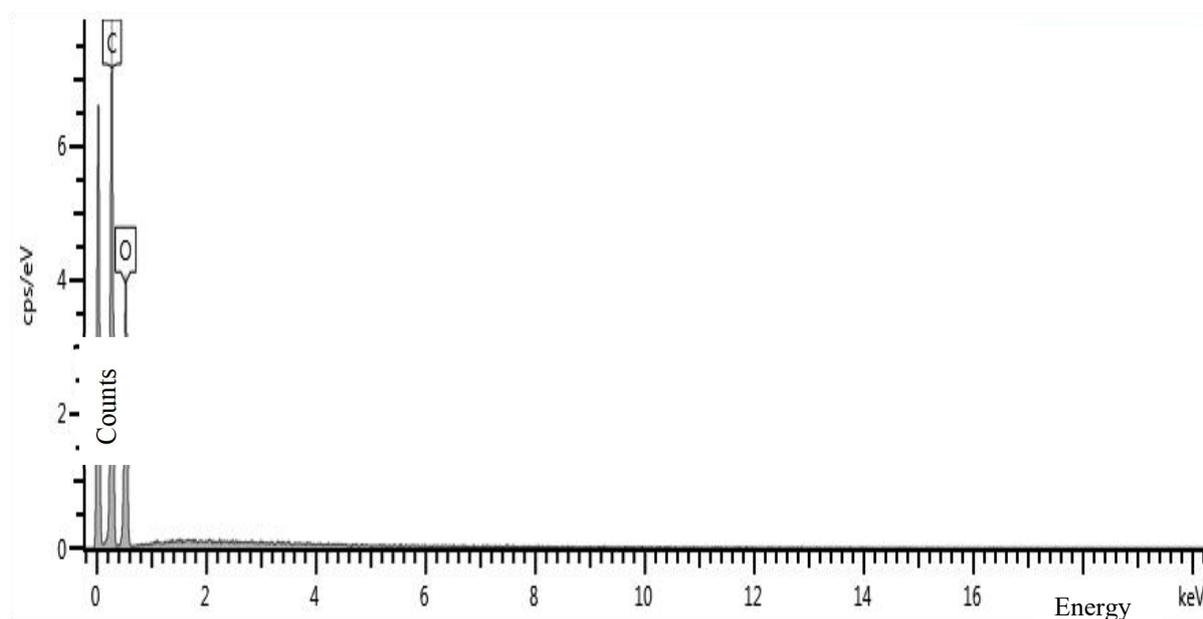
Appendix A: EDX result of unhydrolysed cassava starch

APPENDIX B

The EDX micrograph showing the elemental composition of the hydrolysed cassava starch is shown in Appendix B below.
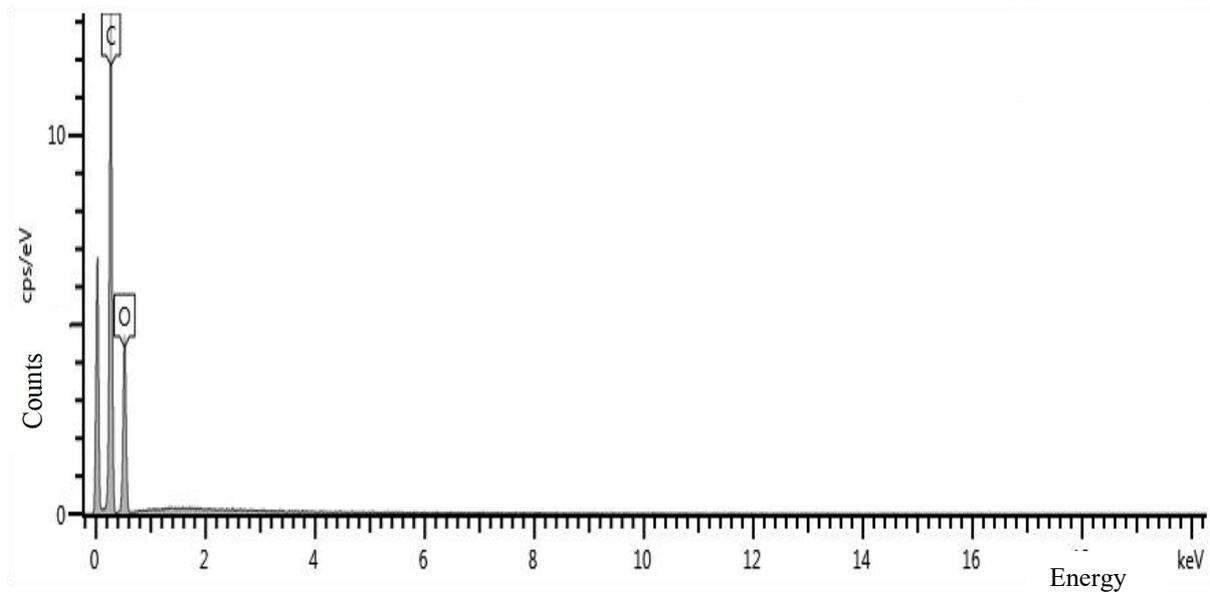
Appendix B: EDX result of Hydrolysed cassava starch

APPENDIX C

The TGA curves of polyethylene and polyethylene waste/hydrolysed cassava starch blends are shown in Appendix C below:
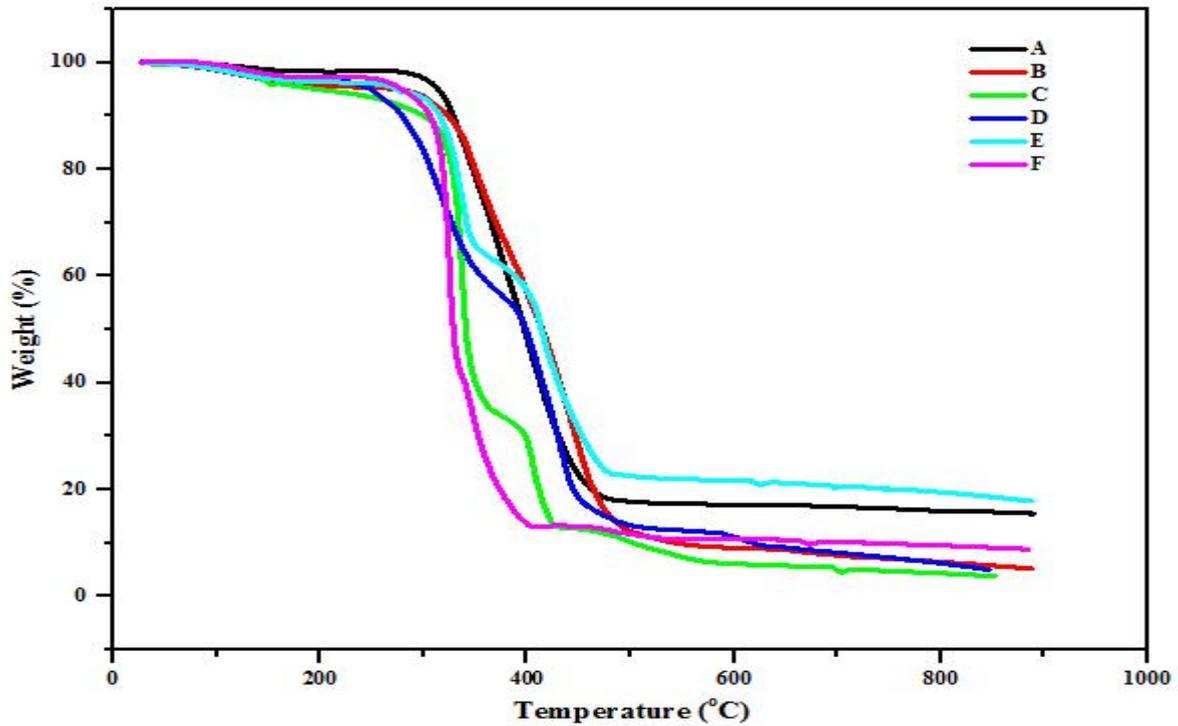
Appendix C: TGA curves of polyethylene waste and polyethylene waste/HCS blends

Keys: A = 0 % HCS, **B** = 10 % HCS, **C** = 20 %HCS, **D** = 30 %HCS, **E** = 40 % HCS, **F** = 50 % HCS
HCS= Hydrolysed cassava starch

APPENDIX D

The DTG curves of polyethylene and polyethylene waste/hydrolysed cassava starch blends are shown in Appendix D below:
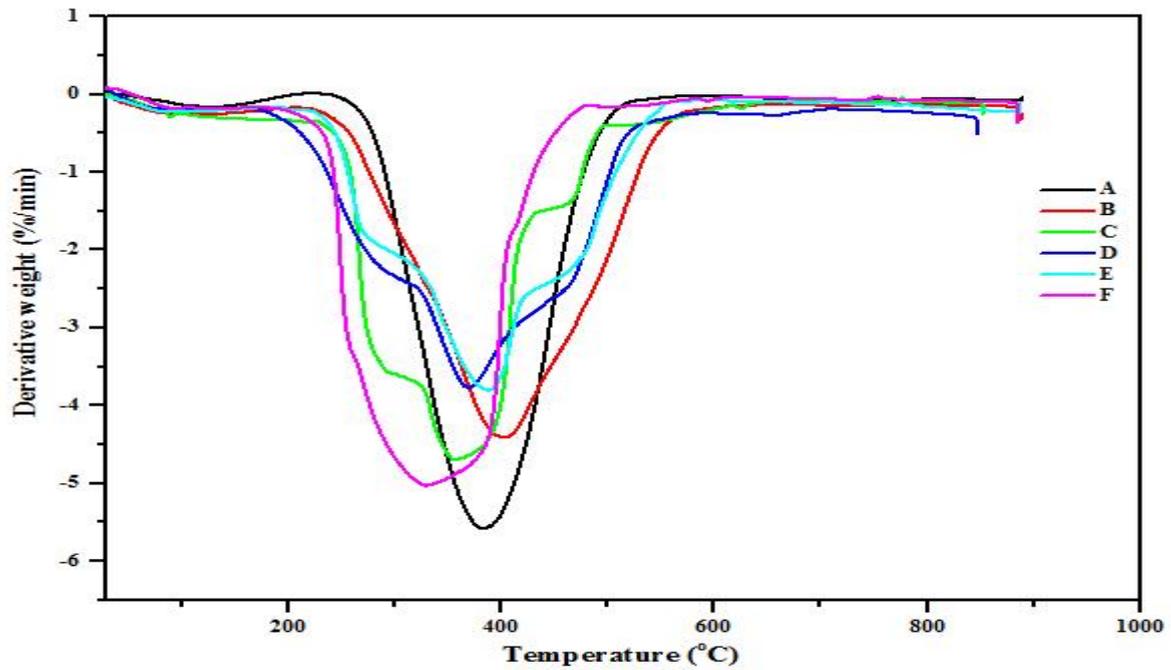
Appendix D: DTG curves of polyethylene waste and polyethylene waste/HCS blends

Keys: A = 0 % HCS, **B** = 10 % HCS, **C** = 20 %HCS, **D** = 30 %HCS, **E** = 40 % HCS, **F** = 50 % HCS, HCS= Hydrolysed cassava starch

The mass of 100% polyethylene wastes and samples of polyethylene containing various percentage of hydrolysed starch recorded over 22 weeks of burial are plotted in Appendix E below.
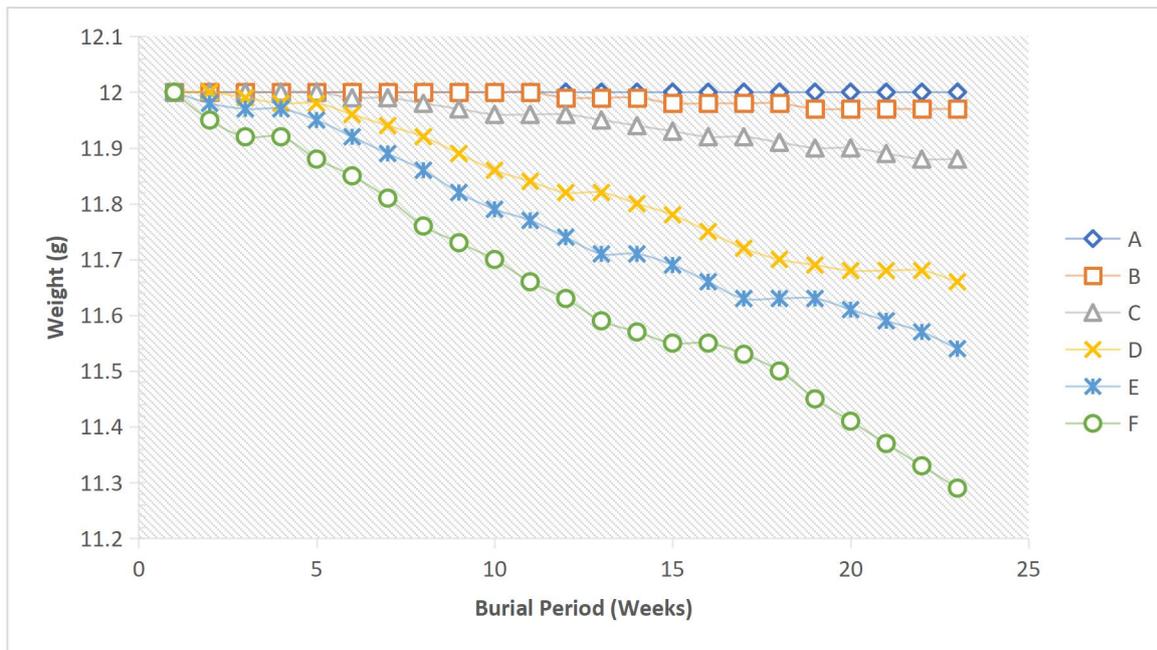

Appendix E: Degradation of polyethylene waste/hydrolysed starch blends

Keys: A = 0 % HCS, **B** = 10 % HCS, **C** = 20 %HCS, **D** = 30 %HCS, **E** = 40 % HCS, **F** = 50 % HCS, HCS= Hydrolysed cassava starch

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APPENDIX F

The EDX micrograph showing the elemental composition of polyethylene waste is shown in Appendix F below.
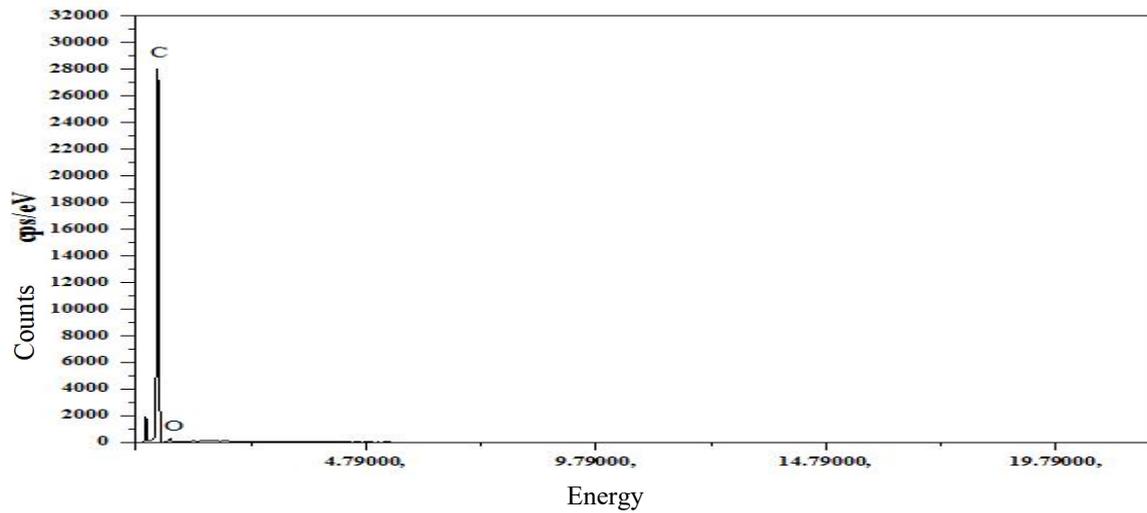
**Appendix F: EDX micrograph of polyethylene waste**

APPENDIX G

The EDX micrograph showing the elemental composition of unburied polyethylene waste/hydrolysed cassava starch blend are shown in Appendix G below.
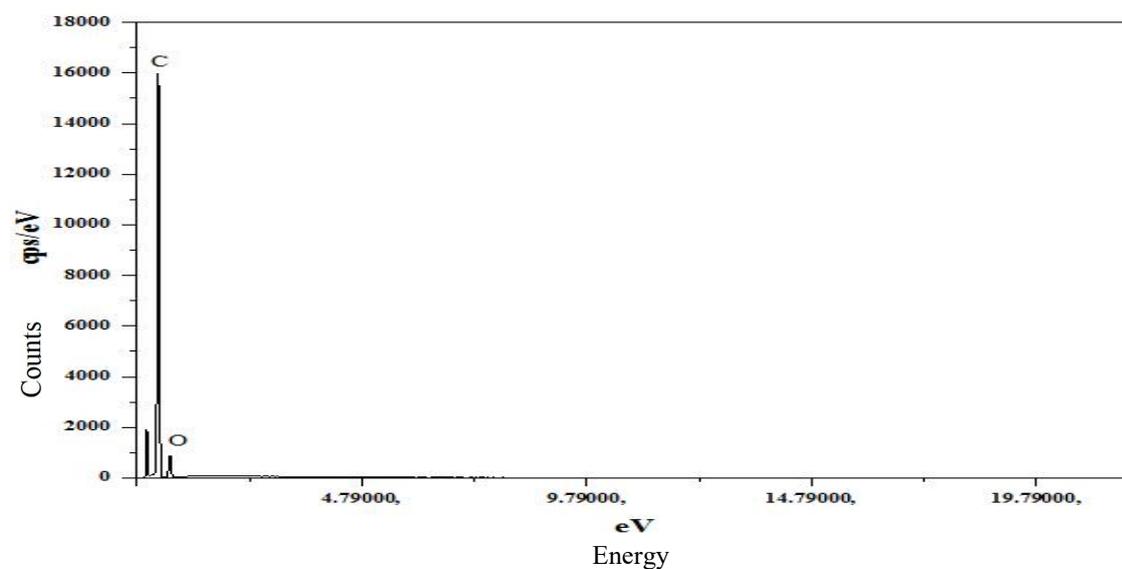
Appendix G: EDX of unburied polyethylene waste/hydrolysed starch blend

APPENDIX H

The EDX micrograph showing the elemental composition of buried polyethylene waste/hydrolysed cassava starch blend is shown in Appendix H below.
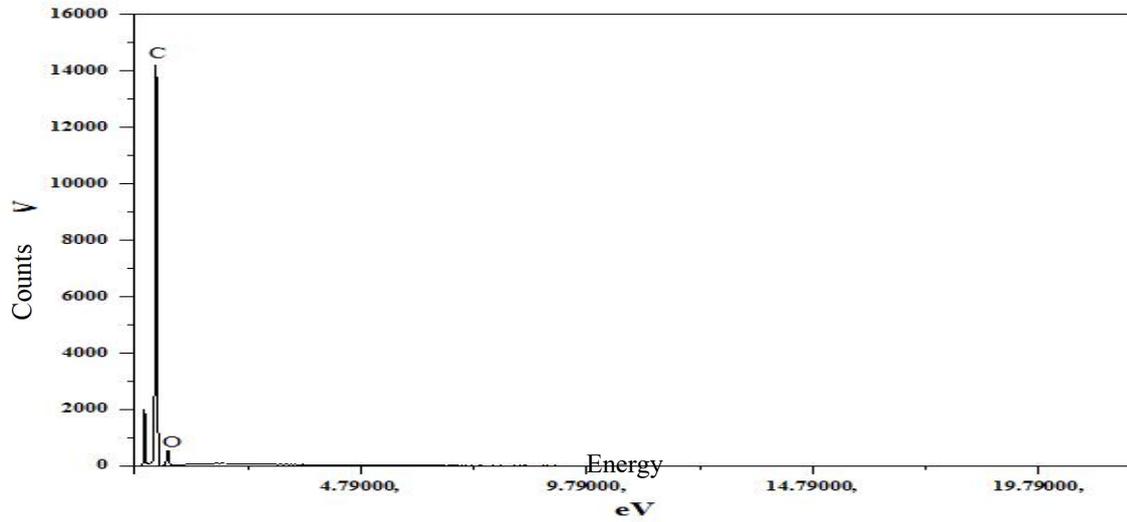
Appendix H: EDX of buried polyethylene waste/hydrolysed cassava starch blend