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Evaluating the decomposition characteristics of organic wastes and synthetic plastics

Wilfred, Osita Ekene

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Evaluating the decomposition characteristics of organic wastes and synthetic plastics



PRIFYSGOL
BANGOR
UNIVERSITY

A dissertation by

Osita Ekene Wilfred

Submitted to the College of Environmental Sciences and Engineering

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Supervisors

Dr Paula Roberts

Dr Vera Fitzsimmons-Thoss

ABSTRACT

Improper waste handling of mixed municipal solid waste (MSW) without material and energy recovery leads to human health problems, environmental pollution, and loss of resources. In contrast, proper handling of these wastes can sustain a circular economy and support an effective and efficient waste management system that reduces the volume of wastes that go into the environment.

This thesis evaluated the decomposition and distribution of 2 key fractions of the waste stream, namely, organic wastes and plastics. The chemical properties of Municipal Solid Waste (MSW) composts made in Nigeria's wet and dry seasons were evaluated to determine their significant differences. These properties included pH, electrical conductivity (EC), organic matter (OM), carbon content, nitrogen content, C/N ratio, phosphorus, potassium, calcium, sodium, and magnesium contents. The heavy metals are chromium, copper, nickel, lead, zinc, and iron. The results revealed seasonal variations in the properties of compost made in Nigeria except for nitrogen content.

The results showed that pH, electrical conductivity (EC), organic matter (OM), carbon content and C/N ratio were significantly influenced by seasonality and higher in the wet season than in the dry season. Phosphorus, potassium, calcium, and heavy metals: chromium, copper, nickel, lead, zinc, and iron were significantly higher in the dry season than in the wet season, except for sodium and magnesium, which were slightly higher in the wet season than the dry season. Higher contents in the dry season were simply from dilution effects; they were leached out during the wet seasons. The EC of composts made in the wet and dry seasons were 4534.17 and 2631.58 μScm^{-1} , higher than the optimal values (750 to 2000 μScm^{-1}). The reason for this is that the type of feedstock (food waste) used in composting was very high in water-soluble salts and will influence the activity of the microorganisms during composting.

The identification and distribution of plastic wastes were conducted in three dumpsites in Owerri, Imo State, in Nigeria. A total of 97, 117 and 129 unknown plastic wastes were collected from Irete, Orogwe and Nekede dumpsites. The unknown plastics were identified using Fourier transform infrared (FT-IR) spectroscopy, ascertaining if the weight of plastic materials was directly related to their mobility off-site (dumpsites). The result revealed that PP, PET and PE were the most abundant plastic polymer wastes (36, 27, and 25%) respectively in the three dumpsites, with the weight of the plastic wastes significantly influencing their movement away from the three dumpsites. The degradation of five plastics (Polyamide 6 (PA-6), Polyethylene terephthalate (PET), High-density polyethylene (HDPE), Low-density polyethylene (LDPE), and Polypropylene (PP)) was investigated in an open field in substrates; soil, compost, and leachate for 24 months in the UK and Nigeria and under laboratory conditions using directly three white-rot fungi (WRF), namely, *Phanerochaete Chrysosporium*, *Ceriporiopsis Subvermispora* and *Trametes Versicolor*, for 12 weeks. At different time intervals, these plastics were studied to track their degradation rate. The degradation study was monitored by visual observation, light microscopy, weight loss, FTIR, carbonyl index (CI), scanning electron microscopy (SEM), and tensile strength analysis.

Visual observation, light microscopy and SEM showed notable changes such as discolouration, roughness, grooves, and biofilm formation on the plastic surfaces, which altered the surface properties of plastics. Their weights fluctuated in the substrates, and with the WRF, HDPE discs from Nigerian soil had the highest weight loss of 5 %, while PP had the most weight gain of 2.1 % from UK compost after 24 months. In the laboratory experiment with the WRF, the PA discs had the highest weight loss of 2% with *T. Versicolor*, while PP had the most weight gain of 1.3 % with *T. Versicolor*. The fluctuations were due to microbial activities or water absorbed from different environments. There were significant differences in weight loss and

reduction in the thickness of plastic discs over time in substrates used for the study.

FTIR spectra and CI revealed reductions in the peak intensities, progressive shifts of peaks, disappearances, and formation of new peaks, which are attributed to oxidation, hydrolysis and depletion of the functional groups of the plastics. Lastly, the tensile strength of all plastics decreased during the degradation study but at different rates. It was also significantly influenced over time in all the substrates used for the degradation study. PET had the highest loss in tensile strength, 22 %, in UK compost, while PP had the least loss in tensile strength, 0.1%, in UK soil after 24 months. These changes became more apparent at 18 and 24 months in substrates and 12 weeks with WRF, especially on the sides of the plastics affected by mechanical shearing.

This research provides underpinning evidence that the properties of MSW composts made in Nigeria were influenced by seasonality. Also, the degradation of synthetic plastics in substrates and white-rot fungi (WRF) was a slow process. It becomes necessary to consider follow-up research by introducing initiators that present new functional groups, thereby producing free radicals on the plastics that will modify and break up their long chains before biodegradation. Also, extending the plastic time in both substrates and WRF could be done to see if it will increase the degradability of plastics.

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ABBREVIATIONS

| | |
|-------------------|----------------------------------------------------|
| AfDB | African Development Bank |
| Al | Aluminium |
| ANOVA | Analysis of Variance |
| ASTM-D | American Society for Testing and Materials |
| ATR | Attenuated Total Reflectance |
| AU | Absorbance Unit |
| BFI | bacterial-Fungal Interaction |
| B.D | Before Degradation |
| C | Carbon |
| Ca | Calcium |
| Cd | Cadmium |
| C-C | Carbon-Carbon |
| C-H | Carbon-Hydrogen |
| CH ₃ | Methyl |
| CH ₄ | Methane |
| CI | Carbonyl Index |
| C.I | Confidence Interval |
| Cl | Chlorine |
| cm | Centimetre |
| C/N | Carbon/Nitrogen ratio |
| Co | Cobalt |
| CO ₂ | Carbon dioxide |
| Cr | Chromium |
| Cu | Copper |
| CuSO ₄ | Copper (II) Sulfate |
| °C | Degrees Celsius |
| DDT | Dichlorodiphenyltrichloroethane |
| DTP | Diethylene glycol terephthalate |
| DEFRA | Department for Environment, Food and Rural Affairs |
| dH ₂ O | De-ionised Water |
| dw | Dry Matter |
| EC | Electrical Conductivity |

| | |
|---------------------------------|-------------------------------------------|
| EPA | Environmental Protection Agency |
| EU | European Union |
| EVA | Ethylene Vinyl Acetate |
| *E | Elements |
| Fw | Fresh Weight |
| FAAS | Flame Atomic Absorption Spectroscopy |
| Fe | Iron |
| FES | Flame Emission Spectroscopy |
| FeSO ₄ | Iron Sulfate |
| FEPA | Federal Environmental Protection Agency |
| FTIR | Fourier Transform Infrared |
| fw | Fresh Weight |
| g | Grams |
| GC/MS | Gas Chromatography Mass Spectroscopy |
| GHGs | Green House Gases |
| GPD | Gross Domestic Product |
| H | Hydrogen |
| HCl | Hydrochloric acid |
| HDPE | High-Density Polyethylene |
| H ₂ O | Water |
| H ₂ O ₂ | Hydrogen Peroxide |
| H ₂ SO ₄ | Dihydrogen Sulfate |
| HPO ₄ | Hydrogen Phosphate |
| H ₂ PO ₄ | Dihydrogen Phosphate |
| ISEPA | Imo State Environmental Protection Agency |
| K | Potassium |
| KH ₂ PO ₄ | Potassium dihydrogen Phosphate |
| kg | Kilogram |
| kg/m ² | Kilogram/metre squared |
| km | Kilometres |
| L | Litre |
| LDPE | Low-Density Polyethylene |
| LLDPE | Linear Low-Density Polyethylene |
| LOI | Loss on Ignition |

| | |
|------------------------------|----------------------------------|
| MC | Moisture Content |
| Mg | Magnesium |
| mg | Milligrams |
| MgSO ₄ | Magnesium Sulfate |
| MnSO ₄ | Manganese Sulfate |
| Mo | Molybdenum |
| MSW | Municipal Solid Waste |
| N | Nitrogen |
| NDC | Nigerian Dry Compost |
| NWC | Nigerian Wet Compost |
| ns | No significance |
| NO ₃ | Nitrate |
| Na | Sodium |
| NH ₄ ⁺ | Ammonium Ion |
| Ni | Nickel |
| OM | Organic Matter |
| OPE | Oxidized Polyethylene |
| P | Phosphorus |
| PA | Polyamide |
| PAHs | Polycyclic Aromatic Hydrocarbons |
| Pb | Lead |
| PAN | Polyacrylonitrile |
| PAS-100 | Publicly Available Specification |
| PCBs | polychlorinated biphenyls |
| PCL | Poly Caprolactone |
| PE | Polyethylene |
| PET | Polyethylene terephthalate |
| PHB | Polyhydroxy butyrate |
| PMMA | Polymethyl methacrylate |
| PP | Polypropylene |
| PS | Polystyrene |
| PUR | Polyurethane |
| PVC | Polyvinyl chloride |
| SDS | Sodium Dodecyl Sulfate |

| | |
|----------------------|----------------------------------------------|
| SE | Standard Error |
| SEM | Scanning Electron Microscope |
| SITA | Société Industrielle de Transport Automobile |
| SPREP | South Pacific Environment Programme |
| SWM | Solid Waste Management |
| TF | Teflon |
| TXRF | Total Reflection X-ray Fluorescence |
| TOC | Total Organic Carbon |
| TN | Total Nitrogen |
| TNT | Trinitrotoluene |
| UK | United Kingdom |
| UN | United Nations |
| UNEP | United Nation Environmental Programme |
| USA | United States of America |
| USEPA | United State Environmental Protection Agency |
| UV | Ultra-Violet |
| μL^{-1} | Microgram Litre |
| μScm^{-1} | Microgram Siemens/centimetre |
| WHO | World Health Organization |
| wm | Wet Matter |
| WRF | White-Rot Fungi |
| XRF | X-ray Fluorescence |
| Zn | Zinc |
| ZnSO ₄ | Zinc Sulfate |

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CHAPTER 1

1.1 Introduction

This chapter describes the background of the research presented in this thesis. It shows the study's justification and the objectives the investigation will achieve. The main hypotheses and general thesis structure are also revealed in this chapter.

The UK generated 509 million tonnes of municipal waste in 2010; however, this figure has reduced to about 463 million tonnes in 2019 (Eurostat- ENV_WASMUN). Though some of this household waste still ends up in landfills, about 67.2% of the total generated waste is recovered (DEFRA, 2021). For example, Stats Wales (2012) suggested that more than one million tonnes of waste were sent to landfills in Wales between 2004-2005, although owing to policies regarding recycling, this figure fell to 592,000 between 2010-2011.

Nigeria, on the other hand, being a developing country with a population of over 200 million people, generates around 43.2 million tonnes of solid waste annually from households, industries, hospitals, artisans, and traders, out of which 20-30% is collected (Rahimi and Garcia, 2017). This makes Nigeria the largest generator of solid waste in Africa. It is also projected that by 2025 with an increase in the population to about 233.5 million people, Nigeria will generate an estimated 72.5 million tonnes of waste annually at a rate of 0.85 kg waste/capita/day; this is $\frac{1}{4}$ of total waste that will be generated in the whole of Africa (Arogundade, 2020). While the total solid waste sent to the landfills in the western countries, e.g., the UK, is reducing, the total waste generated in the developing countries such as Nigeria is increasing. The reason is that the UK has effective structure/legislation to manage waste from generation to disposal, which developing countries lack. In Nigeria and other developing countries, solid waste management is one of the leading environmental challenges which affect these countries. Reasons being because of the rate at which they are generated, improper collection and disposal, high cost accompanying its management across the states, absence of understanding over a range of factors affecting the different phases of waste management and the linkages required to allow the whole handling system to function (Guerrero et al., 2013). Also, because of the lack of legislation enforcing an effective and sustainable waste management scheme, the mixed components of waste generated are sent to landfills, dumpsites, or burnt at times with no form of material and energy recovery. Fig. 1.1 A and B reveal what dumpsites look like in Nigeria.



Fig. 1.1 Picture of a dumpsite set ablaze in Nigeria (Image from Arogundade, S (Nigeria))

The public understands the environmental issues associated with sending waste to landfills/dumpsites in Western and Developing Countries. These environmental issues have led to strict legislation in western countries, but not in developing countries. Because there is minimal control on waste sent to dumpsites in developing countries, solid and liquid wastes from different sectors are disposed of together, leading to contamination of ground and surface water, pollution of the soil, and emission of GHGs (Schiopu and Ghinea, 2013). The production of contaminated water known as dumpsite leachate with a high concentration of heavy metals such as Cd, Zn, Fe, Ni, Pb, Cu and ionic compounds such as NH_4^+ , Na^+ , K^+ , Cl^- , forming soluble salts is also a consequence of sending waste to dumpsites (Aronsson et al., 2010; Zupanc and Justin, 2010). A high concentration of soluble salts such as Na^+ and Cl^- leads to salinity problems, influencing the produced leachate's electrical conductivity. Once the leachate gets to the soil, it affects the soil profile by causing salt stress in plants (Zhu, 2001), osmotic stress (Tuncur et al., 2011) and ionic imbalance (Mukhtar et al., 2018).

Compost is a biologically stabilized product formed from the controlled aerobic decomposition of the organic fraction of Municipal Solid Waste (MSW) (Ayilara et al., 2020). Composting offers advantages over landfilling or burning because its production is cost-effective, generates work, and the usage of its product practically (Ayilara et al., 2020).

The major biodegradable waste used in this research is the solid waste generated by households, businesses, markets, food outlets, and industries, known as municipal solid waste (MSW). The compost produced in Nigeria will be sampled during the rainy and dry season and evaluated to check its physiochemical properties and possible effects of soil application since local farmers solely depend on it for soil amendments.

Plastic is a word from the Greek term 'Plastikos', meaning fit for moulding. They are pliable during production, which lets them be cast, pressed, or extruded into various shapes. The development of plastic materials passed through several historical stages, becoming today the most used material worldwide (Millet et al., 2018). Plastics are significant to our everyday lifestyle and prevalent in the environment after use because they have exceptional properties

compared to other materials. They are cheap, lightweight, durable, sturdy, resist corrosion, and have outstanding thermal and electric lagging properties. Many natural plastics exist, such as asphalt, cellulose, shellac, and rubber. However, the first synthetic plastic production was manufactured in 1909 with the production of a phenol-formaldehyde plastic known as Bakelite by L. H. Baekeland. These phenolic materials made are very significant engineering plastics. The production of other synthetic and semi-synthetic polymeric materials continued mainly from fossil carbon bases such as crude oil and natural gas (Gomez and Michel, 2013). Plastics have gained attention in today's world because of their widespread use. Especially in the packaging industries, where about 42% of plastics have been used for packaging, they mainly comprise PE, PP, and PET (Andrady et al., 2009; Geyer et al., 2017). Plastics are used mainly for packaging applications such as food, pharmaceuticals, cosmetics, detergents, and chemicals. It has replaced paper and cellulose-based products for packaging because of its better properties, including its strength, lightness, and resistance to water (Barns et al., 2009). Plastic materials are produced in large quantities because of their desirable properties. Their production became significant in 1940, with about 1.5 million metric tonnes produced in 1950 (World Plastic Production Report). Since then, an upsurge in the volume of plastic produced each year has been observed, with about 300 million metric tons produced in 2015 (see fig. 1.2).

However, the quantity of plastic production has stayed moderately stable over the last decades (Ivleva et al., 2017). These are the most used plastics; polyethylene (high and low density: HDPE, LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC). The properties that make them desirable are the same properties that raise environmental concerns after their end of life. They are resistant to many environmental influences and end up as pollutants in marine and terrestrial ecosystems, making recycling difficult. The reason is because of the raw materials used in their production, such as plasticizers, stabilizers, fillers, pigments and reinforcing agents, which improve their mechanical properties by reducing or preventing degradation.

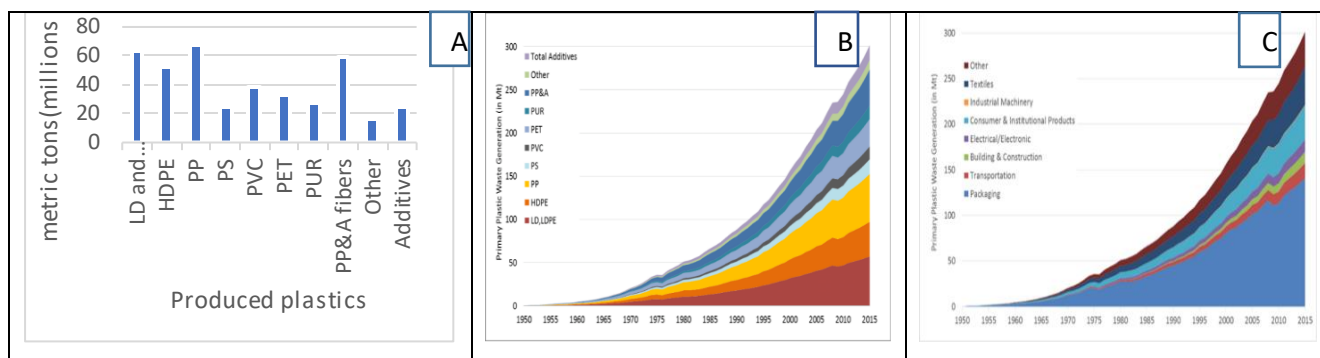


Fig. 1.2 A is the global plastics production, B is plastic waste generation according to polymer type and C the plastic waste generation according to industrial use (all in million metric tons) 1950 to 2015 (Geyer, et al., 2017) .

However, many studies have tried to evaluate the degradation rate of these plastics in natural and controlled environments or employ microorganisms to enhance their degradation rate. Some have also tried blending these plastics with attractive natural biodegradable biopolymers such as starch and cellulose because they are cheap with low density and can be blended with these plastics to produce composites with tailored properties. The increased surface area of the synthetic bulk plastic makes it more susceptible to degradation. Thus, increasing the rate of degradation (Doble et al., 2008; Rivero et al., 2009; Borghei et al., 2010; Wilfred et al., 2018; Luthra et al., 2020).

Efforts to produce plastic materials from renewable resources which will undergo biodegradation in a short period without leaving toxic remains are increasing; the aim here is to replace the long persisting conventional plastics made from non-renewable resources (Song et al., 2009).

It is against this background of tighter regulation, sustainability challenges, and high costs linked to pollution management. This research project investigates two leading components of the municipal solid waste stream, namely, compost, the fastest growing waste, which is a product formed from the breakdown of the biodegradable portion of the dumpsites since middle/low-class farmers use this product to increase soil quality and plant yields. Secondly, plastic materials, also increasing components of waste after biodegradable materials, will be considered. Their identification, abundance, composition, and distribution away from Nigerian dumpsites will be measured, and finally, we will evaluate their rate of degradation in soil, compost, leachate, and with known fungi.

The findings from this study will contribute to the efforts of different governments towards developing and sustaining the circular economy (Velenturf, and Purnell, 2021) towards effective and efficient waste management to help:

- Reduce environmental footprint

- Minimize waste generated
- Reduce resource dependency
- Increase income

Waste processors, waste site operators, policy, and decision-makers will use the findings from this study to enlighten/ educate the public, most especially the local farmers that solely depend on MSW compost for their farmlands, to know the physicochemical properties of such compost, whether their properties are within required standard. The study will provide information about the plastic accumulation and dispersal away from the dumpsites/landfills. Finally, it will reveal the effects of exposing plastic materials to natural environments and employing known fungi in the degradation study, estimating how long it will take to completely degrade these plastics in different substrates.

1.2 Objectives of the study

The general objective of this study is to understand the prevalence of the main leading components of the Municipal Solid Waste (MSW) stream in Nigeria, namely, the compost and the plastics, and evaluate their decomposition characteristics through understanding the specific objectives, which are:

- a) Analysing the chemical and physical properties of compost made seasonally in Nigeria.
- b) Identify plastic wastes from mixed MSW in Nigerian dumpsites using the Fourier transform infrared spectroscopy (FTIR) method.
- c)) Determine the weight and quantity of plastics at distances away from the dumpsites.
- d) Understand the degradation of plastics (PA-6, PET, PP, HDPE, and LDPE) in different substrates, namely, soil, compost, and leachate in temperate and tropical zones—the zones are in the United Kingdom and Nigeria.
- e) Study the rate and effects of microbial degradation of plastic discs; - PA, PET, PP, HDPE, and LDPE using fungi; *P. Chrysosporium*, *C. Subvermispora*, and *T. Versicolor*.

1.3 Hypotheses

This study puts forward the following main hypotheses:

- a) Seasonal variability influences the chemical properties of compost made from Nigerian MSW.
- b) FTIR Spectroscopy can identify unknown plastic materials
- c) PP, PET and PE plastic wastes dominate most dumpsites in Nigeria.
- d) The rate of degradation of PET, LDPE, HDPE, PP and PA-6 differs significantly among plastics in soil, compost, and leachate between temperate to tropical regions.

- e) White Rot Fungi (WRF) alters the surface properties of plastics - PA-6, PET, PP, HDPE, and LDPE.

1.4 Structure of thesis

This thesis is divided into eight chapters. Fig.1.3 displayed the schematic presentation of the thesis outline with the blue boxes showing the chapters from chapters 1 -8 while the research questions are in white boxes beside them. The following is a brief outline of this thesis.

Chapter one covered the general introduction of the research with precise aims and objectives, hypothesis, and research questions which the experimental chapters answered.

Chapter two reviewed related academic research literature published concerning Solid waste management practices in Nigeria compared to other developed countries. It makes available the key definitions that will be beneficial in understanding the rest of the thesis. This chapter is structured in a progressive form of municipal solid waste and its prevailing solutions. Also, this chapter discussed the classification of wastes, the global trend of solid waste management, and the overview of solid waste management in developed and developing countries, including Nigeria. The primary importance of reviewing other literature in this chapter was to find out about the newest trends, required information to conduct further research and support the suggestion to advance further for the experimental research. Studies of the published materials on such a topic led to knowing the controlling and crucial facts in the research before conducting the laboratory experiments. **Chapter three** covered the detailed study area description of the dumpsite locations in Nigeria, locations where we sampled our substrates for degradation purposes, locations where our degradation experiments occurred, and the general methods used during this research. A comprehensive outline of how each laboratory procedure was set up and how the analyses were carried out, including all instruments and apparatuses used.

Chapter four investigated the seasonal differences in physio-chemical properties of organic wastes endpoint. Here we took records of feedstocks and analysed finished composts produced during Nigeria's dry and rainy seasons. Nutrients, heavy metals, and other organic components were tested in the reprocessed organic manure. **Chapter five** examined the relative abundance, composition, and distribution of waste plastics away from three Nigerian dumpsites. Here, FTIR spectroscopy was the analytical technique employed to identify these plastic wastes from these dumpsites, know their most dominant compositions, and check if lighter plastic materials move further away from the dumpsites. **Chapter six** ascertained the degradation of different plastics in soil, compost, and leachate in the temperate zone, the UK, and the tropical zone,

Nigeria. **Chapter seven** evaluated the degradation of plastics using known microorganisms to see how they influence these plastics. **Chapters eight and nine** looked at the general discussion, conclusion, contributions made to the body of the knowledge and industry, limitations, and recommendations from this study.

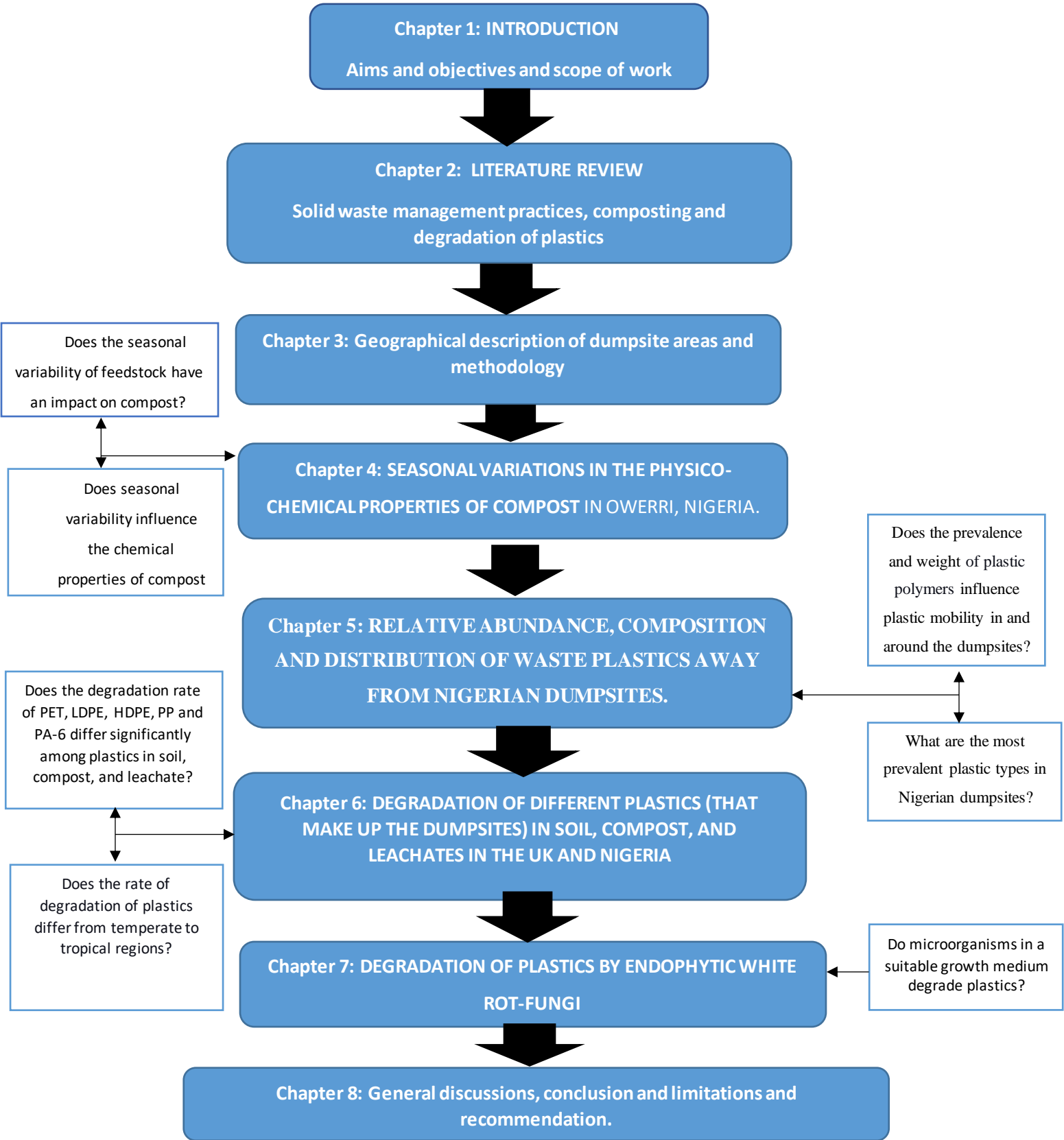


Fig. 1.3 Schematic Presentation of Thesis Outline.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews academic research literature published concerning solid waste management practices in developing countries such as Nigeria compared to other developed countries. It provides the key definitions that will be beneficial in understanding the rest of the thesis. This chapter follows a progressive form. It discusses the classification of wastes, the global trend of solid waste management, and the overview of municipal solid waste and its comprehensive solutions in developed and developing countries, including Nigeria. It considers composting as a branch of solid waste management. The nutrients and heavy metals linked to composting process, plastics as constituents of Nigerian dumpsites and the feedstock (organic wastes) available seasonally for composting, knowing it will affect the chemistry of plastics when used for plastic degradation.

Reviewing other literature in this chapter is important to discover the newest trends and the required information to conduct further research and support the suggestion to advance further for the experimental research. Studies of the published materials on such a topic led to understanding the controlling and crucial facts in composting and plastic degradation before conducting the laboratory experiments.

2.2 Solid Wastes.

All day-to-day activities generate a variety of different wastes arising from several sources. Solid waste (SW) is substantial portions of the thrown-away materials which are not in liquid or gaseous form. It includes agricultural, healthcare, human and animal, mining, mineral, and radioactive waste. AfDB (2002) agreed with United Nations that a decade ago, 2.9 billion municipal residents in the world's cities generated 0.64 kg per person, amounting to 0.68 billion tonnes of solid waste annually. These volumes have increased to approximately 3 billion residents producing 1.2 kg per person daily (1.3 billion tonnes annually). By 2025, city residents should increase to 4.3 billion, each person generating about 1.42 kg daily of municipal solid waste (2.2 billion tonnes annually). A country's population is vital because an increase in a country's population influences the consumption rate, thereby increasing the waste generated (Chalmin and Gaillochet, 2009).

Solid waste is characterized based on the following parameters (EPA, 2010), its sources, nature of waste, generation rates, and composition. Table 1 displays the classification

of solid waste types and sources. These sources are well-defined as giving rise to four or five significant waste classes.

Table 2. 1 Waste is classified by source

| Source | Facilities, activities or where wastes are generated | Types of solid wastes |
|-----------------------------------|---------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Residential | Single-family and multi-family residences; low, medium, and high-density apartments. Can be included in IC&I sector | Food wastes, paper, cardboard, plastics, textiles, yard wastes, wood, ashes, street leaves, special wastes (including bulky items, consumer electronics, white goods, universal waste) and household hazardous waste |
| Commercial | Stores, restaurants, markets, office buildings, hotels, motels, print shops, service stations, and auto repair shops. | Paper, cardboard, plastics, wood, food wastes, glass, metal wastes, ashes, special wastes, hazardous wastes |
| Institutional | Schools, universities, hospitals, prisons, governmental centres. | Same as commercial, and some biomedical wastes |
| Industrial (non-hazardous wastes) | Construction, fabrication, light and heavy manufacturing, refineries, chemical plants, power plants, demolition | Same as commercial |
| Municipal service | Street cleaning, landscaping, parks, beaches, other recreational areas, water and wastewater treatment plants | Street sweepings, landscape and tree trimmings, general wastes from parks, beaches, and other recreational areas, sludge |
| Construction and Demolition | New construction sites, road repair, renovation sites, razing of buildings, broken pavement. | Wood, steel, concrete, asphalt paving, asphalt roofing, gypsum board, rocks and soils |
| Biomedical | Hospitals, nursing homes, morgues, health centres, and medical laboratories. | Sharps such as blades, scalpels, needles, glasses and cannulas. Medicines, Infusion kits, syringes, used and unused bandages. |
| Industrial (Hazardous) | Industries, mills, mining, light and heavy manufacturing factories, refineries, chemical plants, power plants, demolition | Industrial process wastes, scrap materials, chemical and radioactive wastes. |
| Agricultural | Field and row crops, orchards, vineyards, dairies, feedlots, farms | Spoiled food, agricultural waste, hazardous waste |

2.2.1 Municipal solid wastes (MSW)

Municipal solid waste differs among countries due to the types of generators, compositions, sectors collecting it, and the practised waste management processes (Ali et al., 1999). The definition changes over time because of modernization (UN Habitat, 2010). For this research, the European countries' definition of 'municipal waste' will be chosen as follows (EU Council Directive, 1999): "Municipal solid waste is defined as solid waste generated and collected by municipalities or other local authorities." Typically, MSW includes wastes from unwanted items from households, gardens, street sweepings and parks, and non-hazardous solid waste from industrial, commercial, and institutional organizations (Ripa et al., 2017).

MSW is one of the most challenging waste to manage because it consists of various materials such as glasses, electronics, metal scraps, papers, plastics, and organic materials mixed in irregular compositions (Al-Ghouti et al., 2021). Recently, the amount of electronic waste, also known as e-waste, has increased rapidly as individuals become more dependent on electronics, such as computers and mobile phones, which are discarded once damaged. However, professionals claim that "municipal solid waste consists of all sewage, non-air discharges and non-hazardous waste generated in households, business and commercial organizations, institutions. Also, non-hazardous waste from industries which are taken away by private or public authorities in any metropolis is part of MSW.(Cointreau, 1982; Igoni et al., 2007). The physical appearance, nature, and amount of MSW generated vary from area to area. It is likewise a function of the standard of living and lifestyle of residents in a particular area. The increase in a country's gross domestic product (GDP), urbanization, developmental phase, and change in the way of life and food pattern has also led to the rapid increase in the amount of MSW with its composition varying. The connection between MSW generation and income differs concerning the developmental phase of a country. As a country develops, its waste generation rate increases (UNEP, 2005; Buenrostro and Bocco, 2003). MSW could either be biodegradable such as food remains, paper, fabrics and wood or non-biodegradable such as tyres, glass, and plastics.

The composition of municipal solid wastes from developing countries typically differs from those of developed countries. For example, MSW varies significantly in India regarding the composition and hazardous state compared to MSW in developed countries. Most developing countries generate waste comprising over 50% organic materials (Asase et al., 2009; Gupta et al., 1998; Shannigrahi et al., 1997; World Bank 1995 and 1998, UNEP/SPREP 1997).

Another example is the comparison of the composition of waste from Kumasi in Ghana and that from the city of London displays differences in appearances and composition. The waste in Kumasi consists of a high proportion of biodegradable materials (64%) and similarly inert materials such as wood, ash, sand, and charcoal. In comparison, the waste from London has paper and organic constituents in the proportions of 32% and 30%, respectively (Asase et al., 2009). The components of waste are an essential element as it controls the potential for resource repossession, appropriate methods of disposal and the ecological impact the waste has if not suitably handled (UNEP, 2005). The composition and volume of MSW generated provide the base on which type of waste management system is best required to deal with the waste. Improper MSW management is one of the significant environmental problems in developing countries. It causes all types of pollution in the air, soil, and water and causes health hazards to residents living in these countries. Discarding MSW in areas in an unrestrained way causes several problems to the nearby environment, including surface and groundwater supplies.

2.2.2 Municipal Solid Waste Management Process

MSW management process should be a deliberate, systematic control of waste from the point of generation to its final disposal. The process comprises production, sorting, collection, transport, treatment, recycling, recovery, and disposal of solid waste (Skitt, 1992). Generally, all types of waste generated from various sources are collected and transported to a designated site or waste yard, sorted into fractions (usually bio-waste, paper, glass, plastics, etc.). Municipal solid waste management is a complex practise as it involves several skills; it may also be covered by waste legislation and regulatory structure that see that guidance on disposal and recycling is obeyed. Waste management processes vary widely among different countries; for example, some developing countries lack the formal waste collection systems that developed countries have. Therefore, a municipal solid waste management process aims to ensure that municipal solid waste is handled to safeguard both public health and the environment (Henry et al., 2006; Wilson, 2007).

2.3 An Overview of Municipal Solid Waste Management in Sub- Saharan African Countries

Sub- Saharan African countries comprise countries that have not attained a significant level of development and have a low standard of living. They can be addressed as developing countries too. Decades ago, most developing countries did not have problems managing their waste because their waste consisted of mostly agricultural sources such as foodstuffs,

vegetables, and other produce from the farm, which were all biodegradables. They were used as manure for crops. Their habitations were also sparse, and the land was abundant for disposal. Disposal became an issue through the increase of cities and the number of individuals living together in comparatively small areas searching for livelihoods. The increase in the population of individuals also led to a rise in waste generated per unit area (Bello et al., 2016; Daniel and Perinaz, 2012). Globalisation has raised some disturbing concerns for developing countries, including Nigeria. One such worry is the influence of urbanisation and its consequences. Cities are conventionally engines of social modernisation and economic development and are also the platform for globalisation activities. Also, in these developing countries today, concern has risen about poor waste management, primarily in cities where the feeding patterns have changed, and its generation rate has increased significantly (Sakurai, 1990; Achankeng, 2003). MSWM arose as a vital part of providing a healthy and comfortable environment for individuals. The problem posed on the budget towards waste is a consequence of the high costs related to its management, the absence of understanding over issues that affect the diverse phases of waste management and connections essential to enable the entire handling process. Despite the amount of money spent from the budget on solid waste management, its collection is still not entirely covered because the collection systems are often lacking (Bello et al., 2016; Al-Khatib et al., 2010). The most common disposal method in developing countries is open and unrestrained dumping at landfills, while some people burn their wastes in their courtyards.

In contrast, others dumped their waste in streets, gutters, and waterways. In most developing countries, floods, water pollution, and littered lands have been linked to weak waste management exercises (Palczynski, 2002; Henry et al., 2006). Mishandling waste in many third-world countries has led to the predominance of diseases such as malaria, tetanus, cholera, and diarrhoea (McMichael, 2000). This situation places the already desperate authorities in a complicated state, knowing they now have to initiate new solutions to tackle the increasing volumes and different waste varieties (Achankeng, 2004).

2.4 Municipal Solid Waste Management in Nigeria

One apparent significance of speedy urbanisation in Nigeria and other developing countries is the increase in the generation of municipal solid wastes. Several urban authorities face challenges in handling these difficulties and dealing with their collection and disposal (Ogu, 2000). It is traced that from the early 1990s to the present time, environmental law in Nigeria has not been effectively enforced, stating that there is no law on which managing

environmental worries may be recognised, which sums up the above-rated statement (Adelagan, 2004; Olowomeye, 1991; Agunwamba, 1998; Walling et al., 2004).

Walling et al. (2004) and Adelagan (2004) agreed that the Federal Government presently has minimal control over environmental rules throughout the country. The studies suggested further that local governments were envisioned to account for solid waste management. Still, most have dodged this obligation due to a lack of resources and prevalent corruption in the structure. The study puts together the critical causes of the MSW challenges in Nigeria: an increase in population, quick urbanisation, poverty, and insufficient funds released to the state agencies.

Agunwamba (2003) and Onibokun and Kumuyi (1999) encouraged the government to begin embracing integrated MSW management solutions. These solutions are both from the public sector and private sector solution-driven, as they possess a better potential for long-term desired environmental and commercial developments.

2.4.1 Municipal Solid Waste generation, composition, collection, disposal, and recycling in Nigeria

In developing countries such as Nigeria, waste management comprises production, collection, transportation, handling, sorting, recycling, or waste disposal. The varieties of waste in Nigeria originate from residential, commercial, institutional, and industrial sectors contributing to immense challenges to the existing overwhelmed waste management specialists (Nnaji, 2015). Table 2.2 shows us the municipal solid waste generation in nine major cities in Nigeria. The rate at which municipal solid waste is generated in Nigerian cities differs and solely depends on the unique features and activities of residents of that city. The rates at which waste is generated range from 0.44 kg/cap/day to 0.66 kg/cap/day in the towns compared to 0.7-1.8 kg/cap/day produced in developed countries (Cointreau, 1982; Hardoy et al., 2013). This still causes a burden on the municipal budget due to the high costs related to its management (Guerrero et al., 2013). The difference in this range of waste generation between the developing countries and the developed countries is because of the improved and better use of current infrastructure and equipment used in handling wastes generated, for example, the use of more waste collection. The disparity in data on waste generated in Nigeria could be attributed to some factors responsible for conflicting data on solid waste generation, such as coverage of research regarding time and year of data collection, a technique of investigation, the season of research (wet or dry season), and the source of data (Nnaji, 2015). However, Aliyu and Amadu (2017) conducted a study in some cities presented below.

Table 2. 2 Municipal solid waste generation in nine cities in Nigeria (Aliyu and Amadu, 2017)

| City | Population | Tonnes/month (fresh weight) | Density (Kg/m ³) | Kg/Capita/Day |
|---------------|------------|--------------------------------|------------------------------|---------------|
| Lagos | 8,029,200 | 255,556 | 294 | 0.63 |
| Kano | 3,248,700 | 156,676 | 290 | 0.56 |
| Ibadan | 307,840 | 135,391 | 330 | 0.51 |
| Kaduna | 1,458,900 | 114,433 | 320 | 0.58 |
| Port Harcourt | 1,053,900 | 117,825 | 300 | 0.6 |
| Markurdi | 249,000 | 24,242 | 340 | 0.48 |
| Onitsha | 509,500 | 84,137 | 310 | 0.53 |
| Nsukka | 100,700 | 12,000 | 370 | 0.44 |
| Abuja | 159,900 | 14,785 | 280 | 0.66 |

According to Gidarakos et al. (2006), Municipal solid waste composition varies in different cities. He observed that developing countries generate far more organic waste while developed countries generate inorganic waste. Table 2.3 reveals that over 50% of waste generated in Nigeria is organic (biodegradable) with other components as recorded from different States. The organic part is a vital fraction of the MSW because it comprises a large portion of the MSW stream in Nigeria and other developing countries. It has an adverse effect on public health and the total quality of the environment if not accurately treated or discarded. Lastly, it attracts rodents and vector insects that feed on them (Fei-Baffoe et al., 2014). Globalisation has led to the generation of more inorganic wastes such as metal scraps, plastics commodities, glass, and fabrics. Waste compositions differ according to seasons, revenue level, populaces, communal activities, climate, and industrialised invention.

Also, the size of marketplaces for waste constituents and the degree of urbanisation affect waste generation (Ogwueleka, 2009). In Nigeria, the composition of municipal solid waste can be best gotten straight from the source of production: homes, marketplaces, and

offices. The reason is that scavengers alter the composition of municipal solid waste as it is transferred from the source to the open dumps (Lisa and Anders, 2008).

Table 2. 3 Composition of municipal solid waste for some Nigerian cities

| City | Food/Putrescibles | Metal | Glass | Paper | Plastics | Others | References |
|---------------|-------------------|-------|-------|-------|----------|--------|------------------------|
| | (%) | | | | | | |
| Lagos | 56 | 4 | 3 | 14 | 4 | 19 | Cointreau 1982 |
| Abuja | 52 | 5 | 2 | 10 | 11 | 20 | DFID 2004 |
| Port Harcourt | 37.6 | 17.2 | 13.5 | 12.4 | 9.9 | 9.4 | Igoni et al., 2007 |
| Kano | 43 | 5 | 2 | 17 | 4 | 29 | Bichi and Amatobi 2013 |
| Onitsha | 30.7 | 6.2 | 9.2 | 23.1 | 9.2 | 21.6 | Ogwueleka 2009 |

Others = dust, ash, ceramics, rubber, soil, bones

Waste collection and transfer are part of the waste management process. It transfers municipal solid waste collected from the point of generation (residential, commercial, institutional, and industrial) to the point of disposal or treatment. Climate conditions and socio-economic and ethnic customs hinder active waste collection, separation, storage, and transportation of waste in developing countries (Chattopadhyaya et al., 2009).

Collecting municipal solid waste is the most challenging part of solid waste management in developing countries. Ineffectual collection systems regularly lead to waste build-up, causing environmental pollution, driving wildfires, blocking drainages, and threatening the public's physical health (Olowomeye, 1991; Nnaji, 2015). Mbue et al., 2015; Oteng-Ababio et al., 2012, revealed two types of waste collection procedures practised in most Sub-Saharan African countries. The pre-collection at House-to-House type and the general disposal method (fig. 2.1).



A

B

C

Fig 2.1 Shows pictures of A and B being the house-to-house collection methods while C is the communal type of waste collection methods practised in Nigeria. Picture A from WastePoint limited Nigeria, B from Takoulu Jean (Cameroon), and C is Author's picture (Nigeria).

Separation or sorting of waste is another waste management process that has been overlooked by developing countries such as Nigeria. Wastes are mixed from their generation sources, making sorting difficult; in most cases, scavengers are responsible for sorting (Agunwamba,

2003; Kariuki et al., 2019). The scavengers burn wastes at the dumpsites to get valuable items for recycling. Research linked to source separation of municipal wastes in Nigeria is few; despite how important separating the waste generated from the source is, it is not practised (Onibokun and Kumuyi 1999; Ogu, 2000; Agunwamba, 2003). Works of researchers in other developing countries have been reviewed to know their achievements in source separation and apply such procedures to see if they will be effective in Nigeria. (Nnaji, 2015). Nnaji and Utsev (2011) recommended that sorting at source (SAS) can be attained by making different waste containers for different waste classifications. Waste is separated into various categories such as biodegradable (organic waste) and non-biodegradable, which are recyclable in the form of plastic, bottle/glass, and metal, paper/cardboard.

Recycling is a part of resource recovery which has enormous promises for industrial application, particularly in the poor city populaces in many developing countries (AfDB, 2002). Presently, in Nigeria, the private sector conducts recovery through recycling processes. These private sectors sort for recyclable materials through different means, such as scavengers that pick them up from dumpsites and are being paid in return. Agunwamba (2003); Afon (2007) have focused on MSW recycling processes and divulge that it has many advantages both to the economy and the environment. They established that MSW recycling is at a fundamental stage in Nigeria because it has not received much consideration from the government, like formulating laws and structures guiding the effective practice in Nigeria (Afon, 2007).

The disposal of municipal waste is the final process in the solid waste management system. It is essential to move all waste generated from either house to house or communal amenities in a simple and effective means to either recycling centres or final disposal sites. In Nigeria, like most developing countries, wastes are usually dumped in open un-engineered sites, unrestrained dumpsites beside roads, markets, or dwelling places for residents.

2.5 Composting

Composting is a biological breakdown of mixed organic wastes into humus-like material by the action of microorganisms under controlled moisture, temperature, and aeration (Cooperband, 2000). It is the part of controlled conditions that distinguish composting from normal decomposition processes, which occur in an open landfill where the waste pile is not managed well. The main difference is that composting is aerobic while landfilling is anaerobic.

Composting is one of the branches of waste management which reduces the volume of the organic portion of municipal waste going into landfills and utilizes the organic waste. For

example, compost made from animal waste is used in Asian countries where the soils are impoverished as organic matter to enhance the fertility of the soils (Tiquia and Tam, 1998). Decades ago, composting was practised in many ways in the early era, including adding well-decomposed manure or a mix of plant and animal wastes in pits for an extended period before mixing it into the soil (Diaz and de Bertoldi, 2007).

Organic waste used for compost comprises various materials that vary significantly in particle size, nutrient, moisture, and chemical content, and it is grouped into animal manure, garden, and house waste. Garden wastes comprise wooden chippings, grass clippings, tree branches, leaves, crop remains and soil, while house waste is the decomposable portion of household waste. Examples are paper and cardboard, fruits and vegetable wastes from the markets, and food waste. Manures are made from waste from poultry, piggery, and grazing fields for animals such as cows and also all on-farm materials and off-farm residues and wastes (Khater, 2015).

The mixture of these three categories of organic waste (garden, house, and manure) forms municipal compost. Organic waste is presently managed through a variety of systems. While bigger-scale composting methods include in-vessel composting or open windrow composting, smaller-scale composting methods have also been established, including outdoor heap/bin, trench composting, and vermicomposting. Each method has its benefits and shortcomings depending on the quantity of feedstock, the available site and space, and the time required for compost formation.

Composting converts raw organic wastes into a finished product (humus-like material) with the help of soil microorganisms. Finished compost is mature, biologically stable, and less bulky than the feedstock used in its production, making it easy to handle (Rynk, 1992). Finished compost is mature, biologically stable, less bulky than the feedstock used in its production, making it easy to handle (Rynk, 1992).

2.5.1 Factors Affecting Composting

Composting is a biological activity involving microorganisms, so factors affecting their growth and reproduction require monitoring to be within range (Roman et al., 2015). These factors include feedstock, aeration, C/N ratio, pH, and climatic and geographical factors, including moisture and temperature (Cooperband, 2000; Maeda et al., 2010; Roman et al., 2015). The effectiveness of any composting process depends on these factors. The factors are considered in composting process planning and operation (Roman et al., 2015).

2.5.1.1 The particle size

The size and amount of feedstock used in composting will influence the movement of oxygen in a pile, thus also the microbial activities affecting the properties of the final compost formed. For instance, mixing various amounts of feedstock to create compost helps balance the nutrients in the finished compost. Jonsson and Wardle (2008) suggested that mixing different plant wastes gave an excellent mixture effect, with one of the wastes having a higher concentration of nitrogen and phosphorus. Agreeing to Gentile et al. (2001), the quality of feedstock used for composting controls the short-term dynamics of C decomposition, whereas the quantity of the feedstock controls the formation and the stabilisation of soil organic carbon. Massive organic wastes should be chopped or shredded to reduce the particle size to 1-5 cm (Atalia et al., 2015) to ensure an appropriate surface area for decomposition.

2.5.1.2 Aeration

Oxygen is a vital factor for heterotrophic metabolic processes and is very crucial in the composting process (aerobic). Although some breakdown happens in the absence of oxygen (anaerobic breakdown), the process is prolonged with an offensive smell. The more oxygen in a pile, the faster the decomposition will occur, though various strategies are employed to ensure adequate aeration (Zheng et al., 2018).

2.5.1.3 C/N Ratio (Feedstock and nutrient balance)

The carbon to nitrogen (C/N) ratio is an essential factor influencing the composting process and the properties of the final compost formed. Microorganisms consume C and N during composting. Carbon serves as a source of energy and an essential component for organisms. In contrast, nitrogen is a builder of cell structure, vital in synthesising amino acids, proteins and nucleic acids. The microorganisms involved use 15 to 30 times more carbon than nitrogen during the process. (Mustin, 1987). The accepted optimum C/N ratio of compost should be 15- 20 (Gotaas, 1956). Usually, the C/N ratio drops during the composting process. As carbon is lost in carbon dioxide, the nitrogen is either immobilised or used to synthesise amino acids. If the C/N of compost is very high, nitrogen becomes immobilised; thus, compost breakdown is slowed down, but if the C/N is lower than 10 will release N very fast from the compost. High or low C/N ratios can be adjusted by adding either high carbon or high nitrogen wastes. Examples of high carbon sources are shredded papers, Sawdust, wood chips, straws, and autumn leaves. However, nitrogen-rich sources are poultry manure, abattoir waste, and sewage (Atalia et al., 2015).

2.5.1.4 Climatic factors and environmental factors

Climatic factors, as well as environmental factors, influence the composting process. Composting and related nutrient release forms vary with climatic areas among forests where composting rates are enhanced by moisture and temperature (Li-Xin et al., 2003).

Moisture: Moisture content is vital in composting to maintain and sustain the biological breakdown of waste materials. It may become a limiting factor when not controlled. High moisture content influences oxygen available for microbial activity and the oxygen from the spaces between materials leading to higher GHGs emissions. The reason is that it creates anaerobic degradation (Tamura and Osada, 2006) while slightly delaying the dispersal of soluble molecules and microbial activity, reducing the composting rate (Atalia et al., 2015).

Temperature: Temperature is a vital factor in composting. Moderately high temperatures have often been considered essential for compost sanitation. Unusually high or low temperatures should be avoided during composting; they slow or stop decomposition and cause unwanted chemical alterations of the organic matter. High compost pile temperatures are attributed to the biological process of the lysis of carbon bonds in the decomposition (Mustin, 1987). Gotaas (1956) suggested that the optimum temperature range is 50-70°C. Regular turning of the pile should be employed to maintain the temperature by the producers to avoid temperatures higher than 70°C.

2.5.1.5. pH:

De Bertoldi et al. (1983) suggested that organic materials undergo composting process between pH ranges (3–11), with the optimal values between 5.5 and 8. The reason is that microorganisms develop well around neutrality. Though fungi are more tolerant to distant neutral pH than bacteria (Azim et al., 2018). Decomposition affects the pH of compost during the process; while the pH decreases in the early stage of composting, due to the formation of organic acids released during the decomposition of pure organic materials (carbohydrates and lipids), there is an increase in pH at the later stage because the breakdown of protein (lignin and other highly resistant compounds) to release ammonia (McKinley and Vestal, 1985).

2.5.2. Microorganisms

Microorganisms play a crucial role in the breakdown of organic matter and the mineralisation of nutrients. They include many bacteria, protozoa, actinomycetes and fungi and are all involved in decomposing organic waste (AgriLife, 2009). They are the initial dwellers of the waste pile because they come in with the waste that makes up the pile, accounting for

most of the decomposition in a pile. Factors such as temperature changes and the nature of feedstock will influence these microorganisms' population, their growth and how they function (Gotaas, 1956; Roman et al., 2015).

These microorganisms require nutrients, mainly carbon and nitrogen, for energy and growth, which are found in organic waste mixtures. More species of microorganisms appear to be associated with aerobic breakdown than anaerobic decomposition (Cooperband, 2000). In aerobic composting, bacteria, actinomycetes, and fungi are the most active (AgriLife, 2009).

Table 2. 4 Types of microorganisms involved in municipal composting.

| Types | Species | Ref |
|----------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| Bacteria <i>Pseudomonas sp</i> , <i>streptococcus sp</i> | <i>Bacillus casei</i> , <i>Pseudomonas</i> <i>Lactobacillus buchneri</i> , <i>Bacillus</i> <i>subtilis</i> , <i>Azotobacter</i> <i>Azospirillum Micrococcus</i> | Atalia et al., 2015, Rebolledo et al., 2008, Wei et al., 2007. |
| Actinomycetes <i>Streptomyces sp</i> | <i>Streptomyces</i> , <i>Actinomyces</i> | |
| Fungi <i>Polyporaceae sp</i> | <i>Aspergillus</i> , <i>Myxomycota</i> , <i>Hyphomycetes</i> , <i>T. versicolor</i> , <i>P.chrysosporium</i> , <i>Trichoderma</i> , <i>Alternaria</i> , <i>Penicillium</i> | |

Composting is characterised by distinct temperature changes linked to the succession of microbial populations adjusted to the prevailing temperature. Three types of microorganisms are involved in breaking down the waste: fungi, bacteria and actinomycetes. These microorganisms are grouped according to the different temperatures in which they thrive.

Mesophilic microorganisms are organisms that thrive in moderate temperatures, neither too cold nor too hot. (10-50°C). Examples of mesophiles are *Listeria monocytogenes*, *Staphylococcus aureus*, and *Escherichia coli*. They may thrive in both conditions, with and without oxygen.

Thermophilic microorganisms are organisms that thrive at relatively high temperatures (40-122°C). The enzymes in thermophiles function at high temperatures. Examples of thermophiles are *Pyrococcus*, *sulfolobus* or *methanosarcinales*, *Pyrolobus*, and *methanbacteria*.

Extremophilic organisms thrive in physically or geochemically extreme environments. They are harmful to most life on earth. Examples are *Pyrococcus furiosus* and *Pyrolobus fumarii*,

which survive at a very high temperature of over 100°C, and *Synechococcus lividus*, which stays as low as -20°C.

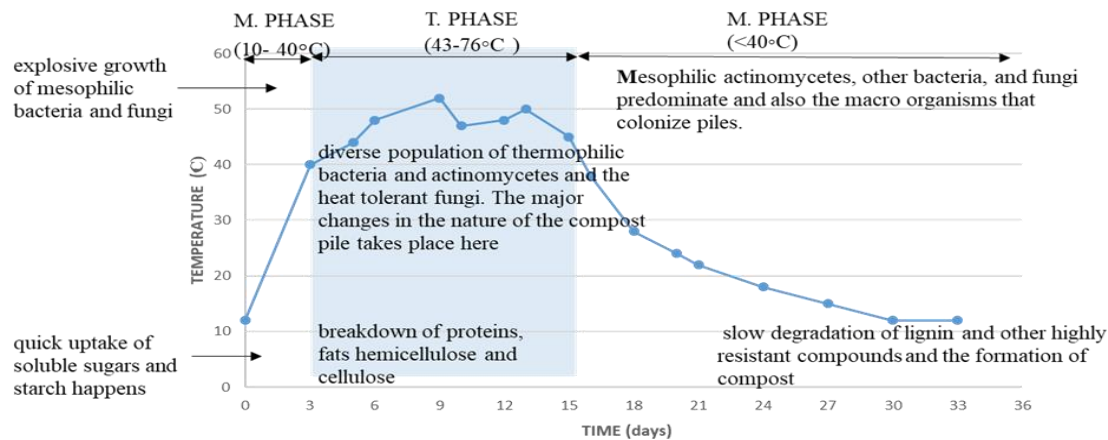


Fig. 2.2 Diagram of the three Phases of Composting (Trautmann and Kransny, 1997).

Three phases can characterise the composting process: mesophilic, thermophilic, and mesophilic, including maturing and cooling. Also, the temperature fluctuations are spatially and temporary variables. The transition between mesophilic and thermophilic phases can result in a loss of degradation efficiency. Fig.2.2 reveals the diagram of the three Phases of Composting (Trautmann and Kransny, 1997).

The increase in temperatures is a by-product of the extreme microbial action in composting. There are three phases in composting:

- The mesophilic phase is the initial phase where mesophilic bacteria colonise in the wastes. They work very quickly, increasing the pile's temperature slowly between 10-50°C. They are the workhorses of waste piles, generating enough heat to raise the temperature over 38°C. The pH decreases due to the organic acids released from the bacteria's breakdown of carbohydrates and lipids. (Kaiser 1983; Tuomela, 2000)
- The thermophilic phase is where thermophilic microorganisms gradually take over the process. This phase is vital for reducing worm eggs, pathogens and bacteria that may have health hazards to people or animals. The microorganisms live and grow in Thermophilic fungi in the waste pile (scorching environment temperature, over 50°C). Actinomycetes become prominent in this stage; they play a vital role in decomposing cellulose within a short duration (Mustin, 1987). This phase continues from a few days to some weeks. Though, depending on the mass of the piles and the constituents of the waste materials. pH increases because the microorganisms break proteins to release ammonia. The decomposition of organic matter slows down at temperatures above 60°C.

- The mesophilic phase is also known as the maturing and cooling phase. This final phase of the composting process is the maturing and the cooling phase, when the pile becomes very stable and mature (Paul, 2009). The compost temperature slowly drops, and mesophilic microorganisms again take over this phase. Here, the mesophilic bacteria, fungi and actinomycetes predominate the pile. They are slowly degrading lignin and other highly resistant compounds. This phase is the curing or maturation phase of the remaining organic matter at ambient temperature. At this phase, there are minor reactions of polymerisation and condensation, which lead to the production of hummus-like material with humic acids and are resistant to degradation (Azim et al., 2018).

Several chemical changes happen throughout composting time, either relatively quick in a typical composting system or more slowly in bins or systems that do not heat up. In all of these compost systems, the chemical breakdown of complex organic compounds is initiated by enzymes produced by microorganisms. Nutrients like nitrogen, phosphorus, potassium, and others are released as the organic matter decomposes.

2.5.3 Formations and emissions of GHGs

The products of composting are CO_2 , CH_4 , H_2O , N_2O , NH_3 and heat (Hellebrand, 1998; Möller and Stinner, 2009; Maeda et al., 2010; Sánchez-Monedero et al., 2010; Sánchez, et al., 2015). These products formed is as a result of microbial activities throughout the composting process. Hao (2001) reported that CO_2 and CH_4 peaked during composting in the middle of the windrows. The production of CH_4 was due to insufficient diffusion of oxygen during composting at the windrow (Sánchez et al., 2015). At the same time, the production of N_2O was due to nitrification and denitrification (Paul, 2009). The release of N_2O is influenced by temperature, nitrate content and oxygen available, though kept at a low rate if aerobic conditions (Hellebrand, 1998). N_2O formed during denitrification can be further reduced to N_2 (Hao, 2001). While the aerobic nitrification of NH_3 to form NO_2^- and NO_3^- may also form N_2O as a by-product (Sánchez-Monedero et al., 2010). During the composting process of animal dung, 47-77% of the N content in the compost material is released in the form of NH_3 , and an increase in temperature and pH increases NH_3 emissions (Martins and Dewes, 1992). Fig. 2.3 shows us the diagram of a composting process in a windrow.

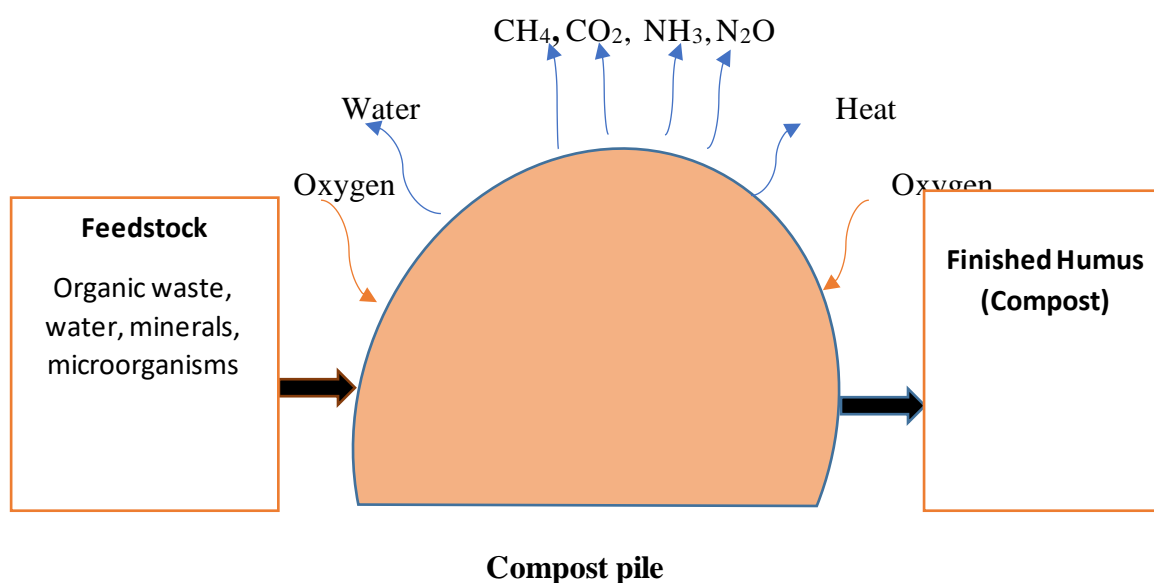


Fig. 2.3 Diagram of composting process in a windrow (Paul, 2009)

2.5.4 Nutrients and toxicity in compost

All composts comprise a range of compounds that are present. These compounds are metals, inorganic ions, soluble salts such as phosphates, carbonates, sulfates, and nitrates), and organic compounds such as proteins, DNA, fatty acids, hydrocarbons, and PAHs, alcohols, lipids etc. These compounds are primarily formed via the microbial action and breakdown of organic waste constituents. These components are vital in supporting bacterial activities and chemical breakdown (Brady, 1984). Using compost as a soil conditioner elevates the soil nutrients influencing soil productivity (Anikwe and Nwobodo, 2002). The amount of nutrients in compost depends on mainly the feedstock used in making it and the processes used. However, the nutrients from finished compost are released more slowly into the soil than from fresh feedstock. It is considered mature with other organic wastes in the right proportion into stable organic form (Mathur, 1998).

The elements essential for plant growth are categorised as macro-nutrients or micro-nutrients. Plants need these elements in different quantities for their optimum growth. Macro-nutrients consist of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), and sulfur (S). At the same time, Micro-nutrients include boron (B), copper (Cu), cobalt (Co), chlorine (Cl), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn). Macro-nutrients can further be divided into essential and minor nutrients. N, P, and K are considered essential because they are most frequently needed for microbial activities.

Besides carbon, hydrogen and oxygen, nitrogen, phosphorus, and potassium are the essential nutrients plants need in the highest quantities and are usually the most restricting nutrients to plant growth (Schoonover and Crim, 2015).

The feedstock used during composting is the primary source of these nutrients in composting. Goswami and Sarma (2008); Okeyode and Rufai (2011) established that the physio-chemical analysis of soils with compost applied to them had more nutrients than typical soils without compost. The toxicity problems in compost are traced to the disposal of all forms of waste (municipal, commercial, or industrial) in landfills. For instance, the feedstock used for compost and some industrial waste rich in heavy metals are seen together in landfills.

However, it becomes vital to monitor the properties of compost formed, such as nutrients, heavy metal, salt contents, and its toxicity, since the feedstock used in its production is sourced from different sectors and is helpful in various applications. These applications include enhancing nutrient management, soil organic matter, and combating soil erosion (Van-Camp et al., 2004; Giagnoni et al., 2020). APEX was the launched quality standard created by the UK's three largest waste management companies, namely (SITA, Cleanaway, Onyx) and Freeland horticulture for composted materials. APEX standard is similar to the PAS-100 standard. They are known standards within the organic recycling sectors and contribute to the circular economy as the base document for composting organic wastes. Compost must meet the specified APEX or PAS-100 standards to be suitable for use.

2.5.5 Decomposition in composting.

Decomposition is vital in composting because of its link to the release of nutrients and the formation of soil organic matter, which is a critical aspect of the ecosystem. Any change in the decomposition rate will affect the role of C and the release of nutrients. Decomposition is a breakdown (physically, chemically, and biologically) of organic matter into moderately stable forms. (Berg and McClaugherty, 2014; Cooperband, 2000). Decomposition follows a progressive way, with diverse organic compounds leading decomposition processes as they proceed (Berg and McClaugherty, 2003).

Organic matter consists of soluble compounds and structural constituents. While the soluble components are the low molecular compounds such as sugar, organic acids amino acids, which are labile with faster turnover units, the structural constituents are high molecular weight complexes. They are naturally highly resistant (Van Hess et al., 2005). They are in the cell

walls of the organic matter, acting as a defence against pathogens (Horwath, 2007). Examples of the structural constituents are hemicellulose, cellulose and lignin. They are naturally depolymerised via hydrolytic cleavage of their bonds. They link their subunits with the extracellular enzymes, consuming them by microorganisms (Van Hess et al., 2005). The production of the extracellular enzymes is strongly influenced by the availability of nutrients in organic matter, affecting the microorganisms' energy demand. The bacteria and fungi are responsible for the decomposition of organic matter (fig. 2.6). The brown rot-fungi decomposes the hemicellulose and cellulose.

In contrast, the lignin is decomposed by the ligninolytic fungi known as white rot-fungi slowly at a later stage because it resists decomposition (Trautmann and Kransny, 1997). Therefore, the decomposition in composting process is divided into two. First is the mass loss in organic matter in the early stage, which is faster due to the decomposition of soluble compounds and non-lignified holocellulose, which improves the microbial hydrolysis of carbohydrates. In contrast, the mass loss of the organic matter in the later stage is reduced due to the exhaustion of these compounds and the slow decomposition of lignified holocellulose and lignin, suppressing the microbial ligninolytic enzymes (Berg and McClaugherty, 2003).

2.6 Plastics

Plastics are materials consisting of a vast collection of monomers into straight, branched, or three-dimensional synthetic large molecules known as polymers. Large quantities of polymeric materials known as plastics are produced yearly, and their significance has been evident in today's world because of their wide range of applications. The production of plastic is rapidly increasing. Since 1939, there has been a steady rise in the volume of plastics manufactured each year, from 300,000 in 1939 to 322 million metric tons produced in 2015 (see Fig. 2.4) (PlasticsEurope, 2015; Neufeld et al., 2016).

They are pliable and moulded into different solid shapes; additives like antioxidants are added to plastics during production to their polymer chains to aid their environmental degradation (Gómez and Michel, 2013; Vroman and Tighzert, 2009). They became prominent in the nineteenth and twentieth centuries. They were preferred because of the properties they exhibit, to provide durability and resistance to various forms of degradation (Hourston, 2010), such as:

- Microbial degradation is the ability of polymers to be attacked by microbial organisms.
- Photo-degradation is the effect of sunlight/ultraviolet rays on the polymers (Cornelia and Zaikov, 2009).
- Thermal degradation is the weight loss of polymers when heated up (Devi et al., 2016).

Their properties range from lightweight, durability, pliable, flexibility, heat-resistance, and the ability to be mixed with other polymers to change their individual properties. (Barnes et al., 2009) Due to these desirable qualities they possess, plastics are manufactured in large quantities. Because they degrade slowly, they occupy most areas of landfills (Tokiwa et al., 2009). Plastic materials have properties that are beneficial to different industries. Its principal market is in making packaging materials, an application whose growth was enhanced by a global change from reusable to single-use containers. (Geyer et al., 2017)

They persist for a long time in the environment, even when exposed to the factors that affect degradation.

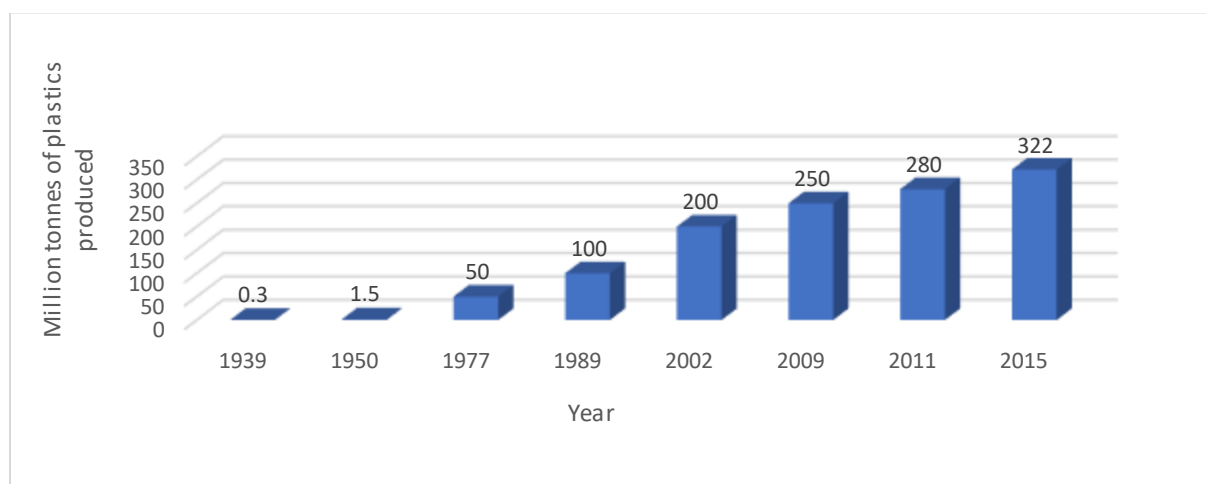


Fig. 2.4 Weight of plastics generated (Plastics Europe, 2015)

2.6.1 Types of plastics

There are two types of plastics; they are synthetic or commodity and natural plastics. Feedstocks derived from non-renewable petroleum resources are used to produce synthetic plastic, while renewable biological resources are used in making natural plastics. Examples are cellulose, starch (Vroman and Tighzert, 2009).

Synthetic plastics are divided into two categories.

- Thermoset plastics tend to retain their shapes after making them and cannot return to their original form. They are hard and durable, and they find their use in auto parts or aircraft parts. Examples include polyurethanes, epoxy resins and phenolic resins.
- Thermoplastics: They are plastics that can soften upon heating to return to their original forms. They are less firm than thermosets, moulded and extruded into films, fibres, and packaging materials. Examples include polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC).

The conventional thermoplastics seen around us today are grouped by their different recycling symbols often used in consumer goods as shown in fig.2.5 (Gregory and Andrady, 2003).

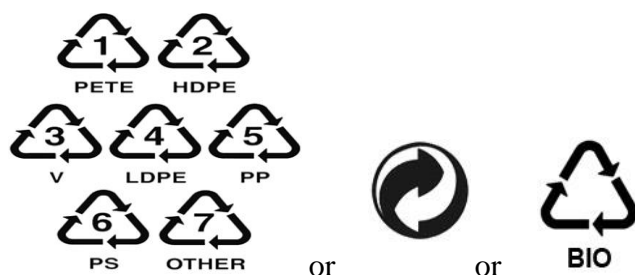


Fig. 2.5 The SPI resin/ recycling codes of some plastics. (Gregory and Andrady, 2003)

The most commonly used plastics in packaging are polyethylene, polyethylene terephthalate, polypropylene, Polystyrene, polyvinyl chloride, high-density polyethylene, low-density polyethylene.

They are used in disposable items such as packaging, eating gear and refuse bags (Gewert et al., 2015).

PET (Polyethylene Terephthalate) is a polar synthetic polymer formed from ethylene glycol and aromatic terephthalic acid condensation. The occurrence of the aromatic ring in the PET repeating parts gives the plastic prominent stiffness and strength. (fig.2.6). They are known as thermoplastic, showing partial crystallisation. PET monomer is written as bis 2 - hydroxyethyl terephthalate. PET produced annually in 2017 exceeded 30 million tons. PET is thermoplastic and partially shows crystallisation. PET is used in making PET bottles, films, and other fibres in the textile industry. PET is made into different fibres, used for butter tubs, soda, water bottles.

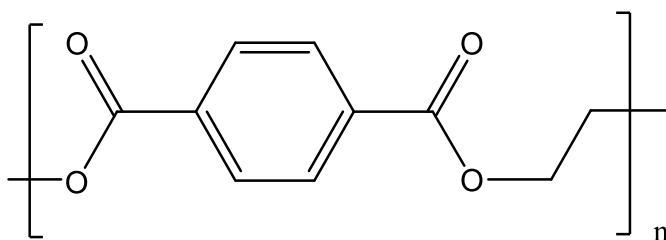


Fig. 2.6 The structure of Polyethylene terephthalate.

PE (Polyethylene) is made up of long-chain polymers of ethylene, and it is mainly made either as high-density (HDPE) or low-density polyethylene (LDPE). PE is chemically produced by the polymerization of ethane which is very flexible since side chains can be gotten dependent on the manufacturing process (Danso et al., 2019).

HDPE (High-density polyethylene) is a light, short-branched synthetic resin made from polyethylene (PE) at low temperatures and pressures using activated chromium oxide as catalyst or Ziegler-Natta and metallocene catalysts. Their polymer chains pack closely together, resulting in a dense, highly crystalline material of high strength and moderate stiffness (fig. 2.7). It is used for milk, juice, agriculture mulch, bleach, and detergent bottle head caps of bottles.



Fig. 2.7 The structure of polyethylene

LDPE (Low-density polyethylene) is a light, branched synthetic resin made from gaseous ethylene under very high pressures and high temperatures in the presence of oxide initiators. LDPE is a very flexible material, more branched than HDPE. It is used for squeezable bottles, agricultural mulch, bread and frozen food bags, grocery bags.

PP (Polypropylene) is made through chain-growth polymerisation from a propylene monomer. It has properties similar to polyethylene but is slightly more complex and more heat resistant than PE. Its structure is shown in fig. 2.8. It is used for packaging and labelling, yoghurt containers, syrup bottles, ketchup bottles, straws, battery cases, ice scrapers.

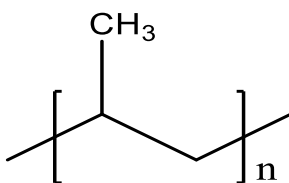


Fig. 2.8 The structure of Polypropylene

PA (Polyamide) is a polymer made from repeating units of aliphatic, semi-aromatic or aromatic molecules connected via amide bonds. Nylon and Kevlar are the most used synthetic polyamides. They are mainly used in textiles, automotive applications, floorings, and sports clothing. Notably, proteins and natural silk are polyamides. Fig. 2.9 shows us the structure of polyamide.

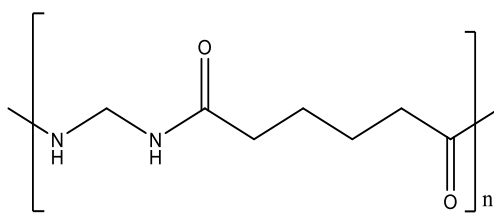


Fig. 2.9 The structure of polyamide.

For this research, we are considering the degradation of five of these synthetic plastics (namely, high-density polyethylene (HDPE) and low-density Polyethylene (LDPE), polypropylene (PP), polyamide (PA), also known as nylon-6 and polyethylene terephthalate (PET)) in different media and at controlled conditions.

2.6.2 Plastic Waste

There is an upsurge in the global challenge emanating from the end life of plastic materials because of the large-scale production and applications of plastics globally (Shen et al., 2020). Most mixed plastic wastes become pollutants in marine and terrestrial ecosystems, making recycling difficult (Zhu and Wang, 2020; Gundogdu and Walker, 2021). The disruptive effects of plastics have been identified as a threat to wildlife and food webs because of a lack of knowledge of plastic composition in landfills, and their environmental degradation is yet limited. About 20%-30% of plastic materials comprise a high proportion of industrial and municipal wastes in most sub-Saharan African countries. Rahimi and Garcia (2017) found that about 150 million tonnes of plastic end up in landfills yearly, and less than 30% of the plastic waste is recovered and recycled.

Plastics are abundant and present disposal difficulties when their worth ceases because they degrade slowly (Devi et al., 2016) in landfills. Plastic waste is a worldwide concern; currently, the problem of the disposal of plastic waste has attracted growing attention, resulting in the fast growth of plastic wastes (Gewert et al., 2015). Although some of these plastics can be recycled, recycling is not practised in all the cities of developing countries because it is not cost-effective. Therefore, they are released into the environment; they accumulate and are spread to landfills/dumpsites, waterbodies and gutters through environmental effects such as wind (Shim and Thompson, 2015, Tokiwa et al., 2009). It is reported that plastics in the marine environment are of growing concern because of their perseverance and effect on the water bodies, wildlife and possibly, humans. More than 60% of all floating rubbishes in the water bodies are plastics and are increasing yearly (Thompson et al., 2009; Jambeck et al., 2015).

2.6.3 Plastic degradation

Any change in plastics is caused due to environmental factors such as physical, biological, and chemical conditions known as plastic degradation. Degradation processes change the properties of any plastic, causing bond scission and the formation of new functional groups of the plastic. Degradation alters the properties of plastics such as colour, shape, molecular weight, or strength under the influence of one or more factors, such as heat, light or chemicals (Pospisil and Nespurek, 1997).

Table 2. 5 Degrading routes and types of degradation (Olayan et al 1996; Vasile and Dekker, 2000).

| DEGRADING AGENTS | TYPES OF DEGRADATION |
|----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Light (ultraviolet, visible), Plasma radiation, laser light, x-rays, light, and oxygen | Photo- degradation is degradation caused by the absorption of photons, mainly those wavelengths from sunlight, such as ultraviolet radiation, visible light, and infrared radiation. The physical and mechanical properties of the plastic is affected. It could be photo-thermal, photo-chemical or photo-oxidation degradation. |
| Heat, oxygen, ozone, heat and oxygen | Thermal-degradation is the weakening of molecular structure by high temperature causing molecular scission, discoloration, crack and breakage which could be oxidation, ozonolysis and thermo-oxidative degradation. |
| Microorganisms, Enzymes | Biodegradation which could be bioerosion, hydrolysis or dissolution. |
| Stress and Abrasive forces | Physical degradation which could be wear and tear, ageing, cracking or environmental stress. |
| Chemicals (acids, alkalis, salts water or solvents) | Chemical degradation is degradation caused by attack from chemical reagents, affecting the polymer chain, causing molecular scissions of the polymer. It could be reaction with gases, hydrolysis, solvolysis. |

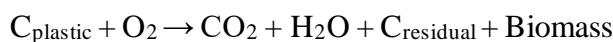
➤ Biodegradation of plastics

Biodegradation of plastics is a procedure in which plastics are degraded by soil or organic wastes at given temperatures in an aerobic or anaerobic environment with the aid of microorganisms. The extent of biodegradation of plastics could be checked by the loss of mechanical properties, molecular weight distribution, functional groups on the surface, surface topography, fragmentation, or the action of living organisms. The properties of these plastic

wastes enhance biodegradation under different media because the microorganisms liable for degradation vary from each other and possess their peak growth conditions in the medium. (Vijaya and Reddy, 2008). Plastics degradation occurs faster in substrates with more collection and activity of diverse microorganisms and other components. High temperature and moisture increase microbial attack, which favours biodegradation. These factors, put together, affect the scission of the polymer chain bonds through hydrolysis leading to a decrease in the molecular mass of the polymers. The strength of the plastics decreases as their molecular weight drops (Patrick, 2001).

Though some of these plastics are considered non-biodegradable or degrade differently because of their differing properties, certain microorganisms can degrade them very slowly after being exposed to abiotic factors such as heat light and chemicals (Vroman and Tighzert, 2009). Biodegradation is the mineralisation of plastics requiring microorganisms. Such as bacteria and fungi and is very specific, attacking the chemical structures and bonds of the plastics (Gómez and Michel, 2013). This occurrence happens in two phases. The first one is the abiotic reactions that weaken or fragment the plastic into lower molecular weight monomers, followed by the final bio-integration of the new smaller molecular weight species by microorganisms leading to their mineralisation (Vroman and Tighzert, 2009). UV- heat, energy from the sun, and oxygen are critical in the degradation of plastics with a carbon-carbon skeleton, leading to the carbon chain breaking up into smaller polymers fragments known as oligomers or monomers. The oligomers or monomers formed by the chain breakup are more prone to biodegradation. Degradation follows this route; thermal and photodegradation, hydrolysis, and biodegradation (Andrady, 2011). The final products from the degradation of plastics are reduced molecular weight polymer fragments, such as monomers and oligomers, and the formation of different end groups, mainly carboxylic acids (Gewert et al., 2015). The visual effects of plastic degradation are colour change and a network of cracks on its surface (Vasile and Dekker, 2000). Cracking on the surface causes the inside of the plastic to be accessible for more degradation, which finally leads to embrittlement and breakdown of the plastics (Vasile and Dekker, 2000).

There are two pathways for the degradation of plastics: plastics with a carbon-carbon skeleton with a backbone made of carbon atoms and plastics with hetero-atoms in their main chain. Examples of plastics with a C-C backbone are PE, PP, PS and PVC. In contrast, PET and PU are plastics with heteroatoms in the main chain (Andrady, 2011).



Although plastics can take a long time to degrade in the natural environment, degradation can be hastened by the action of some microorganisms.

2.6.4 Plastic degrading microorganisms

Microorganisms such as bacteria and fungi are actively involved in the degradation of plastics (Gu et al., 2000b). Vijaya and Reddy (2008); Wilkes and Aristilde (2017); Tsuchii et al. (1980); Griffin (2007) studied the degradation of different plastics in different media such as soil and compost. They revealed that the microorganisms involved in the degradation of plastics differ, and they have conditions that they thrive on in these media. Fig. 2.10 shows the general mechanism of plastic biodegradation.

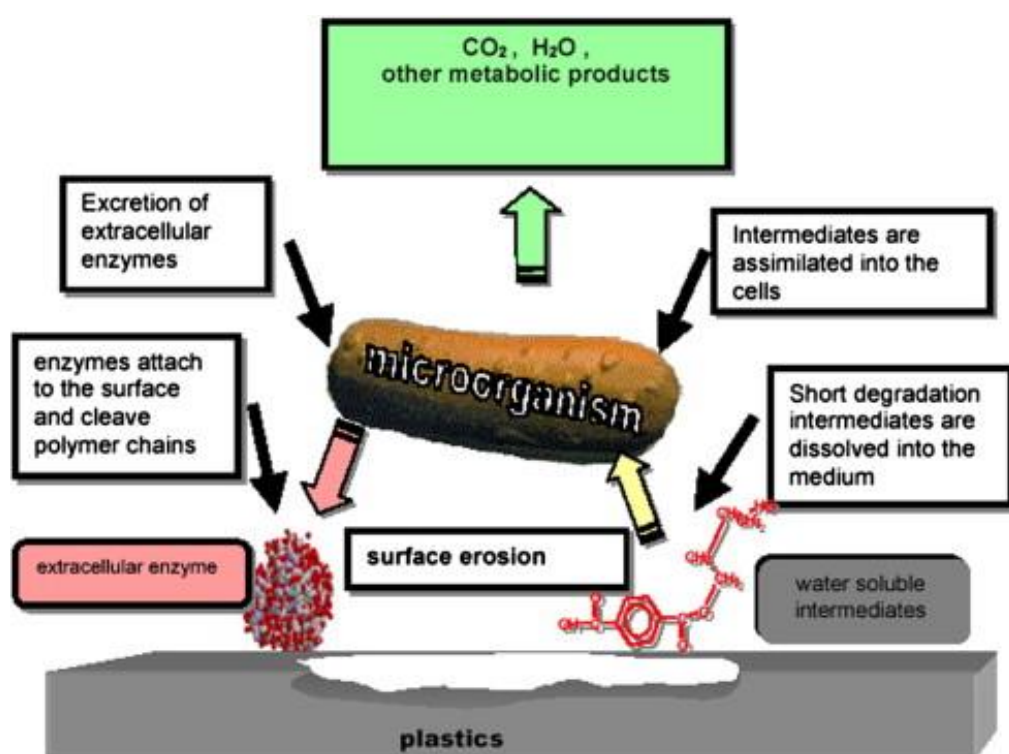


Fig. 2.10 General mechanism of plastic biodegradation under aerobic conditions (Mueller, 2006).

These microorganisms ranged from bacteria species, such as *Bacillus* sp., *Staphylococcus* sp., *Streptococcus* sp., *Pseudomonas* sp., *Arthrobacter* sp., *Diplococcus* sp., *Moraxella* sp. and *Micrococcus* sp. At the same time, the fungal species are recognised as *A. glaucus*, *A. candidus*, *A. ornatus*, *A. flavus*, *A. cremeus*, and *A. nidulans*. These microorganisms are abundant in aquatic and terrestrial environments and have been revealed to break down synthetic plastics because of their various metabolic abilities and genetic plasticity (Devi et al.,

2016; Wierckx et al., 2015). These microorganisms present in the environment use the plastic material as their carbon source for their growth and thus degrade the plastic materials.

Pseudomonas species are most active at degrading a wide range of plastic polymers characterised by low-density PE (LDPE) and high-density PE (HDPE). Kyaw et al. (2012) studied the extent of biodegradability of LDPE plastics with four various strains of *Pseudomonas* bacteria: *Pseudomonas aeruginosa* PAO1 (ATCC 15729), *Pseudomonas aeruginosa* (ATCC 15692), *Pseudomonas putida*, and *Pseudomonas syringae*. Degradation was accessed by weight loss, morphological changes, mechanical and spectroscopic differences. Their results revealed that these species of *Pseudomonas* degraded LDPE films. According to Cregut et al. (2013), several *Pseudomonas* species, including *P. fluorescens*, *P. aeruginosa*, *P. cepacia*, *P. protegens*, and *P. chlororaphis*, have been identified as PU degraders.

Han et al. (2020) used *Arthrobacter* and *Streptomyces* species isolated from agricultural soils to degrade PE films. The formed significant biofilms on the surface of the PE films using the films as a sole carbon source. Each strain degraded the PE films within a 90-day inoculation experiment by forming biofilms on the films' surfaces, decreasing the films' hydrophobicity and increasing carbonyl index and CO₂ release. In contrast, Shah et al. (2013) added that *P. aeruginosa* strain MZA-75 was found to degrade and metabolise polyester PU. Extensive degradation of polyurethane Impranil DLN was also accomplished by *P. protegens* Pf-5 and other *P. protegens* strains (Hung et al., 2016).

Kathiresan (2003) used two species of fungi: *A. glaucus* and *A. niger* isolated from mangrove soil to degrade polyethene and plastics cups. The fungal species degraded 28.80% of polyethene and 7.26% of plastic cups in one month period.

The process requires the breakdown of the polymer into smaller oligomers and, eventually, monomers that can pass through the cell membrane, followed by assimilation and subsequent intracellular metabolism (Singh and Sharma 2008). Biodegradation of structurally different plastics and their associated by-products is species-dependent due to the required enzymes.

2.6.5 Enzymes Involved in Plastic Decomposition

The action of enzymes on plastics remains a complex process because most plastics are not the specific substrates for some enzymes (Kumar Sen and Raut 2015). Enzymes contribute to the degradation of plastics, joined with other biotic and abiotic factors put together. Microorganisms involved in the degradation process get attached to the surface of the plastic starts growing by using the plastic as the carbon source. At this point, extracellular enzymes

are secreted by these microorganisms (Table 2.7), attach themselves firmly to the plastic surface, cleaving to the polymer chains and then catalyses a hydrolytic cleavage (fig. 2.15). The enzymes attach themselves to the surface of the plastics in different concentrations, depending on the number of enzymes secreted by the microorganisms. There is the formation of low-molecular-weight compounds known as monomers, dimers, or oligomers (Vasile and Seymour 1993). The process is called depolymerisation. These smaller pieces formed are further consumed by the microorganisms as carbon and energy sources.

Table 2. 6 Some microbial enzymes for biodegradation of plastics.

| Microbe | Enzyme | Polymer as substrate | References |
|------------------------------------|----------------------|--------------------------------------|-----------------------|
| <i>Aspergillus oryzae</i> | Cutinase | Polybutylene succinate (PBS) | Howard 2002 |
| <i>Aspergillus flavus</i> | Glucosidases | Polycaprolactone (PCL) | Shimao 2001 |
| <i>Thermobifida fusca</i> | Hydrolase | Polyethylene terephthalate (PET) | Muller 2006 |
| <i>Fusarium sp.</i> | Cutinase | (PCL) | Dashtban et al., 2010 |
| <i>Phanerochaete chrysosporium</i> | Manganese peroxidase | Polyethylene | Deguchi et al, 1998 |
| <i>Phanerochaete chrysosporium</i> | manganese peroxidase | Nylon-6 | Iiyoshi, et al. 1998 |
| <i>Rhizopus arrizus</i> | Lipase | Polyethylene adipate (PEA), PBS, PCL | Shimao 2001 |
| <i>Amycolaptosis sp.</i> | unknown | Polylactic acid (PLA) | Dashtban et al., 2010 |

2.6.6 The role of biofilm on the hydrophobicity/hydrophilicity of plastics

The hydrophobicity or hydrophilicity of any polymeric material depends on the nature, extent and position of the functional groups existing in that plastic (Al-makhlafi et al., 1994). If the degree of the degradation of any material is higher than the extent of depletion of its functional groups, then there will be an increase in the hydrophilicity of that material; equally, if the rate of reduction of functional groups of a polymeric material is higher than the rate of degradation. An increase in hydrophobicity will be detected. Most plastics are hydrophobic because they

are made to be durable, rugged, and resist degradation. Therefore, hydrophobicity is a vital factor to be considered in the chemistry of plastic biodegradation since it is between plastic and microorganisms (Cunliffe et al., 1999). However, as soon as plastic enters the environment, be it on land or the aquatic system, biofilm, one of the signs of biodegradation of plastics in different environments, quickly grows on the plastic surface. The reason is that physicochemical weathering and microbial activities in that environment influence plastic behaviour in such an environment (Arunkumar et al., 2020). For instance, UV radiation causes the release of free radicals that trigger photo-degradation processes and alter the plastic surface properties (Pinto et al., 2019). These photo-degradation processes reduce the hydrophobicity of such plastic, thereby increasing its hydrophilicity. The more the hydrophilic surfaces of a polymeric material, the more quickly the plastic is covered with biofilm formed by microorganisms (Wang et al., 2012). The reduction in the plastic's hydrophobicity aids biodegradation processes. i.e., allowing microorganisms to form biofilm on the plastics' surface and reducing the plastic's light transmittance (Sudhakar et al., 2007; Eich et al., 2015; Horton and Dixon, 2018). Biofilm colonization, therefore, depends on differences in the surface properties such as additives, coarseness, wettability, and exposure to solar radiation (Pinto et al., 2019).

2.6.7 Effects of plastic wastes in the environment

Synthetic plastic materials are naturally inert and resilient to microbial attack and therefore stay long in the environment before degradation (Reddy, 2008). When found in soil, it reduces soil usefulness, hinders the growth of plant life, and reduces water permeation into the soil. They are a hazard to aquatic life when they are located in water bodies, affect aquatic plants, and cause bioaccumulation of plastics in the bodies of marine animals when they feed on them; a case of choking or death may occur with such animals (Gopal et al., 2014). The quality of drinking water is reduced as plastics release some toxic chemicals for which most of them are known to be carcinogens, for example, styrene, phthalates, bisphenol A, benzene, and vinyl chloride that are by-products of PS, PE, PET and PVC (Government India, 1997).

Several wandering animals consume plastic materials and bottles from landfills due to inadequate, open, and un-engineered disposal structures, which can lead to their death.

Throughout the wet season, the plastic waste dropped on the roadsides is carried away into water pools, channels, and gutters, leading to their blocking and overflowing. These blockages due to plastic build-up become a breeding ground for dangerous insects such as mosquitoes that cause human sickness. Also, Gopal et al. (2014) concluded after their research that the

water quality gets decayed due to the accumulation of these synthetic materials. People living around landfills where these plastic wastes are burnt face respiratory problems because the atmosphere has been polluted with fumes from these toxic chemicals. Fig. 2.11 reveals plastic wastes in the marine body (A) and the landfill (B).



Fig. 2.11 Plastic wastes in the environment, A the marine body (Author's picture) and B, the landfill (Wilfredor, 2006).

CHAPTER 3

DESCRIPTION OF OWERRI, IMO STATE AND PENHESGYN, NORTH WALES

3.1 Background of Study.

As the world continues developing, consumption rates keep rising—an unavoidable concern because the rise in consumption rates directly influences the amount of solid waste generated. Solid waste management is a multidimensional concern that combines political, institutional, public, environmental, and financial sectors (Mitchell et al., 2015). Therefore, this chapter will cover the detailed study description of the dumpsites where feedstocks for composting will be collected. Dumpsites where plastics will be sampled from and identified using ATR FTIR spectroscopy. Lastly, the sites where plastic degradation will be conducted in Nigeria and the United Kingdom. Comparison between the temperate and tropical zones, i.e., (the United Kingdom and Nigeria) for degradation of plastics will be studied because of the differences in the climatic conditions and the chemistry of the substrates used in both zones, which all will affect the rate of degradation of plastics.

However, the choice of Owerri metropolis in Imo State, the eastern part of Nigeria, for this study was because of its urban status. It is a small city in Nigeria which is also faced with municipal solid waste management challenges like most cities in developing countries. Imo State is the researcher's State, which made the fieldwork and access to sites for the study more accessible. Also, most studies on solid waste management in Nigeria have mainly focused on the larger cities, neglecting smaller cities.

3.2 Owerri (Imo State)

One significance of speedy urbanization in Nigeria is the increase in the generation of solid wastes. Several urban authorities face challenges in handling these difficulties and dealing with their collection and disposal (Ogu, 2000). Waste management challenges vary with the sizes of municipalities in Nigeria. Owerri is the capital of Imo State and is located on coordinates 5.485°N and 7.035°E on a landmass of 551km². Owerri is one of the fastest-growing state capitals out of 35 other States in Nigeria and has a population of about 1.4 million people as of 2016 and is approximately 100 square kilometres (40 sq mi) in area. The high population density seen in Owerri could be ascribed to rising rural-urban migration as seen in Fig 3.1, resulting in the increased generation of waste and pressure on the current lowly and insufficient waste management structure. With the changes in the way of life and migration of people to

this area, the municipal solid waste generated has not only increased in quantity, but the constituents have also become more wide-ranging.

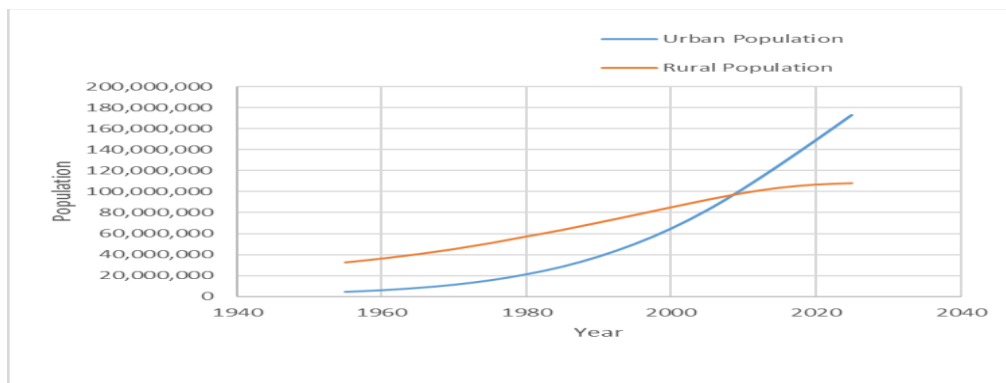


Fig. 3.1 Nigeria's Urban and Rural population, Year 1950-2025 (UN, 1986).

The city is in the tropics and has a West African monsoonal climatic type marked with two different seasons (rainy or wet and dry or harmattan season) during April to October and November to March, respectively. The average annual rainfall is 1500- 2200mm (60-80 inches), having the wettest season about June-August (Imo State government, 2016; Oguntoyinbo, 1994). The average yearly temperature is 31°C, and the annual relative humidity is 75% in Owerri, with a slight difference in the different seasons of the year (Amadi et al., 2012; Imo State government, 2016). There is a high moisture content (52.6%-66.2%) of waste generated in the wet season, like other tropical countries with the same pattern of rainfall (Chua et al., 2011; Hassan et al., 2001). This is because the wet seasons influence the moisture content of waste materials (feedstock) generated, thereby influencing the composting process (Dayal et al. 1993). There are two chosen collection methods of wastes generated in Imo State: the door to door and communal disposal methods. However, illegal disposal methods such as open dumping in unregulated dumpsites and burning wastes are still practised. Because residents often feel that these are the only options available for solid waste management (Mwanthi and Nyabola, 1997; Goett, 1998; Hilburn, 2015).

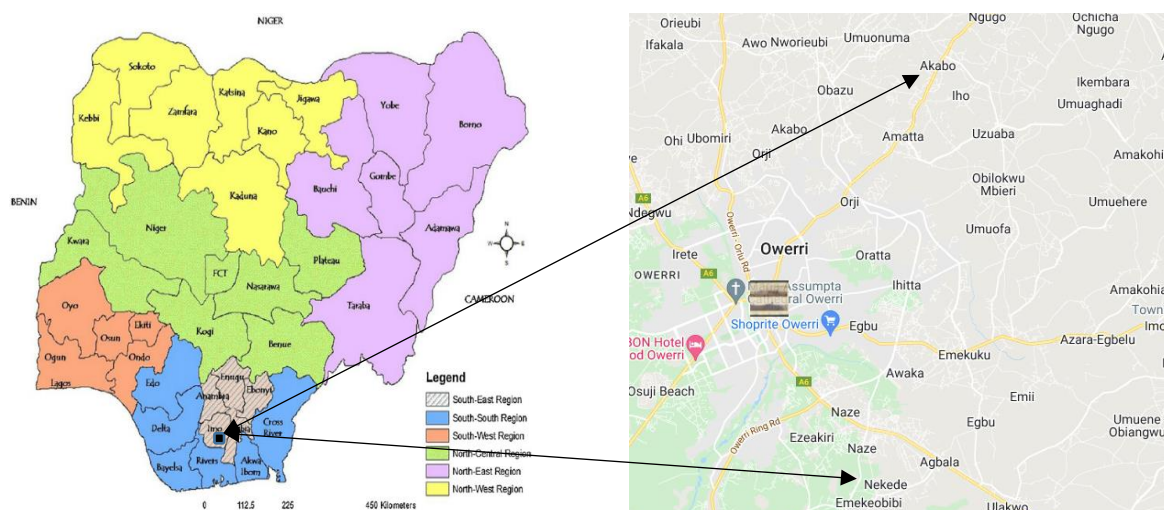


Fig. 3.2 Map of Nigeria showing Owerri in Imo State the location of the composting site and the Nekede dumpsite for sourcing feedstock.Source: (<http://www.nigeriamasterweb.com/5mbebe/NigeriaStatesMap>)

Fig. 3.2 shows the maps of Nigeria and Owerri/Akabo where (Jeniv fertilizer is made) windrow composting takes place and Nekede dumpsite where some of the organic feedstock used for composting is obtained. The feedstock used for composting is obtained by sorting organic portions directly from dumpsite or buying organic waste from vegetable, fruit, or foods markets. Therefore, compost made from organic portions of municipal solid waste in Owerri in Nigeria will be used for this research.

Identifying different types of plastics that make up the dumpsites is essential if operational solid waste management must be practised and sustained. Knowing that about a 150 million tonnes of plastics enter dumpsites yearly and less than 30% of this plastic waste is recycled. This research will collect at least 95 different unknown plastics from three dumpsites and will be identified using FTIR spectroscopy. Fig. 3.3 shows the maps of Nigeria and Owerri revealing the locations of the three dumpsites, Irete, Orogwe and Nekede, where different unknown plastics will be sampled and used for analysis and Irete where the degradation of the plastics will happen.

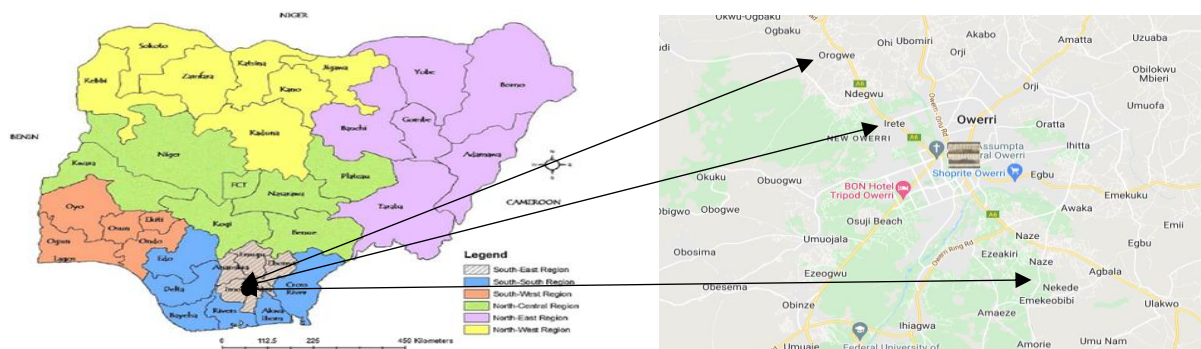


Fig 3.3 Map of Nigeria and the three communities with three dumpsites in Imo State where plastics wastes where sampled. Source: <https://placeandsee.com/s?as=mapa&n=imo-state>

Irete, Orogwe and Nekede dumpsites are within the Owerri zone of Imo State, Nigeria. Thus, are the dumpsites where plastic wastes will be sampled. The choice for these three dumpsites in Imo State is because the researcher lived and worked around Irete and Orogwe, which housed the two small dumpsites. In contrast, Nekede dumpsite is a big dumpsite that accepts waste materials from the small dumpsites, making the fieldwork for the study more accessible.

3.2.1. Irete dumpsite

Irete is a community in Owerri west local government of Imo State in Nigeria. The following neighbouring communities surround the community; umuguma by the North, Orogwe and Akwakuma by the East, Okuku by the West and Ndegwu by the South. Ogbaku Ohii and ndegwu. It comprises 18 villages, of which they are subdivided into three, Ezi-Irete, Amaikpu and Umuoma. The dumpsite is located along Onitsha-Owerri express road, opposite Irete market. The waste generated in this dumpsite is mixed and comes from the villages that make up Irete and nearby communities. Irete dumpsite is a very small and illegal because it is at the federal express road. Waste generated causes both air and land pollution because of the inefficient waste management in the state

3.2.2. Orogwe dumpsite

Orogwe is one of the communities in Owerri west local government of Imo State in Nigeria. The following neighbouring communities surround the community; Irete, Ogbaku Ohii and Ndegwu. It is made up of smaller villages Umueze, Ubah, Umuafom, Umunjanwoke, Umuokpiri and Umunnomo, with a population of about 10,000 people, predominantly farmers. The dumpsite is located at the boundary between Irete and Orogwe, along Onitsha-Owerri express road, about 7km to the state's capital. The waste generated in this dumpsite is mixed

and comes from both communities (Irete and Orogwe). Orogwe dumpsite is a small and illegal because it is at the federal express road connecting two major Cities (Imo and Anambra State). Waste enters the drainages and blocks them when not attended to and very smelly leachate formed enters a water body behind the dumpsite. Inefficient waste management in the state has resulted in both land and air pollution in this community.

3.2.3. Nekede dumpsite

Nekede is a town in Owerri West local government of Imo State in Nigeria. It comprises three different towns, namely, Umuoma, Umualum, and Umudibia. It lies at the junction of Otamiri and Nworie Rivers. It cuts across the Aba-Owerri express road. It is fast becoming a city, with a growing population due to the citing of the federal-government owned higher institutions, federal polytechnic Nekede and Federal University of Technology Owerri located 5km from Nekede. An increase in the population of people in this town led to a rise in the waste generated. Also, this dumpsite is the authorised large dumpsite built by the Imo State government for receiving waste materials from smaller dumpsites. Nekede dumpsite is the only active dumpsite since the government reclaims others for recreation purposes. It receives 45-60 trucks of waste from around the state. The sources of waste in the metropolis dumped at this dumpsite are households, markets, hotels, schools, hospitals, and offices. It is noteworthy to state that no factories or industries exist within the metropolis.

There has been slight progress in the seventeen Sustainable Development Goals (SDGs) established, one of which is ensuring environmental sustainability. It has been sluggish, with Nigeria ranking 160 on the 2020 SDG Index (Sachs et al., 2020).

Owerri has several waste sources, mainly from households, offices, markets, companies, hospitals, hotels, and schools. Organic wastes make up more than 50% of the entire waste generated in the state (Nnaji, 2015). These waste materials generated in the city find their way into over 120 dumpsites dispersed around the city. Only about 41 of these dumpsites are legal, where basic waste amenities have been made available for disposal from recognised collection points in various parts of the city. Most times, the wastes in these dumpsites are set on fire, increasing air and soil pollution. Handling solid waste has become one of the major challenges facing the federal, state, and local government environmental protection agencies. In Owerri, like other States in Nigeria, solid waste generation is influenced by some factors such as urbanisation, industrialisation, economic growth, income level, people's lifestyle, and climatic conditions (Odoemene and Ofodu, 2016).

In 1989, the Federal Government of Nigeria established a policy governing the environment (FEPA 1988) in response to the severe challenges caused by environmental degradation. This policy aimed to attain sustainable development in Nigeria cities, and they are:

- To provide all Nigerians with a quality environment suitable for their health and wellbeing.
- To safeguard and use the environment and natural resources for the advantage of present and future generations.
- To restore, sustain and improve ecosystems and ecological practices vital to the functioning of the environment and for the protection of natural diversity.
- To promote public consciousness and encourage understanding of vital links between environment and development by encouraging individual and public participation.
- Co-operate with government bodies and agencies to optimise transboundary natural resources and reduce environmental pollution.

The Federal government established State Environmental Protection Agency (SEPA) and local government environmental protection agencies in the mid-1990s for each city. Imo State's government organisation responsible for solid waste management is the Imo State Environmental Protection Agency (ISEPA). Their roles cover City cleaning (local contractors in a municipal/private involvement plan), street sweeping, waste control, solid waste collection and transfer and vegetation control. Although informal solid waste collection operations exist parallel with official agencies in some major cities like Onitsha, Lagos, etc., the collectors provide the service for a fee.

Studies have also revealed that about 30-60 % of solid waste generated in Nigerian cities is not collected and that the current environmental legislation in the state is poorly enforced (Ogwueleka, 2009). These setbacks mentioned can be accredited to these factors: little accessibility caused by poor road systems, operational, financial, and managing flops on the side of waste management authorities, poor services, limited use of waste reduction activities, lack of regulated dumpsites, denial to pay stipulated bills for collection and non-execution of method optimisation.

Solid waste management is hence one of the essential obligations of the Agency. ISEPA solid waste department is responsible for the collection, transfer, and disposal.

Usually, food waste was found to comprise over 50% of overall municipal solid waste in most cities in Nigeria (Ogwueleka, 2009; Nnaji, 2015).

According to Halla and Majani (1999), composting the organic portion of MSW is a part of waste management since it reduces waste generated and transport costs while simultaneously creating financial and employment prospects.

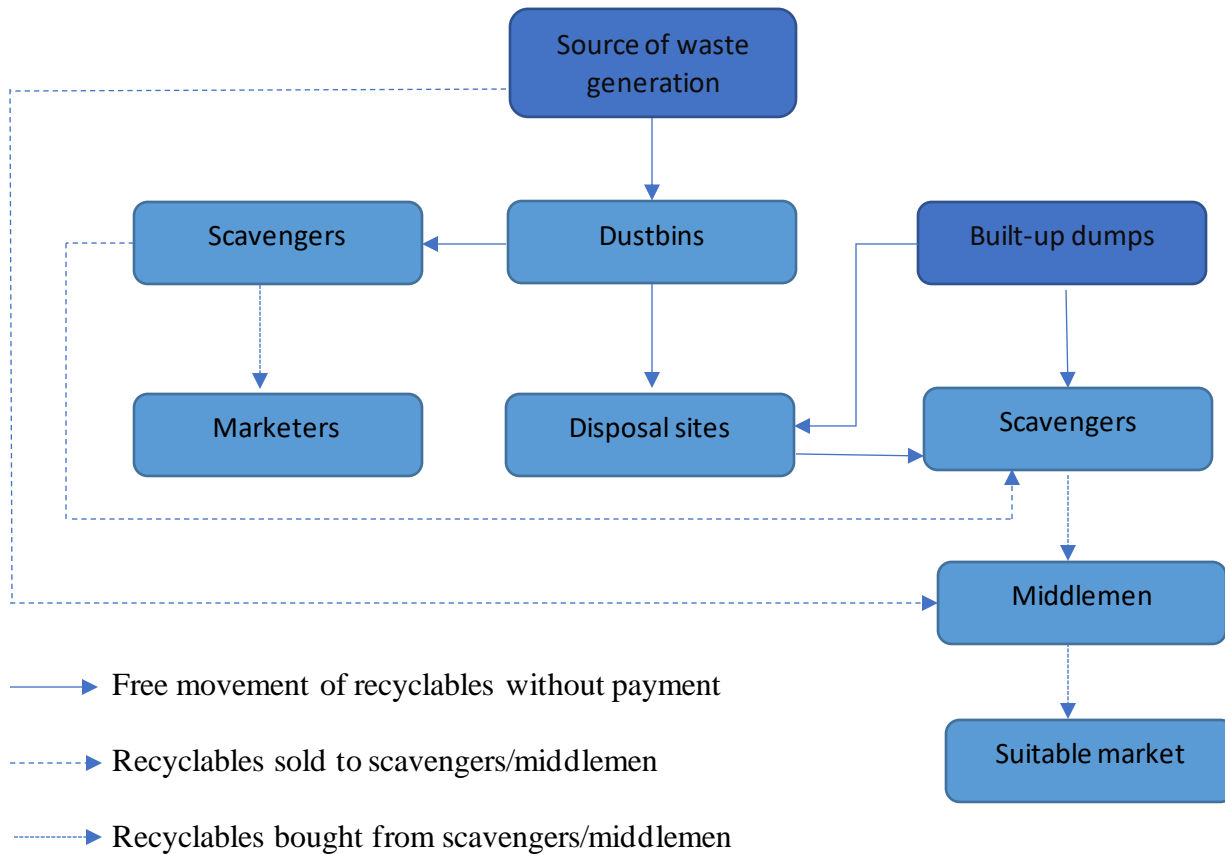


Fig. 3.4 Diagram of scavenger activities in MSW management in Imo- State Nigeria (Agunwamba, 2003)

The diagram (Fig. 3.4) shows clearly how recyclable waste materials are handled and managed at the State level by scavengers.

3.3 Anglesey (North Wales)

Anglesey is an island off the north coast of North Wales with an area of 276 square miles (715 km²). It has a temperate climate, most humid, tending to be wetter with less sunshine than England. It is characterised by four seasons, spring, summer, autumn, and winter. There is ample rainfall all year round, with the usual wind from the southwest bearing regular spells of mild and wet weather from the Atlantic Ocean (United Kingdom, Factbook 2008). Rainfall is heaviest between September and January. The temperature varies with the seasons between -11 and 35° C. The vegetation of Anglesey covers a wide range of grassland and wetland plant

species for rearing animals. The population of Anglesey was estimated at 69,800 people in 2017.

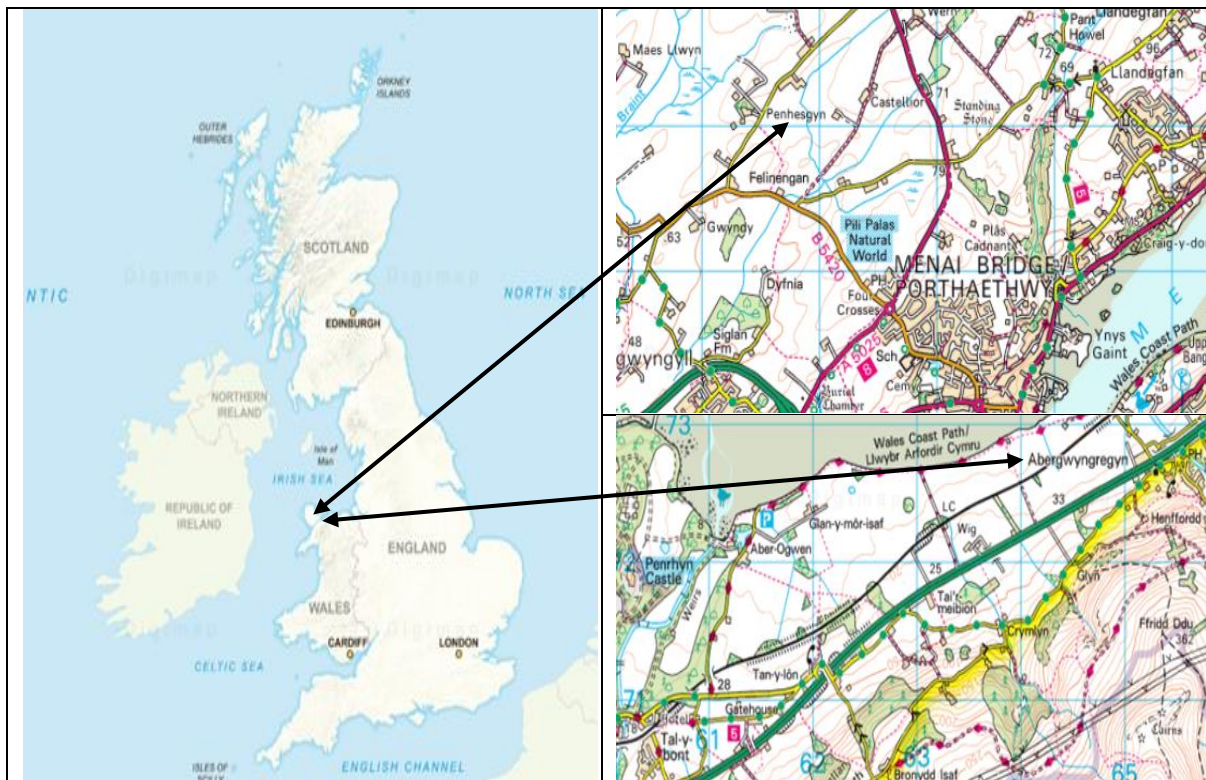


Fig. 3.5 Map of the United Kingdom and North Wales showing Anglesey the composting site and the site for the experimental study was setup. Source: <https://digimap.edina.ac.uk/roam/map/os>

Fig. 3.5 shows the maps of the United Kingdom and North Wales; in Penhesgyn where compost is made, and Abergwyngregyn location where the degradation of the plastics was studied. Penhesgyn recycling site is where the in-vessel composting of the organic waste materials takes place, and it is located in Anglesey. Lots of woody waste is brought to this composting site during winter and stored together until more fresh material appears in spring. The woody waste is shredded and mixed with greener waste for composting. The Anglesey council manages the Penhesgyn recycling site.

The rising profile of solid waste management in North Wales is best reflected by the level of activity generated within the sector. The waste disposal methods employed in North Wales are well-structured, which entails reducing waste generated through recycling and reusing them. The MSW management in Wales is a shared responsibility; even though Natural Resources Wales holds general responsibilities for environmental regulation, District Councils collect waste generated and transport them to landfills. In the case of Unitary Authorities, the Disposal and Collection Authority functions are combined under one layer of local government (Phillips et al., 1999).

The resource and waste strategy focused on preserving material resources mainly by reducing waste, encouraging continued use of natural resources, and moving towards a circular economy in England. The Welsh Government released its first circular economy strategy, including plans to make Wales the world's best country at recycling. This new strategy aims at keeping resources in use and avoiding waste. This new strategy forms part of plans for a 'green recovery' in Wales, which tackles the effects of the Covid-19 pandemic, Brexit, and climate change.

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Waste Strategy (2007) drew the next instant and strategic 47 objectives as it concerns municipal solid waste management in all parts making up the United Kingdom:

1. To reduce waste growth by prioritising waste prevention and reuse.
2. To meet and surpass the Landfill Directive, which requires reducing the amount of biodegradable municipal waste (BMW) landfilled in 2010, 2013 and 2020.
3. To protect the asset in infrastructure required to divert waste from landfills.
4. To attain the best environmental benefits from reserves through better recycling resources and energy recovery, using various technologies.

While the Resources and Waste Strategy introduces some policies to a more circular economy, such as waste prevention through reuse, reduction and recycling actions, the Waste Strategy (2007) for England focuses on waste arising and their national management plan management. The significant difference between the UK and Nigeria in handling and managing municipal solid waste generated within its region is that while the UK has the proper infrastructures and observes set out waste management strategies and rules, Nigeria is faced more with the challenges associated with municipal solid waste management. The reason is the lack of infrastructure and poor enforcement of the waste management strategies and rules (Waste Strategy (2007); Ogwueleka, 2009).

CHAPTER 4

SEASONAL VARIATIONS IN THE PHYSICO-CHEMICAL PROPERTIES OF COMPOST PRODUCED IN OWERRI, NIGERIA.

4.1 Introduction

Seasonal variations influence the composting of organic fractions of the municipal solid wastes, affecting the final properties of compost made (Boldrin and Christense, 2009). The components of organic waste used for composting consist of a wider variety of seasonal materials (garden waste, organic house waste and manure). The garden waste, organic house waste and manure that make up an organic fraction of MSW are used in compost production in some developing countries, e.g., Nigeria.

Wet seasons affect the moisture content of the feedstock and, subsequently, the moisture content of the final compost made. Like a windrow setup without a shield, it may leach out vital components of the final compost formed because of rainfall. Moreover, the seasonal variation in the properties of compost is linked to the varying feedstock used for making them, which vary seasonally, too (Well, 1994; Ward et al., 2005). Ward et al. (2005) observed that the chemical composition of composted organic waste varied widely with seasonal variation in raw input across the UK. He evaluated dry matter (DM), Cl, N, C, and K contents and the C/N ratio. The study showed seasonal patterns for some parameters (N and K). Some researchers from different countries looked at the effects of seasonal variations on the Physico-chemical properties of final compost made, as shown in table 4.1.

Table 4. 1 Comparative table to show seasonal differences in values obtained from compost analysis of some countries.

| Country | Seasons | Parameters % dry weight | | | | | | References |
|---------|---------|-------------------------|--------------|----------------------|-----------|----------|----------|----------------------|
| | | pH | EC (dS/m) | Salinity Meq/100g | TOC | TN | C/N | |
| Spain | Winter | 8.5±0.17 | 0.4±0.04 | - | 47.3±1.87 | 1.6±0.14 | 29.4±2.6 | Benito et al 2006 |
| | Summer | 8.6±0.17 | 0.5±0.03 | - | 46.7±1.36 | 1.5±0.29 | 33.7±6.7 | |
| Italy | Winter | 8.2 | - | 18 | 33 | 2.7 | 9.3 | Negro et al 2018 |
| | Summer | 8 | - | 21 | 28 | 3 | 12.9 | |

(The values shown are the average of 3 values from each season, n=3)

The parameters checked seasonally gave variation in some results obtained from Table 4.1. Results revealed that the pH values of all composts analysed in winter and summer were above 8, respectively. The EC values followed the winter compost < summer compost agreed with declining values of rainwater received. The change in the EC was due to the difference in the leaching of soluble salts due to seasonal rainfall (Benito et al., 2006). While the C/N ratios

from Benito et al. (2006) were 29.4 and 33.7% for winter and summer, which were all higher than the typical values of 15–20, Negro et al. (2018) had their C/N ratio to be 9.3 and 12.9% lower than the standard ranges. However, the C/N ratios of all the composts made in the summer were higher than those made in the winter because of more grass clippings and green plants produced during the summer/wet season (Benito et al., 2006).

Therefore, C/N and EC were only affected by seasonal variations because composts had less air space and were more easily accessible for water absorption. While the analysis by Negro et al. (2018) gave opposite results except for the values of C/N ratios that agreed with that of Benito et al. 2006.

These feedstocks were taken periodically from the composting facility in Madrid, Spain, over 18 months to determine if seasonal variability influenced the properties of the compost made. Moreover, Ward et al. (2005) observed that across the UK, the chemical composition of composted organic waste varied widely with seasonal variation in raw input. Ward et al. (2005) revealed that seasonal differences affected some compost parameters from the UK after collecting feedstock in different year seasons.

Hurley et al. (2017) and Huang et al. (2017) also revealed that essential nutrients were leached out more during the composting process in the wet/summer seasons. Therefore, seasonal variations have influenced the properties of composts made.

4.1.2 The seasonal variation in feedstocks used for compost production

The results of the Physico-chemical analysis conducted on garden waste sampled five times from two seasons at four different composting amenities in the USA by Bary et al., 2005 revealed compositional variation among the facilities. The main reason for the compositional difference was that grass clippings were the primary source of seasonal differences. For instance, green waste will contain more dead leaves and woody material in the dry/winter seasons and more grasses and green plant stock in the wet/summer seasons. Therefore, the available feedstock in a particular season will influence the process and the final properties of compost. This is because the feedstock balances nutrients and carbon/ nitrogen ratio, which is of the utmost importance in all phases of the breakdown of organic waste.

Some foods, vegetables, and fruits used for composting are seen in specific seasons in Nigeria. Gidakos et al. (2006) agreed that the composition of solid waste varied in different areas of Greece. The quantity of waste generated was influenced by a seasonal variation on the Island of Crete. Reason being that the amount of waste generated in the summer period was more prominent than the ones produced in other seasons of the year, especially in the tourist regions.

Fig. 4.1 revealed the seasonal variation in waste generation (A) in Akure Ondo state (2016-2018) and (B) in three towns in Oyo State, Nigeria (Afon, 2007). From fig. 4.1A and B, more wastes were generated in Akure and Oyo between August and December, with the peak occurring in December. This differentiation is apparent because of the harvest of produced maize husks, fruit, and food peels between July and December. Being a festive period, December gives rise to lavish spending and extravagant lifestyles, increasing the amount of waste generated. Afon (2007) also studied and found that 1093 tons of waste were generated in the wet season (July) while 774 tons were generated in the dry season (February) in the southwestern state of Nigeria. This seasonal variation of municipal solid waste is not peculiar to Nigeria but to most countries (Wahab and Ola, 2018; PCI, 2008). Boldrin and Christensen (2010) concluded that seasonal variation influenced the quantity, the physical and the chemical composition of garden wastes generated in Aarhus, Denmark. They said that the amount of garden waste generated varied from 2.5 kg/ person/month in winter to 19.4 kg/ person/ month in summer, with a minor increase recorded in autumn (October), perhaps due to the collection of leaves. Volatile solids like dead leaves and woody materials make up the green waste in the winter.

In contrast, fresh green grasses and vegetables with substantial soil make up the green waste, giving rise to high ash content in the summer. Most recoverable nutrients are higher and more in garden waste in the summer months. Therefore, seasonal differences in the feedstock and their adjustments are vital aspects to consider during the composting process (The Composting Council of Canada (b), 2002).

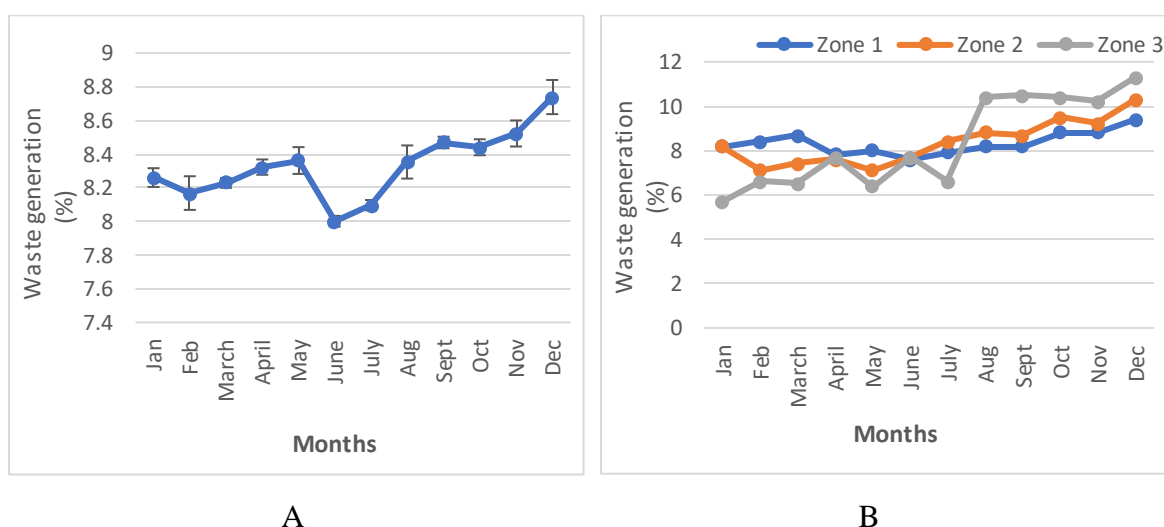


Fig 4.1 A. seasonal variation in waste generation in Akure Ondo state (2016-2018), B. percentage of seasonal variation of waste generation in three towns/zones in Ogbomosho, Nigeria (Afon, 2007).

4.1.3 The variation in the properties of compost

The characterisation of the Physico-chemical properties of the compost produced is an essential aspect of MSW management because its feedstock varies with seasons, vegetations, localities, lifestyles, demographic, environmental and legislative influences (Atalia et al., 2015). The variations in the factors mentioned influence the physicochemical properties of the final compost. The significant differences in the properties of compost made between Nigeria and the UK are the high electrical conductivity and heavy metal concentration observed in Nigerian compost compared to the UK compost. The reason is that the feedstock used from composting in Nigeria contains food waste that is very high in soluble salts, affecting such compost's electrical conductivity. In contrast, food wastes are not part of the UK's feedstock for composting. Again, feedstocks are sourced directly from the dumpsites, which influences the heavy metal contamination of composts in Nigeria because of the inclusions of other waste materials from other sectors.

In contrast, green and woody wastes characteristically comprise low heavy metal levels. Therefore, the feedstock used in compost production influences its properties (Well, 1994; Ward et al., 2005; Oyesola and Obabire, 2011). Even minor changes in the concentration of some parameters above the standard levels can result in severe environmental problems to the soils treated with it.

4.2 Aims and Objectives

Few studies focused on a seasonal variation on the feedstock used for compost making. Some studies have been published examining the seasonal variation of feedstock without looking at the effect of these feedstocks in the final compost made. This work aims to investigate and report on the feedstock (organic constituents of MSW) and proportions used for composting in both wet and dry seasons and then evaluate the chemical properties of compost made seasonally in Nigeria. By accomplishing these objectives, the study seeks to answer the following questions:

- a) Does seasonal variability of feedstock have an impact on compost?
- b) Does seasonal variability influence the chemical properties of compost from Nigerian MSW?

4.3 Materials and Methods

4.3.1 Background / Materials of Compost produced in Nigeria:

The compost used in this study was purchased from Jeniv fertilisers, located on Owerri/ Akabo express road. Imo State, Nigeria. As mentioned above, the feedstock used for compost making is organic waste from the three categories of waste, ranging from different materials, as seen in fig. 4.2. They include paper and cardboard, fruits, and vegetable wastes, spent grains (waste from the brewery), water hyacinth plants, burnt palm kernels, food remains, crop remains, grasses, and sawdust. To compost, manure is collected directly from poultry, piggery, and grazing fields. Fig.4.2 revealed the records of feedstock used for compost making for both wet and dry seasons were taken from three years (2016-2018), most of the feedstock is seasonal, and the decision of the feedstock to be used is strongly dependent on their availability. The feedstock used for composting were;

Green Waste: It is an organic waste containing a high nitrogen concentration. Examples are grass clippings, leaves, water hyacinth, green vegetables and garden wastes.

Spent grain: It is an essential by-product of brewing industries. It accounts for about 85% of the whole by-products generated. It is rich in cellulose and non-cellulose polysaccharides and can be recycled (Aliyu and Bala, 2011). Because of its high protein level, it is used to boost the nitrogen level in the soil.

Fruits wastes are the remains, peels, or spoilt portions of fruits from either the buyer or seller. They are rich in browns, i.e., high carbon content, and can boost C/N levels in composting.

Food remains: These are portions of food discarded or lost uneaten either from production, handling, retailing or consumption.

Manure: It is an organic material obtained from animal dung and, in such cases, with bedding straw in them. It is rich in nitrogen levels and is used to improve soil fertility. For example, poultry, piggery or from grazing fields for cows)

Others: They could be other organic materials not mentioned, which could be in burnt or unburnt forms; examples are palm kernels, sawdust, ashes, wood, cardboard, and papers. They are also rich in browns, i.e., high carbon content, enhancing C/N levels during composting.

The feedstock is put together in different proportions in the window for 29 days, where regular watering and the temperature were checked to ensure aeration and uniform decomposition. Also, regular turning was done by the composting workers using CAT-front end-loaders. The piles were transferred to the curing bay using the front end-loaders, after which they were left for about 21 days. At this point, the materials were sun-dried and non-degradable materials

were picked up, then moved the batch to the fertiliser house where they were blended to compost. Composts from Nigeria were sampled during the two seasons of Nigeria (wet and dry) to determine seasonal variations in their properties. Composts produced in the wet season were coded Nigerian wet composts (NWC), while those produced in the dry season were coded Nigerian dry composts (NDC).

Compost samples were collected three times at the core of each season to track the seasonal variations in their properties. Therefore, composts were sampled only for six months of the year. The Nigerian wet composts were produced and sampled in April, June, and July 2018, while the Nigerian dry composts were produced and sampled in November, January, and February 2019. The composting workers sampled with gloves, directly collecting the composts from the baler of the blender machine with airtight Ziplock plastic bags.

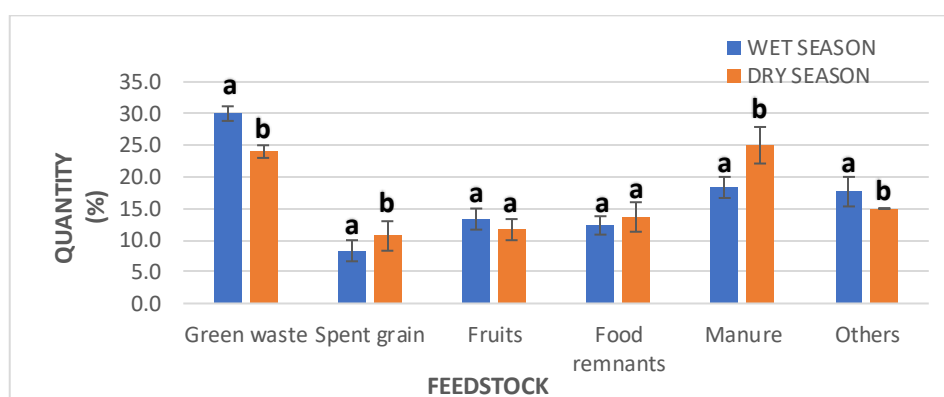


Fig. 4.2 The proportions of feedstock used seasonally in compost making in Nigeria from (2016-2018). (Source from Jenif fertilizers, Owerri Imo State).

4.3.2 Sampling methodology

The composting workers sampled composts from 12 different batches produced each season, four from each month, as mentioned in section 4.3.1. Three replicates (1000g each) were randomly sampled from each batch. Each batch produced 10 – 15 bags of compost, and the determination and purpose for random sampling depended on the availability of composted materials (sample size) to increase the generalizability of the results. The 12 batches from each season were labelled and denoted with (NWC1- NWC12) for the wet season and (NDC1- NDC12) for the dry season.

4.3.3 Sample preparation

The compost samples were air-dried by opening each Ziplock bag with the samples under the sun at 30°C for 48 hours in Nigeria in case some were still damp, which was part of the

requirements of the cargo company to provide relatively dry samples. Afterwards, they were packed in a thick sealed plastic bag and securely transported to the UK through DHL services according to the procedures for receiving foreign samples. They were transferred to the Thoday laboratory at Bangor University, where analysis will be conducted. The compost samples were labelled and kept in polythene bags and stored in a laboratory plastic box at room temperature until further analysis.

4.3.4 Analytical methods

4.3.4.1 Control and assurance of the resulting quality

We will attain precision and accuracy of study results using standard laboratory procedures, including analytical grade chemicals and ultra-pure water to prepare a 0.1 N HNO₃ solution to clean equipment. Before the analysis, the composts were processed according to British Standards. Table 4.2. reveals the summary of the analytical method and basic conditions applied for compost sampled in the wet and dry season. For all the methods, three replicates were used for the study.

4.3.4.2. Sample analysis

HCl was produced by Fisher scientific Laboratory, the United Kingdom, while the HNO₃ used was from Fluka Analytical France.

The analysis of composts was according to the British Standards (BS) for soil conditioner and growing media. Below table 4.2 is some specified test methods from (PAS) 100 compost accreditation schemes (PAS100, 2018).

Table 4.2 Summary of analytical method and basic conditions applied for compost sampled in the wet and dry season.

| Analysis | Test method | Type, Amount & processing sample | Seasons | |
|------------------------------------------------|----------------------------------------|----------------------------------|---------|-----|
| | | | Wet | Dry |
| pH | BS EN 13037 | F (2g) wm | ✓ | ✓ |
| EC | BS EN 13038 | F (2g) wm | ✓ | ✓ |
| LOI (Organic matter content) | BS EN 13039 | D (10g) dm | ✓ | ✓ |
| % carbon, % nitrogen and C/N | LECO CN-2000 (Direct combustion) | D (0.2g) dm | ✓ | ✓ |
| Possibly heavy metals (Cr, Cu, Ni, Pb, Zn, Fe) | BS EN 13650 | D (0.5g) dm | ✓ | ✓ |
| Nutrients (water soluble) | BS EN 13652 | F (0.2g) dm | ✓ | ✓ |
| Grinding | Kitchen pestle/mortar (lab. Mill ball) | D (20-25g) dm -hand grinding | ✓ | ✓ |

Sample type: F (fresh), D (dry), wm (wet-matter) and dm (dry matter).

Before the analysis, the composts were processed according to British Standards (BS 2000). For all the methods, three replicates were used for the study.

4.3.4.3 Compost pH and electrical conductivity (EC)

The compost solution was prepared for pH and electrical conductivity (EC) measurements. 2g of each compost sample was weighed into 25mL centrifuge tubes, and 10mL of deionised water (dH₂O) was added to each compost sample (1:5 compost: water (w/v) ratio). Three replicates of each compost were performed for both measurements. The samples were shaken for 30mins at 250rpm (SW2 Shaker Table, Edmund Buhler GmbH). The pH of the compost solution was measured with (HANNA instruments pH 209 meter, UK) after it had been calibrated by using buffer solutions (pH = 7 and 4). The EC was measured on the same solution with a standard probe (HANNA instruments EC 215 conductivity meter, UK) at 18°C. The EC meter was previously calibrated using a 0.01M potassium chloride solution. This solution has an EC of 1413 μScm^{-1} .

4.3.4.4 The determination of organic matter (OM)

For correct results, the measurement of organic matter was measured gravimetrically. For one to measure the organic matter of compost, about 10g of each compost sample (WB) was weighed into clean crucibles (WA); and the samples dried overnight in an oven at 105°C

(n=3). After drying, the crucibles were removed from the oven, cooled in a desiccator, and reweighed (WC). The change in mass obtained gave the water content (Faithful, 2002).

For the OM determination, the compost samples (WC) were placed overnight in a muffle furnace (Carbolite, UK) at 450°C. We removed the crucibles from the furnace and allowed them to cool in desiccators; it was reweighed (WD). The difference in percentage from the dry state gave the organic content. The soil moisture content and organic matter as percentages were calculated as follows:

$$\text{Loss on ignition (\% LOI)} = \frac{\text{WC} - \text{WD}}{\text{WC} - \text{WA}} \times 100 \dots\dots\dots (\text{Equ.4.1})$$

4.3.4.5 Determination of total carbon and nitrogen in compost

0.05-0.2g of oven-dried compost was used to determine compost's total carbon and nitrogen content using Direct Combustion, Thermal Conductivity, and IR absorption (CHN-2000 analyser LECO TruSpec®). Samples were ground with pestle and mortar. Sieved to 1mm using 630µm sieve. Dry at 105°C overnight in an oven and carefully weigh out 0.05-0.1g of compost samples into a special tin foil cup. Wrap well after putting samples, then record the weight. Samples are ready to be run in a LECO machine (Abdalgader, 2014).

4.3.4.6 Direct determination of compost total element concentrations

Total X-ray fluorescence spectroscopy (TXRF) analysis was conducted on an S2 PICOFOX TXRF (Bruker AXS Microanalysis GmbH, Germany) to ascertain the element content in compost samples. The S2 PICOFOX is a benchtop TXRF instrument with a Silicon detector and an X-ray tube with a molybdenum target. It uses software SPECTRA (Bruker, v. 7.2.5.0); this automatically stores spectral information obtained during analysis and converts individual files to CSV. Format. Sample discs are prepared by pipetting 10 µL of Serva Silicon solution onto the centre of cleaned discs and allowed to dry for 15 mins at 80°C on a hot plate, then returned to the disc carrier. 20 mg (recorded to 2 decimal places) of oven-dried compost, samples were ground down to < 70µm, weighed into 1.5mL Eppendorf centrifuge tubes and mixed with 1 mL of Triton-X solution (1% v/v) to each compost sample. Each sample was internally standardised using new pipettes with 5 µL of Gallium stock solution (1000 mg L⁻¹). A vortex device is used to homogenise the samples for 30 seconds. Then 10 µL of the

suspended sample was pipetted onto a centre of treated discs kept in the disc carrier and dried under a glass cover on a hot plate for 15 minutes at 50°C until completely dry.

A gain correction was conducted at the start of each run after every 20 samples using an un-siliconised disc carrying 10 µL of Gallium stock solution (1000 mg L⁻¹). Then Insert discs with dried samples into the disc carrier of the machine, then analyse for 600 seconds. We deliberately chose 15 representative compost samples with various properties and elemental concentrations to calibrate the S2 PICOFOX for total element analysis in composts and an additional 20 soil samples as an independent validation set (Bruker, 2007b).

4.3.4.7 Acid extraction for compost

Weigh out 0.5g of dried compost samples into 10 Pyrex tubes (n=3 including a blank tube). Then place the tubes in racks into a half-filled water bath in a fume hood at 85°C. Add 5ml of HNO₃ gently into the Pyrex tubes with samples and the blank and leave the samples to digest for 1 hour. Then add 2.5mL HNO₃ to the samples digesting already and continue digesting until no more brown fumes are seen. Add 5ml HCl and leave to digest further for half an hour. The mixtures are left to cool and then placed in a container filled with ice. 10mL dH₂O is added to the Pyrex tubes. The mixtures were filtered with 42-Whatman filter papers and made up to 25mL with deionised water into 25ml volumetric flasks. The extracts are transferred into polyethene bottles and stored in the refrigerator at 4°C for analysis. The extracts in the refrigerator were used for Flame atomic absorption spectrometer (FAAS) and flame photometry analysis after diluting the extract in the ratio of (1:100) extract: dH₂O. All analyses were conducted in triplicate.

- Flame atomic absorption spectrometer (FAAS) Heavy metal analysis for Cu, Fe and Zn was conducted using a Varian flame atomic absorption spectrometer (FAAS) model 220-FS fitted with an impact bead, fitting hollow cathode lamps and an air-acetylene gas. The analytical conditions and linear range for the equipment fitted with the impact. We used eight multi-metal standard solutions for calibration. They were prepared in the same matrixes used to extract target metals in different steps in the progressive extraction scheme. They are made up of a 50 mgL⁻¹ working solution for each target metal distinctly. The working solutions were prepared from stock solutions (obtained from Sigma-Aldrich), with 1000 mgL⁻¹ within the linear ranges. The blank solutions were injected during the analysis after 10-15 unknown samples were analysed to zero

the instrument. The dilution factors for extracts were determined by trial and error. We calculated the detection limits by injecting five blank solutions (15 ml of dH₂O + 5 ml concentrated nitric acid) into the equipment to obtain a linear curve on FAAS (Miller and Miller, 2005; Rinklebe and Shaheen, 2014).

- Flame emission spectrometer (FES) A flame photometer is an atomic optical emission spectroscopy method that uses the flame as the source of atoms excitation to determine alkali elements with low excited states. We used it to analyse compost made in Nigeria for Na and Mg. The diluted extract solutions were aspirated into a flame as a fine aerosol. It is vaporised, atomised by a mixture of heat and the action of reducing gas. Then, it was excited into higher electronic states by the heat at the distinctive wavelengths producing light as the electron returns to the ground state.

4.3.5 Statistical Analysis

Statistical analyses were completed with SPSS version 25 for Windows. Levene's T-test for equality of variances was used to check if the feedstock used had a significant difference seasonally. One-way ANOVA showing significant differences are as probability (P) values was used to compare the differences in feedstock generated for compost making and physicochemical properties of compost made between seasons. Two-way ANOVA was used to know the effects of seasonality on the physio-chemical properties of composts, while Tukey's HSD post hoc test was used for multiple comparisons between batches means where ANOVA F statistics were significant at P. Finally, excel 2016 was used to present the data graphically. Descriptive analysis was used to determine the measure of the variability of the compost formed.

4.4 Result and Discussions

Some parameters can considerably affect the overall properties of compost. They include the nature and source of feedstock, sorting, and composting (He et al. 1992). These parameters tested are vital to understanding the compost characterisation for it to be effectively taken as a soil conditioner as suggested in the literature (Hoitink et al., 1997; Atiyeh et al., 2001) relating to their physicochemical and biological properties (He et al., 1995). Fig. 4.2 revealed the seasonal differences in feedstock used in compost making in Nigeria for three years, while table 4.3 reveals the post Hoc tests and their significance levels between the means of feedstock produced in three years in Nigeria.

Table 4. 3 Post Hoc tests (Tukey B^a) and significance levels for the means of feedstock produced seasonally in Nigeria.

| VOLUME | | | | | |
|-------------------------|---|----------|----------|----------|----------|
| Tukey B ^a | | | | | |
| Subset for alpha = 0.05 | | | | | |
| Feedstock | N | 1 | 2 | 3 | 4 |
| Spent grain | 6 | 9.50000 | | | |
| Fruits | 6 | 12.50000 | 12.50000 | | |
| Food remnants | 6 | 13.00000 | 13.00000 | | |
| Others | | | 16.33333 | | |
| Manure | 6 | | | 21.66667 | |
| Green waste | 6 | | | | 27.00000 |

Both the one-way ANOVA conducted on the volume of feedstock generated (% dry weight) between 2016 and 2018 and the post hoc test (Tukey B^a) conducted on the feedstock as seen in table 4.3 revealed that the volume of feedstock generated that was used in the production of compost in Nigeria differ between three years sampled, (One-way Anova: $F_{5,30} = 19.878$, $P = 0.000$). While the T-test (Levene's test for equality of variances) carried out on the feedstock generated revealed no significant difference seasonally (between dry and wet seasons) (t-Test: $t_{34} = 0.00$, $P = 1.000$; difference = 0.000, 95% C.I. = -4.750 to 4.750).

4.4.1 Physical and chemical properties of compost made in the wet season

The composts made and sampled in the wet season were brownish, dense with a mild odour. Batches 1-12 are the same as NWC 1-12. Table 4.3 displays the chemical properties (pH, and EC) of 12 batches of compost made in the wet season in Nigeria.

Table 4. 4 pH, and electrical conductivity of compost made in the wet season. (Mean SE, (n=3)).

| Batches of compost | pH | EC (μScm^{-1}) |
|--------------------|-------------------------------|-------------------------------------|
| NWC1 | 8.35 \pm 0.03 ^b | 4780 \pm 100.17 ^{bc} |
| NWC2 | 8.63 \pm 0.01 ^{cd} | 4926.67 \pm 147.42 ^{bc} |
| NWC3 | 8.97 \pm 0.04 ^e | 5030 \pm 334.51 ^{bc} |
| NWC4 | 8.55 \pm 0.03 ^c | 4793.33 \pm 27.28 ^{bc} |
| NWC5 | 8.67 \pm 0.04 ^{cd} | 3886.67 \pm 600.04 ^{ab} |
| NWC6 | 8.65 \pm 0.03 ^{cd} | 3450 \pm 125.30 ^a |
| NWC7 | 8.32 \pm 0.01 ^b | 4493.33 \pm 150.70 ^{abc} |
| NWC8 | 7.90 \pm 0.03 ^a | 4673.33 \pm 293.62 ^{bc} |
| NWC9 | 8.62 \pm 0.01 ^{cd} | 4800 \pm 60.83 ^{bc} |
| NWC10 | 8.59 \pm 0.04 ^c | 4270 \pm 97.13 ^{abc} |
| NWC11 | 8.73 \pm 0.01 ^d | 3943.33 \pm 84.52 ^{ab} |
| NWC12 | 9.04 \pm 0.01 ^e | 5363.33 \pm 47.02 ^c |
| APEX | 7.0-8.7 | 750-2000 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P<0.05$. (NWC1-12 means batches of Nigerian wet compost).

The mean pH of the different batches of compost from Nigeria ranged from 7.90- 9.04 (Table 4.4). They are basic and typically mature composts. All composts from Nigeria were within the accepted APEX standard limits of compost pH, which is 7.0-8.7, except for NWC 3 and 12, which were significantly higher than other batches. pH affects the availability of nutrients to the microorganisms. The increase in compost pH caused mineralisation of C and subsequent production of OH ions by ligands exchange and the introduction of basic cations K^+ , Ca^{2+} , Mg^{2+} . Brady and Weil (1996) suggested that micronutrients and metal cations are most soluble and available for plant and microbial biomass for use under acidic conditions; thus, compost would help moderate the availability of heavy metals. Therefore, pH significantly differed among batches made in the wet season ($F = 110.39$, $P<0.05$).

EC is an important parameter to determine in compost because it measures the soluble salts concentration in compost. When used alone or as soil boosters, very high salt concentration can inhibit microbial biomass and plant growth (He et al., 1995; Brito, 2001; Castillo et al., 2004; Dimambro et al., 2006). The mean values of EC of the compost were very variable, ranging from 3450 μScm^{-1} to 5363 μScm^{-1} . The EC of all batches of compost exceeded the Apex EC limit, which is 750 to 2000 μScm^{-1} , possibly due to the feedstock used in composting that contains high water-soluble salt concentration as food waste (He et al., 1995). For example, high EC in mixed MSW compost (5300 μScm^{-1}) caused growth inhibition in lettuce and

cabbage (Brito, 2001). So, the EC of compost made between batches in the wet season was significantly different, with batches 6 and 5 having significantly lower EC than batch 12 ($F = 5.69$, $P < 0.05$). Fig. 4.4 revealed the post hoc test (Tukey B) on the pH and EC of compost made in the wet season. The result revealed that the means of the pH and EC of different batches of compost made in the wet season in Nigeria were significantly different.

The results from the chemical properties (OM, carbon and nitrogen content and C/N ratio) of the different batches of compost made in the wet season in Nigeria are displayed in Table 4.5.

Table 4. 5 Organic matter, Carbon, Nitrogen, and C/N ratio of compost made in the wet season (Means \pm SE, (n=3)).

| Batches of compost | OM | Carbon | Nitrogen | C:N Ratio |
|-----------------------|---------------------------|---------------------------|--------------------------|---------------------------|
| | (% dry weight) | | | |
| NWC1 | 40.03±2.12 ^{cde} | 22.23±1.30 ^{bc} | 1.47±0.04 ^{abc} | 15.13±0.60 ^{def} |
| NWC2 | 22.94±0.66 ^a | 14.10±1.97 ^a | 1.16±0.16 ^a | 12.17±0.33 ^{ab} |
| NWC3 | 32.17±0.58 ^b | 20.17±1.92 ^{abc} | 1.24±0.07 ^a | 16.16±0.70 ^f |
| NWC4 | 36.89±0.25 ^{cd} | 20.47±1.47 ^{abc} | 1.79±0.09 ^{cd} | 11.39±0.27 ^a |
| NWC5 | 40.45±0.31 ^{de} | 22.73±0.23 ^{bc} | 1.37±0.02 ^{ab} | 16.60±0.10 ^f |
| NWC6 | 25.38±0.47 ^a | 14.70±1.65 ^{ab} | 1.13±0.12 ^a | 13.06±0.28 ^{abc} |
| NWC7 | 44.23±1.66 ^e | 25.60±0.75 ^c | 1.69±0.01 ^{bcd} | 15.19±0.41 ^{def} |
| NWC8 | 50.81±0.89 ^f | 27.33±3.06 ^c | 1.93±0.14 ^d | 14.08±0.56 ^{cde} |
| NWC9 | 35.15±0.66 ^{bc} | 21.40±0.35 ^{abc} | 1.31±0.02 ^{ab} | 16.35±0.46 ^f |
| NWC10 | 38.41±0.51 ^{cd} | 21.77±0.29 ^{abc} | 1.37±0.12 ^{ab} | 15.82±0.29 ^{ef} |
| NWC11 | 38.91±1.25 ^{cd} | 21.37±1.34 ^{abc} | 1.27±0.06 ^{ab} | 16.78±0.31 ^f |
| NWC12 | 25.04±0.39 ^a | 15.67±0.78 ^{ab} | 1.17±0.04 ^a | 13.34±0.40 ^{bcd} |
| APEX | 25-65 | <10 | 0.9-2.0 | 15-20 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P < 0.05$ (NWC1-12 means batches of Nigerian wet compost).

The mean of organic matter (loss on ignition) of the compost from Nigeria tested varied significantly from 22.94% (NWC2) to 50.81% (NWC8) in table 4.5. Compost NWC 2, 6 and 12 gave the lowest mean significantly for OM of compost along with column $P > 0.05$. While other composts had significantly higher mean values for OM.

Generally, the OM of compost made in the wet season was significantly different between batches ($F = 60.69$, $P < 0.05$), with NWC 7 having significantly higher OM content than other batches. It could be that they compost with higher OM mean values contain more woody and green waste, which leads to higher cellulose and lignin concentrations influencing the organic

matter content (Dimambro et al., 2007). The OM can be enhanced by adding high manure to cellulose, lignin, sludge, or garden waste (He et al., 1995). The carbon to nitrogen ratio is one of the significant factors that affect the growth of microorganisms that drive the decomposition of organic wastes and release nitrogen during composting.

The carbon content values of compost made in Nigeria ranged from 14.1% (NWC2) to 27.3 % (NWC8). Batjes (1996) and Khater et al. (2015) suggested that these results agreed with the specified standard value of organic carbon, which must be higher than 10%. Therefore, the Carbon content of compost made in the wet season was significantly different between batches ($F = 6.23$, $P < 0.05$).

The nitrogen content values ranged of compost made in the wet season ranged from 1.13% (NWC6) to 1.93 % (NWC8) for the different batches of compost made in Nigeria, meaning that the nitrogen content of compost made in the wet season was significantly different between batches ($F = 8.77$, $P < 0.05$). These obtained results agree with those obtained by Benito et al. (2005) that found that the total nitrogen rate of MSW compost ranged from 0.99 to 2.01%. The nitrogen content of any compost is dependent on the amount of protein source from feedstock or manure used. An example of protein sources that increase nitrogen contents is food waste, animal manure and sludge. At the same time, straw, cardboard and wood clippings and sawdust will reduce the nitrogen content of compost.

The wet season's C/N ratio of compost from Nigeria was significantly different between batches ($F = 18.63$, $P < 0.05$). It ranged significantly from 11.39% (NWC4) to 16.78% (NWC11). For C/N, NWC 11 was observed to have significantly higher C/N content than the other batches. The C/N ratio of all composts was below the acceptable range of 20% as recommended by APEX. The low C/N ratios of the composts could be from the proportions of the feedstock added during the process. C/N ratios of composts with large amounts of food waste, manure or green plant material (e.g., grass clippings) will have a low C/N ratio regardless of whether they are fully composted or not. Several authors reported that this ratio could be amended by adding more high carbon sources waste materials (Rawat et al., 2013).

According to Table 4.5, there was a trend in the mean values of the three variables checked (OM, C and N content). When compost had the highest values in OM, it still had the highest values in both C and N values. Also, the lowest OM gave rise to the lowest C and N. An increase in OM will increase C, which increases the microbial activities and warmer and moister substrate (Davidson, 1994). Therefore, table 4.5 reveals the post hoc test (Tukey B) conducted on the chemical properties (OM, carbon and nitrogen content and C/N ratio) of the different batches of compost made in the wet season. The result revealed that the (OM, carbon

and nitrogen content and C/N ratio) of compost made in the wet season differed significantly between batches.

The results shown in table 4.6 displayed the mean values of the nutrient contents from the 12 batches (NWC1-12) of compost sampled in Nigeria during the wet season and their significant differences.

Table 4. 6 The contents of nutrient elements of compost made in the wet season (Means % of dry matter \pm SE, (n=3)).

| Batches of compost | P | K | Ca | Na | Mg |
|--------------------|-------------------------------|-------------------------------|------------------------------|------------------------------|-----------------------------|
| | (%) | | | | |
| NWC1 | 1.2 \pm 0.04 ^{bc} | 1.5 \pm 0.05 ^{abc} | 8.8 \pm 0.57 ^{ab} | 0.1 \pm 0.01 ^{ab} | 0.4 \pm 0.00 ^a |
| NWC2 | 1.2 \pm 0.05 ^{bc} | 1.6 \pm 0.06 ^{abc} | 8.8 \pm 0.30 ^{ab} | 0.1 \pm 0.01 ^c | 0.4 \pm 0.01 ^a |
| NWC3 | 1.0 \pm 0.07 ^{ab} | 1.3 \pm 0.14 ^{abc} | 8.1 \pm 1.40 ^{ab} | 0.1 \pm 0.01 ^{bc} | 0.5 \pm 0.01 ^b |
| NWC4 | 1.0 \pm 0.04 ^{abc} | 1.4 \pm 0.06 ^{abc} | 8.4 \pm 0.94 ^{ab} | 0.2 \pm 0.01 ^d | 0.5 \pm 0.00 ^b |
| NWC5 | 1.1 \pm 0.10 ^{bc} | 1.6 \pm 0.19 ^{bc} | 9.6 \pm 1.0 ^{ab} | 0.1 \pm 0.01 ^{ab} | 0.4 \pm 0.01 ^a |
| NWC6 | 1.1 \pm 0.07 ^{bc} | 1.5 \pm 0.11 ^{abc} | 9.4 \pm 0.92 ^{ab} | 0.1 \pm 0.00 ^a | 0.4 \pm 0.00 ^a |
| NWC7 | 1.3 \pm 0.13 ^c | 1.8 \pm 0.22 ^c | 8.9 \pm 0.78 ^{ab} | 0.2 \pm 0.01 ^c | 0.5 \pm 0.01 ^b |
| NWC8 | 1.0 \pm 0.06 ^{abc} | 1.4 \pm 0.01 ^{abc} | 7.1 \pm 0.65 ^{ab} | 0.2 \pm 0.02 ^c | 0.6 \pm 0.00 ^b |
| NWC9 | 0.9 \pm 0.09 ^{ab} | 1.5 \pm 0.09 ^{abc} | 8.3 \pm 1.0 ^{ab} | 0.1 \pm 0.00 ^{bc} | 0.5 \pm 0.01 ^b |
| NWC10 | 1.3 \pm 0.05 ^{bc} | 1.9 \pm 0.10 ^c | 11.4 \pm 1.23 ^b | 0.1 \pm 0.00 ^{ab} | 0.5 \pm 0.01 ^a |
| NWC11 | 0.7 \pm 0.06 ^a | 1.1 \pm 0.10 ^{ab} | 8.4 \pm 1.0 ^{ab} | 0.1 \pm 0.00 ^{ab} | 0.5 \pm 0.01 ^a |
| NWC12 | 0.7 \pm 0.02 ^a | 0.9 \pm 0.00 ^a | 6.6 \pm 0.42 ^a | 0.1 \pm 0.01 ^{ab} | 0.5 \pm 0.01 ^b |
| APEX | 0.3-0.9 | 0.5-1.5 | 1.5-3.5 | <0.6 | 0.25-0.7 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P<0.05$ (NWC1-12 means batches of Nigerian wet compost).

The means of total phosphorus (P), potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg) values ranged from 0.7-1.3%, 0.9-1.9%, 6.6-11.4%, 0.1-0.2% and 0.2-0.6 %, respectively, for different batches of compost. The results were different mainly because of the feedstock used during composting (Dimambro et al., 2006; 2007). While the mean values of the Na and Mg contents of all the batches of composts were significantly within the accepted standard range, the mean values of the Ca were significantly higher than the standard range, as suggested by Sullivan et al. (2018). Ca content above 3.5% suggests that feedstock contains soil, gypsum, or lime. The P content of compost made in the wet season was significantly different between batches ($F = 7.616$, $P < 0.05$), and all the mean values of batches produced had P content above the accepted standard range except NWC 9, 11 and 12.

Also, the K content of compost made in the wet season was significantly different between batches ($F = 4.213$, $P < 0.05$), and the mean values for K were all within the acceptable range except NWC 2, 5, 7 and 10. P and K contents exceeding 0.9 and 1.5%, respectively, suggest that the feedstock contains more food wastes or manure. While the Ca content of compost made in the wet season was not significantly different between batches ($F = 1.861$, $P > 0.05$), the Na and Mg contents of compost made in the wet season were significantly different between batches (Na: $F = 29.136$, $P < 0.05$ and Mg: $F = 37.828$, $P < 0.05$). The vital nutrients were present in all the batches of composts analysed, though in high quantity as seen in phosphorus for batches (NWC 1, 2, 3, 4, 5, 6, 7, 8, and 10), in potassium for batches (NWC 2, 5, 7, 10 and 11) and all batches of composts for calcium. The high nutrient contents recorded in table 4.5 for the different batches of compost analysed in the wet season correlate with the very high electrical conductivity obtained from table 4.3 ($3886\text{--}5363\mu\text{Scm}^{-1}$), i.e., the feedstock used in composting contained high soluble salts, therefore influencing the properties obtained compost formed.

Therefore, the total nutrient contents of compost do not determine that the compost will be appropriate for agricultural purposes. Still, the concentration of individual nutrients is vital. For instance, while high levels of nitrate may benefit plants, high levels of Na of more than 0.6% may reduce the growth of plants (Dimambro et al., 2006).

The mean of the heavy metal concentrations of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn) and iron (Fe) values are displayed in table 4.7 and range significantly from 8.8-22.4, 96.1-217, 6.6-17.9, 9-24.5, 483.1-1289.5 and 5338.2-16408.6 mgkg^{-1} respectively, for different batches of compost.

Table 4.7 Concentrations of heavy metals in compost made in the wet season. (Means mg kg⁻¹ of dry matter \pm SE, (n=3)).

| Batches of compost | Cr | Cu | Ni | Pb | Zn | Fe |
|--------------------|--------------------------------|---------------------------------|-------------------------------|--------------------------------|------------------------------------|--------------------------------------|
| | mg kg ⁻¹ | | | | | |
| NWC1 | 18.50 \pm 1.74 ^{ab} | 197.12 \pm 9.18 ^b | 10.86 \pm 0.55 ^a | 19.13 \pm 2.05 ^{ab} | 1013.71 \pm 51.82 ^{bc} | 11399.11 \pm 935.24 ^{ab} |
| NWC2 | 17.64 \pm 0.88 ^{ab} | 195.63 \pm 6.95 ^b | 14.73 \pm 3.40 ^a | 19.32 \pm 0.15 ^{ab} | 1090.87 \pm 34.24 ^{bc} | 10734.68 \pm 339.34 ^{ab} |
| NWC3 | 13.87 \pm 2.14 ^{ab} | 169.13 \pm 19.65 ^b | 13.47 \pm 3.47 ^a | 14.46 \pm 1.77 ^{ab} | 926.34 \pm 85.71 ^{bc} | 9000.40 \pm 1068.12 ^{ab} |
| NWC4 | 15.81 \pm 1.48 ^{ab} | 165.24 \pm 11.37 ^b | 17.51 \pm 4.46 ^a | 17.73 \pm 2.27 ^{ab} | 925.87 \pm 59.21 ^{bc} | 9583.64 \pm 519.81 ^{ab} |
| NWC5 | 22.44 \pm 5.09 ^b | 210.83 \pm 25.75 ^b | 15.21 \pm 2.50 ^a | 24.54 \pm 5.95 ^{ab} | 1160.79 \pm 110.74 ^{bc} | 16408.63 \pm 5425.30 ^b |
| NWC6 | 18.26 \pm 2.47 ^{ab} | 193.37 \pm 12.99 ^b | 17.92 \pm 0.96 ^a | 20.30 \pm 2.69 ^b | 1123.71 \pm 83.80 ^{bc} | 11308.46 \pm 882.69 ^{ab} |
| NWC7 | 17.65 \pm 2.19 ^{ab} | 216.96 \pm 23.38 ^b | 15.76 \pm 1.83 ^a | 21.28 \pm 2.21 ^{ab} | 1289.45 \pm 144.64 ^c | 11454.18 \pm 1197.99 ^{ab} |
| NWC8 | 14.49 \pm 1.80 ^{ab} | 146.35 \pm 7.08 ^{ab} | 11.62 \pm 1.27 ^a | 15.02 \pm 0.98 ^{ab} | 792.314 \pm 2.83 ^{ab} | 9259.10 \pm 831.66 ^{ab} |
| NWC9 | 12.52 \pm 2.57 ^{ab} | 98.08 \pm 10.96 ^a | 9.19 \pm 1.51 ^a | 13.45 \pm 0.94 ^{ab} | 540.25 \pm 58.93 ^a | 7037.74 \pm 965.02 ^a |
| NWC10 | 18.30 \pm 0.77 ^{ab} | 198.25 \pm 17.74 ^b | 13.01 \pm 0.95 ^a | 20.25 \pm 1.58 ^{ab} | 1123.72 \pm 85.04 ^{bc} | 11748.92 \pm 1054.48 ^{ab} |
| NWC11 | 10.86 \pm 1.86 ^a | 88.47 \pm 6.10 ^a | 6.75 \pm 0.68 ^a | 13.18 \pm 4.10 ^{ab} | 483.14 \pm 41.02 ^a | 5656.71 \pm 406.01 ^a |
| NWC12 | 8.87 \pm 0.50 ^a | 96.11 \pm 3.35 ^a | 6.64 \pm 0.13 ^a | 9.01 \pm 0.28 ^a | 528.02 \pm 10.39 ^a | 5338.24 \pm 145.97 ^a |
| APEX | \leq 100 | \leq 130 | \leq 50 | \leq 200 | \leq 300 | \leq 2.0 |
| PAS 100 | \leq 100 | \leq 200 | \leq 50 | \leq 200 | \leq 400 | \leq 1.5 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P < 0.05$ (NWC1-12 means batches of Nigerian wet compost).

Chromium content was significantly different between batches (Cr: $F= 2.825$, $P<0.05$), with NWC 11 and 12 having significantly lower contents than NWC 5. NWC 7 was significantly higher in copper content than the other batches made during the wet season. There was a significant difference in the result obtained for copper content analysis (Cu: $F= 10.280$, $P<0.05$). On the other hand, nickel showed a significant difference between batches in compost made in the wet season (Ni: $F= 2.927$, $P<0.05$), with NWC6 having significantly higher nickel content than the other batches formed also. Lead (Pb) content was also significantly different between batches of compost formed in the wet season (Pb: $F= 2.461$, $P<0.05$). The heavy metal concentrations of all the batches of composts analysed in the wet season showed significant differences between batches. They were within acceptable levels except for Zn and Fe from table 4.6, which were significantly higher than other heavy metals. The reason is that most of the feedstock used during composting was sourced from mixed MSW, contaminated with metals seen with the organic fraction of municipal waste at dumpsites. Examples of materials that increase heavy metal concentrations at landfills are batteries, bottle covers, solder, electrical fittings, and fishing tools seen alongside municipal waste. Also, stabilisers and pigments used in plastic production and sewage sludge/manure may contain some heavy metals (Richard & Woodbury, 1992). Dimambro et al. (2006) suggested that composts made from mixed MSW have higher heavy metal concentrations than composts made from source sorted feedstocks. Both PAS 100 and the APEX accepted standards have bounds for heavy metal concentrations though they vary to some extent in the acceptable amounts (Table 4.6). The more the feedstock used for composting degrades and matures, and the water-soluble carbohydrates and cellulose are broken down, the more the heavy metals become concentrated (Dimambro et al., 2006).

The statistical results from the heavy metal analysis for zinc and iron contents were significantly different between batches of compost made in the wet season (Zn: $F=12.927$, $P<0.05$ and Fe: $F=2.994$,

$P>0.05$). Therefore, compost analysis for heavy metals becomes vital as it affects both its sales and usage if its concentrations are above-accepted range because of the bioaccumulation potential of these metals (Tibu et al., 2019).

4.4.2 Physical and chemical properties of compost made in the dry season

The composts made and sampled in the dry season were black/brown in colour, dusty in appearance, with a faint woody smell. The different batches are the same as NDC 1-12.

Table 4.8 displays the chemical properties (pH, and EC) of 12 batches of compost

Table 4. 8 pH, and electrical conductivity of compost made in the dry season (Means \pm SE, (n=3)).

| Batches of compost | pH | EC (μScm^{-1}) |
|--------------------|------------------------------|------------------------------------|
| NDC1 | 8.30 \pm 0.01 ^c | 2578.64 \pm 2.78 ^{ab} |
| NDC2 | 8.34 \pm 0.01 ^c | 1706.67 \pm 51.32 ^a |
| NDC3 | 8.20 \pm 0.03 ^c | 1649.67 \pm 92.33 ^a |
| NDC4 | 8.05 \pm 0.02 ^c | 2786.00 \pm 241.31 ^{ab} |
| NDC5 | 6.95 \pm 0.12 ^a | 3436.67 \pm 292.42 ^b |
| NDC6 | 7.39 \pm 0.26 ^b | 2771.33 \pm 481.52 ^{ab} |
| NDC7 | 7.95 \pm 0.12 ^c | 2306.00 \pm 142.67 ^{ab} |
| NDC8 | 8.01 \pm 0.10 ^c | 3473.33 \pm 530.86 ^b |
| NDC9 | 8.14 \pm 0.01 ^c | 3310.00 \pm 76.38 ^b |
| NDC10 | 8.27 \pm 0.02 ^c | 2172.67 \pm 36.37 ^{ab} |
| NDC11 | 8.23 \pm 0.02 ^c | 2655.00 \pm 103.78 ^{ab} |
| NDC12 | 8.23 \pm 0.03 ^c | 2736.33 \pm 83.69 ^{ab} |
| APEX | 7.0-8.7 | 750-2000 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P<0.05$ (NDC1-12 means batches of Nigerian dry compost).

The mean pH of the 12 batches of compost made in the dry season was 7.0 to 8.3 (Table 4.8). They are essential and typically mature composts. All composts made in the dry season were within the accepted APEX standard limits of compost pH of 7.0-8.7. Considering the pH of these composts, they could be used for agricultural purposes (Bunt, 1988) because of the availability of nutrients and metals to the microorganisms. Zmora-Nahum et al. (2007) suggested that compost properties varied because of the different feedstocks used during composting. Thus, the pH of compost between batches in the dry season was significantly different ($F = 19.207$, $P<0.05$).

The mean values of EC obtained in the dry season vary according to the number and type of ions in the solution. The EC ranged from 1649.7 μScm^{-1} (NDC3) to 3473.3 μScm^{-1} (NDC8). All the mean values of the EC of batches of composts exceeded the Apex EC limit of 750-2000 μScm^{-1} , except NDC 2 and 3; the reason for the high EC of compost is because food waste in the feedstock has a very high concentration of some water-soluble salts (He et al., 1995). Brito (2001) and Castillo et al. (2004) suggested that composts with high EC could have harmful effects when used for agricultural purposes. Therefore, the EC of compost made between batches in the dry season was significantly different ($F= 4.987$, $P<0.05$), with NDC 6 exhibiting significantly higher EC than other batches. Therefore, fig. 4.8 summarised

the post hoc test (Tukey B) conducted on the pH and EC of compost made in the dry season. The result revealed that the means of the pH and EC of different batches of compost made in the wet season in Nigeria were significantly different.

Table 4.9 displays the chemical properties (OM, C, N and C/N) of 12 batches of compost made in the dry season in Nigeria.

Table 4. 9 Organic matter, Carbon, Nitrogen, and C/N ratio of compost made in the dry season (Means \pm SE, (n=3)).

| Batches of compost | (OM) | Carbon | Nitrogen | C:N Ratio |
|-----------------------|-------------------------|--------------------------|--------------------------|---------------------------|
| | % dry weight | | | |
| NDC1 | 26.11±0.33 ^a | 19.33±0.81 ^{ab} | 1.51±0.04 ^{abc} | 12.76±0.23 ^{bc} |
| NDC2 | 26.27±1.03 ^a | 16.30±0.35 ^a | 1.22±0.00 ^{ab} | 13.35±0.25 ^{cd} |
| NDC3 | 28.87±0.99 ^a | 16.70±0.26 ^{ab} | 1.11±0.02 ^a | 15.07±0.05 ^e |
| NDC4 | 40.94±3.62 ^b | 19.70±0.85 ^b | 1.62±0.12 ^{bc} | 12.20±0.36 ^{bc} |
| NDC5 | 25.97±1.02 ^a | 16.63±0.34 ^{ab} | 1.59±0.08 ^{bc} | 10.48±0.49 ^a |
| NDC6 | 24.58±0.47 ^a | 16.80±0.60 ^{ab} | 1.47±0.09 ^{ab} | 11.48±0.62 ^{ab} |
| NDC7 | 26.77±0.76 ^a | 16.40±0.42 ^a | 1.31±0.04 ^{ab} | 12.50±0.1 ^{bc} |
| NDC8 | 42.32±3.40 ^b | 22.60±0.68 ^c | 2.08±0.23 ^d | 11.00±0.6 ^{ab} |
| NDC9 | 44.80±1.30 ^b | 24.10±1.37 ^c | 1.91±0.09 ^{cd} | 12.62±0.38 ^{bc} |
| NDC10 | 28±1.66 ^a | 18.57±0.34 ^{ab} | 1.35±0.03 ^{ab} | 13.80±0.15 ^{cde} |
| NDC11 | 32.28±1.18 ^a | 18.50±0.55 ^{ab} | 1.09±0.05 ^a | 16.94±0.28 ^f |
| NDC12 | 32.73±0.56 ^a | 18.67±0.50 ^{ab} | 1.26±0.06 ^{ab} | 14.91±0.46 ^{de} |
| APEX | 25-65 | <10 | 0.9-2.0 | 15-20 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P<0.05$ (NDC1-12 means batches of Nigerian dry compost).

The mean of total organic matter (loss on ignition) of the compost varied significantly, from 25.97% (NDC5) to 44.8% (NDC9) in table 4.9 (dry weight). The OM of compost made between batches in the dry season was significantly different ($F= 17.592$, $P<0.05$). These results agree with the 25-65% APEX range for compost to be considered for agricultural use. Also, the results obtained agreed with the result obtained by Benito et al. (2006), which found that the highest value of total organic matter of compost was about 44%.

Montejo et al. (2015) suggested that the main reason compost's organic matter does not meet the required standard lies in the composition of the feedstocks used. The total organic matter of compost can be improved by adding manure high in cellulose and lignin (He et al., 1995).

The mean values of the carbon content of compost made between batches in the dry season ranged significantly from 16.3% (NDC2) to 24.1% (NDC9). Batjes (1996); Khater et al. (2015)

suggested that these results agreed with the specified standard value of organic carbon, which must be higher than 10%. The nitrogen content values ranged significantly from 1.1% (NDC11) to 1.93% (NDC8) for the different batches of compost made in the dry season. These results agree with both the APEX range and the result obtained by Benito et al. (2005), which should range between 0.99 to 2.01% for MSW compost.

There were significant differences between batches from the results obtained from carbon and nitrogen content (C: $F = 14.376$, $P < 0.05$ and N: $F = 11.513$, $P < 0.05$). It was owing to the difference in the amount of feedstock used within the batches in the same season. Batches of compost with the highest mean values of organic matter of 44.8% (NDC9) significantly had the highest total carbon concentrations of approximately 24.1%. On the other hand, the lowest mean values of organic matter, 25.97% (NDC5), significantly corresponded to samples with the lowest mean values of total carbon, 16.3%, agreeing with the results obtained by Montejó et al. (2015).

The C/N ratio of compost made between batches in the dry season ranged significantly from 10.5% (NDC5) to 16.9% (NWC11) and was significantly different ($F = 24.142$, $P < 0.05$). The C/N ratios of all composts were below the acceptable range of 15-20% as recommended by APEX of an ideal ready-to-use compost except NDC3 and NDC11 with 15.01 and 16.9%, respectively. Because of the type and the nature of feedstock used during composting, manure or garden wastes. The carbon/nitrogen ratio is a vital factor to note during composting as it influences the growth and activity of microorganisms responsible for decomposing organic wastes. Low C/N, carbon and the total organic matter of composts can be improved by adding feedstocks high in carbon sources, for example, straw, cardboard and wood clippings and sawdust. Therefore, the results from the OM, C, N and C/N analysis of compost made in the dry season differed significantly between batches ($P < 0.05$).

Table 4. 10 The contents of nutrient elements of compost made in the dry season (Means % of dry matter \pm SE, (n=3)).

| Batches of compost | P | K | Ca | Na | Mg |
|-----------------------|------------------------------|-------------------------------|--------------------------------|------------------------------|-----------------------------|
| | % of dry matter | | | | |
| NDC1 | 0.76 \pm 0.10 ^a | 2.1 \pm 0.30 ^a | 2.6 \pm 0.40 ^a | 0.04 \pm 0.01 ^a | 0.5 \pm 0.01 ^b |
| NDC2 | 1.6 \pm 0.10 ^a | 2.6 \pm 0.30 ^a | 6.6 \pm 0.70 ^a | 0.04 \pm 0.00 ^a | 0.5 \pm 0.01 ^b |
| NWC3 | 1.1 \pm 0.20 ^a | 2.6 \pm 0.40 ^a | 4.3 \pm 0.80 ^a | 0.04 \pm 0.01 ^a | 0.5 \pm 0.00 ^b |
| NDC4 | 2.2 \pm 0.10 ^a | 3.1 \pm 0.10 ^a | 8.1 \pm 0.40 ^{ab} | 0.1 \pm 0.01 ^c | 0.4 \pm 0.01 ^a |
| NDC5 | 3.6 \pm 1.50 ^{ab} | 9.4 \pm 3.90 ^{ab} | 14.7 \pm 6.00 ^{abc} | 0.04 \pm 0.00 ^a | 0.5 \pm 0.01 ^b |
| NDC6 | 6.6 \pm 0.90 ^c | 17.1 \pm 2.20 ^c | 27.1 \pm 4.90 ^{cd} | 0.04 \pm 0.00 ^a | 0.4 \pm 0.00 ^a |
| NDC7 | 5.5 \pm 1.20 ^{bc} | 12.7 \pm 2.80 ^{bc} | 21.1 \pm 5.50 ^{bc} | 0.1 \pm 0.01 ^a | 0.5 \pm 0.00 ^b |
| NDC8 | 11.3 \pm 0.30 ^d | 17.7 \pm 0.60 ^c | 40.6 \pm 1.00 ^e | 0.12 \pm 0.02 ^c | 0.4 \pm 0.01 ^a |
| NDC9 | 9.2 \pm 0.40 ^d | 19 \pm 1.80 ^c | 35.8 \pm 1.90 ^{de} | 0.43 \pm 0.02 ^d | 0.4 \pm 0.01 ^a |
| NDC10 | 6.2 \pm 0.40 ^{bc} | 18 \pm 1.10 ^c | 23 \pm 2.10 ^{cd} | 0.1 \pm 0.00 ^a | 0.4 \pm 0.01 ^a |
| NDC11 | 3.6 \pm 0.30 ^{ab} | 13.6 \pm 1.40 ^{bc} | 15.1 \pm 2.50 ^{abc} | 0.1 \pm 0.00 ^{ab} | 0.4 \pm 0.01 ^a |
| NDC12 | 1.8 \pm 0.10 ^a | 3.1 \pm 0.30 ^a | 8.7 \pm 0.80 ^{ab} | 0.1 \pm 0.00 ^{bc} | 0.4 \pm 0.01 ^a |
| | 0.3-0.9 | 0.5-1.5 | 1.5-3.5 | >0.6 | 0.25-0.8 |

**Means with the same letter are not significantly different along columns according to the Tukey B test $P<0.05$
(NDC1-12 means batches of Nigerian dry compost)**

Table 4.10 shows the results of the mean values of the water-soluble nutrients checked (total phosphorus (P), potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg)) of composts made in the dry season in Nigeria, (NDC1-12).

The nutrients were significantly present in all the batches of composts in very high quantities except in Na and Mg. The means of total P, K, Ca, Na and Mg values significantly ranged from 0.8-11.3%, 2.1-19%, 2.6-40.6%, 0.04-0.1% and 0.4-0.5 %, respectively, for different batches of compost. The mean values of all Na and Mg contents of all the batches and the mean values of P and Ca contents for NDC1 composts were within the accepted standard range. In contrast, others significantly had a high amount of nutrients above the accepted standard range, as Sullivan et al. (2018) suggested. The lower amounts of nutrients recorded from the NDC1 compared to other batches may be because NDC1 compost was from the end of the wet season/beginning of the dry season.

The excess Ca content observed suggests that feedstock contains soil, gypsum, or lime, while the excess of P and K contents indicates that the feedstock contains more food wastes or manure. The high nutrient contents recorded in table 4.9 for the different batches of compost analysed in the dry season correlate with the high electrical conductivities obtained from table 4.7 ($1949.7\text{--}3473.3\mu\text{Scm}^{-1}$). It also indicates a high amount of nutrients in the feedstock (Dimambro et al., 2006).

The variations in the nutrient contents were mainly due to the food waste feedstock, which was relatively nutrient-rich with high soluble salts, which then increased the nutrient contents of the compost formed. Another reason for very high nutrients observed could be less rainfall in the dry season, reducing run-off or dilution effects of the nutrients. For example, Mamo et al. (2002) conducted a study with over 200 composts made in the USA, and the results revealed between 5-100-fold variations in compost nutrients.

Therefore, the total nutrient contents of compost do not determine that the compost will be appropriate for agricultural purposes. Still, the concentration of individual nutrients is vital. For instance, while high levels of nitrate may benefit plants, high levels of Na of more than 0.6% may reduce the growth of plants (Dimambro et al., 2006). Hence, the results of the analysis of nutrient contents (P, K, Ca, Na and Mg) of composts made in the dry season in Nigeria all showed significant differences between batches (P: $F= 27.498$, $P<0.05$; K: $F= 16.918$, $P<0.05$; Ca: $F= 17.491$, $P<0.05$; Na: $F= 144.141$, $P<0.05$ and Mg: $F= 32.762$, $P<0.05$). Table 4.11 revealed the means of the heavy metal concentrations of the compost (NDC1-12) made in the dry season.

Table 4. 11 Concentrations of heavy metals in compost made in the dry season (Means mg kg⁻¹ of dry matter \pm SE, (n=3)).

| Batches of compost | Cr | Cu | Ni | Pb | Zn | Fe |
|-----------------------|----------------------------------|------------------------------------|----------------------------------|----------------------------------|--------------------------------------|---------------------------------------|
| | mg kg ⁻¹ | | | | | |
| NDC1 | 12.81 \pm 1.99 ^a | 50.19 \pm 6.22 ^a | 13.74 \pm 5.93 ^a | 14.74 \pm 1.05 ^a | 364.28 \pm 59.51 ^a | 8426.87 \pm 326.83 ^a |
| NDC2 | 24.39 \pm 2.93 ^a | 214.34 \pm 19.74 ^{ab} | 12.36 \pm 0.97 ^a | 27.42 \pm 3.86 ^a | 1511.70 \pm 159.52 ^{abc} | 12355.94 \pm 1646.35 ^a |
| NDC3 | 16.16 \pm 1.87 ^a | 119.83 \pm 21.49 ^a | 9.96 \pm 1.79 ^a | 22.80 \pm 7.31 ^a | 565.20 \pm 90.50 ^a | 10224.80 \pm 1265.02 ^a |
| NDC4 | 17.30 \pm 2.06 ^a | 190.11 \pm 19.66 ^{ab} | 28.06 \pm 13.40 ^a | 20.61 \pm 0.98 ^a | 1082.07 \pm 120.31 ^{ab} | 10386.75 \pm 586.37 ^a |
| NDC5 | 63.82 \pm 32.09 ^{ab} | 381.49 \pm 163.70 ^{abc} | 65.85 \pm 29.36 ^a | 83.71 \pm 35.28 ^{ab} | 1865.92 \pm 741.28 ^{abcd} | 51106.47 \pm 23601.78 ^{ab} |
| NDC6 | 118.64 \pm 22.49 ^b | 539.09 \pm 82.60 ^{bc} | 64.18 \pm 8.94 ^a | 144.91 \pm 25.37 ^{bc} | 3428.99 \pm 455.86 ^d | 78510.64 \pm 13570.92 ^b |
| NDC7 | 75.33 \pm 5.37 ^{ab} | 648.07 \pm 152.07 ^c | 69.83 \pm 10.11 ^a | 95.86 \pm 19.24 ^{abc} | 3514.69 \pm 678.68 ^d | 59960.86 \pm 6516.97 ^{ab} |
| NDC8 | 94.64 \pm 4.34 ^{ab} | 631.83 \pm 32.58 ^c | 64.87 \pm 3.43 ^a | 96.91 \pm 7.85 ^{abc} | 3074.54 \pm 155.36 ^{cd} | 47859.74 \pm 4682.36 ^{ab} |
| NDC9 | 118.65 \pm 10.26 ^b | 1096.52 \pm 37.97 ^d | 498.84 \pm 406.64 ^b | 159.47 \pm 11.56 ^{bc} | 5725.33 \pm 390.19 ^e | 77389.55 \pm 3199.57 ^b |
| NDC10 | 135.05 \pm 28.79 ^{bc} | 551.72 \pm 63.82 ^{bc} | 131.72 \pm 65.16 ^a | 135.03 \pm 20.12 ^{bc} | 3277.55 \pm 447.67 ^{cd} | 91230.28 \pm 15341.57 ^b |
| NDC11 | 196.41 \pm 29.78 ^c | 496.42 \pm 82.17 ^{bc} | 115.71 \pm 15.54 ^a | 169.68 \pm 21.40 ^c | 2687.33 \pm 515.01 ^{bcd} | 137502.49 \pm 20428.08 ^c |
| NDC12 | 29.80 \pm 2.86 ^a | 305.51 \pm 37.81 ^{abc} | 14.54 \pm 1.68 ^a | 39.02 \pm 4.27 ^a | 1162.02 \pm 106.99 ^{ab} | 17005.07 \pm 1500.02 ^a |
| APEX | \leq 100 | \leq 30 | \leq 50 | \leq 200 | \leq 300 | \leq 2.0 |
| PAS 100 | \leq 100 | \leq 200 | \leq 50 | \leq 200 | \leq 400 | \leq 1.5 |

Means with the same letter are not significantly different along columns according to the Tukey B test $P < 0.05$
(NDC1-12 means batches of Nigerian dry compost)

The means of heavy metal checked; chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), and iron (Fe) values significantly ranged from 16.2-196.4, 119.8-1096.5, 9.9-498.8, 19.1-169.7, 565.2-5725.3 and 10224.8-137502.5 mgkg⁻¹ respectively, for different batches of compost. The heavy metal concentrations of all the batches of composts analysed in the dry season were very high. While the levels of Pb for all the batches were significantly within the acceptable range, the Zn and Fe concentrations for all the batches significantly exceeded acceptable concentrations. It was not so for Cr, Cu, and Ni checked. Table 4.11 displayed different trends in their mean levels of heavy metals; while the mean concentrations of Cr and Cu for some batches of compost were significantly within the acceptable range, others significantly exceeded. The reason is that most feedstocks used during composting have been sourced from mixed MSW dumpsites which contain organic materials and other diverse non-degradable components (Richard & Woodbury, 1992; Mamo et al., 2002; Dimambro et al., 2005). Hence, composts made from source sorted feedstocks give lower heavy metal concentrations than those made from mixed MSW. So, the heavy metal analysis becomes very important throughout composting process to when the final products are formed because of bioaccumulation in the final products (Dimambro et al., 2006; Tibu et al., 2019).

It is observed in the results also from table 4.10 that the batches (NDC 9-11) had significantly higher mean concentrations of heavy metals than other batches, and this is because of lack of rainfall, i.e., leaching out/dilution effect of heavy metals. These composts were made at the peak of the dry season. Chromium, lead, and iron contents were significantly different among the batches, with NDC 11 having significantly highest content than other batches. NDC 9 was observed to have significantly higher copper and zinc contents than the other batches for copper and zinc. Though nickel content was highest in NDC 9 than in other batches, it did not significantly differ.

Therefore, we can summarise that the statistical results from the heavy metal analysis of different batches of compost made in the dry season revealed that there were significant differences between batches for all the metals checked (Cr: $F=12.054$, $P<0.05$; Cu: $F=13.875$, $P<0.05$, Pb: $F=11.994$, $P<0.05$ and Zn: $F=15.031$, $P<0.05$ and Fe: $F=13.611$, $P<0.05$), except in Ni, which showed no significant difference between batches made from the same season (Ni: $F=1.273$, $P>0.05$).

4.5 Seasonal Differences in the Physio-Chemical Properties of the Compost made in Nigeria.

Seasonality influences the availability of feedstocks used for composting and the final compost produced in Nigeria. It controls the composting process done outside if not managed well. However, composting happens naturally in all climates and places; climatic conditions such as temperature, wind, and rainfall delay or accelerate the process. That is why they must be managed well, depending on where the composting takes place (Ryndin and Tuuguu, 2015). E.g., Systems that are indoors or have shelter over them may only be affected by feedstocks used in composting. At the same time, systems without shelter over them are affected by climatic conditions and feedstocks too. Solomon (1993) suggested that wind drops the temperature and dries out heaps, while the scorching sun dries out moisture from the heap, and heavy rains can chill and waterlog the compost heap. Fig. 4.3 shows the total rainfall and the temperatures throughout the year at Owerri in 2018 when the compost was made. The diagram was obtained from the internet.

Wet and dry seasons in Owerri vary significantly throughout the year. Temperatures in Owerri are adequately warm year-round. While the wet season lasts from April to November, its peak June- September, the dry season lasts from November to March.

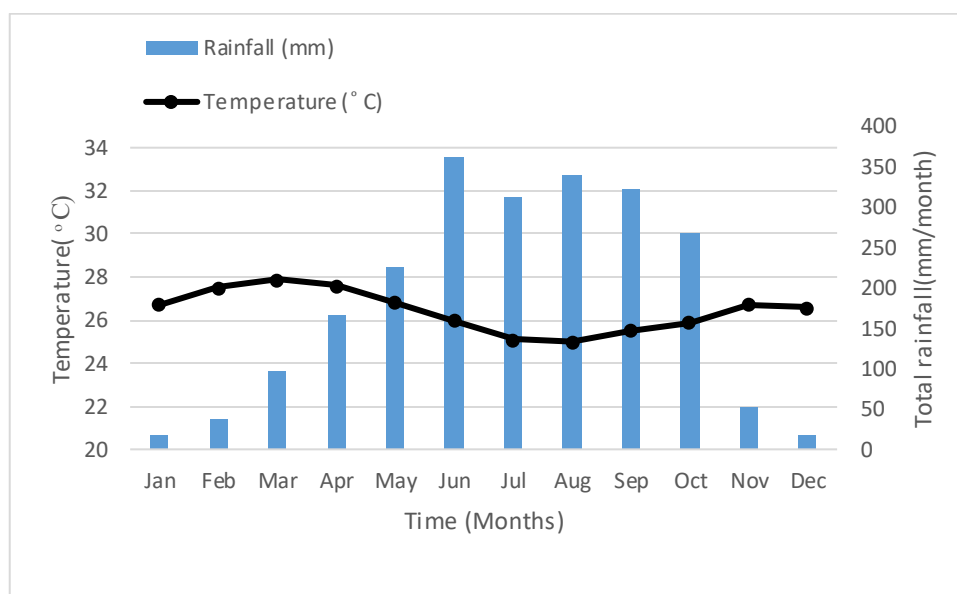


Fig. 4.3 Total rainfall and the average temperature at Owerri in 2018 at the time of compost production(Owerri climate-<https://en.climate-data.org>).

4.5.2 Seasonal differences in physical properties of compost

The physical properties of composts made seasonally were seen from their colour to their textures. The composts were brown and blackish brown (fig. 4.4). In comparison, the

composts made in the wet season had more grass trimmings and green components, resulting in a smoother compost. That is why its brownish colour, dense with mild odour unlike the ones made in the dry season which had a blackish-brown colour, very dusty in appearance having a faint woody smell. The fig. 4.4 are the composts made both in the wet and dry seasons. Benito et al. (2006) also agreed that more grass clippings that made most of the feedstock during the summer caused the production of smoother compost with small air space.

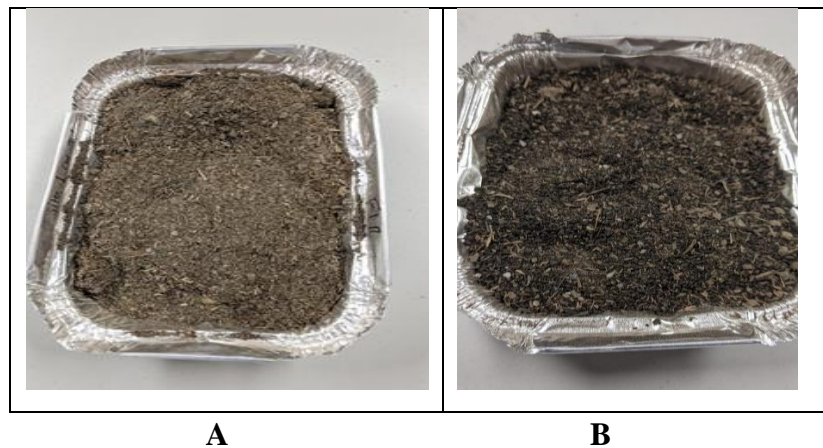


Fig. 4.4 Pictures of composts made in A, wet and B, dry seasons.

For this chapter, temperature and rainfall were not tracked during compost production in Nigeria. However, data on temperature and rainfall were collected online, as mentioned in fig.4.4, so no correlation was performed on the results. In this section, the parameters tested seasonally presented significant variation in some results obtained below:

4.5.3 Seasonal differences in chemical properties of compost

The seasonal differences in the chemical properties of composts made in Nigeria are seen in this section. It includes the pH, EC, organic matter, Carbon, Nitrogen, and C/N ratio, nutrients, and heavy metals concentrations. The seasonal mean values for pH of compost made in Nigeria are displayed in fig.4.5

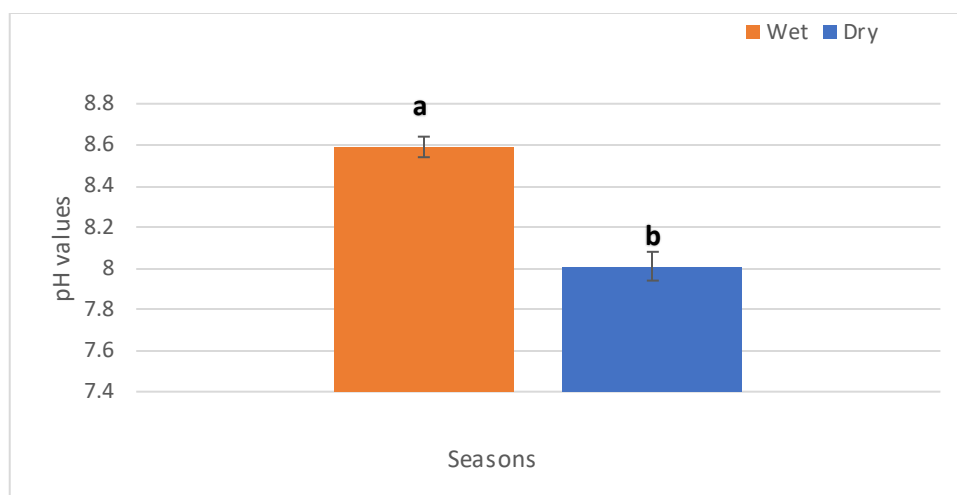


Fig. 4.5 Seasonal mean values for pH compost. Error bars indicate the 95% confidence level of the (Mean \pm SE, (n=36). Means with the same letter are not significantly different.

The pH of compost typically varied for both wet and dry. Results revealed that the mean pH value of all the batches of composts analysed in the wet season was 8.6, while the mean pH value of all the batches of composts analysed in the dry season was 8. The pH value of the composts obtained in both seasons was within the accepted APEX standard limits of pH of compost which is 7.0-8.7.

They are alkaline, mature composts, and the results agreed with the conclusion of pH obtained by Benito et al. (2006). The compost made in the wet season was significantly higher than those in the dry season. The reason is that the compost produced in the wet season might be from the feedstock used (see fig. 4.2 more commercial wastes used in the wet season).

Moreover, the faster the synthesis of phenolic (mineralisation of carbon and subsequent production of OH⁻ ions by ligand exchange allows the introduction of basic cations, such as K⁺, Ca²⁺ and Mg²⁺ during the composting process. That is faster degradation of organic fractions in the wet season period. While, in the dry season, pH values were lower, signifying slower degradation and higher production of organic acids (humification) (Benito et al., 2006). Because pH influences the availability of nutrients to the microorganisms, Bunt (1988) suggested that for growing media purposes, composts with pH higher than 5.2-6.3 should be improved with other materials for plants sensitive to alkaline conditions, e.g., Blueberry and rhododendron. Therefore, seasonal differences significantly influenced the mean pH of compost made in Nigeria (F=407.224, P<0.05).

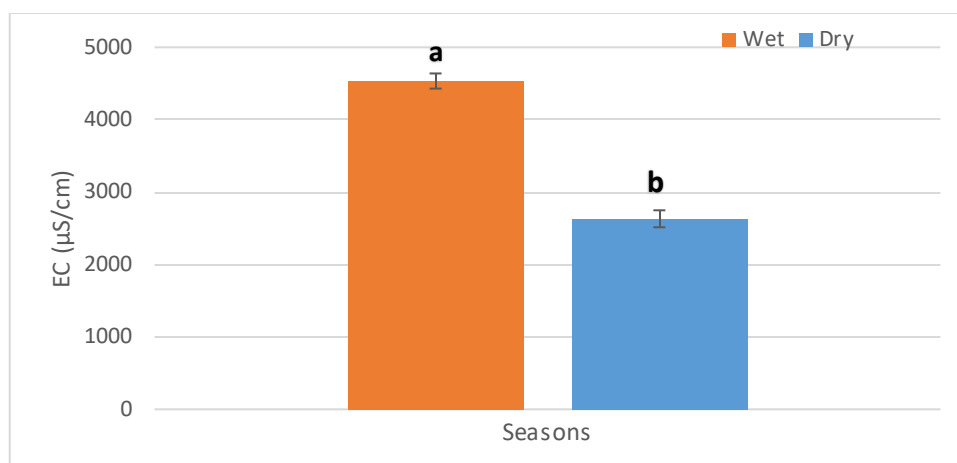


Fig. 4.6 Seasonal mean values for EC of compost. Error bars indicate the 95% confidence level of the (Mean \pm SE, (n=36). Means with the same letter are not significantly different

The mean EC values of composts made in the wet and dry seasons were 4534.17 and 2631.58 μScm^{-1} , as displayed in fig. 4.6. The EC results of composts from the wet and dry seasons were significantly higher than the optimal values, the Apex EC limit (750 to 2000 μScm^{-1}). The reason is probably due to the food waste, i.e., feedstock used in composting that contains high water-soluble salt concentration as food waste (He et al., 1995). Thus, seasonal differences significantly influenced the EC of compost made in Nigeria ($F=8.011$, $P>0.05$).

Fig. 4.7 reveals the mean values of the composts' seasonal variations of organic matter (LOI), carbon, nitrogen, and carbon/nitrogen ratios.

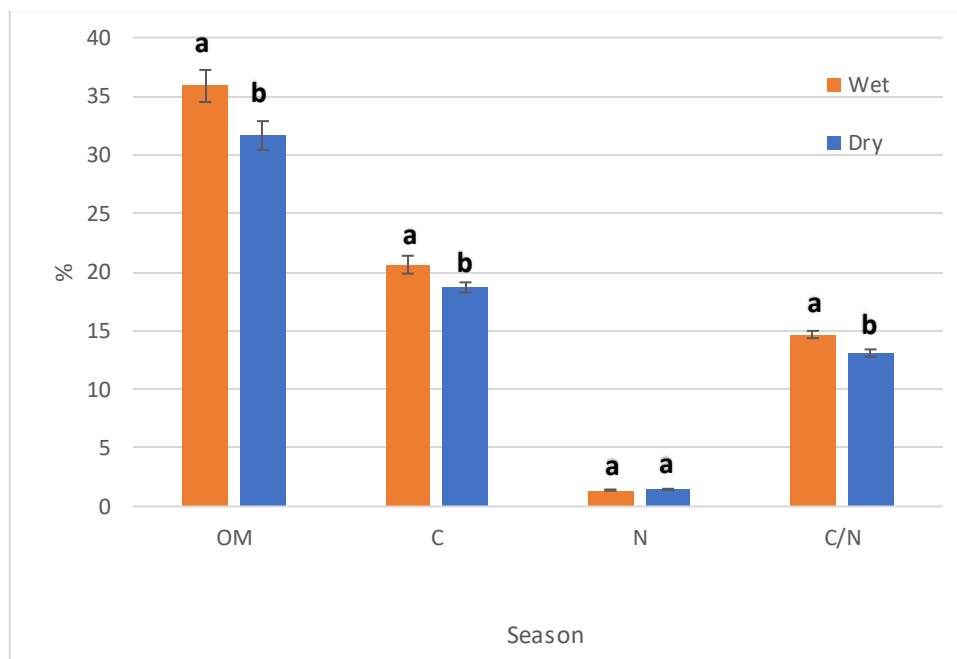


Fig. 4.7 Seasonal organic matter, Carbon, Nitrogen, and C/N ratio contents of compost. Error bars indicate the 95% confidence level of the (Mean \pm SE, (n=36). Means with the same letter are not significantly different.

The following results from Fig.4.7 agree that the nature of the feedstocks affected the properties of compost formed. The organic matter (loss on ignition) is the most valuable constituent of compost for soil improvement. Therefore, the organic matter and carbon are expressed as a percentage of dry compost weight (Sullivan et al., 2018). Organic carbon (C) gives about half of the organic matter weight. From fig. 4.7, from all the batches of composts analysed seasonally, results revealed that the mean total organic matter of composts was significantly 35.9% in the wet season and 31.6% in the dry season, of which were all within the ideal values of good compost (25-65%). Also, results obtained from the mean organic carbon of composts were significantly 20.6% in the wet and 18.7% in the dry seasons. Results agreed with the specified standard value of organic carbon, which must be higher than 10% (Batjes, 1996; Khater et al., 2015).

The mean values of nitrogen content were 1.4% in the wet season and 1.5% in the dry season. Moreover, these results agree with those obtained by Benito et al. (2005), who found that the total nitrogen rate of MSW compost ranged from 0.99 to 2.01%. Finally, the mean C/N ratio of compost was significantly 14.7% in the wet season and 13.1% in the dry season. However, the mean values of the C/N ratio of composts made in the wet and dry seasons were below the acceptable range of 15-20% as recommended by APEX.

The results revealed that all the parameters checked in fig. 4.7 were dependent on the feedstock composition and thus have seasonal dependence except for nitrogen content. i.e., seasonal differences significantly influenced the organic matter, carbon, and C/N ratio contents of composts made in Nigeria (OM: $F=53.299$, $P<0.05$; C: $F=14.568$, $P<0.05$ and C/N: $F=93.339$, $P<0.05$). While seasonal differences significantly influenced nitrogen contents in all composts made were not significantly influenced seasonally (N: $F=2.083$, $P>0.05$). The seasonal variations observed in the properties of the composts checked in fig. 4.7 are due to either seasonal variation in feedstock used (Negro et al., 2018) or the partial maturation of the pile, which leads to loss of carbon as CO_2 . (Fig. 4.7), also revealed that the mean values of organic matter, carbon and C/N ratio were significantly higher in the wet season than those of the ones made in the dry season. The reason why nitrogen contents of the composts made did not show any significant differences may be that poultry manure, a source of nitrogen content, may have been gotten from the same poultry farm in both wet and dry seasons, therefore, not having a significant effect on the compost made seasonally.

The reason for the high C/N ratio obtained in compost made in the wet than the C/N ratio of compost made in the dry season is due to reduced rainfalls in the dry season. The feedstock

used in composting in the wet seasons may be more branches of plants or more commercial wastes, which increases the C/N of the composts, as described by Bary et al. (2005) and Boldrin and Christensen (2010). Also, the increase of C contents of the composts and decrease of N in the wet season reflects the increase observed in the C/N ratio in the wet season. C/N ratios of compost are an essential factor during composting. The low C/N ratios of the composts obtained in both wet and dry seasons could be because they contain more manure or green materials. These composts can be amended by adding more constituents of high carbon sources (Rawat et al., 2013). Though the results obtained from the Organic matter (%) were within the required range, Abad et al. (2001) suggested that total organic matter above 80% is suitable for potting media. An increase in OM will increase C and C/N values, leading to increased microbial activities (Davidson, 1994). The seasonal total organic matter content could be increased by adding materials that are high in cellulose and lignin concentrations or sludge or garden waste (Dimambro et al., 2005, He et al., 1995)

Fig. 4.8 displays the seasonal variation of the mean values obtained from the nutrient contents of compost.

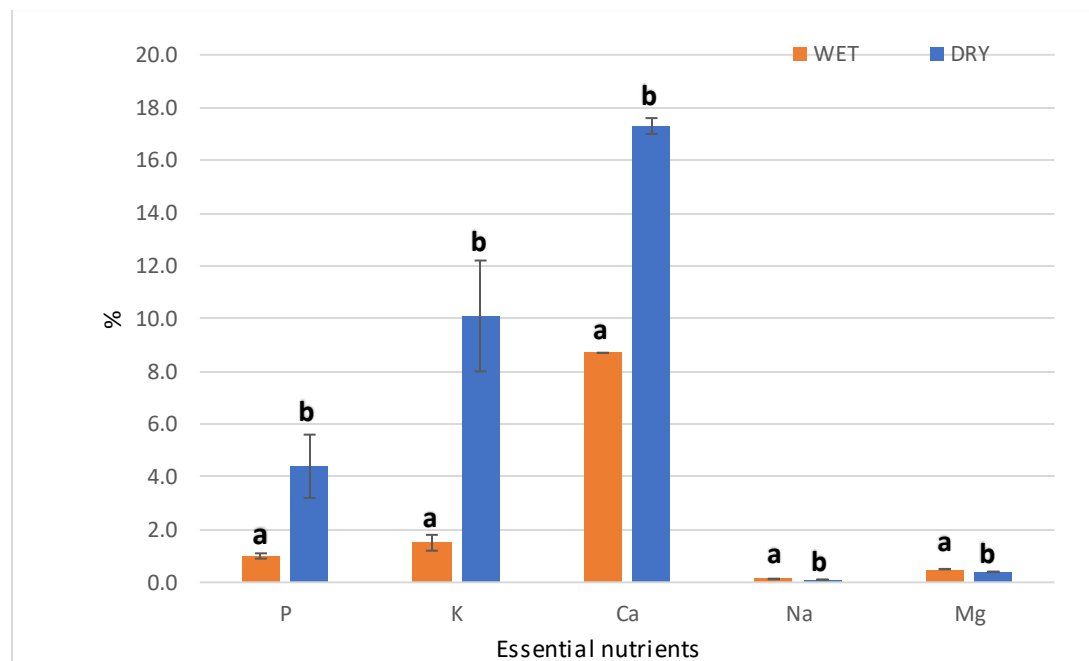


Fig. 4.8 Seasonal contents of nutrient elements of compost. (Error bars indicate the 95% confidence level of the (Mean \pm SE, (n=36). Means with the same letter are not significantly different.

Potassium and calcium were the most significantly plentiful nutrients, reflecting the nature of the compost. Ca had the highest values of 8.7 and 17.3 % in both wet and dry seasons, while Na significantly had the least concentration of 0.13 and 0.10 % in both wet and dry seasons.

Usually, these nutrients are not limiting because they are in sufficient concentration in the compost source materials. The levels of the nutrients are highest in this order of (Ca > K > P) for both wet and dry seasons as recorded than the concentrations of other nutrients as seen in fig. 4.8. They reflected the nature of the compost, which is vital to study when evaluating the nutrient recovery potential from green waste.

Composts with high soluble salts affect the plant's germination and growth by triggering water stress and ion toxicities (Recycled Organics Unit 2003). The mean contents of nutrient (P, K, and Ca) composts obtained during the dry season were significantly higher than the mean of nutrients recorded during the wet season, except for Na and Mg contents that were significantly higher in the wet season than in the dry season. The reason is that the increased number of precipitations received by the heap during the wet season during the composting leached the nutrients out and dissolved more soluble ions in the samples. Nutrients like Mg held more tightly than potassium can be depleted due to excessive rainfall (Hardy, 2013).

According to Sullivan et al. (2018), the results from fig. 4.8, only the mean values of the concentrations of Mg and Na were significantly within the standard range of compost nutrients, while others were significantly far above the recommended standard values. Ca exceeded 4% in both wet and dry, which is the accepted standard, suggesting that feedstocks used in composting contained soil, gypsum, or lime, while P and K exceeded 0.9 and 1.5%, respectively the dry season. It indicates that the feedstock contained more food wastes or manure.

However, statistically, seasonal differences significantly influenced the phosphorus, potassium, calcium, sodium, and magnesium contents of composts made in Nigeria (P: $F=333.359$, $P<0.05$; K: $F=302.864$, $P<0.05$; Ca: $F=92.675$, $P<0.05$; Na: $F=74.982$, $P<0.05$; and Mg: $F=676.629$, $P<0.05$).

Fig. 4.9 presents the obtained heavy metals concentrations of Cr, Cu, Ni, Pb, Zn and Fe (mg kg^{-1}) in both wet and dry seasons.

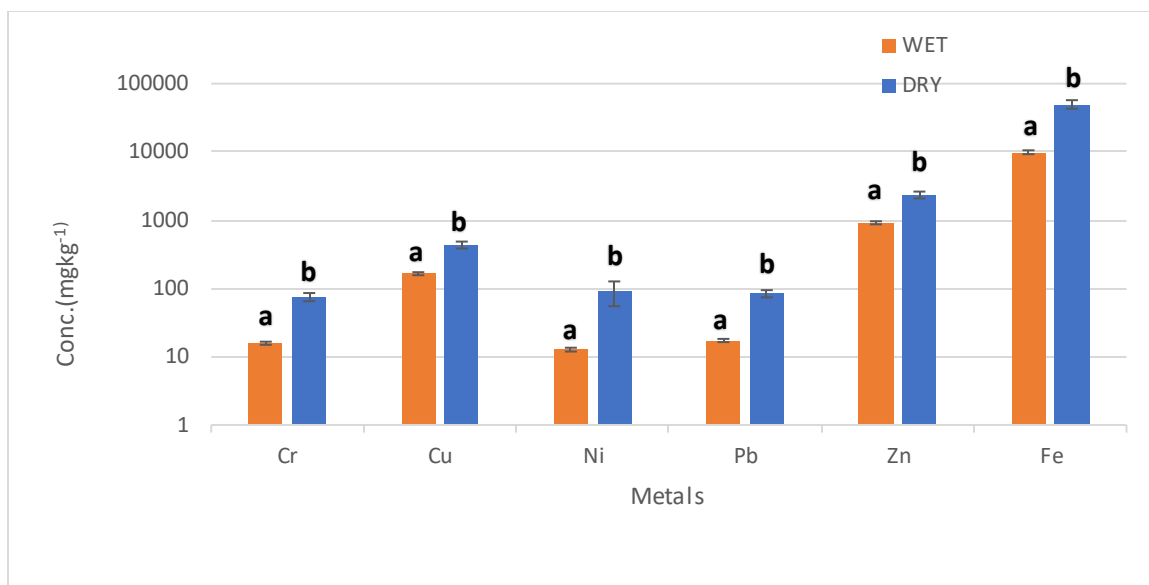


Fig. 4.9 Seasonal concentrations of heavy metals in compost (mg kg⁻¹ means of dry matter, error bars indicate the 95% confidence level of the (Mean \pm SE, (n=36)). Means with the same letter are not significantly different.

The results obtained from fig. 4.9 showed that all the mean values of concentrations of heavy metals from composts made in Nigeria were significantly influenced seasonally, with the concentrations of all the heavy metals significantly higher in the dry season than those in the wet season. The reason might be rainfall, which aided the dilution of heavy metals during composting in the wet season.

Heavy metal concentrations observed in composts made from mixed waste streams have been broadly studied by some researchers (Cai et al., 2007; Gao et al., 2008; Chen et al., 2010; Andersen et al., 2011) mainly because of their toxic effects on microorganisms and possible long-term build-up in the food chain.

The sequence of metal concentrations in compost was Fe>Zn>Cu>Pb>Cr>Ni in the wet season and Fe>Zn>Cu>Ni>Pb>Cr in the dry season. Fe had the highest values of 9910.8 and 50163.3 mgkg⁻¹, in both wet and dry seasons, while Ni and Cr significantly had the least concentration of 12.7 and 75.3, respectively. Fe and Zn significantly exceeded the accepted standard of heavy metals concentrations in both seasons.

The reason is that compost could be from contaminated feedstock (through the food cycle), metals discarded alongside other MSW which are bioavailable to organic waste and leaking of batteries that end up in the compost. It could also be from livestock manure or sewage sludge used in composting (Basta et al., 2005; Khan et al., 2008), metal mining industries around composting facilities/landfills, which release the metal ores into the air and later settles on compost/ organic waste (Sposito and Page, 1984).

Besides, stabilisers and pigments used in plastic production may contain heavy metals (Richard and Woodbury, 1992) and, finally, improper waste sorting, contaminating the Feedstock (Planet Natural.html.) The heavy metal concentrations are higher in mixed MSW composts than in composts made from source-separated organic waste (Richard & Woodbury, 1992; Ciavatta et al., 1993).

Compost contaminated with heavy metals applied to farmland can release these heavy metals into the soil, hence, into the food chain (Petrizzelli, 1996). Therefore, a detailed assessment of the effect of heavy metals through compost application may be supported by the facts about their performance in the soil (Petrizzelli, 1996). Richard and Woodbury (1996) suggested inconsistent evidence of whether heavy metals from MSW composts can hurt soil microorganisms, including nitrogen-fixing bacteria that soils that have been cropped for decades may be deficient in nutrients. MSW compost could alleviate such deficiencies over the years. Therefore, statistically, the seasonal differences significantly influenced the heavy metal concentrations of the compost made in Nigeria (Cr: $F=145.823$, $P<0.05$; Cu: $F=140.159$, $P<0.05$, Pb: $F=184.705$, $P<0.05$ and Zn: $F=15.704$, $P<0.05$ and Fe: $F=154.260$, $P<0.05$).

4.6 Conclusion

The results obtained here answered the research questions, which are:

1. Does the type and proportions of wastes (feedstock) used in compost making vary seasonally?

2. Does seasonal variation affect the chemical composition of compost from Nigerian MSW?

After some interviews with the makers of the locally made compost and seeing the records of the raw materials/feedstock used annually. It was established that most of the feedstock used for composting is seasonal, and the feedstock to be used is strongly reliant on the availability of these feedstocks. Fig. 4.2 revealed the seasonal feedstock used for composting. Statistically, the volume and type of feedstock generated and used in compost production in Nigeria differ between the three years sampled. The T-test (Levene's test for equality of variances) on the feedstock generated revealed no significant difference seasonally (between dry and wet seasons).

Also, results from this study show seasonal variations in the chemical properties of compost made in Nigeria. This study evaluated and compared three replicas of 12 batches of composts produced in wet and dry seasons, and most of their feedstocks were sourced from mixed MSW. Composts were analysed for pH, electrical conductivity, organic matter, carbon, nitrogen, and C/N ratios. Also, nutrients and heavy metals contamination were checked. It can be concluded that for both seasons, compost's pH was significantly higher in the wet season than in the dry season. Likewise, The EC of composts made in the wet season was significantly higher than those made in the dry season. It suggested that seasonal differences significantly influenced the means of EC from composts made in both wet and dry seasons. The results obtained from the organic matter, carbon (C), and C/N ratios displayed seasonal dependence and were higher in the wet season. Reasons are the type and composition of Feedstocks (Bary et al., 2005; Boldrin and Christensen, 2010), which were highly seasonal and the fast mineralisation of carbon and subsequent production of OH^- ions during composting process (Benito et al., 2006). The C/N ratios for wet and dry seasons were 14.7 and 13.1% lower than the acceptable range of 15-20. The composts could be enhanced by adding more feedstocks of high carbon sources (Rawat et al., 2013). The electrical conductivity/salinity of composts made in the wet season was higher than those made in the dry season. This could be due to seasonal climatic differences, and the feedstock used is very high in water-soluble salts (He. et al., 1995). The annual contents of nutrients and heavy metal concentrations of composts checked revealed seasonal variabilities but higher in the dry seasons than in the wet season, except for sodium and magnesium, which

were higher in the wet seasons. Reasons for this may be attributed to the dilution effect/leaching during wet seasons, reducing their concentrations in compost. Though magnesium is known to be held more tightly in composts, this is the reason why it was not reduced in the wet season (Hardy, 2013). While calcium exceeded the 4% accepted standard in both wet and dry, depicting that feedstock may have contained soil, gypsum or lime, phosphorus and potassium exceeded 0.9 and 1.5%, respectively, in the dry season, suggesting that the feedstock contained more food wastes or manure. Also, the high EC obtained from this study correlates with the high soluble nutrient contents observed for all batches of compost.

Finally, Fe and Zn concentrations exceeded the accepted standard in both seasons from all the heavy metals analysed. The reason is that most feedstocks used were sourced from the dumpsites directly. For example, metal scraps, batteries that leak and plastics that contain pigments and stabilisers, which are all discarded alongside other MSW, can increase the concentrations of these heavy metals (Brinton and Brinton, 1992; Richard & Woodbury, 1992; Ciavatta et al., 1993; Montejo et al., 2015).

Therefore, as seen from figs. 4.5 - 4.9, this study revealed significant differences in the chemical properties of the composts seasonally except for moisture content and nitrogen content, which did not show any significant differences.

CHAPTER 5

RELATIVE ABUNDANCE, COMPOSITION AND DISTRIBUTION OF WASTE PLASTICS AWAY FROM NIGERIAN DUMPSITES.

5.1 Introduction

Plastic waste is the third leading component of municipal waste in cities after food and paper waste (United Nations Environmental Programme et al., 2009). Over 300 million metric tons of polymeric materials known as plastics are generated yearly worldwide. Their significance has been observed in today's world because of their wide range of applications (Geyer et al., 2017). It is estimated that less than 30% of plastic waste that enters the landfill yearly in Europe is recycled (Plastics Europe, 2015). Landfills or dumpsites and marine environments are the leading sinks for plastic wastes generated annually through littering, waste disposal, sewage treatment and environmental factors (Shim and Thomposon, 2015). These plastic wastes seen accumulating in the environments are seen moving away from where they are dumped through human and environmental factors.

Therefore, there is an upsurge in the global challenge emanating from the end of life of plastics. The reason is that they are chemically persistent and abundant in the broader environment, making recycling difficult (Rios et al., 2007; Jambeck et al., 2015).

While developed countries have made significant progress toward establishing operational approaches to waste management, they include identifying diverse waste sources, separating, and recycling them (Scheinberg, 2003; Saarikoski, 2006; UNCHS, 2010). The situation is not so for African countries; it is below standard because of the ineffective handling of solid waste (Crook and Ayee, 2006; Van Dijk, 2006; Oosterveer, 2009).

The disruptive effects of plastic waste have been identified in marine and terrestrial environments as a threat to wildlife and the food web due to a lack of knowledge of plastic composition. Fig. 5.1 shows us what a typically mixed waste with plastics on dumpsites and in a marine environment. Also, their environmental degradation is limited because they are usually mixed with additives, which strengthen them, making them more durable to the environment (Andrady, 2011). These additives could be stabilizers, plasticizers, fire retardants, UV stabilizers, dyes, opacifiers, or gloss additives which all raise the risk of adverse health issues, such as the case of plasticizers (Crompton, 2007; Koch and Calafat, 2009; Oehlmann et al., 2009; Tripathi et al., 2016; Turner, 2018).



Fig. 5.1 Pictures of mixed plastic wastes in the environment (Author's own images)

These Plastic polymers are primarily synthetic because they are derived from fossil fuels (crude oil) to produce different types of monomers through a polymerisation reaction. They include polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polyamide (PA), polyacrylonitrile (PAN), polyurethane (PUR), Polyamide (PA), etc. (Gewert et al., 2017; Jehanno et al., 2019). Which fig. 5.2 will display the molecular structures for most plastic materials generally used, as seen in the chosen dumpsites.

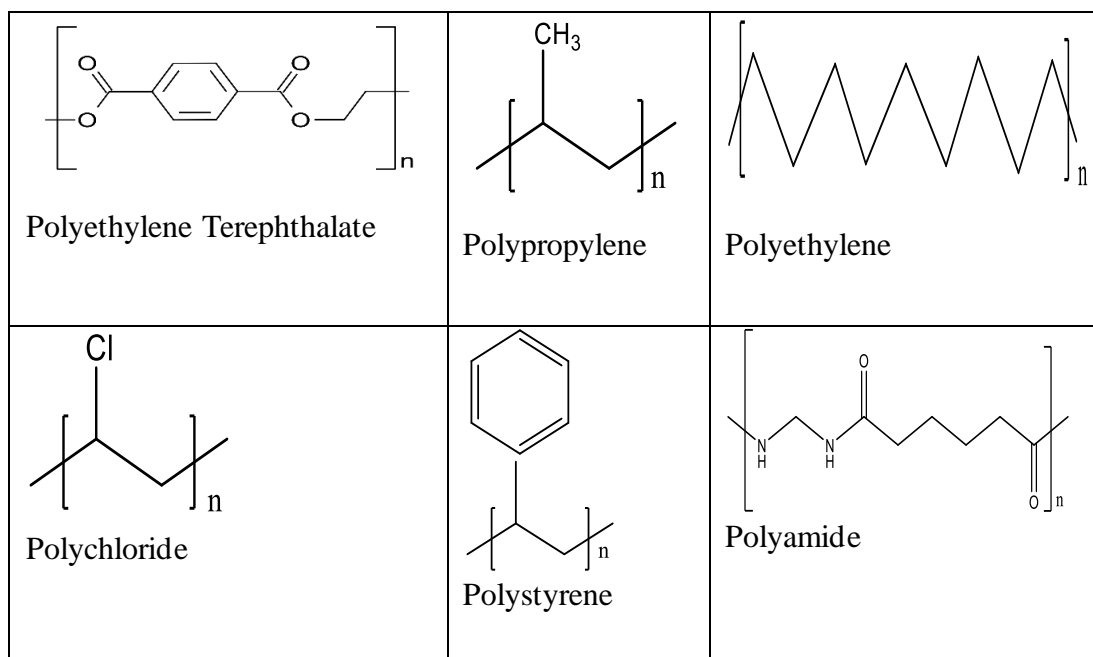


Fig. 5.2 Molecular structures for most of the plastic polymers seen in the chosen dumpsites

5.1.1 Factors influencing the spatial patterns of plastic wastes

Despite the several global benefits of plastics in our society today, there are challenges caused by these plastics. Different factors play a role in the presence and spatial distribution of plastic wastes in the environment. These factors consist of the types of plastic materials used daily, which are frequently seen in huge quantities and are used in packaging applications. Climate

conditions such as wind and rainfall (Browne et al., 2010; Geyer et al., 2017), size and density of plastics wastes (Thiel et al., 2003; Ryan et al., 2009) are factors influencing their distribution in the environment. Finally, human activities such as fishing, tourism, scavenging, and animals moving plastics from one place to another also affect their spatial distribution in the environment (Dahlén and Lagerkvist, 2008; Rillig, 2012).

Although the density of plastic can differ significantly, it depends on the polymer's nature and the processes it goes through during making (Browne et al., 2010). Duis and Coors (2016) and Ryan et al. (2009) explained that most plastic particles move from the environment into water bodies through wind, flood, or stormwater run-off due to rainfall.

Thornton and Jackson (1998); Browne et al. (2015); and Galgani et al. (2015) also investigated the different types and sizes of plastics along the shores away from land-based sources. They concluded that the environment and composition of wastes were affected by physical factors and the climatic conditions, which agrees with the submissions of (Thiel et al., 2003; Ryan et al., 2009 and Browne et al., 2010).

These plastics produced are labelled with a resin code marked under the plastic in a triangle showing the polymer type as seen in fig. 2.7 in chapter 2 (Gregory and Andrady, 2003). The resin codes are hardly readable in plastic wastes (large or in fragments); therefore, identifying the plastic waste is essential using chemical analysis. Characterizing unknown plastic helps eliminate concerns surrounding their prevalence and end of life in the environment (Jung et al., 2018).

Plastic identification

Identifying these various types of plastic wastes in the environment is essential to help tackle and sustain effective and efficient solid waste management. For instance, knowing the type of plastic waste prior recycling process helps save time in guessing what type of plastic it is and gives us near accuracy in recycled products. Presently, a variety of spectroscopic methods are widely used for plastic identification (Andrady, 2017). Such as thermal desorption and pyrolysis gas chromatography-mass spectrometry (GC/MS) used to identify indicator chemicals used in plastics production and microplastics from rivers (Nilsen et al., 2014; Dümichen et al., 2015; Fischer and Scholz-Böttcher, 2017). The GC/MS methods were limited to only unstable or ionisable compounds, such as small oligomeric fragments within the bulk material. The Fourier-transform infrared spectroscopy, the Raman (FT-IR), and X-ray fluorescence (XRF) using vibrational spectroscopy are other methods used in the identification of plastics; they analyse the entire sample with less sample preparation (Frère et al., 2016). However, a common feature among these spectroscopic methods is the challenge associated

with analysing polymeric mixtures. It records the spectrum of individual plastic materials one at a time, consuming time.

FTIR Identification

PLASTICS + *FOURIER-TRANSFORM INFRARED* = IDENTIFICATION



Fig. 5.3 Diagram showing the identification of polymeric materials by FT-IR (Author's image)

Fig. 5.3 shows the identification of unknown polymeric materials by FT-IR. The FTIR spectroscopy method was used for this study and no other method because the FTIR machine was the only equipment accessible at the time of analysis. Uses light absorption by the molecules of the material measured in the infrared region of the electromagnetic spectrum, causing frequency change due to molecular vibration. This absorption corresponds precisely to the bonds existing in the molecule. As the light is absorbed, it induces a dipole movement during interaction with the material (Hahn, 2007). FTIR has become the most preferred technique for identifying both micro and macro plastic waste and various additives used in making them in different environments (Mecozzi and Monakhova, 2016; Cincinelli et al., 2017). It is simple, effective, and non-destructive for characterising and separating plastic polymers, using infrared absorption bands showing the exact chemical and molecular functional groups existing in the plastic, as seen in table 5.1 (Rotter and Ishida, 1992; Beltrán and Marcilla, 1997; Verleye et al., 2001; Nishikida and Coates, 2003; Noda et al., 2007; Asensio et al., 2009; Jung et al., 2018).

Usually, the FTIR spectrum of complex molecular polymers often shows several peaks, and due to their high chemical heterogeneity, their visual interpretation generally requires a skilled operator. The external agents such as the interaction of the plastics with hydrological factors, living organisms and the natural ageing process of the polymer can modify its spectral features, making the identification of the plastic even more complex.

Table 5. 1 List of important vibration modes and mod assignments for the FT-IR of some polymers identified.

| Polymers | Frequency (cm ⁻¹) | Assignment | Intensity | Ref |
|-----------|----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (PET) | 1713(a) 1239(b) 1091(c) 872 (d) 723 (e) | C=O stretch C-O stretch C-O stretch C-H bend (aromatic) C-H bend (aromatic) | s s s m s | (Rotter and Ishida, 1992; Beltrán and Marcilla, 1997; Verleye et al., 2001; Nishikida and Coates, 2003; Noda et al., 2007; Asensio et al., 2009; Jung et al., 2018). |
| LDPE | 2914(a) 2848(b) 1467(c) 1462(d) 1377(e) 730 (f) 718 (g) | C-H stretch C-H stretch C-H bend C-H bend C-H bend C-H rock C-H rock | s s m m w m m | |
| HDPE | 2914(a) 2848(b) 1467(c) 1462(d) 730 (e) 718 (f) | C-H stretch C-H stretch C-H bend C-H bend C-H rock C-H rock | s s m m m m | |
| PP | 2951(a) 2915(b) 2838(c) 1455(d) 1377(e) 1166(f) 997 (g) 972 (h) 840 (i) 808 (j) | C-H stretch C-H stretch C-H stretch C-H bend C-H bend C-H bend, C-H rock, C-C stretch C-H rock, C-H bend, C-H rock, C-C stretch C-H rock, C-CH stretch C-H rock, C-C stretch, C-CH stretch | s s s m s m w w w w | |
| PA(Nylon) | 3298(a) 2932(b) 2858(c) 1634(d) 1538(e) 1464(f) 1372(g) 1274(h) 1199(i) 687 (j) | N-H stretch C-H stretch C-H stretch C=O stretch N-H bend, C-N stretch C-H bend C-H bend N-H bend, C-N stretch C-H bend N-H bend, C-O bend | m m m s s w w w w w | |
| PS | 3024(a) 2847(b) 1601(c) 1492(d) 1451(e) 1027(f) 694 (g) 537 (h) | C-H stretch(aromatic) C-H stretch Aromatic ring stretch Aromatic ring stretch C-H bend C-H bend(aromatic) C-H bend(aromatic) Aromatic ring bend | w w w m m w s m | |

| Polymers | Frequency (cm ⁻¹) | Assignment | Intensity |
|--------------|--------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|
| PVC | 1427(a) 1331(b) 1255(c) 1099(d) 966 (e) 616 (f) | C-H bend C-H bend C-H bend C-C stretch C-H rock C-Cl stretch | m w s w m s |
| EVA | 2917(a) 2848(b) 1739(c) 1468(d) 1375(e) 1241(f) 1020(g) 720(h) | C-H stretch C-H stretch C=O stretch C-H bend C-H bend C(=O)O stretch C-O stretch C-H rock | s s m w w m w w |
| PMMA | 2992(a) 2949(b) 1723(c) 1432(d) 1386(e) 1236(f) 1188(g) 1140(h) 985(i) 964(j) 750(k) | C-H stretch C-H stretch C=O stretch C-H bend C-H bend C-O stretch C-H rock C-O stretch C-H rock C-H bend C-H rock | w w s w w m w m w w w |
| (PTFE)Teflon | 1200(a) 1145(b) 779(c) 742(d) 720(e) 638(f) 552(g) | C-F stretch C-F bend C-F scissoring C-F scissoring C-F scissoring C-F deformation C-F bend | s s w w w m m |

The letters in () mean number of peaks and “s” means strong peaks, “w” means weak peaks and “m” means mild peaks.

5.2 Aims and Objectives

This chapter aims to

- Identify the plastic wastes from mixed MSW in Nigerian dumpsites using the Fourier transform infrared spectroscopy (FTIR) method.
- Evaluate the accumulation and distribution pattern of the different plastic wastes at Nigerian dumpsites.

Significance of the study

Recycling is part of the waste management process, and it is imperative to identify and group plastic wastes by type and other similar qualities to maximize their recycling process. Therefore, exploring an effective and sustainable approach is pertinent; this includes analytically using modern technology to identify and separate plastic waste into similar groups before recycling. The results will contribute significantly to the body of knowledge by helping

identify polymeric materials, know plastic diversity in the broader environment such as dumpsites and understand the distribution patterns of plastic wastes at distances around and away from the dumpsites.

Hypothesis

- FTIR Spectroscopy can identify unknown plastic materials
- PP, PET and PE plastic wastes dominate most dumpsites in Nigeria.

By achieving the aims, this study seeks to answer the search question

Research Questions

RQ1 Does the prevalence and weight of plastic polymers influence plastic mobility in and around the dumpsites?

RQ2 What are the most prevalent plastic types in Nigerian dumpsites?

5.3 Materials and Methods

5.3.1 Study sites and Sampling strategy

Several factors impact the manufacture and consumption of plastic products in Nigeria, such as socioeconomic, climatic, political settings, population, and cultural factors. The significance of this is observed in waste generation patterns and their management. Unknown plastic wastes were collected in June 2019 (wet season) from three different locations (dumpsites) from Irete, Orogwe and Nekede in Owerri Imo-State, as described in sections 2.2.1, 2.2.2 and 2.2.3.

Sampling Strategy

Plastic wastes were collected at the active dump area (A.D.A) fig. 5.4E, the grey centre part, is within 0-100m and is distant away from the dumpsites. For the active dump areas of the dumpsites, 2m x 2m quadrat was randomly thrown four times across the four quadrants of each (A.D.A) dumpsite. At each point, surface sampling was observed from the quadrat. While a belt transect was employed to measure the dispersal and distribution of plastic wastes at distances away from the dumpsites. Plastics were collected from the surface of the quadrat across the four quadrants of the dumpsites at a range of distances (50, 150, 250, 350 and 450m) from the grey centre part/active dump area of the dumpsites) as seen in fig. 5.4 E. Each distance transect was repeated four times at each dumpsite. At the smaller dumpsites (i.e., Irete & Orogwe), further coverage was limited due to perimeter fencing; the total of mixed plastic wastes was collected from the three dumpsites, respectively: Irete, 97, Orogwe, 117 and Nekede, 129.

Fig. 5.4A-D are the dumpsites where plastic wastes were collected, while Fig 5.4.E shows a rough sketch of the sizes of dumpsites and the sampling strategy employed in this study. Fig. 5.4A-D are the dumpsites where plastic wastes were collected, while Fig 5.4.E shows a rough sketch of the sizes of dumpsites and the sampling strategy employed in this study.

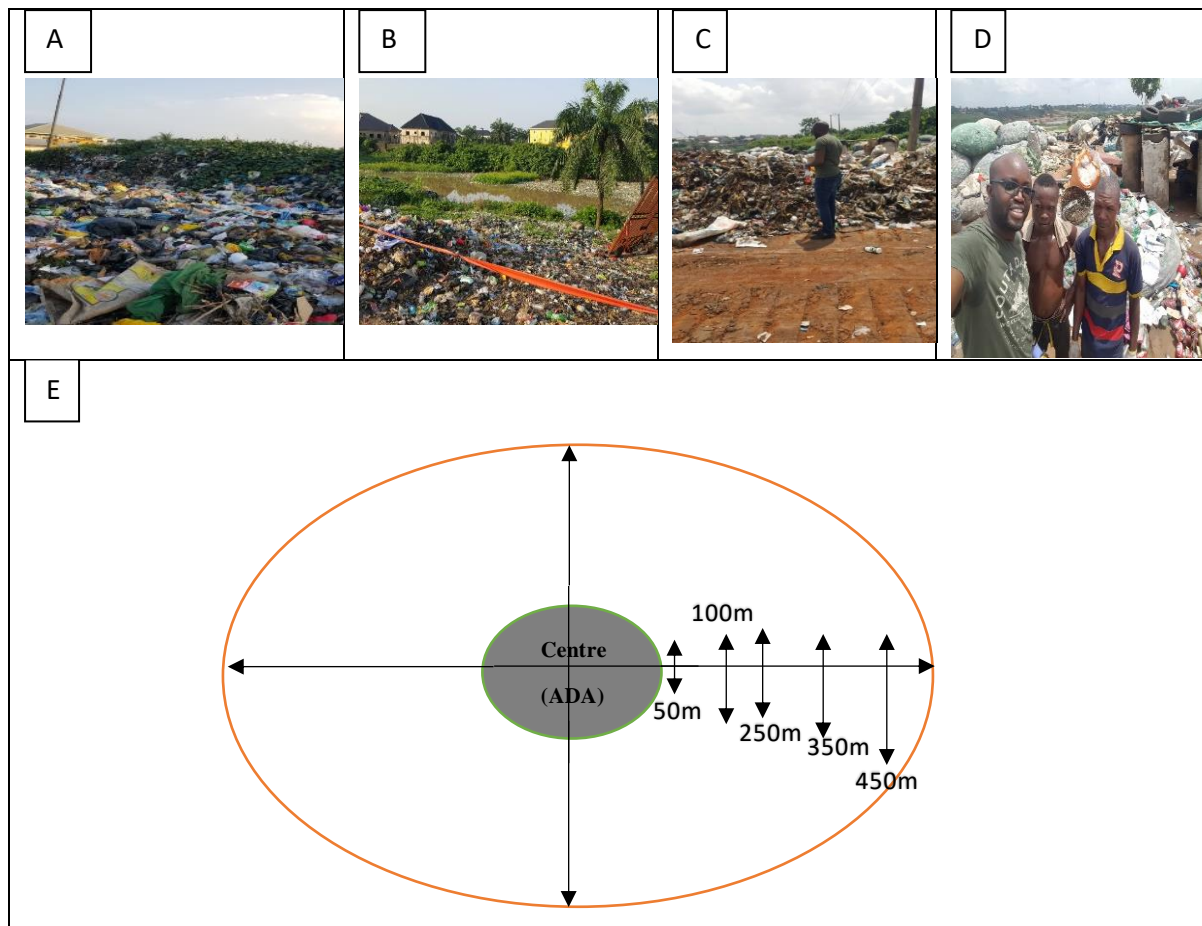


Fig. 5.4 Pictures taken at A, Irete, B, Orogwe, C and D, Nekede dumpsites and E, rough sketch of the three dumpsites in Owerri Imo state (green is Irete, blue is Orogwe and orange is Nekede).(Author's own images)

Two dumpsites were small (Irete and Orogwe), while Nekede dumpsite was larger receiving waste materials from smaller dumpsites in the state. Fig. 5.5 are the procedure employed from sampling, processing and analysis carried out on the plastic wastes.

5.3.2 Sample preparation

Sampled plastic wastes were counted, washed with detergent to get rid of organic matter residuals from several dumpsite sources and rinsed with deionised water. They were cleaned with a dry cloth, air-dried at 25°C for 48 hours, securely packaged in a well-labelled plastic bag, and couriered to Bangor University. The weight of these plastic wastes was recorded in

the laboratory and then stored under laboratory conditions. All samples were cut into 5-6mm discs/pieces and then kept in labelled polythene bags in the laboratory until further analysis. To help ascertain the spectra of the plastic samples collected from the dumpsites in Nigeria, new/virgin plastic samples of known spectra were commercially purchased from Direct Plastics, UK. The new plastic samples were subjected to FT-IR spectroscopy to determine their spectra. Their spectra were compared to the known spectral range in the ICA library to see if they were the same and then used as a reference for the unknown plastic samples from the dumpsites in Nigeria. FTIR technique was conducted on the surface and inside the cut plastic wastes to know if they exhibited identical spectra. They were then analysed one at a time using tweezers to pick them up and place them on the sample slot. The pressure was applied on the plastic wastes to maximise the contact surface using the pressure tower and compression tip with the ATR crystal. The background spectrum was recorded before each sample was measured. Then each spectrum was obtained by scanning over a range of $4000 - 650 \text{ cm}^{-1}$ at a resolution of 8 cm^{-1} , with sixteen scans for each measurement. OPUS 7.5 software was used to obtain the measurements, and baseline correction was applied to each spectrum. Fig.5.5 shows the diagram for the procedure employed for plastic waste sampling, processing, and analysis.

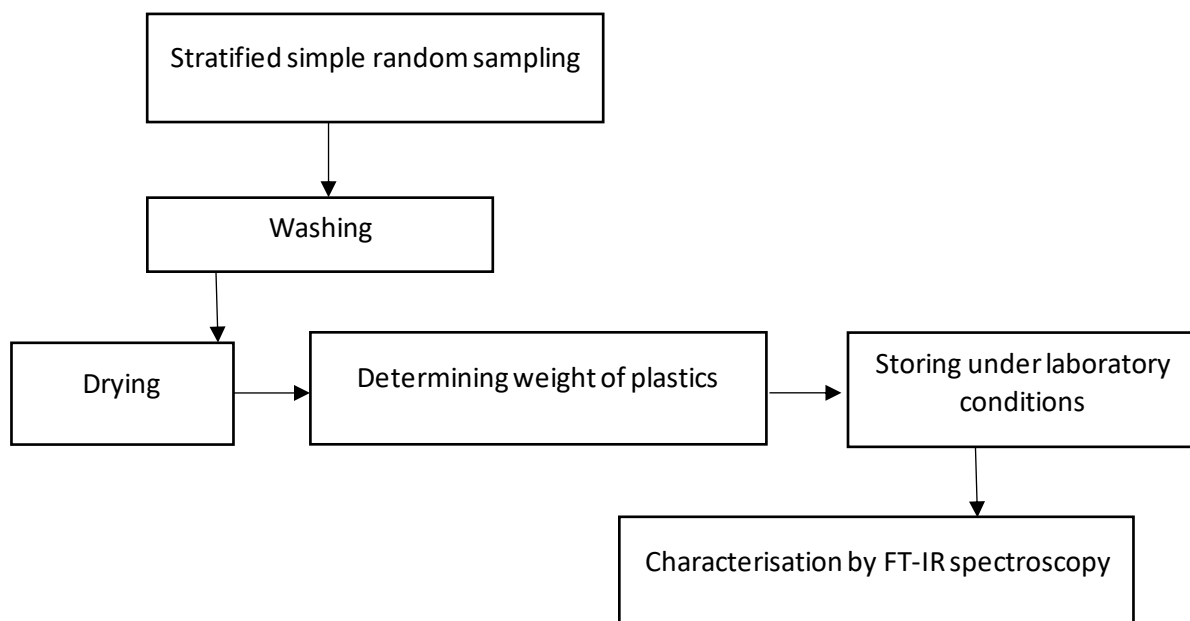


Fig. 5.5 Procedure employed for plastic waste sampling, processing, and analysis

5.3.3. Analytical method

FTIR is a technique commonly used to identify these plastic samples. Usually, FT-IR is used for the identification of polymeric materials within the same plastic classification. The samples

differed in spectral features depending on their conformational characteristics and the presence of plastic additives.

5.3.3.1 Fourier Transform Infrared (FT-IR):

FT-IR is a non-destructive analysis that studies the structural features of plastics and uses PerkinElmer precisely spectrum 100 FTIR spectrometer (USA) to identify the composition of plastic samples. FTIR spectra by attenuated total reflectance (ATR) will be obtained at room temperature. The infrared light of varying wavenumber range will be 4000-400cm⁻¹ onto the samples of interest, and we determine the absorption bands. All spectra will be recorded at a resolution of 4 cm⁻¹ and 64 cm⁻¹. Sixteen scans will be averaged for each sample. The structural features cover the changes which appear mainly on the carbonyl regions / functional groups on the discs during degradation, which is responsible for a drop in the weight of the plastics.

5.3.3.2 Shannon Diversity Index

Is an index that is usually used in ecology to characterise species diversity, richness and their relative abundance which is known as evenness. Here, it will be used to check the diversity of plastics as it reflects the variation of the number of individual plastics in a dumpsite. In addition, it allows us to describe the presence of plastics, the number of plastics (richness) and their relative abundance (evenness) in dumpsites. The Shannon diversity index is denoted as H', and it's calculated as follows.

$$H' = - \sum_{i=1}^s p_i (\ln p_i) \dots\dots\dots(\text{Equ.5.1})$$

where H' is the plastic diversity index,

s is the number of plastics,

p_i is the proportion of individual plastic belonging to the ith species in the data set of interest.

$$\text{Equilibrium/ Evenness} = \frac{H'}{H'_{\max}} \dots\dots\dots(\text{Equ. 5.2})$$

H'_{max} is the maximum possible value of H' (If every plastic was equally likely)

5.3.4. Data and statistical analysis

Data obtained from the FT-IR analysis assisted us in the identification of the total plastic wastes from these three dumpsites and their accumulation away from the dumpsites. Obtained data were statistically analysed using SPSS V20.0 (SPSS Inc., CHICAGO, IL).

The graphs and diagrams were processed using Excel software. The descriptive statistics were expressed as Mean \pm SE and compared using one-way ANOVA, while the comparison between dumpsites was analysed using two-way ANOVA. Tukey B post Hoc tests were carried out on the data for a confidence level of 95 % (significant difference ($p < 0.05$)).

5.4. Result and Discussions

5.4.1 Relative composition of polymers (plastics) identified by FT-IR from landfills

Fig. 5.6 shows the spectral complexity for each unknown plastic sample from the dumpsites, while fig. 5.7 reports the results of the chemical characterisation for the total composition of the plastic wastes coming from the three dumpsites sites. The plastic wastes sampled from the three dumpsites consist of PET, PP, PA-6, HDPE, LDPE, PS, PVC, EVA, TF, and PMMA.

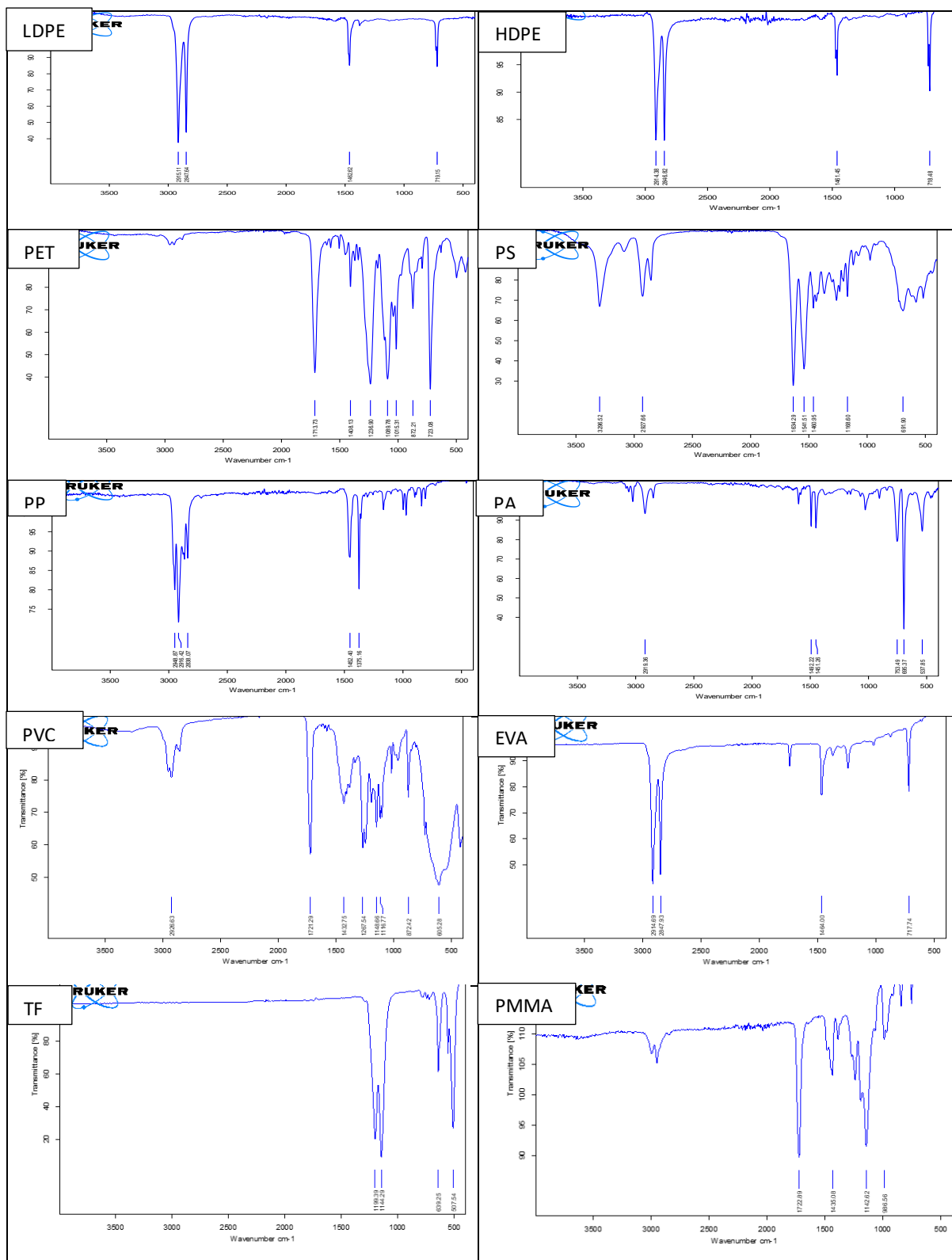


Fig. 5.6 FTIR spectra of some plastic materials common in the landfill starting from the top they are : LDPE, HDPE, PET, PS, PP, PA, PVC, EVA, TF and PMMA

The FT-IR spectra of most unknown plastic wastes matched the spectra of the individual known plastics. The absorption bands identified for most of these unknown plastic wastes were either

an exact match or a few shifts (left or right) in the wavenumbers of the absorption bands of the ICA library. (See Table 5.1). We found the absorption bands from $2800\text{--}3000\text{cm}^{-1}$ in most plastic samples analysed. The bands revealed a strong C-H asymmetric and symmetric vibrations characteristic, familiar to all polymers with a saturated C-C backbone except PET and PVC, which had weak C-H asymmetric and symmetric vibrations.

For the FT-IR of PET plastics checked, the carbonyl stretch is depressed to 1714cm^{-1} by conjugation with the aromatic ring. The other strong peak at 1239cm^{-1} is the asymmetric C-C-O stretch containing the carbon in the aromatic ring. The asymmetric O-C-H stretch is split at 1093cm^{-1} . The carbonyl group also affects the aromatic C-H stretch and shifts to a strong peak at 723cm^{-1} . The bands corresponded to the PET spectra (Verleye et al., 2001; Noda et al., 2007; Asensio et al., 2009). PP plastic wastes showed strong absorbance bands at the same wavenumbers as the known plastics. Polypropylene is formed from adding of a methyl group to any carbon atom in polyethylene. There are now methyl and methine groups present. The methyl peaks appear at 2950 , 2838 and 1377cm^{-1} (split peaks). An overlap occurs with the methylene deformation shifting peak to 1455cm^{-1} vibrations at the C-H bend (Barbeş et al., 2014).

All types of PA-6 (nylon 6,6 and nylon 6) gave the same absorption bands. Their polymers could not be distinguished by FT-IR spectroscopy though they gave their strongest peaks 1634 and 1538cm^{-1} , which belong to Amide I and Amide II peaks. Also, an intense peak was seen at 3300cm^{-1} , which is the N-H stretch. The infrared spectrum of PS is a combination of methylene and mono-substituted aromatic ring peaks. Its spectrum has weak peaks at 3082 , 3061 and 3027cm^{-1} , which are absorptions from the aromatic C-H stretches, and 2926 and 2851cm^{-1} from the methylene stretches. The out-of-plane C-H bends of the aromatic ring are strong at 698 and 756cm^{-1} . The aromatic ring stretching appear at $1,601$, $1,493$ and $1,452\text{cm}^{-1}$.

PE is a chain of methylene units terminated on each end by methyl groups. The spectra of PE samples are expected to contain only methylene stretches and bends because they share the same structural units, chemical bonds, and functional groups. Moreover, having many identical wavenumbers (Asensio et al., 2009) (Table 5.1) is not so because of the differing densities and crystallinities. They have strong, sharp absorption bands that dominate the spectrum, and the methylene stretches at $2914\text{--}2848\text{cm}^{-1}$ and the methylene deformations at 1463 and 718cm^{-1} . LDPE has an additional weak band at 1377cm^{-1} . However, the degree of branching in LDPE is more than that of HDPE, though very small is observed in their spectral region of $1400\text{--}1330\text{cm}^{-1}$, with LDPE having greater intensity at 1377cm^{-1} . The small intensity is due to methyl bending deformation of the branched-chain ends in LDPE (Gulmine et al., 2002; Nishikida and

Coates, 2003; Asensio et al., 2009). The increased branching in LDPE caused an increase in the intermolecular forces and constricted packing within the structure. These results showed that FT-IR spectroscopy is an efficient and reliable method for analysing plastic polymers. FTIR spectroscopy was able to identify the unknown plastics seen in the three dumpsites. Results confirm the presence of different plastic wastes from the dumpsites with different abundances among dumpsites. Fig.5.7, 5.8 and 5.9 revealed the results of all the plastic wastes checked using FT-IT spectroscopy from the three dumpsites.

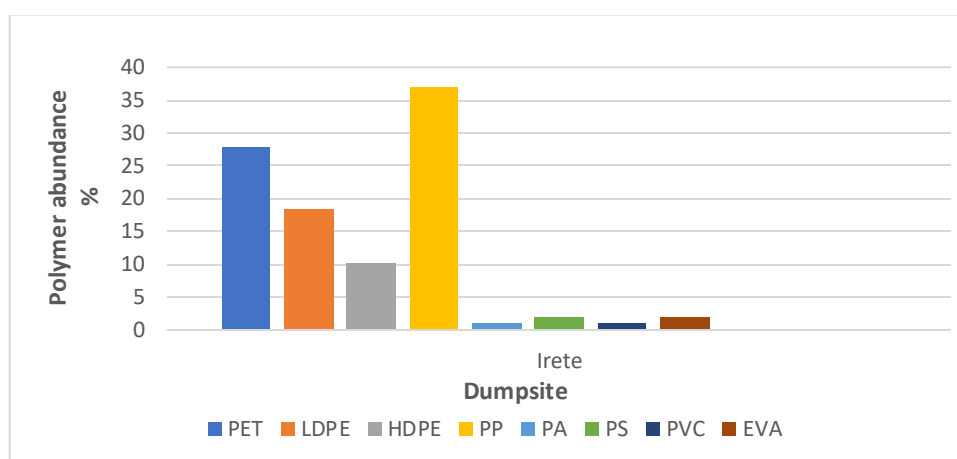


Fig 5.7 Histogram of all polymers (plastic wastes) identified by FT-IR from Irete dumpsite in Imo State, Nigeria. (Measured in %)

FTIR results revealed the occurrence and abundance of different plastic wastes from Irete dumpsite (Fig.5.7). From 97 plastic wastes sampled from the Irete dumpsite, PP had the highest percentage, 36%, while PA and PVC had the least percentage, 1%. Thus, the FTIR of the plastic wastes revealed that the dumpsites consist of plastic types in decreasing order of abundance is - PP>PET>LDPE>HDPE>PS>EVA>PA>PVC.

PP, PET, LDPE and HDPE were significantly highest in abundance (%) than other polymers, making them more prevalent plastics at the Irete dumpsite. Therefore, statistically, the accumulation of these plastics in Irete dumpsite was significantly different ($F=30.246$, $P<0.05$). Fig. 5.8 reveals FTIR results of plastic wastes' occurrence and abundances from the Orogwe dumpsite.

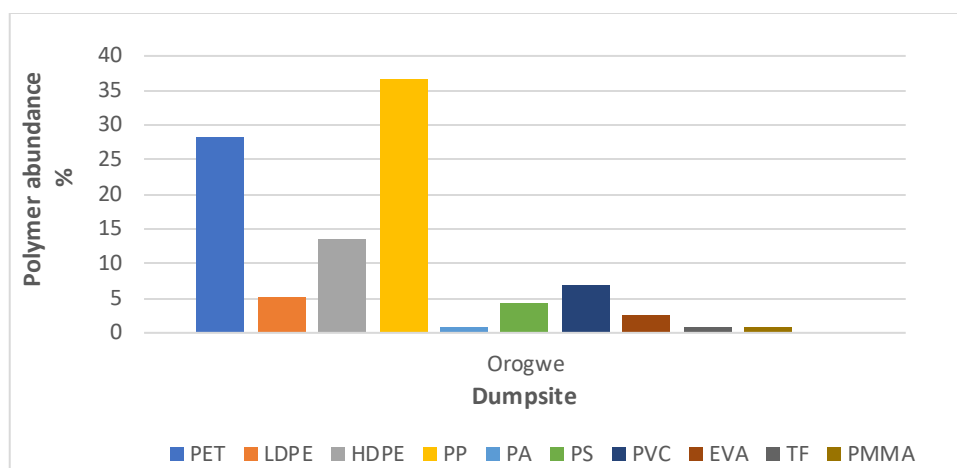


Fig 5.8 Histogram of all polymers (plastic wastes) identified by FT-IR from Orogwe dumpsite in Imo State, Nigeria. (Measured in %)

From 117 plastic wastes sampled from the Orogwe dumpsite, PP had the highest percentage, 37%, while PA, TF and PMMA had the least percentage, 1%. Thus, the FTIR of the plastic wastes revealed that the dumpsites consist of plastic types in decreasing order of abundance is - PP>PET>HDPE>LDPE>PVC>PS>EVA>PA>TF>PMMA.

Polymers: PP, PET, HDPE, and LDPE, were significantly highest in abundance (%) than other polymers, making plastics more prevalent at the Orogwe dumpsite. Hence, the build-up or the accumulation of these plastic wastes in the Orogwe dumpsite significantly differed. ($F=42.216$, $P<0.05$).

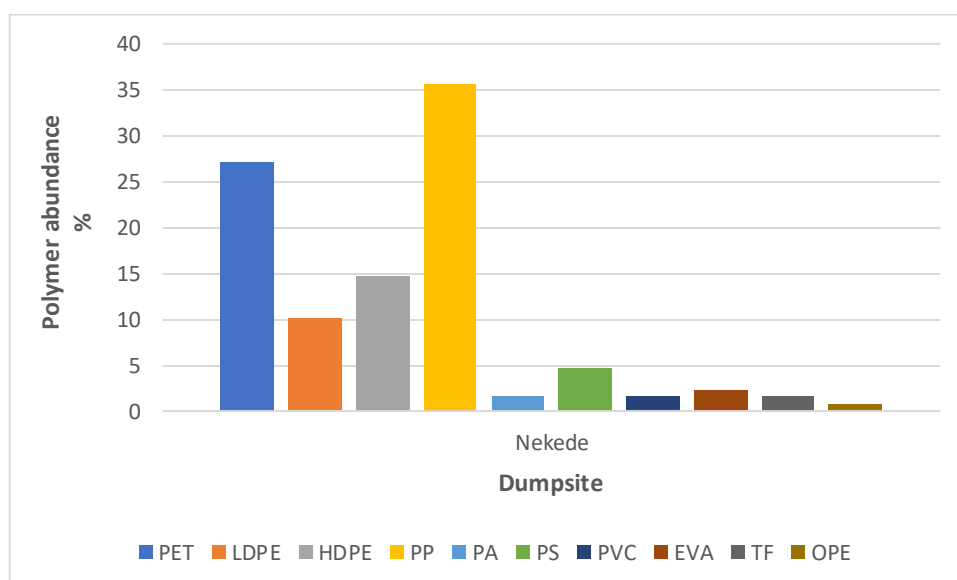


Fig 5.9 Histogram of all polymers (plastic wastes) identified by FT-IR from Nekede dumpsite in Imo State, Nigeria. (Measured in %)

FTIR results revealed the occurrence and abundance of plastic wastes from the Nekede dumpsite (Fig.5.9). From 129 plastic wastes sampled from Nekede dumpsite, PP had the highest percentage, 36%, while OPE had the least percentage, 1%. So, the FTIR of the plastic wastes revealed that the dumpsites consist of plastic types in decreasing order of abundance is - PP>PET>HDPE>LDPE>PS> PA>PVC>EVA>TF>OPE. Polymers, PP, PET, HDPE, and LDPE were significantly highest in abundance (%) than other polymers, making them more prevalent plastics at Nekede dumpsite. Statistically, the accumulation of these plastic wastes in the Nekede dumpsite was significantly different ($F=48.027$, $P<0.05$).

About 3.7% of the plastic wastes sampled were not identified using FTIR. The reason is that either their spectra had no readable fingerprints, or the spectrum could not be attributed to the spectral range of known plastics in the ICA library because of the degradation effect (Gewert et al., 2017). However, these plastic types represented many detected waste particles and were also found distances away from the dumpsites. One of the reasons synthetic polymers such as PP, PE, PVC, and PS are seen as waste in our environment is that about 30% of the plastics used globally are used in different packaging applications for items like food, pharmaceuticals, cosmetics, detergents, and chemicals. While 21% were used in building and construction, 7% in automotive, 6% for electrical and 28% for other divisions (Tripathi et al., 2016). PP polymers were the most abundant in three dumpsites. Also, results from figs. 5.7, 5.8, and 5.9 revealed that PP, PET, HDPE, and LDPE were most significant in abundance (%) than other polymers from three dumpsites and more prevalent than other plastics at these dumpsites.

Furthermore, the British framework of available plastics as a single-use packaging material has an abundance of 40% based on PET, PE, PP, PS and PVC, with a demand of around.

(Zhang et al., 2016; Canopoli et al., 2016; Thompson, 2017), revealed that after identifying plastic wastes that were buried at four MSW sites in the UK, using FTIR spectroscopy and other methods, he found out that PE and PP plastics were dominant at these sites., Forbid (2012) revealed that 29% of the mixed plastic wastes make up the waste stream in Lagos, Nigeria. Nicholson (2017) suggested that the two most abundant plastic wastes in the environment are polyethylene and polypropylene because they are very resistant to biodegradation.

Also, most microplastics seen floating in the oceans and rivers were collected and analysed using FTIR. It was reported that they were either PE or PP because not only are they single-use plastics that are discarded immediately after use, but their lightweights make them possible to be transferred from one place to another (Browne et al., 2010; Nor and Obbard, 2014; Thiel et al., 2003). Another reason could be because of their physical and chemical properties, which make them resistant to seawater (Zhang et al., 2015) and the fact that they represent 30 and

27% of the worldwide manufacture of polymeric materials in 2015 and a bulk of their compounded products even with additives and fillers, still float in seawater (Andrady, 2017; Geyer et al., 2017)

The production of plastics over the years, most especially the ones used in packaging applications, keeps increasing significantly than other plastic materials. These plastics are PP, LDPE, HDPE, PVC, PET, PUR and PS. The properties such as toughness and resistance to degradation make them useful in many applications (Geyer et al., 2017).

Beckman (2018) revealed that the manufacture of synthetic polymers worldwide is dominated by the main polyolefins, PP and PE. They dominate for the following reasons: They have low densities and are very light synthetic polymers, very easy to shape into products leading to their large-scale production. They are manufactured with moderately inexpensive natural gas, and most of their final products are made to resist environmental damage.

5.4.1 Spatial distribution of different plastic wastes away from active dumping areas of three dumpsites

In the dumpsites, plastic wastes, similar to other natural materials, are not evenly transported. Their spatial distribution strongly depends on factors such as size, form, density, surface smoothness, and conveyance conditions. Fig. 5.10 shows us the trend in decreasing the weight of the plastic wastes further away from the dumpsites. So, we sampled plastics up to 450m and did not see anything after this point (fig. 5.11). Fig. 5.11 gave the distribution in weight of the plastic wastes distances away from the active dumping areas of dumpsites (0metres).

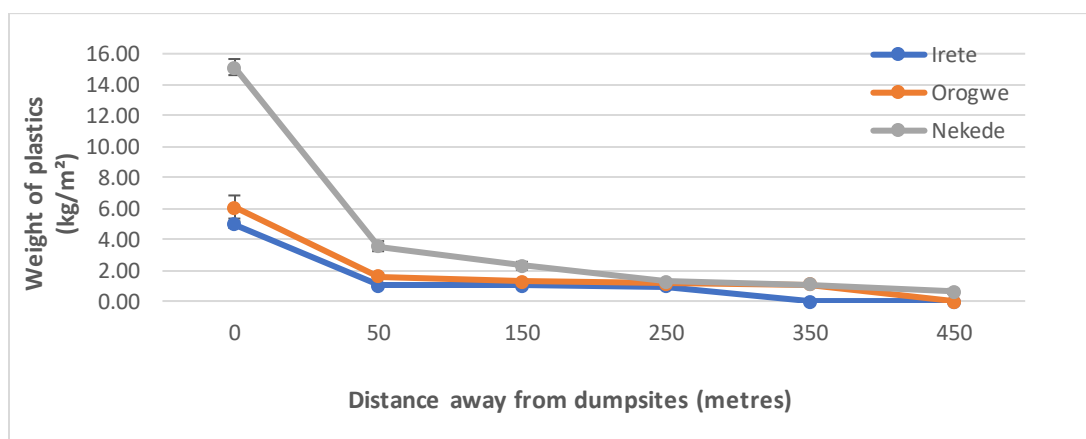


Fig. 5.10 Diagram of the trend in the decrease of the weight of the plastic wastes further away from the active dumping areas. (n= 4 at each dumpsite while n=4 at each measured metre away from the dumpsite)

We identified the total composition of the plastic wastes before checking their spatial dispersion away from the dumpsites. It is vital as it offers essential information on individual plastic waste, which could be traced back to its origin.

The weight of plastic wastes reduces significantly as they move farther from the dumpsite centre (Fig 5.10; $F= 27.714$, $P<0.05$). Fig. 5.11 revealed the changes in the plastic-type and weight away from the dumpsite centre. The reduction in the weight of the plastic wastes (i.e., light ones) away from the landfills supported that the total average mean of the identified plastic wastes reduced distance from the dumpsites. Types of plastics frequently used, climatic conditions, size and density of plastics and human/ animal activities are factors influencing the dominance of the plastic wastes seen in the environments and their movements away from the dumpsites (Thornton and Jackson, 1998; Thiel et al., 2003; Dahlén and Lagerkvist, 2008; Ryan et al., 2009; Browne et al., 2010; Browne et al., 2015; Galgani et al., 2015).

There was a general decrease in the average number of plastic wastes seen at a measured distance away from the active dumping areas of dumpsites (fig. 5.11).

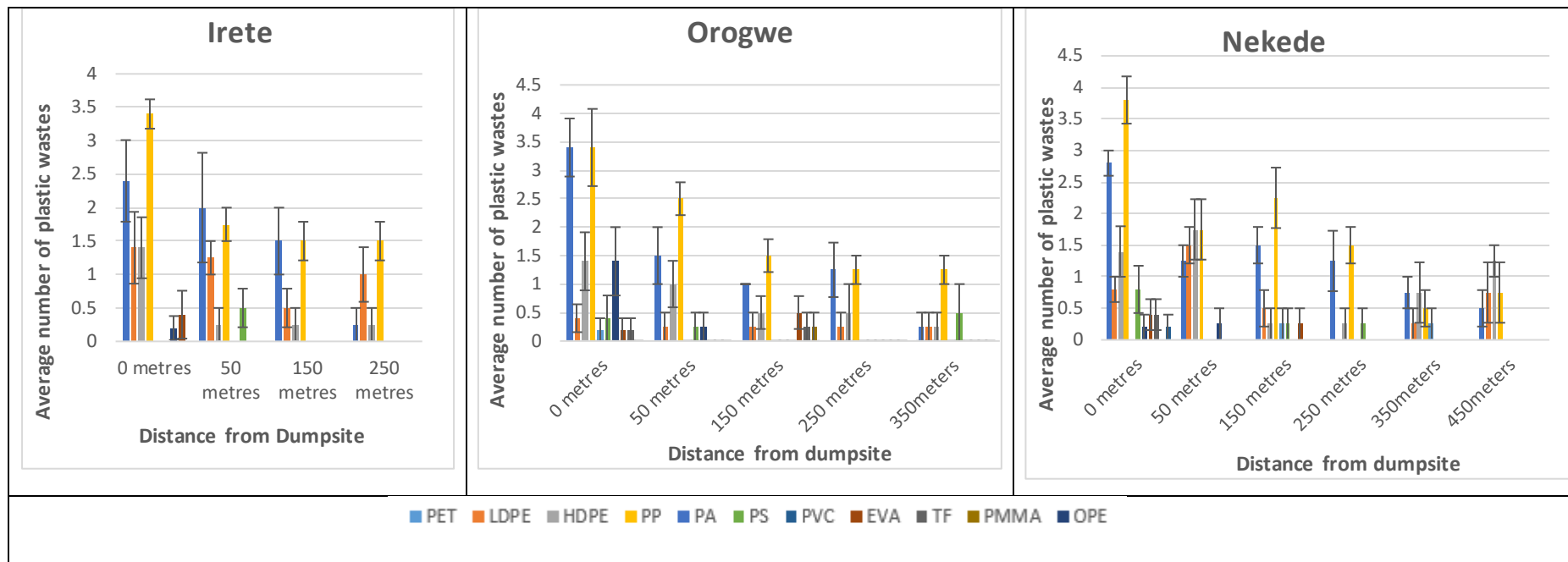


Fig. 5.11 Graph of spatial distribution of average number of plastic wastes sampled further away from dumpsites.((Mean±SEM), Irete n=17, Orogwe n=21, and Nekede n=25)

Fig. 5.11 revealed the average number of plastic wastes collected from both the active areas of dumpsites (0m) and distances away from the dumpsites (50m, 150m, 250m) for Irete (50m, 150m, 250m and 350m) for Orogwe and (50m, 150m, 250m, 350m and 450m) for Nekede dumpsite respectively. The result from fig.5.11 also displayed that PP, PET, and PE were the most prevalent plastic wastes in and distance away from the three dumpsites.

The result agrees with the submissions from other researchers (Browne et al., 2010; Forbid, 2012; Zhang et al., 2015; Canopoli et al., 2016), which suggested that the above name three waste plastics are the most seen in our environment. The reason is that they are used broadly in domestic and industrial applications as everyday single-use plastics and the low densities they possess. When dumped in uncontrolled environments such as those studied here, they disperse easily. We also saw plastics like PA, PS, PVC, EVA, TF, and OPE in small quantities compared to PP, PET and PE in large quantities.

The average number of plastic wastes in each dumpsite had a significant difference. However, their occurrence away from all the dumpsites decreased with the lighter ones: PP, PET and PE, i.e., (HDPE and LDPE).

The heavier plastic wastes were seen more in the dumpsites at 0meters, while the lighter plastic such as wrapping sheets, pure water sachets, and biscuit wraps were spread further away from the dumpsites (50 to 150 to 250 to 350 and 450m). From the result obtained, plastic waste accumulated is significantly more in all the dumpsites than in distances further away from the dumpsites. The same plastics seen at the dumpsites were also seen distances away from these dumpsites except in the case of the average number of PS in Irete dumpsite and EVA in Orogwe.

IRETE DUMPSITE

The average number of PP plastics sampled directly from the active areas of Irete dumpsite (0m) was 3.4, and it decreased further away to 150m, then remained constant till 250m. At the same time, PET had an average number of 2.4, the second-highest, in Irete dumpsite and reduced this progression away from the dumpsite. Both LDPE and HDPE waste plastics sampled from Irete dumpsite at 0 metres had an average number of 1.4, the third-highest, and both also reduced further away from the dumpsite to 250mtetres. While HDPE average number reduced this trend (1.4, 0.25, 0.25 and 0.25), LDPE had (1.4, 1.25, 0.5 and 1), respectively. The average number of EVA plastic sampled was 0.4, while PVC had the average number of 0.2 waste plastic was sampled at the dumpsite and was not seen again away from

the dumpsite. PS and PA had different progression; they were not seen at the dumpsite, but we sampled two pieces of PS waste plastic 50m away from the dumpsite, and one piece of PA was seen at 250m. Reasons could be an action of wind, animals, or humans moving these further away from the dumpsites (Browne et al., 2010; Dahlén and Lagerkvist, 2008). All the plastic wastes seen at the dumpsite were reduced further away from the dumpsite except PA and PS. Therefore, statistically, there was a significant difference in the movement of the plastics further away from the Irete dumpsite ($F=6.832$, $P<0.05$).

OROGWE DUMPSITE

The average number of PP and PET waste plastics sampled from this dumpsite was 3.4, and both were reduced further away from the dumpsite. PP reduced in this progression (3.4, 2.4, 1.5, 1.25 and 1.25) away from the dumpsite, while PET took this way in the reduction (3.4, 1.5, 1, 1.25, and 0.25), respectively. Also, the average number of HDPE and PVC waste plastics sampled from the Orogwe dumpsite at 0 metres was the second-highest, and both of them were reduced further away from the dumpsite. LDPE and PS had an average number of 0.4, the third-highest at the dumpsite. LDPE reduced from 0.4 at dumpsite to 0.25 and remained constant till 350m (0.4, 0.25, 0.25, 0.25 and 0.25) and PS waste plastic reduced in this progression (0.4, 0.25, 0, 0 and 0.5). PA, EVA, and TF followed by having only an average number of 0.2 plastic wastes at the dumpsite. While PA and TF had this progression (0.2, 0, 0, 0 and 0), EVA had (0.2, 0, 0.25, 0 and 0). No PMMA plastic waste was seen at the dumpsite, but only one piece was sampled 150m away from the dumpsite. Also, the plastics seen at the Orogwe dumpsite reduced further away from the dumpsite. So there was a significant difference in the movement of the plastics further away from the Orogwe dumpsite ($F=11.085$, $P<0.05$).

NEKEDE DUMPSITE

Here, because the dumpsite is big, we sampled plastic wastes up to 450m away from the dumpsite. PP had the highest average number of plastic wastes sampled at the Nekede dumpsite and distances away from the dumpsite. PP reduced further away from the dumpsite. PET had the second-highest average number of plastic wastes at the dumpsite and further reduced distances away from the dumpsite. It had (2.8, 1.25, 1.5, 1.25, 0.75 and 0.5). HDPE waste plastics sampled at the Nekede dumpsite had an average number of 1.4, the third-highest, and had this trend (1.4, 1.4, 0.25, 0.25, 0.75 and 1.25). The average number of HDPE waste plastics reduced from 1.4 to 0.25, further away from the dumpsite to 150 meters. It remained constant at 0.25 at 250 meters. Then it increased to 0.75 at 350m and then to 1.25 plastic wastes at 450m.

Nothing was seen after 450m. Both LDPE and PS waste plastics sampled at Nekede dumpsite had an average number of 0.8, the fourth-highest, and reduced further away from the dumpsite. While LDPE had (0.8, 1.5, 0.5, 0, 0.25 and 0.75), PS had (0.8, 0, 0.25, 0.25, 0 and 0) respectively. EVA, TF, PVE, and OPE followed the same trend in reducing distances away from the active areas of the dumpsite. PA plastic waste was not seen at the dumpsite, but the average of 0.25 waste plastic was sampled at 150m and 350m away from the dumpsite. This result from Nekede statistically concludes that there was a significant difference in the movement of the plastics further away from the Nekede dumpsite ($F= 7.608$, $P<0.05$).

Generally, the results gotten from this study show that plastic wastes were present in Irete, Orogwe and Nekede dumpsites, and they are seen reducing further away from the dumpsite, The current results also revealed a decrease in the total number of collected plastic wastes further away from the dumpsites. Reasons could be climate conditions (Browne et al., 2010) or human/animal factors, especially scavengers and animals seen around landfills (Dahlén and Lagerkvist, 2008). June is a wet month in Nigeria. Consistent heavy and long rainstorm with little wind during the city's monsoon season moves plastic wastes away from the dumpsites.

5.4.2 Shannon diversity index of the plastics in the dumpsites

Fig. 5.10 revealed the Shannon diversity index (SDI) plots and equability for different plastic waste distribution and abundance in Irete, Orogwe and Nekede dumpsites. The higher the values obtained from the SDI, the more the diversity of the plastics from the dumpsite.

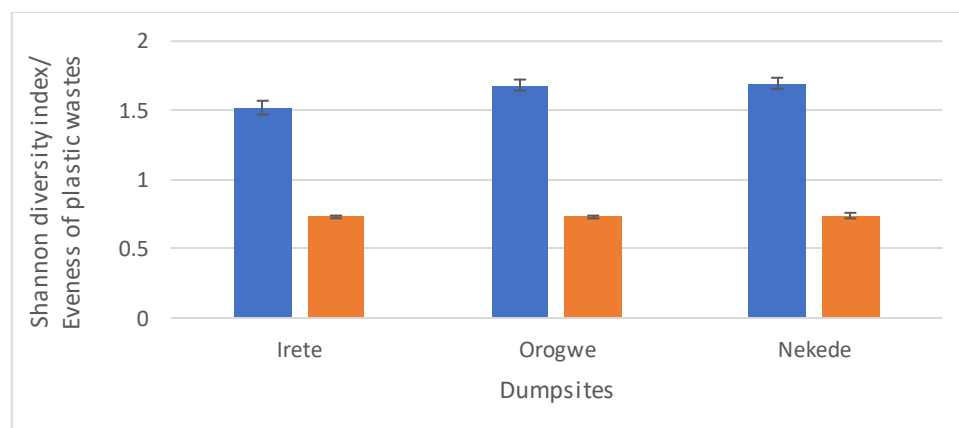


Fig. 5.12 Shannon diversity index and Equilibility plots for different plastic wastes distribution and abundance in Irete, Orogwe and Nekede dumpsites.

From Fig. 5.12, we observed the diversities in the three dumpsites. Nekede and Orogwe dumpsites had the highest diversity, while Irete had the least. Statistically, the result can be summarised that the number of plastic wastes significantly differed in the dumpsites.

Each plastic waste was evenly represented in the different dumpsites and showed no significant differences. However, the dumpsites were highly rich in all plastic wastes. The differences in this result could be as follows: Sizes of dumpsites because bigger dumpsites contain more waste materials than smaller ones. The human population around these dumpsites will bring about richness, diversity, and accumulation differences. Lastly, animals and scavengers moving these plastic materials about the dumpsite could also contribute.

5.5 Conclusion

In today's world, the use of plastic materials is inevitable. Therefore, it becomes necessary to use suitable techniques such as FTIR in characterising plastic wastes seen in dumpsites, which this chapter exhibited. The procedure employed for plastic waste sampling, processing, and analysis is shown in fig.5.5.

As demonstrated in this study, the accuracy of using the FT-IR technique for identifying plastic wastes from dumpsites has the advantage of rapid analysis and no destruction of collected waste samples. However, it requires much time since samples are run one at a time. In agreement with the results obtained in this work, FT-IR spectroscopy becomes the analytical technique suitable for analysing plastic wastes from landfill systems. It allows the analysis of plastic surface layers with different chemical features exposed to diverse forms of processing and the modifications in the layer structure affected by all forms of physical and normal weathering activities (UV light, marine and soil exposure). It simply offers information on the surface of the plastic being examined. Thus, when additives or other polymers are blended with plastics being analysed, it characterises polymer mixtures, identifying additives, plasticisers and absorbers used in their production. The plastic wastes found in these dumpsites are more macroplastics than microplastics. The fragmentation of these plastics in the dumpsite results from prolonged exposure to sunlight and physical abrasion (Andrady, 2003). This chapter presents the first-ever outcome on the abundance of plastic wastes in dumpsites in Owerri, Imo State, Nigeria.

Finally, the FT-IR analysis of 350 plastic wastes collected from Irete, Orogwe and Nekede dumpsites have been displayed in figs. 5.7 -5.9. The results revealed that PP, PET and PE were the most abundant plastic polymer wastes. PP consists of over 36%; PET had 27%, LDPE had 12%, HDPE had 13%, PS had 4%, EVA had 2%, PA had 1%, and 5% of the plastic wastes were not identified. Reasons may be from either photo-degradation/weathering of these plastics, which caused variations in the spectroscopic spectra of the plastic wastes or a lack of a comprehensive spectra library to identify complex samples. The results from this study reveal

that plastic wastes at the dumpsites were significantly higher in abundance than the plastic wastes seen a distance away from the dumpsites.

The result also revealed significant differences in weight distribution as a function of the polymer type of the plastics, as seen in fig. 5.10. Finally, fig.5.12 revealed the Shannon diversity index of the plastics. It shows that the number of plastic wastes in Nekede and Orogwe dumpsites significantly were more diverse than the number of plastic wastes in Irete dumpsite. However, the dumpsites were moderately even and highly rich in all plastic wastes. The next chapter will look at the degradation rates of these widely used plastics in different substrates, namely, soil, compost, and leachate and in the temperate zone, the UK and tropical zone, Nigeria.

CHAPTER 6

PLASTIC DEGRADATION-DEGRADATION OF PLASTICS IN SOIL, COMPOST AND LEACHATE IN BOTH TROPICAL AND TEMPERATE REGIONS.

6.1 Introduction

Plastics are long-chain polymers from petrochemicals formed by various chemical processes of joining the monomer units together (Shimao, 2001). Plastic materials have recently been used in many applications because of their versatility, such as in the packaging industries.

Though plastic materials are a vital part of the world economy, problems related to the wide use of plastic cannot be ignored. Pollution caused by plastics littered all around the environment has been listed by the UN Environmental Programme (UNEP, 2014) as one of the topmost environmental challenges due to their slow degradation rate, occurrence, and damaging effects on aquatic and terrestrial environments (mainly soils). Also, they can transport vectors for other possible contaminants, including human pathogens, biological contaminants, and heavy metals (Qi et al., 2020). Plastic wastes find their way to the environment through human activities. It is projected that 60 % of plastic formed since 1950 has ended in landfills or natural ecosystems (Gourmelon, 2015). The main types of plastics seen in the environment are – namely, polyamide (PA), poly (ethylene terephthalate) (PET), polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), and polystyrene (PS) (Alimi et al., 2018).

Some methods have been projected to treat the problems associated with plastic waste in the environment; they include recycling, incineration, and energy recovery. However, all these solutions have drawbacks, such as high cost (Zhao et al., 2018) formation of toxic compounds, such as dioxins, furanes and acid emissions (Verma et al., 2016).

Several scientific studies have examined the degradation of plastics under natural or simulated environmental conditions (Zhang et al., 2021) with estimated lifetimes that can change intensely based on recent evidence. For instance, Ward et al. (2019) discovered that polystyrene exposed to sunlight degrades faster and at a very short pace than the thousands of years in earlier estimations (Ward et al., 2019)

Most of these studies concentrated on plastic degradation in marine environments such as seawater (O'Brine and Thompson, 2010; Zhao et al., 2018). This research has chosen to degrade some of these plastics seen in the environment to track their rate of degradation in substrates like soil, compost, and leachates, where microorganisms partake in breaking them down. This method aims to reintegrate the elemental components of the plastics into the natural cycles, diminishing the effects related to their accumulation.

Plastic degradation in substrates can be triggered thermally, photo, mechanically, catalytic, ozone-induced, and biologically in the environment. These routes increase oxygen-holding functional groups, thus changing the plastics' surface properties and chemical structure (Zhu et al., 2019). Though, among these degradation routes, photodegradation, ozone-induced degradation, and biodegradation are primarily responsible for environmental degradation, such as in soils, composts, landfills etc. The degradation of these plastics is subject to the.

1. Nature of plastics and their physicochemical features, such as size, molecular weight, chemical bonding, flexibility, crystallinity, and surface hydrophobicity.
2. Environmental conditions, namely, pH, temperature, UV radiation, humidity, availability of appropriate microorganisms and enzymes (Shah et al., 2008; Zhu et al., 2019).

6.2 Physico-chemical degradation of plastics.

Physicochemical degradation is any process that alters the properties of plastics, i.e., weakening functionality due to chemical or physical reactions resulting in bond scission and then chemical changes. Recent decomposition studies focus on degradation by physical or chemical factors. An example of such is photodegradation, which happens under the actions of ultraviolet (UV) radiation, decreases the mechanical properties of a plastic, weight, appearance, and alterations on both the physical and biofilm formation when exposed to seawater. The extent of surface damage of some plastic materials in different environments depends on the type of plastics, UV radiation intensity and exposure time (Andrady et al., 2011; Jelle and Nilsen, 2011). Most biopolymers undergo photolytic or photo-oxidative degradation in the environment due to UV radiation, reducing their half-life (Andrady et al., 2011). Also, plastics contain different functional groups known as chromophores, such as alkene, ester, or aromatic groups. These chromophores can absorb UV radiations and rise these chromophores to an excited state. If the plastics cannot release the absorbed radiation a free radical is released, triggering photo-oxidation through a free radical reaction known as autooxidation (Rabek and Rånby, 1974; Andrady et al., 2011).

Biologically mediated degradation of plastics

Biological degradation, on the other hand, is any process that causes modifications to the properties of plastics due to biological breakdown by microorganisms leading to the breaking of bonds of such plastic. Biofilm formation is one of the signs of biodegradation of plastics in different environments, and it is caused by microorganisms seen in these environments (Rummel et al., 2017; Arunkumar et al., 2020). The microorganisms involved in

degrading both natural and synthetic plastics are bacteria and fungi (Gu et al., 2000a). They affect the light transmittance of such plastics and cause biodegradation (Sudhakar et al., 2007; Eich et al., 2015; Horton and Dixon, 2018). Microorganisms responsible for the degradation of plastics vary because each one has its ideal optimal environmental growth conditions, such as soil. Therefore, biodegradation of plastics will proceed naturally under diverse soil conditions giving to their properties. plastics are, therefore possible base for heterotrophic microorganisms in the soil. (Glass and Swift, 1989). Considering the biodegradation of natural and synthetic polymers is essential since their increased production is rising. The environmental accumulation causes a pollution problem that could persist for centuries and therefore requires understanding the interactions between materials and microorganisms and the biochemical changes involved. Microorganisms produce at least two enzymes actively involved in the biodegradation of plastics: extracellular and depolymerases (Doi, 1990; Gu et al., 2000b). While intracellular enzymes are responsible for breaking random internal bonds of the main polymer chain of the plastic, the extracellular enzymes break down the polymer chains successively (Jain and Tiwari, 2015). During biodegradation, plastics undergo bio-deterioration, where plastics undergo chemical, mechanical, and physical change as a result of the extracellular enzymes, i.e., microbial biological activity on the surface of the plastics producing biofilm. Then its bio-fragmentation, where the microbial activity leads to the breaking down of plastics into smaller units such as dimers, oligomers, and monomers (Harrison et al., 2018). Finally, the microorganisms' assimilation or further utilisation of fragmented or smaller units as carbon and energy sources convert them to end products, such as CO₂, H₂O and biomass (Bano et al., 2017; Emadian et al., 2017). The degradation is called mineralisation when the end products are CO₂, H₂O, or CH₄ (Frazer, 1994; Hamilton et al., 1995). Table 6.1 shows us some studies done by some researchers on the biodegradation of some plastics in different environments with the physical changes observed in the plastics over a given period.

Table 6. 1 Summary changes found in the literature for plastics after exposure to different environmental conditions.

| Plastic | Degradation time/substrate | Analytical methods | Changes Observed | References |
|--------------------------|---------------------------------------------------------|---------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|
| LDPE, PP, PS | 24 h in a rotating laboratory mixer with sediment added | FTIR, SEM, Visual Observation | The rougher the sediment, the more the fragmentation of plastics | Chubaren ko et al. 2020 |
| PE | 33 days in seawater at 3 m depth and seafloor | Dynamometer, SEM | Decrease in the mechanical properties, biofilm formation and signs of surface degradation. | Eich et al. 2015 |
| PE, PVC | Buried 24 months in soil at 5cm depth | FTIR, AFM, spectrophotometer | Increase in surface roughness, release of plasticizers | Sullivan et al. 2019 |
| LDPE, HDPE | Buried 8 weeks in mangrove soil | Weighing balance | Weight loss | Kumaret al 2007 |
| PA, PE PP, PET | 6.5 months UV exposure in seawater | Instron universal materials testing machine, TGA, SEM, AFM | Loss of elasticity; Increase in stiffness; Waning of the plastics; Observation of granular oxidation, fragments, and cracks on surfaces; Loss of homogeneity on surface. | Inguez et al. 2018 |
| LLDPE, HDPE, PP | 280 days in air | FTIR, DSC, GPC, Instron universal materials testing machine. | Reduction of in average molar mass; reduction in mechanical properties, increased carbonyl index, changes in crystallinity. | Ojeda et al. 2011 |
| PA, PVC, PS, PE, PP, PUR | 24 Months in air sheltered from UV and precipitation | Colorimeter | Yellowing and changes in lightness | Pastorelli et al. 2014 |
| PHB | Buried 150 days in compost | Instron universal materials testing machine Weight change. | Reduction in mechanical properties, 6% mass loss. | Mergaert et al 1994 |
| | Compost at 55°C | Weight change, CO ₂ measurement. | 80% biodegradation and CO ₂ evolution. | Tabasiet al. 2015 |
| | Buried 200 days in tropical soil | Weight balance | Mass loss due to microbial activities | Mergaert et al 1994 |

6.3 Biodegradation of plastics in substrates:

Substrates here are the same with environments, including soil, compost, and leachate/ marine environments. One advantage of degrading plastics in the natural environment is the possibility

of evading plastic waste build-up in the environment. Therefore, the mineralization or breakdown of large polymers to monomers involves several collections of microorganisms in these substrates. Adding plastics to substrates that contain these collections of bacteria and fungi capable of degrading large organic polymers with other factors, such substrate becomes conducive to degrading the plastic polymers.

Plastic will totally or partially biodegrade in an environment solely depends on some factors. These factors are physical and chemical factors (temperature, moisture, pH, and properties such as crystallinity and additives) and biological factors (the presence of the right microbes in that environment) (Mohee and Unmar, 2007). Also, Rujni'c-Sokele and Pilipovi (2017) suggested that plastic's thickness will affect its biodegradation rate. The thicker the plastic, the longer its biodegradability. Therefore, plastic might degrade in one environment but not in another (Tuomela, 2002). Consequently, it is crucial to evaluate the behaviour of different plastics in different environments and determine whether they show any sign of biodegradation under different conditions (Narancic and O'Connor, 2019). Under aerobic conditions, microorganisms use oxygen to oxidize carbon and form carbon dioxide as one of the significant metabolic end products.

There was little attention to plastic degradation in the soil until Rillig (2012) raised the issue of plastic disposal, accumulation, and degradation in soil. While several researchers concentrated on marine plastic degradation, a few have investigated plastics in terrestrial systems. Therefore, knowledge gaps concerning their dispersal, fate and environmental effect are still unknown (Horton et al., 2017; Chae and An, 2018; de Souza Machado et al., 2018; He et al., 2018; Guo et al., 2020). Restrepo-Florez et al. (2014) and Krueger et al. (2015) were among the few researchers that considered the degradation of synthetic plastics in soil, compost, and leachate. They suggested that the properties of these plastics, such as durability, lead to accumulation in almost all environmental substrates. However, they concluded that a few degradation pathways for synthetic plastics in the environment, mainly in coastal areas or surface water caused by UV radiation and physical abrasive routes (Moore, 2008; Song et al., 2017). Analytical methods, including qualitative and quantitative analysis, need to be enhanced to properly evaluate the rate and impact of plastics in the terrestrial systems.

6.3.1 Biodegradation of plastics in soil

When plastic is buried in soil, its rate of degradation is not just influenced by the nature of the plastics but also by the type and characteristics of chosen soil, the microbial biomass and the and physical factors such as pH since the biodegradation process can change from place to

place and season to season (Emadian et al., 2017; Siracusa, 2019). For example, PLA and PCL degraded faster in alkaline soil than in neutral and acidic soil. However, the polymeric material's features accounted for most of the alterations in the biodegradation rates (Elsawy et al., 2017). Plastics buried in soil may slightly undergo photo-oxidative degradation because of reduced light and oxygen in the soil. At the same time, plastics will undergo thermo-oxidative (slow oxidative) alongside hydrolysis, metal ions from wet soil and microbial activity.

Also, plastics in soil may be clanged to microorganisms and other pathogens in the soil environment, requiring water since water is the medium of most microorganisms in the soil. Therefore, the absorption of water from the soil initiates the hydrolysis reaction with slightly photo-oxidative degradation because of reduced light and oxygen in the soil, thermo-oxidative (slow oxidative) leading to physical and optical changes of plastics such as chain scission, crosslinking, reduced ductility, colour change, cracking and reduction in most desirable physical properties (Sang et al., 2020).

6.3.2 Biodegradation of plastics in compost

Burying plastics in soil and compost takes the same degradation pathway because they are typical environments where degradation is partly aerobic and partly anaerobic. Compost is a biological-rich, organic material made by humic complexes, and it is a relatively stable type of organic matter with a unique physical and nutritional structure. This explains its vast microbial diversity (Song et al., 2009) and why it is suitable for soil amendment (Kale et al., 2007). Both macroorganisms and microorganisms break down plastics buried in compost in the presence of oxygen, CO₂, water, and heat (Rudnik, 2019). Petroleum-based plastics such as PHB has shown high degradability up to 80% in less than four months in different compost environments (Cho et al., 2011; Tabasi and Ajji, 2015). leachates from MSW composting site

6.3.3 Biodegradation of plastics in leachate

Biodegradation of plastics in marine environments is subject to primarily environmental conditions, such as temperature and the presence of nutrients (Sang et al., 2020). The degradation of plastics in marine environments can be either aerobic or anaerobic. However, most researchers have reported in the literature referring to degradation in the marine environment to be aerobic. Leachate from MSW in-vessel composting site was used for this study, and it is more like seawater with complex chemistry, containing various chemicals and microorganisms. It is likely to result in more Physico-chemical degradation because of the biological processes happening in it. Therefore, leachates consist of different plastic-degrading

microorganisms, a vital factor in biodegradation (Tosin et al., 2012; Emadian et al., 2017). The UV radiations from sunlight initiate the photo-oxidative degradation of plastics, thermooxidative proceeds with autocatalytic hydrolysis, where water diffuses the amorphous regions of the plastics, causing cleavage to ester bonds (Sang et al., 2020). Su et al. (2019) stated that the carbonyl index (CI) of polyethene placed in landfill leachate increased from 0.18 to 1.3 over time; they suggested that oxidative degradation was one of the plastics' main pathways in landfill leachate.

6.4 Aims and Objectives

Presently, several polymeric materials are marketed now and claim to be decomposable. They could be termed “degradable”, “oxo-biodegradable”, “biological”, “compostable”, and “green” are frequently used to refer to different types of plastics (Gomez and Michel, 2013). These materials include conventional plastics, amended with additives meant to improve biodegradability.

This study aims to

- Evaluate the rate and impact of degradation on a wide range of commercially made plastics (PET, HDPE, LDPE, PP and PA) used for different applications.

Degradation of these plastics was studied in different substrates, namely, soil, compost, and leachate, and in different countries depicting temperate and tropical zones—the United Kingdom and Nigeria. The objective of this part of the research is.

To evaluate and compare the rate of degradation of PET, LDPE, HDPE, PP and PA6 in soil, compost and leachate in Nigeria and the United Kingdom for two years.

Achieving these objectives, the study, therefore, seeks to answer the following research questions (RQs):

RQ: 1. Does the degradation rate of PET, LDPE, HDPE, PP and PA-6 differ significantly among plastics in soil, compost, and leachate between temperate to tropical regions?

RQ: 2. Does the degradation rate of these different plastics differ from temperate to tropical regions?

Hypothesis

- The rate of degradation of PET, LDPE, HDPE, PP and PA6 differs significantly among plastics in soil, compost, and leachate between temperate to tropical regions.

6.5 Materials and Methods

6.5.1 Materials

This study used the HPDE, LDPE, PP, PA, and PET plastic polymers. Virgin lightweight plastics (HDPE, LDPE, PP, and PA) in natural sheet form were purchased from Direct plastics, UK. The plastics were: PE300 High-density polyethylene (HDPE), PE300 Low-density polyethylene (LDPE), PPH Polypropylene (PP), and cast Polyamide (nylon 6). The dimension of the natural plastics was 1000 m* 100 m *1.5 mm. (the dimension of height is 1000 m, the dimension of width is 100 m, while the diameter is 1.5 mm). While Polyethylene terephthalate (PET) sheet used (dimension- 600*600*1.5mm) was purchased from GOOD FELLOW50 (UK). This study used these plastics because they are globally used in different packaging applications. Sodium dodecyl sulfate (SDS) was purchased from Sigma Aldrich, UK. 1.5 mm colour-coded liros whipping twine was purchased from Force 4 Chandlery, UK. The soil used in the UK was collected from Henfaes located in Abergwyngregyn. At the same time, the compost and leachate were obtained from the Penhesgyn recycling site located in Anglesey, both in North Wales, UK. The soil samples used in Nigeria were collected from Uhuala Udo, while the compost was obtained from Jeniv fertilisers in Imo State. The soils used for the field experiments in the two zones were collected from the surface to the depth of 0-50cm of typical plant vegetation.

6.5.2 Plastic preparation

Each homopolymer plastic was cut with a laser cutter and manual cutter into discs of 25mm diameter and 150/20mm for the dog bones (fig.6.1) to ensure equal surface exposure and consistency between plastic types; initial properties are presented in table 6.3. Enough discs and dog bone plastics were cut for the experiment, and replicate samples of these plastics were removed at different time intervals: discs, 6, 12, 18, and 24 months; dog bones 12 and 24 months. Few impacts were observed from the mechanical shearing of the plastics used for this study. However, they were negligible following the FTIR and SEM results before the degradation study, so the study did not focus so much on them. However, the impacts of cutting and removing plastics from the substrates may increase or aid the degradation of plastics since physical and mechanical factors contribute to the degradation of plastics (Fotopoulou and Karapanagioti, 2017). Three discs and three dog-bone-shaped plastics were removed from three replicate bags of compost and soil and three leachate cans each time. Plastic discs and dog bone-shaped plastics were removed from the soil, compost and leachate and washed with 2%

SDS to denature cells, tough dirt, and distilled water. They were air-dried for 24 hours and then kept in a desiccator before analysis. We observed the plastic samples recovered from the substrates.

Table 6. 2 Physical properties of some plastics used for experimental set-up.

| PLASTIC TYPE | COLOUR | DENSITY (g/cm ³) | WEIGHT (g) | | Thickness (mm) |
|--------------|-------------|------------------------------|------------|----------|----------------|
| | | | DISC | DOG-BONE | |
| PET | Transparent | 1.38-1.45 | 0.94 | 3.96 | 1.5 |
| LDPE | White | 0.91-0.94 | 0.75 | 2.94 | 1.5 |
| HDPE | White | 0.93-0.97 | 0.70 | 2.80 | 1.5 |
| PP | White | 0.89-0.92 | 0.59 | 2.54 | 1.5 |
| PA | White | 1.13-1.35 | 1.09 | 4.68 | 2 |

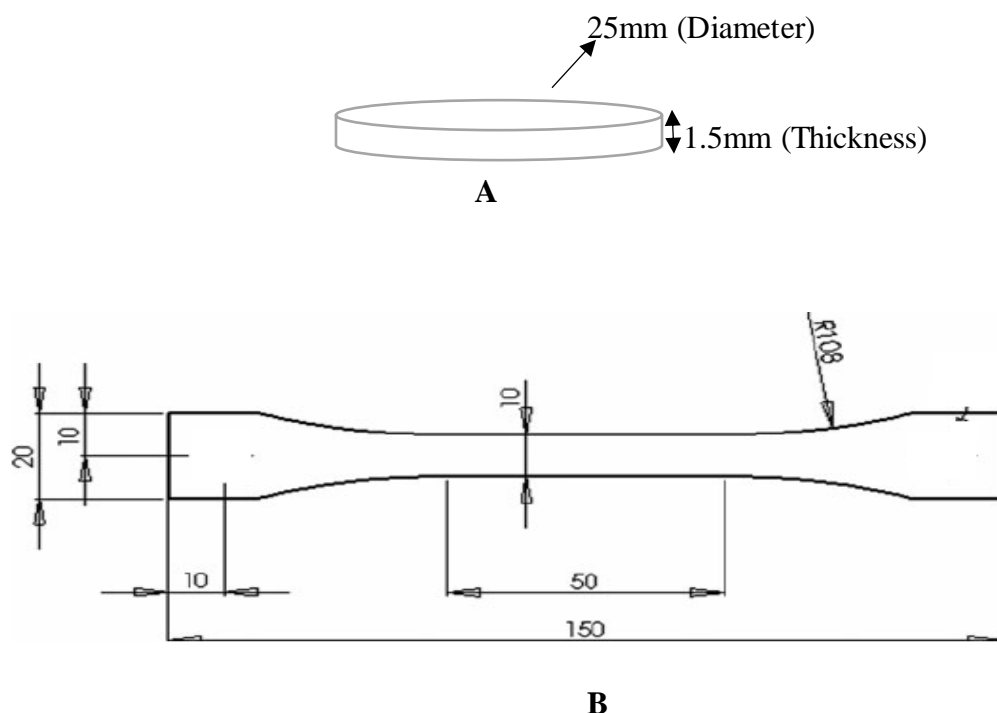


Fig. 6.1 Plastic shapes: A disc and B dog-bone used for degradation studies

6.5.3 Background of study cities

Our studies were conducted from January 2018 to January 2021 at Henfaes Research Station, United Kingdom, and from August 2018 to August 2021 at Uhuala Udo, Nigeria. We chose two villages for contrasting zones and climatic conditions but similar in size, space, and topography. Henfaes is the University of Bangor's experimental yard (53.23 N, 4.02 W, 10 m above sea level) located in Abergwyngregyn, North Wales, United Kingdom. Abergwyngregyn

is close to Bangor and has a temperate climate, with cool, wet winter and warm wet summers. Hottest in July with a temperature of about 18°C, coldest in February with a temperature of about 2°C and wettest in October at about 3.1 inches while Uhuala Udo (5.47 N, 7.32 E, 148 m above sea level) located near Owerri, the capital of Imo State in Nigeria. Uhuala Udo has a tropical climate with wet and dry seasons. Hottest in February with a temperature of about 28°C and wettest in September at about 12.6 inches. The field experiments, such as burying plastic samples in soil or compost or placing it in a river or leachate obtained from a landfill, give an ideal practical environmental condition (Scalenghe, 2018).

6.5.4 Experimental Design

The experiment was set up in the open air to study the biodegradability of various plastics under natural conditions in the soil, compost, and submerged in composting leachate in the UK and soil and compost in Nigeria (fig.6.2). Leachate was not used in Nigeria because the windrow composting site in Owerri, Nigeria, lacked the infrastructure for gathering MSW leachate produced. Three 1 m³ dumpy bags (n=3) were filled each with 1 tonne of soil, and compost in Nigeria and the UK, while three 20 L plastic cans (n=3) of leachate were used for this study in the UK. Each substrate bag and can in the UK had 20 plastic discs, of which 4 were of the identical plastic-type of HDPE, LDPE, PP, PET, PP, and PA and 10 different dog-bone shaped plastics, of which 2 were of the identical plastic-type of HDPE, LDPE, PP, PET, PP, and PA for the 2 years degradation study. Also, each bag of substrates in Nigeria had the same number of plastic discs and dog bone shapes as mentioned for the UK except for not having leachate. There was no particular order or protocol in burying them. The plastics were buried in the soil and compost at a depth of 20 cm from the surface and placed in leachate with 1.5mm colour-coded liros whipping twine attached to them to identify the plastic types. At the time for removal, 5 plastic discs of each plastic type (HDPE, LDPE, PP, PET, PP, and PA) were removed from each dumpy bag and can on each time interval, 6, 12, 18, 24 months while and 5 dog-bone plastics (HDPE, LDPE, PP, PET, PP, and PA) of each plastic-type were removed from each dumpy bag and can on each time interval 12, and 24 months.

The plastics, discs and dog-bone shapes used for the experiment were washed with SDS to denature cells and with distilled water, dried with a dry cloth, air-dried for 24 hours, and then stored in the desiccator after they were recovered from the substrates. They were weighed before and after the degradation study.

Before the experimental set-up, soils, composts and leachate were sampled to determine their basic chemical and physical conditions. Soil, compost, and leachate were collected from each

dumpster bag and can at depth up to 10cm from both experimental sites in January 2018 and August 2018. Immediately after sampling, 20 g of each soil and compost sample (n=3) were collected using a small hand digger and well packaged in Ziplock bags. The substrates from Nigeria were securely transported to Thoday laboratory in Bangor University, following all rules and guidelines in accepting and working with foreign samples. In contrast, the substrates from the UK were stored in a plastic box in Thoday laboratory until analysis.



Fig. 6.2 Experimental setup of A, compost and soil, B, leachate in the UK, and C, compost and soil in Nigeria.

The properties of the substrates used for degradation prior to analysis was also checked (Margesin and Schinner, 2005). The soil and compost solution were prepared for pH and electrical conductivity (EC) measurements. 2g of soil and compost samples were measured into 25mL centrifuge tubes, then 10mL of deionised water (dH₂O) was added to the samples (1:5 (soil/compost: water (w/v) ratio). At the same time, 10mL of leachate was measured out also into 25mL centrifuge tubes. Measurements were performed in three replicates of each soil and compost sample. The samples were shaken for 30mins at 250rpm (SW2 Shaker Table, Edmund Buhler GmbH). We measured the soil and compost solution's pH and EC using (HANNA instruments pH 209 meter, UK).

The total carbon and C/N content of soil and compost were determined using Direct Combustion, Thermal Conductivity, and IR absorption (LECO TruSpec®). 0.2g of soil/compost were oven-dried at 60°C and ground with pestle and mortar. Sieve to 1mm using 630µm sieve. Then dried at 105°C overnight in an oven and carefully weighed out 0.1-0.2 of soil and 0.05-0.1g of compost samples into a special tin foil cup. Wrap well after putting samples, then record the weight. Samples are ready to be run in a LECO machine.

The moisture content of soil and compost was measured gravimetrically. We weighed 10g of soil and compost sample (B) into clean crucibles (A), and the samples were dried overnight in

an oven at 105°C (n=3). After drying, the crucibles were removed from the oven, cooled in a desiccator, and reweighed (C). The change in mass obtained gave the water content (Faithful, 2002; Margesin and Schinner, 2005).

$$\% \text{ Moisture content} = \frac{B-C}{C-A} \times 100 \dots\dots\dots (\text{Equat. 6.1})$$

6.5.5 Climate data

Data on the mean daily air temperature from both the UK and Nigeria were monitored during the degradation experiment of plastics using I-buttons. Some I-buttons were buried together with the plastics samples in dumpy bags about 20cm deep. While the remaining I-buttons were affixed with leachate at the side of the plastic cans.

6.5.6 Analytical Methods

6.5.6.1 Visual observations

We checked the visible changes on plastics practically in all tests. Visible features used to refer to degradation include roughening of the surface, fractures, colour changes, and biofilms formations on the surfaces (Ikada, 1999). Visual changes can first suggest the first step of degradation. For insight on more evidence about the degradation mechanism, more analytical tests could be carried out on samples to confirm the extent of degradation. Below are some analytical techniques that we use to check for degradation.

6.5.6.2 Light microscopy

Light microscopy is a non-destructive visual analysis used to check the plastics discs after sampling and washing using a Leica microscope (model is DM6000 M) with an attached camera at magnification of 200µm. This method identifies fractures and colonies of possible microorganisms on the surface of the discs responsible for degradation. Three photographs were taken from each plastic disc.

6.5.5.3 Weight Change of plastics

Weight changes of plastic discs and dog bone shapes were recorded at each sampling time interval. The weight change of plastics in combination with other analytical tests will reveal detailed information regarding the degradation process (Witt et al. 2001).

Weight change was calculated as follows:

$$\text{Weight (\%)} = \frac{W_0 - W_m}{W_0} \times 100\% \dots\dots\dots (\text{Equat 6.2})$$

W₀ is the original sample weight of plastics

W_m is the measured plastic sample weight after burial in moist soil, compost, and leachate.

6.5.5.4 (FT-IR)

FT-IR is a non-destructive analysis that studies the structural features of plastics and uses PerkinElmer precisely spectrum 100 FTIR spectrometer (USA) to identify the composition of plastic samples. FTIR spectra by attenuated total reflectance (ATR) will be obtained at room temperature. The infrared light of varying wavenumber range will be 4000-400cm⁻¹ (Ter-Halle et al., 2017). on to the samples of interest, and we determine the absorption bands. All spectra are recorded at a resolution of 4 cm⁻¹ and 64 cm⁻¹; scans will be averaged for each sample. OPUS 7.5 software was used to obtain the measurements, and baseline correction was applied to each spectrum.

The structural features cover the changes which appear mainly on the carbonyl regions / functional groups on the discs during degradation, which is responsible for a drop in weight of the plastics. 3 replicate discs were analysed at each sampling time.

6.5.5.5 Carbonyl Index:

From the FTIR spectra result of the plastics, the carbonyl index will also be calculated from the peaks of plastic discs to check for changes. The reason is that most plastics are made up of carbonyl groups with C=O ending, which are the most chemically reactive portion of their structure, thus ideal sites where biodegradation is started. Carbonyl index (CI) was used to check the degree of biodegradation mostly on carbonyl groups (C=O) and methylene groups (-CH₃) as its value relies on the degraded carbonyl bond. CI is obtained by the formula given in

$$\text{Carbonyl Index (CI)} = \frac{\text{Absorbance at } 1740\text{cm}^{-1}(\text{the maximum carbonyl peak})}{\text{Absorbance at } 1460\text{cm}^{-1}(\text{the maximum carbonyl peak})}\dots\dots\dots (\text{Equ.6.3})$$

6.5.5.6 Scanning electron microscopy

SEM is a non-destructive analysis that uses a high beam of electrons from a Phenom desk-top SEM (Phenom, FEI, USA), with samples affixed to aluminium stubs using conductive carbon

pads. It has a gold coating at an accelerating voltage of 5 kV in a magnification range of 500-20,000x at a resolution of 30 nm.

The plastics' topography and morphology, including surface roughness, cracking, porosity, and notches, will be determined using the Phenom pro-suite surface analysis software. Measurements were taken at a replication level of 3 measurements from each plastic sample. From the desiccator, 10µm-25mm (diameter) of each Plastic sample are pasted onto the SEM sampler on a stub using a carbon tube and sputtered coated with gold. Then morphology of plastic discs will also be checked in 3 replicates at all sampling times.

6.5.5.6 Tensile Strength

The dog-bone thermoplastic samples will be analysed before and after degradation. Tensile strength testing was conducted on exposed plastics samples at room temperature on an Instron 5800 testing machine (Instron, UK) according to the ASTM D638 standard. The tests were recorded by Instron Bluehill software, including PC data acquisition, which automatically calculates the obtained data directly. It is highly accurate equipment as it has high-resolution angle measurement, which allows excellent repeat accuracy. The crosshead speed in the tensile test was 2.0 and 1.2 mm/min (Hamidon et al., 2019). The tensile machine should be able to produce sufficient force either slowly or quickly to break the plastic. Finally, the machine must be able to measure the gauge length and forces applied accurately.

The mechanical features were obtained from the stress-strain curves: the tensile strength, the results are averaged from 3 different measurements. Tensile strength of the dog-bone plastics was checked at months 0,12 and 24 for the dog-bone plastics to check for changes.

The tensile strength of the plastics is calculated as follows.

$$= \frac{\text{Force}}{\text{Cross sectional area of plastics}} \dots\dots\dots(\text{Equat. 6.4})$$

$$= \frac{\text{Maximum load (N)}}{\text{Width x Thickness of plastics (mm}^2\text{)}} \dots\dots\dots(\text{Equat. 6.5})$$

Force in Newton, distance in millimetres was calculated from the data according to the technical datasheets of the sensors. Maximum tensile stress and tensile engineering strain at the rupture point were calculated using equations 6.4 and 6.5.

6.5.7 Data and statistical analysis

Data obtained statistically was analysed using SPSS version 25.0 (SPSS Inc., CHICAGO, IL). One-way ANOVA showing significant differences are as probability (P) values was used to

track the changes in properties of plastics. Two-way ANOVA was used to know the effects of substrates and zones on the physio-chemical properties of substrates used and the changes in plastics' properties. At the same time, Tukey's HSD post hoc test was carried out on the data for a confidence level of 95 %. (Significant difference ($p < 0.05$) on multiple comparisons between plastic groups means where ANOVA F statistics were significant at P. Finally, the graphs and diagrams were processed using Excel software 2016. Errors bars reveal the standard error of three replicates for each experimental point.

6.6 Results and Discussion

Results obtained from the experimental studies of plastic degraded in soil, compost, and leachate in Henfaes Bangor and Uhuala Udo, are discussed in this chapter. The results obtained from the analysis before, during, and after the degradation study are the most effective way to understand plastic fate and behaviour in different environments. The degradation process and its results depend on several factors, and external environmental conditions, when combined, assist in altering plastic properties (Kliem et al., 2020). They include the nature/properties of the plastic, temperature, pH, moisture content and the microorganisms present. This study looked at some properties of the substrates used to degrade plastics, which may have influenced their microorganisms.

Also, the temperature was tracked and presented in table 6.4 using the i-buttons affixed to the body of the dumpy bag and cans with leachates since the experiment was set up in 2 different zones (in the UK and Nigeria).

6.6.1 The properties of the soil, compost and leachate used to degrade plastics

Fig. 6.3 shows the properties of the three substrates, namely, soil, compost, and leachate, used to degrade plastics. These fundamental properties will influence the availability of nutrients for the microorganisms; thus, the microbial biomass that will help degrade plastics as they may source plastic derived C for growth. Leachate only had data for pH and EC and not carbon and C/N ratio. The reason is because of a flaw in the trial experiment to dry up leachate for the carbon content, and a C/N ratio analysis which did not go well.

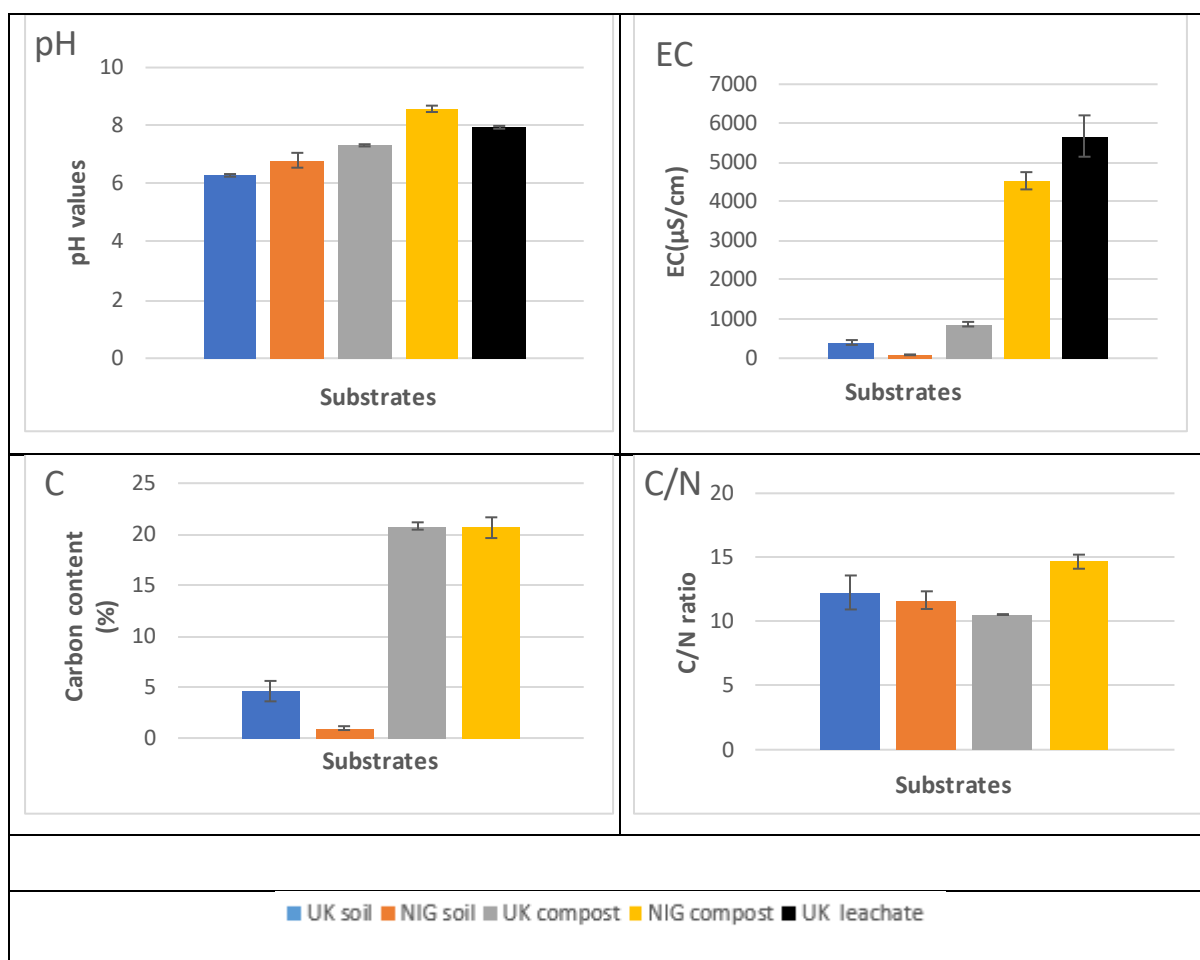


Fig. 6.3 Graphs showing the values of pH, electrical conductivity, carbon content, and C:N ratios of substrates from the UK and Nigeria used in the degradation of plastics (Mean SE, (n=3) are presented).

Out of the solid substrates, the highest pH was recorded in composts, with some significant differences between those sources in the UK and Nigeria ($P < 0.05$). Soil pH was significantly higher in Nigerian soils than in UK soils and is probably due to soil management practices and underlying geology. The pH obtained from soil and composts in the UK and Nigeria was within the ideal pH values between 5.5 and 8 because naturally, microorganisms in soil and compost thrive well around neutrality (Azim et al., 2018). Nigeria compost, therefore, had the highest pH of 8.6, which could have influenced the microorganisms involved in the degradation of the plastics. Hashimoto et al. (2002); Massardier-Nageotte et al. (2006); Alsaraf and Aljailawi, (2013) all revealed that various plastics subjected to degradation with microorganisms, soil, compost, and leachate had their properties altered with the pH values of 6.5, 7 -8, and 7.5 -7.6. On the other hand, the EC of the solid substrates, as presented in fig. 6.3 revealed that the highest EC was recorded in composts where Nigerian composts ($4534.1 \mu\text{Scm}^{-1}$) were significantly higher than UK composts ($870 \mu\text{Scm}^{-1}$) ($P < 0.05$), possibly due to the feedstock used during composting, which contains high water-soluble salt concentration as seen in food

waste (He et al., 1995). While, for Soil EC, UK soils had significantly higher EC than Nigerian soils and is perhaps a result of continuous precipitation in the UK than in Nigeria during composting that dissolved several ions. High EC reduces substrate microbial activity and influences critical soil processes such as respiration, nitrification, denitrification, and decomposition (USDA, 1954).

For carbon content, out of the solid substrates, composts significantly had the highest carbon content with the UK's composts than Nigerian's composts ($P < 0.05$). Also, the carbon content in UK's soils was more elevated than Nigerians' carbon content. CN's highest content was recorded with Nigerian composts of solid substrates (14.7%). In comparison, UK composts had the lowest CN content (10.5%), and there were no significant differences between soil and compost in the UK and Nigeria ($P > 0.05$). The C/N ratios from soil and compost from the UK and Nigeria were below the acceptable range of 20:1 as recommended by APEX. They may influence the microorganisms involved in the degradation of plastics.

The soil and compost moisture content took the trend of carbon content, where composts significantly had the highest moisture content with the UK's composts than Nigerian's composts ($P < 0.05$). Also, the moisture in UK's soils was significantly higher than Nigerians' soil moisture content. Here, the reason could be differences in precipitation levels.

From the liquid substrate checked for pH and EC, the average pH of leachates was (7.9) and was significantly within the ideal pH values, which should support the activity of microorganisms. While the average EC of leachates was significantly the highest among other substrates checked, thus exceeding the Apex EC limit, which is 750 to 2000 μScm^{-1} , possibly due to its toxic/polluted nature containing high concentrations of dissolved and suspended heavy metals, inorganic chemicals, and organic matter (Youcai, 2018). These features of leachate can affect the type and microbial biomass which can degrade plastics. Anstey et al. (2014) revealed that various plastics subjected to degradation with microorganisms in the soil, compost, and leachate had their properties altered with the pH values of 6.5, 7 -8, and 7.5 -7.6. Therefore, these parameters play an essential role in substrates because the degradation process depends on the activity of microorganisms with nutrients which are either used, lost, or stored differently as substrates properties vary (Wiatrak et al., 2009).

6.6.2 The temperature tracked with the I-buttons during the degradation of plastics

An I-button is a small device with a microchip enclosed in it, which tracked the temperature of the location of the study. In this study, i-buttons were placed 20cm inside each dumpy bag of soil and compost and affixed to the side of the cans of leachate to track the temperatures for

two years. Data obtained from the temperature readings from the buried/affixed i-buttons in the UK and Nigeria substrates were taken out to know the maximum, minimum and average temperature. The result is displayed shown in Table 6.3.

Table 6. 3 The maximum, minimum and average temperature at Henfaes, UK and Uhuala Udo, Nigeria January -December 2018 at the time of compost production (n=2063 for zone).

| Temperature | UK | Nigeria |
|--------------------------|-----------|-----------|
| Maximum temperature (°C) | 21.5 | 38 |
| Average temperature (°C) | 12.5±0.11 | 25.3±0.03 |
| Minimum temperature (°C) | 1.5 | 24 |

6.6.3 Visual Observation

Visual check of the plastic discs and dog bone shaped after being buried in soil, and compost and placed in leachate for two years was carried out in the UK was shown in figs. 6.4, 6.5, 6.6, and 6.7 below. We observe changes in the appearance and surface of the plastics during degradation easily. There were apparent differences between the degraded discs and dog bone shaped plastics such as discolouration, the roughness of the surfaces, loss of gloss and formation of biofilm on the plastics was observed .i.e., altering the surface properties during degradation

Figs. 6.4 and 6.5 are the visual observation of discs and dog bone shapes of PA-6 and PET plastics after cleaning while figs. 6.6 and 6.7 are visual observations of discs and dog bone shape of PP, HDPE, and LDPE plastics after cleaning.
















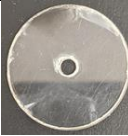
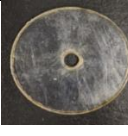



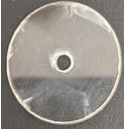
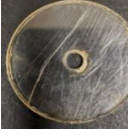


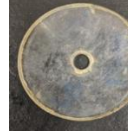





| Plastic/ substrate | 0 month | 6months | 12 months | 18 months | 24 months |
|-----------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PA-6 Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| Leachate |  |  |  |  |  |
| PET Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| Leachate |  |  |  |  |  |

Fig. 6.4 Visual observation of plastics discs- polyamide-6, polyethylene terephthalate, before degradation (0 months), and after degradation (6, 12, 18, and 24 months) in soil, compost, and leachate in the United Kingdom (Goggle pixel camera).















| | Before degradation | Soil 1 Year | Soil 2 years | Compost 1 year | Compost 2 years | Leachate 1 year | Leachate 2 years |
|------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| PA-6 |  |  |  |  |  |  |  |
| PET |  |  |  |  |  |  |  |

Fig. 6.5 Visual observation of dog bone plastics- polyamide-6, polyethylene terephthalate, before degradation and after degradation (12 and 24 months) in soil, compost, and leachate in the United Kingdom (Goggle pixel camera).

Figs. 6.4 and 6.5 revealed the visual observation of discs and dog bone shape PA and PET plastics buried in the soil, compost, and submerged in leachate in the UK. All PA plastics displayed discolouration compared to their control samples at 0 months, especially those placed in leachate. One could notice that while PA disc/dog bone shape plastics in the soil at the 24th month had a roughness of surface with mild biofilm formation on it, PA discs in the leachate at 12, 18, and 24th months exhibited roughness and with what appeared to be mycelial like network on their surfaces. PET plastics in both figs. 6.4 and 6.5. On the other hand, slight discolouration was observed in all substrates used with obviously damaged surfaces from the 6th to the 24th month, most especially at the 18th and 24th months. Another observation was the abrasion marks on PA and PET discs, particularly on PET discs from the 6th month in soil and compost. These marks may have been done on the discs while pulling the plastics from coarse soil and compost. Fig. 6.5 revealed that all dog bone-shaped PA and PET plastics buried in the UK lost their shapes compared to the control plastics.





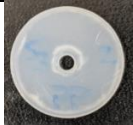






































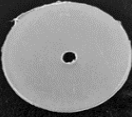

| Plastic/ substrate | 0 month | 6months | 12 months | 18 months | 24 months |
|-----------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PP Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| Leachate |  |  |  |  |  |
| HDPE Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| Leachate |  |  |  |  |  |
| LDPE Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| Leachate |  |  |  |  |  |

Fig. 6.6 Visual observation of plastic discs- polypropylene, high-density polyethylene, and low-density polyethylene before degradation (0 months) and after degradation (6, 12, 18, and 24 months) in soil, compost, and leachate in the United Kingdom (Goggle pixel camera).





| | Before degradation | Soil 1 Year | Soil 2 years | Compost 1 year | Compost 2 years | Leachate 1 year | Leachate 2 years |
|------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PP |  |  |  |  |  |  |  |
| HDPE |  |  |  |  |  |  |  |
| LDPE |  |  |  |  |  |  |  |

Fig 6.7 Visual observation of dog-bone plastics- high-density polyethylene, and low-density polyethylene before degradation, after 12 and 24 months in soil, compost, and leachate in the United Kingdom (Goggle pixel camera).

Figs. 6.6 and 6.7 revealed the visual observation of discs and dog bone shape PP, HDPE and LDPE plastics buried in the soil, compost, and submerged in leachate in the UK for 24 months. All PP discs showed signs of physical degradation with biofilm growing on discs from the 18th – 24th-month in all the substrates used. At the same time, PP dog bone-shaped plastics did not only exhibit discolouration but lost their shape, and mild biofilm was seen on them after the

24th month compared to their control samples before degradation. HDPE discs and dog bone-shaped plastics had mild discolouration, rough surfaces, and biofilm formation for the discs from the 18th – 24th month. In contrast, the dog bone shape HDPE had their surfaces become irregular, with biofilm on some parts and then lost their shapes mostly in soil and compost. All LDPE discs and dog bone-shaped plastics lost their gloss, had slight brownish discolouration, abrasion marks on their surfaces, biofilm on the surfaces from 18th – 24th month for the discs in soil and compost at 24th month for the dog bone-shaped plastics in all the substrates used. Figs. 6.8 and 6.9 revealed the visual observation of discs and dog bone shape PA-6 and PET plastics buried in the soil and compost in Nigeria.

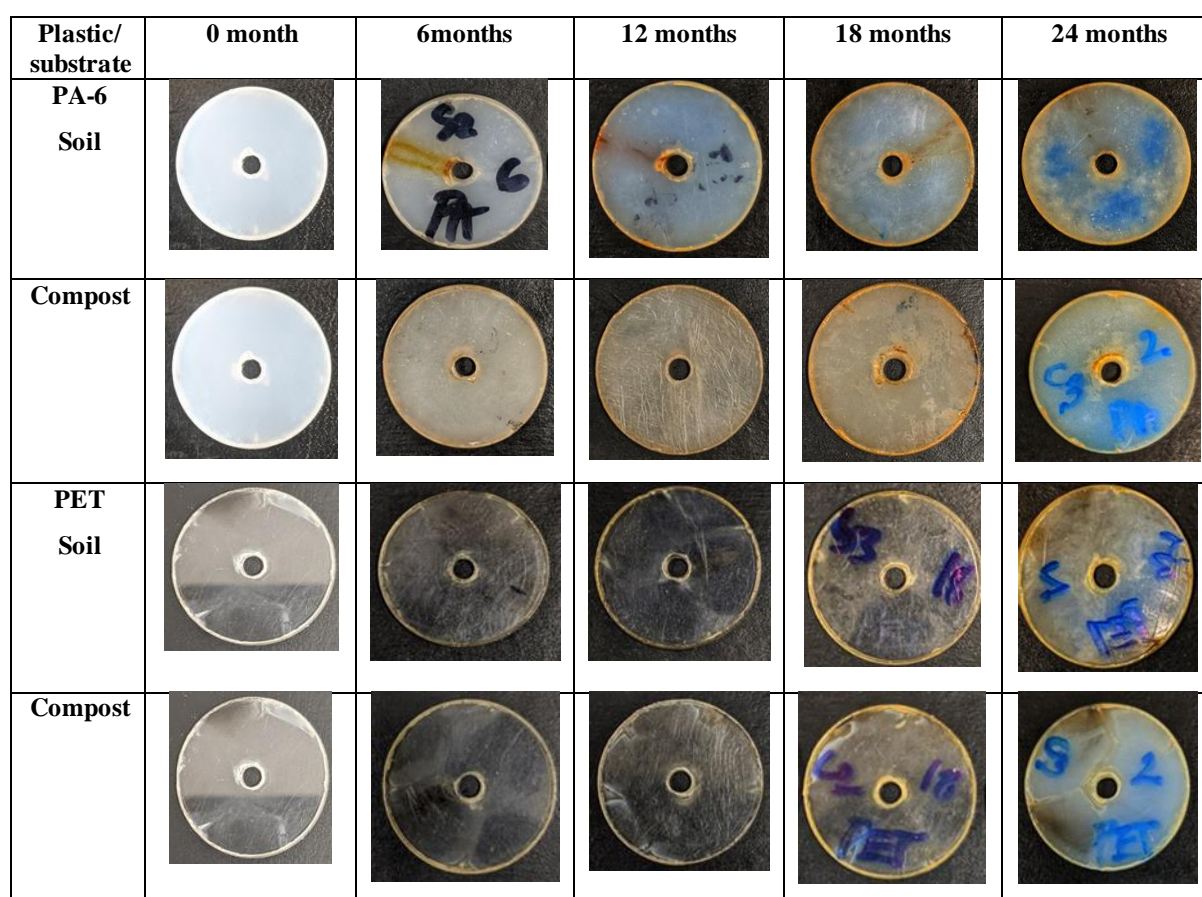


Fig. 6.8 Visual observation of plastics discs- polyamide-6, polyethylene terephthalate, before degradation (0 months) and after degradation (6, 12, 18, and 24 months) in soil and compost in Nigeria (Goggle pixel camera).

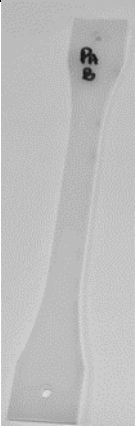




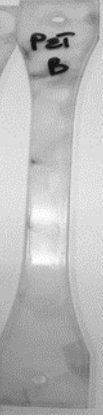




| | Before degradation | Soil 1 Year | Soil 2 years | Compost 1 year | Compost 2 years |
|------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| PA-6 |  |  |  |  |  |
| PET |  |  |  |  |  |

Fig. 6.9 Visual observation of dog-bone plastics- polyamide-6, and polyethylene terephthalate, before degradation, and after degradation at 12 and 24 months in soil, and compost in Nigeria (Goggle pixel camera) .

All PA-6 plastics showed brownish discolouration and slight abrasion/roughness on their surfaces from the 6th month to the 24th month for the discs and the 12th and 24th months for the dog bone shaped in both soils and compost. While biofilm-like patches were mainly seen on the degraded PA-6 discs at the 18th and 24 months, it was apparent on the dog bone shaped PA-6 at the 24th. PET plastics in both figs.6.8 and 6.9 also exhibited slight discolouration in soil and compost with visible rough surfaces from 12th month to 24th month, most especially at the 18th and 24th month for the discs and dog bone shaped. Fig. 6.8 revealed biofilms seen on the PET discs in soil and compost at 18 and 24th months and the dog bone shaped after 24th months. Also, Fig. 6.8 reveals that both PA-6 and PET discs in soil and compost at the 24th month lost their gloss and became more brittle than their control samples, and Fig.6.9 revealed that all dog bone-shaped PA-6 and PET plastics lost their shapes. Figs. 6.10 and 6.11 revealed the discs and dog bone shaped of PP, HDPE, and LDPE plastics.









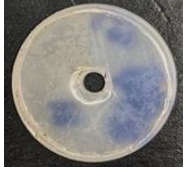





















| Plastic/ substrate | 0 month | 6months | 12 months | 18 months | 24 months |
|-----------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PP Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| HDPE Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |
| LDPE Soil |  |  |  |  |  |
| Compost |  |  |  |  |  |

Fig. 6.10 Visual observation of plastics discs- polypropylene, high-density polyethylene, and low-density before degradation (0 months) and after (6, 12, 18, and 24 months) in soil and compost in Nigeria (Goggle pixel camera).


| | Before degradation | Soil 1 Year | Soil 2 years | Compost 1 year | Compost 2 years |
|------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PP |  |  |  |  |  |
| HDPE |  |  |  |  |  |
| LDPE |  |  |  |  |  |

Fig. 6.11 Visual observation of dog-bone plastics- polyamide-6, polyethylene terephthalate, polypropylene, high-density polyethylene, and low-density polyethylene before degradation, and after degradation at 12, and 24 months in soil, and compost in Nigeria (Goggle pixel camera).

Discs and dog bone PP plastics showed slight discolouration in soil and compost. We observed little biofilm growing on the discs from the 12th to 24th month in soil and compost. HDPE and LDPE discs, as seen in fig. 6.11 displayed brownish discolouration and biofilm formation, which are very distinct in the soil at 12, 18, and 24. In contrast, we saw minor changes in biofilms on discs in compost instead of abrasions marks, which were evident on the HDPE and

LDPE discs in compost. Also, in Nigeria, all the dog bone-shaped HDPE and LDPE plastics lost their original shapes and had more biofilms colonisation on their surfaces in soil than in compost.

From the results obtained in figs. 6.4-6.11, both discs and dog bone-shaped plastics shown above had some form of degradation, such as stress, and abrasive forces, which could be a physical degradation from environmental stress, and they looked dull and shrunk from sunlight during summer or dry season (Pospisil and Nespurek, 1997; Vasile and Dekker, 2000). The most noticed change was the discolouring of the discs, mostly PA and PET (figs, 6.4,6.5,6.8 and 6.9). While the dog-bone exhibited forms of degradation ranging from physical to discolouring, the reason was their properties. PA and PET are plastics with heteroatoms in their main chain (Andrady, 2011). Their chemical structures had sites that encouraged microbial attack (Fig. 6.5). Comparing the substrates in this section, plastics, especially PA-6 and PET in leachates 6.4 and 6.5, exhibited this colour change from the 6th month to the 24th month.

6.6.4 Light microscopy

We used light microscopy to study the plastic discs before and after degradation at chosen intervals at 0, 6, 12, and 24 months in soil, compost, leachate in the UK, and soil and compost in Nigeria. We noted the changes and contrasts in figs. 6.12, 6.13, and 6.14. These changes allowed us to evaluate the superficial differences in plastic surfaces. This section obtained the three images of the plastic discs from the experiments. They followed the same trend in detected changes, so we picked the best image each to represent both before and after degradation for all the different time intervals that sampling took place.






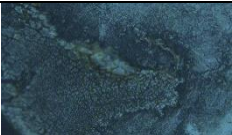




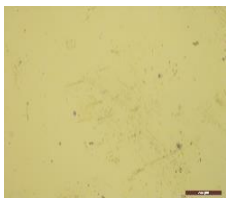









| Control | 6 months | 12 months | 24 months | Substrates |
|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------|
|  Polyamide-6 |  |  |  | Soil |
| |  |  |  | Compost |
| |  |  |  | Leachate |
|  Polyethylene terephthalate |  |  |  | Soil |
| |  |  |  | Compost |
| |  |  |  | Leachate |

Fig. 6.12 Microscopy images of plastic discs- polyamide-6 (PA-6), and polyethylene terephthalate (PET), before degradation (0 month), and after degradation (6, 12, and 24 months) in soil, compost, and leachate in the United Kingdom.

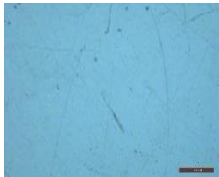






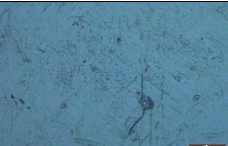









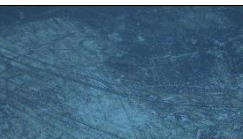




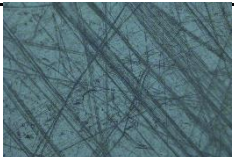

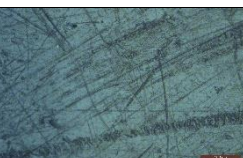



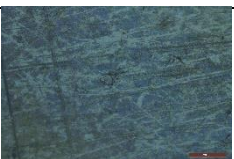

| Control | 6 months | 12 months | 24 months | Substrates |
|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------|
|  Polypropylene |  |  |  | Soil |
| |  |  |  | Compost |
| |  |  |  | Leachate |
|  High-density polyethylene |  |  |  | Soil |
| |  |  |  | Compost |
| |  |  |  | Leachate |
|  Low-density polyethylene |  |  |  | Soil |
| |  |  |  | Compost |
| |  |  |  | Leachate |

Fig. 6.13 Microscopy images of plastic discs- polypropylene (PP), high-density polyethylene (HDPE), and low-density polyethylene (LDPE) before degradation (0 month), and after degradation (6, 12, and 24 months) in soil, compost, and leachate in the United Kingdom.

While fig. 6.12 revealed the microscopic images of the control and degraded PA-6 and PET plastic discs. Fig. 6.13 revealed the UK's microscopic images of the control and degraded PP,

HDPE, and LDPE plastic discs in soil, compost, and leachate after 6, 12 and 24 months. PA and PET's surfaces from 6th -24th month in fig. 6.12 clearly shows surface irregularities as compared with the control surface. At six months, PA-6 and PET plastics in soil, compost, and leachate had mild abrasion marks, colour change, and a few patches of biofilm colonisation like dirt seen growing on the surfaces. These patches grew and became more conspicuous at 12 months; at 24 months, they became even more visible, stronger, and thicker. PA-6 surfaces had these damages more than PET surfaces in all substrates used in the UK, and from their optical evaluation, damages are in this order:

Time= 6months<12months<24months and

Substrates=leachate<soil<compost.

PP, HDPE, and LDPE degradation followed a similar trend. There were abrasion marks and dark patches on the surfaces of these discs in all the substrates after six months, though least on PP in leachate and more on LDPE probably because of its soft, flexible, and transparent nature. These visible damages became stronger after 12 months making cavities on the discs as seen in fig.6.13; under PP in soil, compost, and leachate at 12 months and patches on HDPE and LDPE at 12 months. At 24 months, these damages were more intense than at 12 and 6 months and control discs.

Therefore, figs. 6.12 and 6.13 suggested that the discs of all the plastics buried and submerged in soil, compost and leachate were all affected from 6 months and became more affected with time, i.e., the longer the plastic discs were in these substrates, the greater the damages noticed on their surfaces.



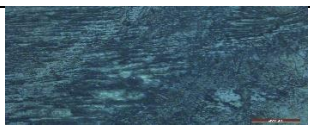
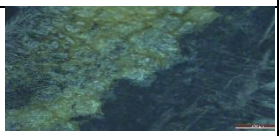
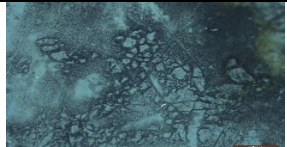



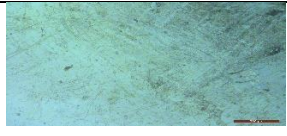





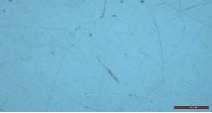


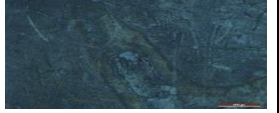

















| Control | 6 months | 12 months | 24 months | Substrates |
|-------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|----------------|
|  Polyamide-6 |  |  |  | Soil |
| |  |  |  | Compost |
|  Polyethylene terephthalate |  |  |  | Soil |
| |  |  |  | Compost |
|  Polypropylene |  |  |  | Soil |
| |  |  |  | Compost |
|  High-density polyethylene |  |  |  | Soil |
| |  |  |  | Compost |
|  Low-density polyethylene |  |  |  | Soil |
| |  |  |  | Compost |

Fig. 6.14 Microscopy images of plastic discs- polyamide-6 (PA-6), and polyethylene terephthalate (PET), polypropylene (PP), high-density polyethylene (HDPE), and low-density polyethylene (LDPE) before degradation (0 month), and after degradation (6, 12, and 24 months) in soil, and compost in Nigeria.

Fig. 6.14 revealed the microscopic images of the control and degraded PA-6, PET, PP, HDPE and LDPE plastic discs in soil and compost in Nigeria after 0, 6, 12 and 24 months. After six months of degradation in Nigeria, significant surface damage was seen on all the plastics, with

PA-6 exhibiting the most surface damage. These damages include dark patches, biofilm colonisation and abrasion marks. After 12 months, these surface damages became more potent in all the plastics in soil and compost, as seen in fig.13, making network-like structures on the discs. These surface damages on plastic discs became worse and strongest after 24 months, i.e., no plastic disc was left out in both soil and compost after 24 months. The biofilm colonisation became broader and thicker with yellowish and black patches under the microscopy. The surface damage of all plastic discs buried in soil and compost in Nigeria followed: Time= 6months< 12 months < 24 months.

Also, fig. 6.14 revealed that surface damages were seen and noticed more through micrographs in the soil environment than compost. The reason was that plastics' degradation rate was proportionate to the microbial load in substrates used; for instance, naturally, soils have a higher microbial load compared to compost, i.e., degrading microorganisms exist more in some environments than others (Ohtake et al., 1998; Andrady, 2003; Cai et al., 2018). Therefore, degrading microorganisms may have lived more in Nigerian soil than in Nigerian compost. The function of time also affected the plastic discs. As seen in fig.6.14, the longer the plastics stayed in soil and compost, the more their surfaces were affected.

6.6.5 Weight change of plastics (WC)

Weight change is one of the techniques used to track degradation in plastics. The soil, compost, and leachate microorganisms may have initiated degradation by forming enzymes that trigger oxidation or hydrolysis of the polymer chains /bonds of plastics. This attack on the polymer chains of the plastics changes the properties of the plastics. We observed the experimental weight change of the plastic discs buried in soil, compost, and leachate in the UK and soil and compost in Nigeria for 24 months, expressed in grams and presented in figs. 6.15 and 6.16, respectively. Although there were fluctuations in the results obtained from the weight change of plastics subjected to degradation as seen in figs. 6.15 and 6.16, still most plastics reduced in weight after 24 months compared to their initial weights before degradation .

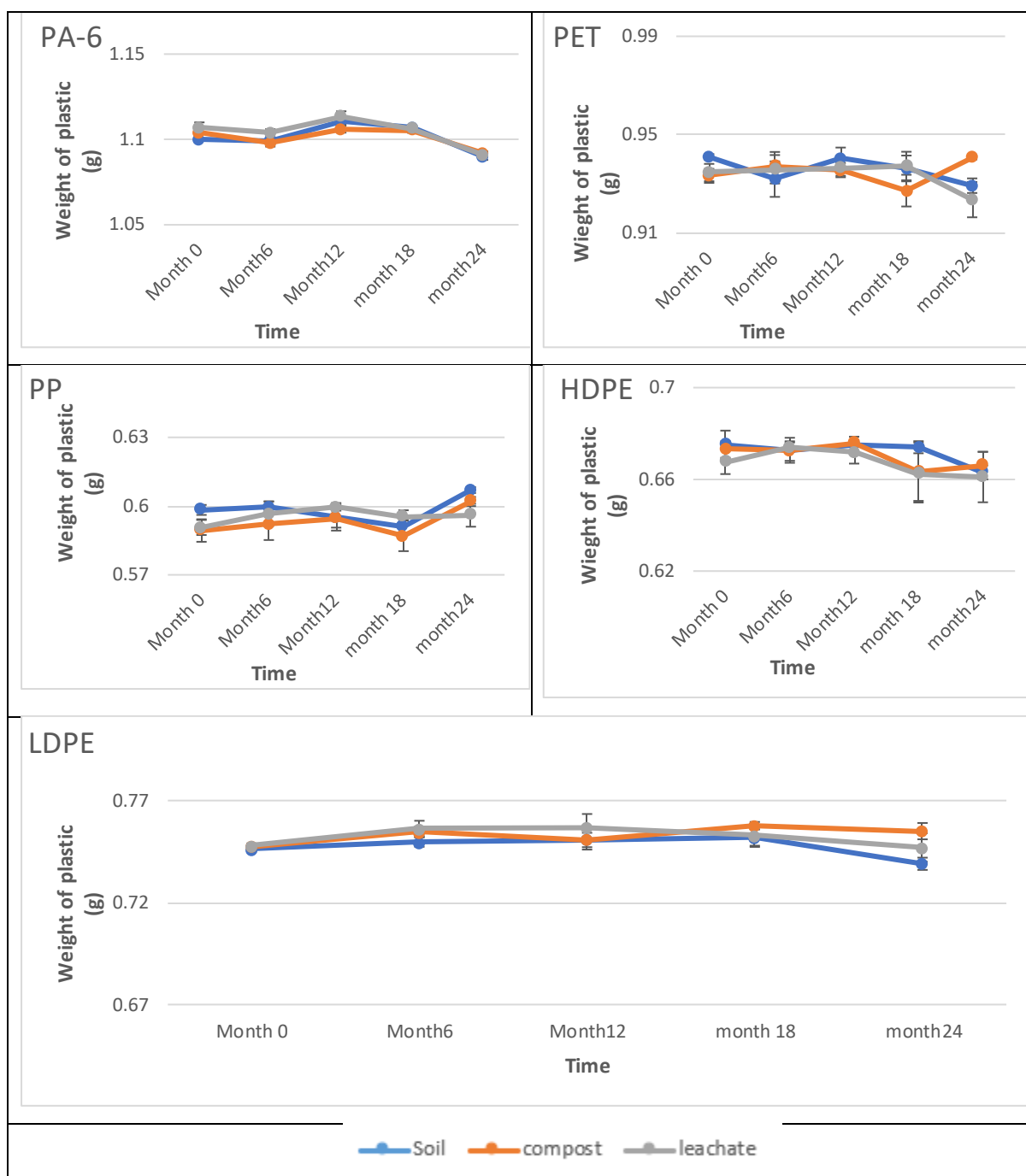


Fig. 6.15 Plots of the weight change of the plastics discs: PA-6, PET, PP, HDPE, and LDPE after 0, 6, 12, 18 and 24 months in soil, compost, and leachate in the United Kingdom. *Y-Axis values differ. Data represents mean \pm SE (n = 3).

Fig. 6.15 presents the results from the average of the three replicates used for the degradation study of plastic discs buried in soil, and compost and submerged into leachate for over 24 months in the UK. Fig. 6.15, displayed the fluctuations observed by the plastic discs in the 6th, 12th, and 18th months as most plastics discs were gaining and losing weights. However, after the 18th-month discs such as PA-6, LDPE gradually lost weight in the three substrates, while PET and HDPE only lost weights in soil and leachate. Their weight changes in the substrates were similar and inconsistent.

While fig. 6.15 revealed that degradation/ weight loss was observed more after 24 months in soil and leachate than in compost. Table 6.4 below summarises the weight change (%) observed after 24 months of degradation of plastic discs in soil, compost, and leachate in the UK.

Table 6. 4 The weight change (%) of the plastic discs in the soil, compost, and leachate after 24 months in the UK. Data represents mean \pm SE(n=3).

| PLASTICS | SUBSTRATES | | |
|-----------------------------------|------------------|------------------|------------------|
| | Soil (%) | Compost (%) | Leachate (%) |
| Polyamide-6 | -0.9 \pm 0.002 | -1.1 \pm 0.001 | -1.4 \pm 0.001 |
| Polyethylene terephthalate | -1.2 \pm 0.003 | 0.8 \pm 0.001 | -1.2 \pm 0.007 |
| Polypropylene | 1.4 \pm 0.013 | 2.1 \pm 0.002 | 0.9 \pm 0.005 |
| High-density polyethylene | -1.8 \pm 0.003 | -1 \pm 0.006 | -1 \pm 0.011 |
| Low-density polyethylene | -1 \pm 0.003 | 1 \pm 0.004 | -0.1 \pm 0.007 |

PA-6 and HDPE discs had weight losses in all three substrates studied, with HDPE discs having the highest weight loss in the soil after 24 months, about -1.8%. PET discs had a weight loss of -1.2% in soil and leachate and had a weight gain in the compost of 0.8%. LDPE discs also lost weight in both soil and leachate (-1 and -0.1%), respectively, while the discs gained weight (1%) in the compost after 24 months. The weight reduction of plastics in substrates is due to the breakdown of the carbon backbone. The microorganisms in the substrates utilise the resulting monomers and oligomers as carbon and energy sources (Deepika and Jaya, 2015). There was a negative trend in weight loss of PP irrespective of the substrate type. In the first 12 months, PP discs gained weight instead of losing (fig. 6.15); however, after 24 months, there was a further increase in the weight gain of PP discs in all substrates used, especially in the compost, where the discs had the highest significant weight gain. The reasons for the weight gain observed by the PP discs in all the substrates, PET discs and LDPE in compost could be the activities of microorganisms in the substrates. They secrete enzymes and form biofilms that increase with time in the substrates and attach themselves to the surface and cracks on the plastic discs. They were hard to wash away or absorb water molecules from the substrates used for degradation. Either of the routes may cause weight gain by plastic discs. El-Shafei et al.,

1998; Taghavi et al., 2021 also experienced an increase in the weight of films subjected to degradation. They attributed the weight gain to microbial colonisation and the metabolites secreted into the polymer structure. For fig.6.15 and table 6.4, statistically, media and time had no significant influence on plastics' weight change (media: $F = 0.003$, $P > 0.05$; time: $F = 0.008$, $P > 0.05$), while plastic types had a significant effect on the weight change (plastic-type: $F = 28671.347$, $P < 0.05$)

Fig. 6.16 displays the results from the average of the three replicates used for the degradation study of plastic discs buried in soil and compost for over 24 months in Nigeria.

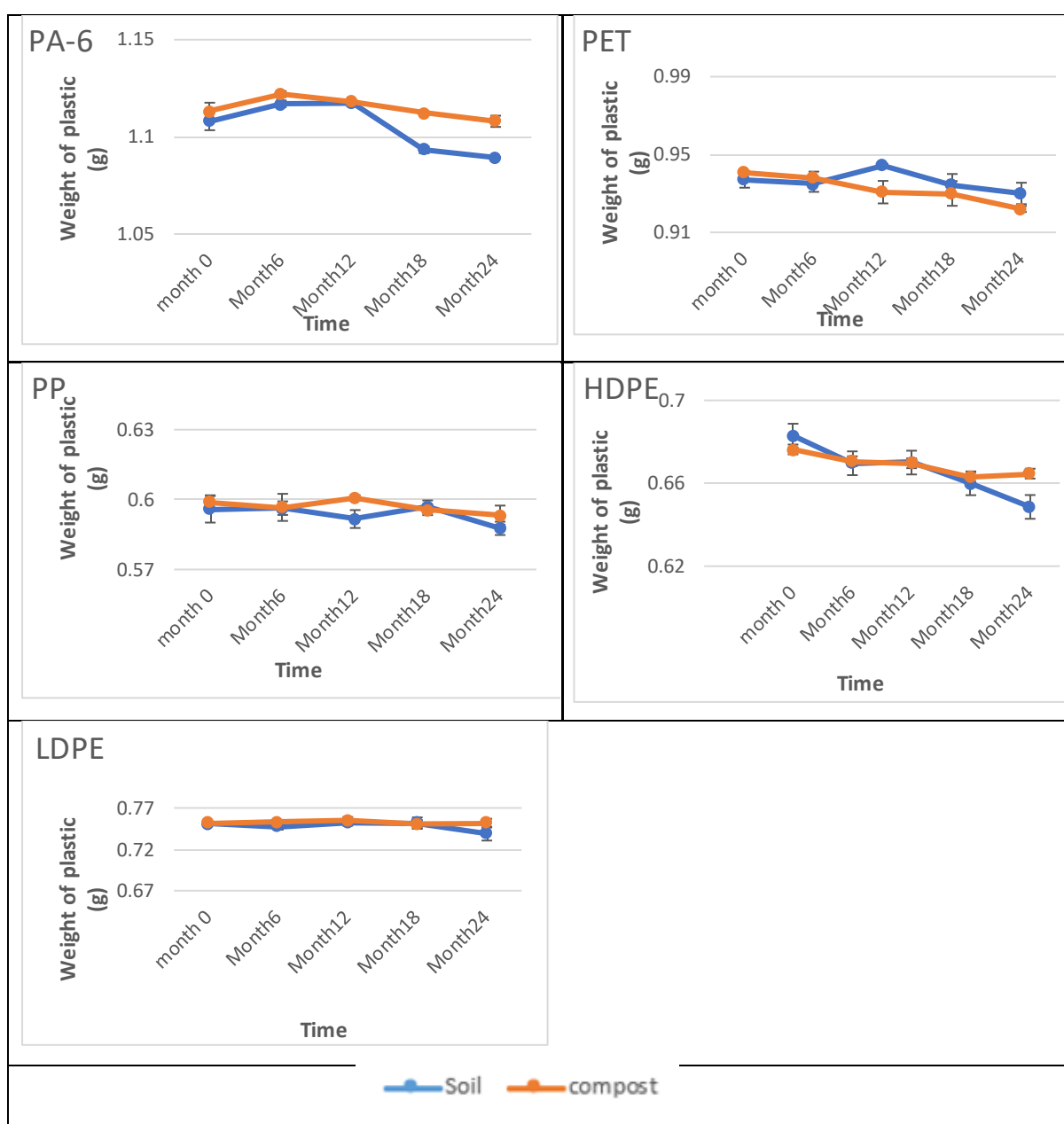


Fig. 6.16 Plots of the weight change of the plastics discs: PA-6, PET, PP, HDPE, and E LDPE after 0, 6, 12, 18 and 24 months in soil, compost, and leachate in the United Kingdom. *Y-Axis values differ. Data represents mean \pm SE (n = 3).

From fig. 6.16, there were fewer fluctuations in the weight change of plastic discs between the 6th and 18th months in Nigeria. The weight loss in plastics buried in Nigeria was uniform in soil and compost, with the degradation/weight loss observed more after in soil than in compost except for PET that showed more weight loss in compost than soil throughout the study in Nigeria. Table 6.5 below summarises the weight change (%) observed after 24 months of degradation of plastic discs in soil and compost in Nigeria.

Table 6. 5 The weight change (%) of the plastic discs in the soil, and compost after 24 months in Nigeria. Data represents mean \pm SE(n=3).

| PLASTICS | SUBSTRATES | |
|-----------------------------------|------------------|------------------|
| | Soil (%) | Compost (%) |
| Polyamide-6 | -1.7 \pm 0.00 | -0.5 \pm 0.003 |
| Polyethylene terephthalate | -0.7 \pm 0.006 | -1.9 \pm 0.002 |
| Polypropylene | -1.4 \pm 0.003 | -0.9 \pm 0.004 |
| High-density polyethylene | -5 \pm 0.009 | -1.7 \pm 0.008 |
| Low-density polyethylene | -1.3 \pm 0.008 | -0.1 \pm 0.005 |

All the plastic discs exhibited weight loss in all the substrates used for degradation in Nigeria, with HDPE discs showing the highest weight loss in soil, about 5%, while LDPE in compost had the least weight loss of 0.1%. The table above showed no weight gain by the plastic discs. Also, plastic discs had more % weight loss in soil than in compost, except for PET, which had more weight loss % in compost.

For fig.6.16 and table 6.5, statistically, media and time had no significant influence on plastics' weight change in Nigeria (media: $F= 0.010$, $P>0.05$; time: $F= 0.020$, $P>0.05$), while plastic types significantly influenced the weight change of plastics in Nigeria ($F= 15938.463$, $P<0.05$). We observed fluctuations in the weight of plastics examined. Such as the gain and loss of weight displayed by these plastic discs exposed to different substrates in the UK and Nigeria as used for this experimental study presented signs that the discs were attacked by microorganisms in the substrates leading to a change in their structural integrity, thereby causing degradation.

Shovitri et al. (2017) buried plastics in beach sand and mangrove sediment for over 16 weeks. Their results also revealed that the percentage of plastic degradation was increasing over this time of burial. Han et al. (2020) buried three types of plastic films in agricultural soil over 30 months, and their results suggested that the weight loss of plastic films observed was linked to the type of soil, although the extent of weight loss depends on the plastic film type. Vargha et al. (2016), on the contrary, after checking the behaviour of different polyethylene films in soil over one year, concluded that the films only suffered physical degradation, not biodegradation.

6.6.6 Fourier Transform Infrared (FT-IR)

FTIR spectroscopy gives vital and practical information about the chemical bonds existing between molecules and provides an essential interaction of those chemical bonds with Infrared radiation. The results from figs. 6.17-6.21 reveals the FTIR of plastic discs before and after degradation at chosen intervals at 12, 18, and 24 months in soil, compost, leachate in the UK and figs. 6.22 – 6.26 reveal results in soil and compost in Nigeria. There were appearances, losses, reductions and shifts of peaks in this section which shows that bonds of molecules and the functional groups present in plastics buried have been weakened due to degradation in all plastics.

6.6.6.1 Fourier Transform Infrared (FT-IR) of plastics buried in the UK

Polyamide-6 (PA-).

The FT-IR result, as shown in fig. 6.17 A, B and C displayed the combined spectra of the PA-6 before and after degradation at 12, 18, and 24 months in soil, compost, and leachate in the UK. There were differences in the spectra of PA-6 discs after degradation when compared to the spectra of the original PA-6 discs. Also, the result demonstrated differences in PA-6 spectra both in the substrates used and over time. The control spectra of PA-6 discs, as seen in (fig. 6.17 A, B, and C), displayed some peaks reflecting the nature of PA-6, which are at wavenumbers; 3294, 3080, 2930, 2858, 1633, 1538, 1459, 1262 and 975 cm^{-1} . The main changes observed from the spectra of PA-6 after degradation in soil, compost, and leachate are as follows.

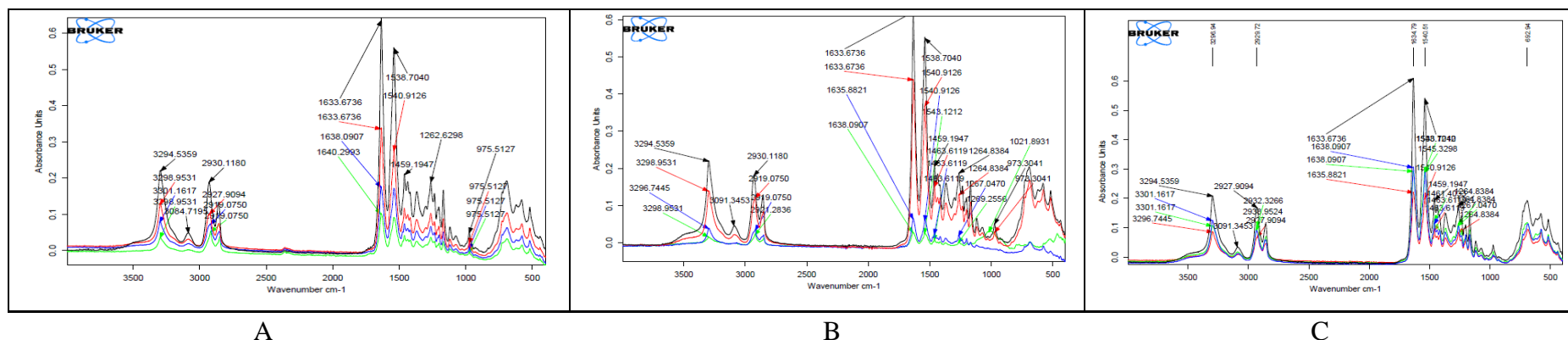


Fig. 6.17 FTIR spectra of the degraded PA discs (black peak shows original PA, red peak shows PA after 12 months, blue peak shows PA after 18 months, and green peak shows PA after 24 months) buried in media, namely, (A) soil, (B) compost, and (C) leachate for 12, 18 and 24 months in the United Kingdom.

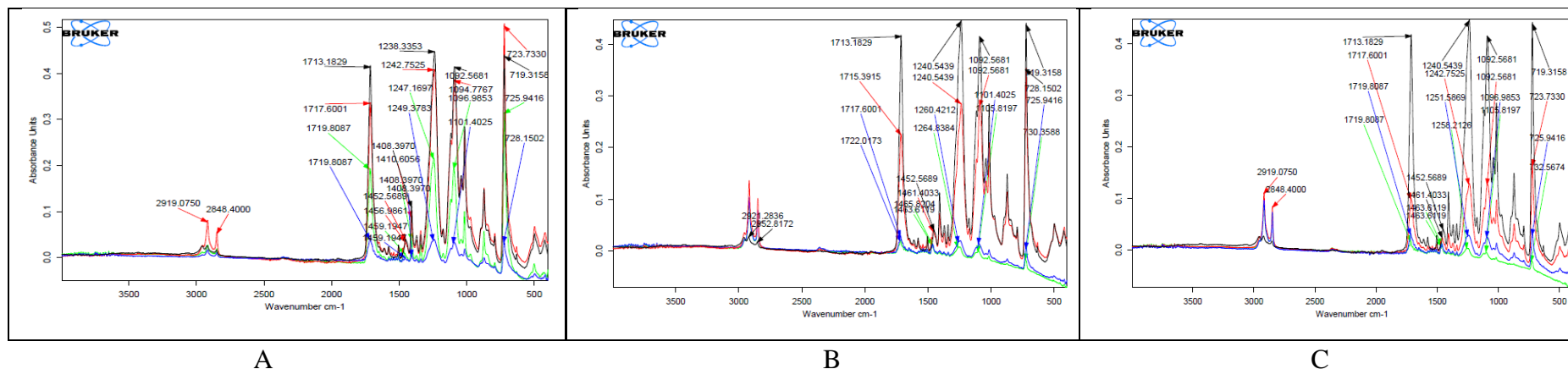


Fig. 6.18 FTIR spectra of the degraded PET discs (black peak shows original PET, red peak shows PET after 12 months, blue peak shows PET after 18 months, and green peak shows PET after 24 months) buried in media, namely, (A) soil, (B) compost, and (C) leachate for 12, 18 and 24 months in the United Kingdom.

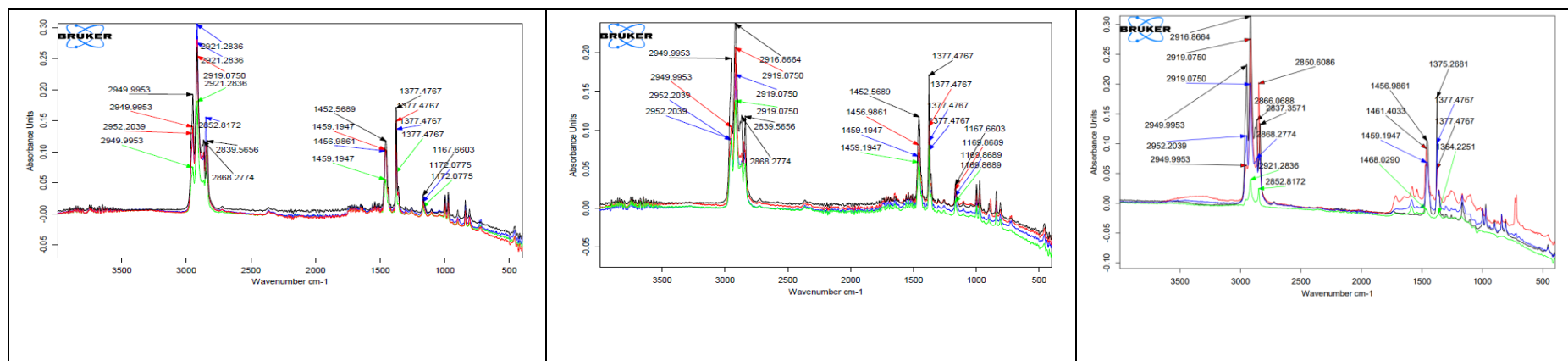


Fig. 6.19 FTIR spectra of the degraded PP discs (black peak shows original PP, red peak shows PP after 12 months, blue peak shows PP after 18 months, and green peak shows PP after 24 months) buried in media, namely, (A) soil, (B) compost, and (C) leachate for 12, 18 and 24 months in the United Kingdom.

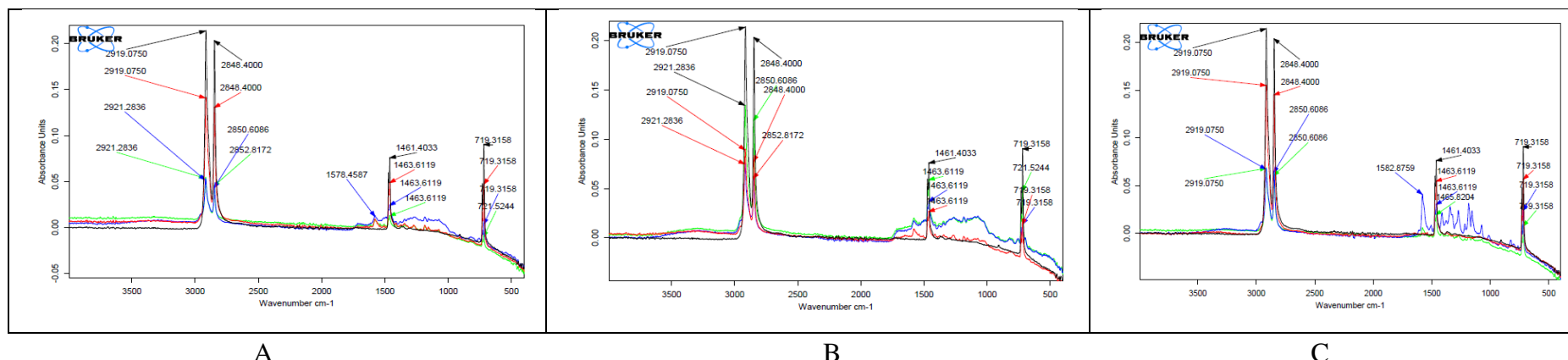


Fig. 6.20 FTIR spectra of the degraded HDPE discs (black peak shows original HDPE, red peak shows HDPE after 12 months, blue peak shows HDPE after 18 months, and green peak shows HDPE after 24 months) buried in media, namely, (A) soil, (B) compost, and (C) leachate for 12, 18 and 24 months in the United Kingdom.

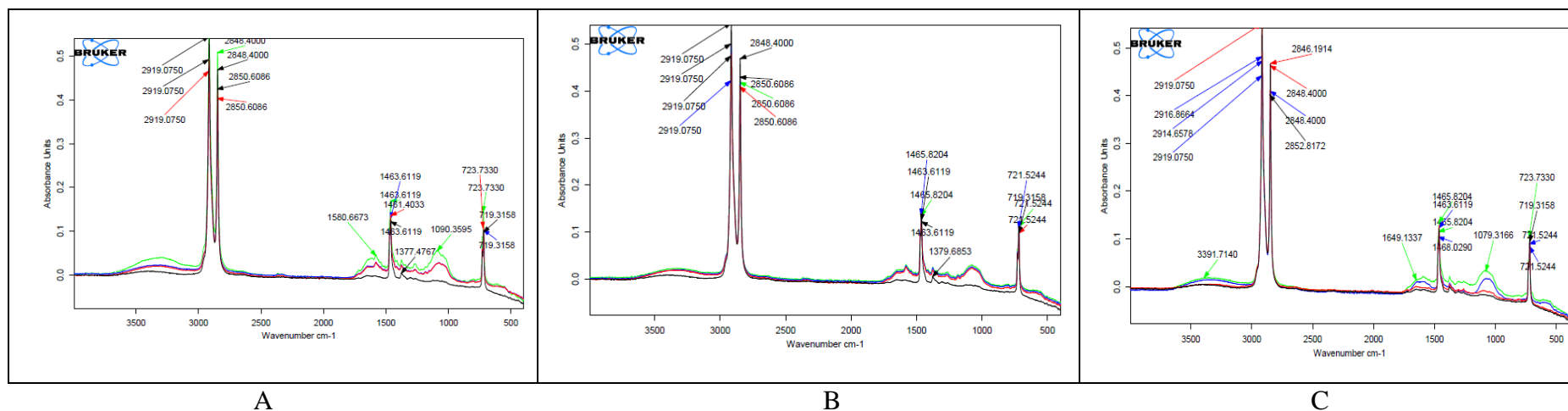


Fig. 6.21 FTIR spectra of the degraded LDPE discs (black peak shows original LDPE, red peak shows LDPE after 12 months, blue peak shows LDPE after 18 months, and green peak shows LDPE after 24 months) buried in media, namely, (A) soil, (B) compost, and (C) leachate for 12, 18 and 24 months in the United Kingdom.

There was a reduction in PA discs' peak intensity/absorbance units at all points of interest compared to their peaks before degradation. In this reduction of the peak intensities, all PA-6 discs followed a trend in soil and compost (control>12 months>18 months>24 months) except in leachate (control>24 months>18 months> 12 months). The peak intensities/absorbance units of the original PA-6 disc before and after degradation at 12, 18 and 24 months are shown in Table 6.6. In soil and compost, the peaks reduced after 12 months and had further reduction after 18 months and had most reduction after 24 months, while in leachate, the peaks of PA-6 discs had most reduction after 12 months, following at 18 then the least reduction at 24 months. Generally, from table 6.6, the reduction in the peaks of degraded PA-6 discs was uniform and more in compost than in soil and leachate from the UK.

Table 6. 6 The Absorbance units of peaks of control and degraded PA-6 discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| PA-6 | Peak intensities/ Absorbance units | | | | | | |
|--------------------|------------------------------------|-------------|-------------|-------------|-------------|-------------|------------|
| | 3294 | 3080 | 2930 | 1634 | 1539 | 1459 | 1263 |
| Control | 0.22 | 0.05 | 0.18 | 0.63 | 0.55 | 0.21 | 0.2 |
| Soil 12 | 0.14 | 0.03 | 0.1 | 0.34 | 0.25 | 0.12 | 0.11 |
| Soil 18 | 0.09 | 0.02 | 0.08 | 0.17 | 0.18 | 0.08 | 0.09 |
| Soil 24 | 0.05 | 0.01 | 0.07 | 0.11 | 0.1 | 0.05 | 0.04 |
| Compost 12 | 0.12 | 0.02 | 0.1 | 0.45 | 0.37 | 0.15 | 0.1 |
| Compost 18 | 0.04 | 0.00 | 0.04 | 0.04 | 0.04 | 0.02 | 0.01 |
| Compost 24 | 0.02 | 0.00 | 0.03 | 0.03 | 0.03 | 0.01 | 0.01 |
| Leachate 12 | 0.09 | 0.02 | 0.08 | 0.21 | 0.2 | 0.09 | 0.05 |
| Leachate 18 | 0.12 | 0.02 | 0.1 | 0.31 | 0.3 | 0.11 | 0.07 |
| Leachate 24 | 0.13 | 0.03 | 0.11 | 0.31 | 0.31 | 0.12 | 0.09 |

Another change observed was the disappearance of peaks at wavenumber 3080cm^{-1} (between wavenumbers 3294.5 and 2930.1cm^{-1} after 12, 18 and 24 months in soil and compost and increase of the peak intensities/ absorbance units as seen in fig. 6.16 A, B and C and Table 6.6 Cannon (1960) and Gonçalves et al.(2007) also observed the disappearance of the peak at 3080cm^{-1} after trying to degrade polyamides. They attributed it to an oxidation reaction of the stretching of C-N bonds and deformation of N-H bonds which causes the degradation of the PA discs. i.e., the transformation of (CO-NH-CH_2) monosubstituted amide groups to (CO-NH_2) non-substituted amide groups (Gonçalves et al. 2007).

Table 6. 7 The shift of FTIR peaks of (control) before degradation and degraded PA discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | | Leachate (cm ⁻¹) | | |
|---------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|---------------------------------|--------------|--------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks | 12 months | 18 Months | 24 months |
| PA-6 | 3295 | 3299 | 3301 | 3299 | 3299 | 3297 | 3299 | 3301 | 3301 | 3297 |
| | 2930 | 2928 | 2919 | 2919 | 2919 | 2919 | 2921 | 2932 | 2939 | 2927 |
| | 1633 | 1633 | 1638 | 1640 | 1634 | 1636 | 1638 | 1638 | 1638 | 1636 |
| | 1538 | 1539 | 1541 | 1541 | 1541 | 1541 | 1543 | 1544 | 1545 | 1541 |

Lastly, table 6.7 revealed another change observed from the spectra of PA-6 after degradation in soil, compost, and leachate after 12, 18, and 24 months. There was a progressive shift of the peaks to a higher and lower wavenumber than their control spectra. A shift of peaks of plastics to a higher or lower wavenumber causes an increase in vibrational frequency. There was a shift of all the PA-6 peaks to higher wavenumbers in soil, compost, and leachate at all control points except at wavenumber 2930cm⁻¹, which were had lower wavenumbers in the soil at the 12th, 18th, and 24th months, compost at 12th, 18th, and 24th months and leachate at 24th month. Shifting of the peaks away from a control wavenumber) depicts the degradation of these PA-6 discs.

All the changes observed after degradation of PA-6 discs in soil, compost, and leachate at the different wavenumbers are caused by hydrolysis and oxidation reaction from the action of microorganisms in these substrates used in this study (Chonde et al., 2012) and proved the change of the amides (-CONH-) functional groups of PA-6 polymer chains.

Polyethylene terephthalate (PET)

Figs. 6.18 A, B, and C reveal the FT-IR result of combined spectra of the PET discs before degradation and after degradation at 12, 18, and 24 months in soil, compost, and leachate in the UK. The control spectra of PET wavenumbers identified were at 1713, 1236, 1088, 870 and 724 cm⁻¹. They displayed differences in their spectra after degradation compared to the spectra of the control PET discs in the substrates used.

Table 6. 8 The Absorbance units of peaks of control and degraded PET discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| PET | Peak intensities/ Absorbance units | | | | | |
|--------------------|-------------------------------------------|-------------|-------------|-------------|-------------|-------------|
| Substrate/year | 1713 | 1452 | 1408 | 1238 | 1093 | 719 |
| Control | 0.42 | 0.03 | 0.12 | 0.46 | 0.41 | 0.45 |
| Soil 12 | 0.34 | 0.02 | 0.1 | 0.43 | 0.4 | 0.5 |
| Soil 18 | 0.05 | 0.01 | 0.02 | 0.05 | 0.05 | 0.06 |
| Soil 24 | 0.19 | 0.02 | 0.03 | 0.25 | 0.2 | 0.3 |
| Compost 12 | 0.22 | 0.03 | 0.06 | 0.28 | 0.28 | 0.33 |
| Compost 18 | 0.03 | 0.01 | 0.02 | 0.04 | 0.03 | 0.03 |
| Compost 24 | 0.02 | 0.01 | 0.01 | 0.03 | 0.02 | 0.02 |
| Leachate 12 | 0.12 | 0.03 | 0.04 | 0.15 | 0.15 | 0.17 |
| Leachate 18 | 0.03 | 0.02 | 0.01 | 0.05 | 0.05 | 0.06 |
| Leachate 24 | 0.02 | 0.01 | 0.01 | 0.04 | 0.02 | 0.04 |

Table 6.8 shows the reduction in the absorbance units at peaks of interest of all degraded PET discs at 12, 18 and 24 months compared to their peaks before degradation. All PET discs followed a trend in compost, and leachate (control>12 months>18 months>24 months), except in soil (control>12 months> 24 months> 18months). In compost and leachate, the peaks reduced after 12 months and had further reduction after 18 months and had the most reduction after 24 months. While in soil, the peaks of PET discs had most reduction after 18, following at 24 months and then the least reduction at 12 months, i.e., table 6.8, summarised that reduction in the peaks of degraded PET discs was uniform and more in leachate, then following in compost and then the soil from the UK.

All the peak intensities of all PET degraded discs reduced overtime except in soil at 12th month and at wavenumber 719cm^{-1} (where there was an increase from 0.45 control to 0.5).

Also, all PET peaks after degradation from 12-24 months directly correlate to the PET discs' peaks before degradation, except for some peaks of PET that disappeared at 18 and 24 months in all the substrates at wavenumbers between 1236 and 1088cm^{-1} .

Table 6. 9 The shift of FTIR peaks of (control) before degradation and degraded PET discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | | Leachate (cm ⁻¹) | | |
|---------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|---------------------------------|--------------|--------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks | 12 months | 18 Months | 24 months |
| PET | 1713 | 1718 | 1720 | 1720 | 1715 | 1718 | 1722 | 1718 | 1720 | 1720 |
| | 1453 | 1457 | 1459 | 1459 | 1461 | 1466 | 1464 | 1461 | 1464 | 1464 |
| | 1238 | 1243 | 1249 | 1247 | 1241 | 1260 | 1265 | 1241 | 1260 | 1265 |
| | 1093 | 1095 | 1097 | 1101 | 1093 | 1101 | 1106 | 1093 | 1097 | 1106 |
| | 719 | 724 | 728 | 725 | 728 | 726 | 730 | 724 | 726 | 733 |

Finally, table 6.9 revealed another change observed from the spectra of PET after degradation in soil, compost, and leachate after 12, 18, and 24 months. There was a progressive shift of all the PET peaks to a higher wavenumber after 12 months except at wavenumber 1093cm⁻¹ in compost and leachate, which remained at 1093cm⁻¹ further after 18 months and most after 24 months. All the changes observed from this PET FTIR results, including reduction of peaks intensities and disappearances of peaks at different wavenumbers, are caused by the ester bonds' autocatalytic hydrolysis reaction from the action of microorganisms in these substrates (Edge et al., 1991; Sang et al., 2020), which can change the carboxyl end groups (-COOH-) functional groups of PET chains.

Polypropylene (PP)

The FT-IR result, as shown in fig. 6.19 A, B, and C displayed the combined FTIR spectra of the PP before degradation and after degradation at 12, 18, and 24 months in soil, compost, and leachate in the UK. The control disc displayed its characteristic peaks at wavenumber: 2950-2837, 1745, 1456, 1375, 1167 and 995cm⁻¹, corresponding to C-H stretching, C=O stretching, CH₃ bending, CH₂ wagging, and asymmetric CH₃ bonds, respectively.

Some changes were observed from the degraded discs' spectra compared to the control disc in the substrates used. Figs. 6.19 A, B and C all revealed a slight reduction in the intensities of all the peaks of the PP spectra after degradation at 12th month and further reduction at 18th and 24th months in all the substrates except at wavenumber 2917cm⁻¹ for 12th and 18th month in soil which had their peaks more in height than the control peaks.

Table 6. 10 The shift of FTIR peaks of (control) before degradation and degraded PP discs in soil, compost, and leachate after 12, 18, and 24 months in the UK .

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | | Leachate (cm ⁻¹) | | |
|---------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|---------------------------------|--------------|--------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks | 12 months | 18 Months | 24 months |
| PP | 2949 | 2950 | 2952 | 2950 | 2950 | 2952 | 2952 | 2950 | 2952 | 2957 |
| | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2921 |
| | 2866 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | 2837 | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | - | 2850 | 2850 | 2853 | 2850 | 2850 | 2850 | 2850 | 2848 | 2848 |
| | 1456 | 1459 | 1457 | 1459 | 1457 | 1459 | 1459 | 1461 | 159 | 1464 |
| | 1377 | 1377 | 1377 | 1377 | 1377 | 1377 | 1377 | 1377 | 1377 | 1364 |

ND -Not Detected

The shift of some peaks of the PP spectra as observed after degradation. from the table 6.10, at wavenumbers; 2949, 2919, 2866, 2837, 1456 and 1377cm⁻¹. The shifts to a higher wavenumber in degraded PP peaks only occurred at wavenumbers; 2949, 2837, and 1456cm⁻¹, while no shift was recorded at wavenumbers: 2919 and 1377cm⁻¹ in all substrates. The reason is that the peaks of degraded PP discs at this wavenumber remained the same as those of control PP discs.

Also, there were four peaks at wavenumbers: 2949, 2919, 2866, and 2837cm⁻¹, corresponding to C-H stretch functional groups in the control PP spectra, as seen in figs. 6.19 A, B and C and Table 6.10. The peaks at wavenumber 2866 and 2837cm⁻¹ disappeared from the spectra of the degraded PP discs at 12, 18, and 24 months in all substrates; also, new peaks appeared at wavenumbers: 2850cm⁻¹ at 12, 18, and 24 months in all substrates, mostly in leachate. Fig. 6.19 C. There was an appearance of a broad and weak peak at hydroxyl region at wavenumber 3450 cm⁻¹ of PP discs in the leachate at 12th and 18th month and the weak peak in the carbonyl region at wavenumber 1720cm⁻¹ of PP control discs became more prominent with time in all the substrates as seen in fig. 6.19.

The disappearance and formation of these new peaks after degradation in soil, compost, and leachate suggested the microorganisms present in the substrates attacking the polar groups of PP, making the discs more susceptible to microbial degradation with time. Therefore, the appearance of the broad peaks of PP at the hydroxyl group in leachate was due to the surrounding intermolecular hydrogen-bonded hydroperoxides and alcohols. In contrast, the prominent peaks at the carbonyl regions of ketones occurred compared to the control PP spectra is caused by the oxidation process, leading to oxidative degradation of PP discs (Moldovan et al., 2012).

Polyethylene (PE):

Figs. 6.20 and 6.21 reveal the FTIR spectra of HDPE and LDPE plastic discs, respectively. HDPE and LDPE share some properties due to the same methyl group (C-H bonding) linked together and Figs. 6.20 and 6.21 hence reveal their characteristic peaks before and after degradation in soil, compost, and leachate at wavenumbers: 2914, 2846, 1467, 1461, 730 and 718cm^{-1} . However, the only difference between their characteristic peaks is the extra small peak at 1377cm^{-1} because of the more methyl group in the branched LDPE. This additional methyl group in LDPE chains also brings about their different properties (Nishikida and Coates, 2003; Asensio et al., 2009).

High-Density Polyethylene (HDPE):

Here are some changes displaying the combined FTIR spectra of the HDPE discs before degradation and after degradation at 12, 18, and 24 months in soil, compost, and leachate in the UK, as seen in (fig. 6.20 A, B and C).

Firstly, there was a reduction of peaks and absorbance of peaks after 12 months in soil, compost, and leachate, further reduction after 18 months, and most reduction occurred after 24 months. Reduction of peaks follows this trend: Control > 12 > 18 > 24 months except in compost where HDPE degraded peaks had least reduction at 24th month after control HDPE discs at wavenumbers 2919 and 2848cm^{-1} in this trend: Control > 24 > 12 > 18 months.

Secondly, there was the formation of new broad peaks at wavenumber 3450cm^{-1} for all the HDPE discs buried in soil, compost, and leachate (fig. 6.20 A, B, and C) and from wavenumbers: $1710\text{-}1500\text{cm}^{-1}$ in all the degraded HDPE discs in all substrates after 12, 18 and 24 months. On the other hand, small and weak peaks were lost, giving rise to a broad peak from wavenumbers $1000\text{-}1750\text{cm}^{-1}$ after 12, 18, and 24 months in soil and compost and spectra with new and many small peaks at the 18th month in leachate.

Table 6.11 displays the major HDPE control disc at wavenumbers: 2919, 2848, 1461, 719cm^{-1} . There was a slight shift of peaks to higher wavenumber region as observed from the spectra of the HDPE degraded discs. In the soil, at wavenumbers: 2919 and 2848cm^{-1} , there was no peak shift after 12 months. However, there was a shift to the wavenumber of 2921cm^{-1} after 18 and 24 months and to wavenumbers of 2851 and 2853cm^{-1} . There was no shift at wavenumber 1461cm^{-1} in all the substrates over 24 months except in leachate at 24 months, where the shift occurred from $1461\text{-}1466\text{cm}^{-1}$.

Table 6. 11 The shift of FTIR peaks of (control) before degradation and degraded HDPE and LDPE discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | | Leachate (cm ⁻¹) | | |
|-------------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|---------------------------------|--------------|--------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks | 12 months | 18 Months | 24 months |
| HDPE | 2919 | 2919 | 2921 | 2921 | 2921 | 2919 | 2919 | 2919 | 2919 | 2919 |
| | 2848 | 2848 | 2851 | 2853 | 2853 | 2851 | 2848 | 2848 | 2851 | 2851 |
| | 1461 | 1464 | 1464 | 1464 | 1464 | 1464 | 1464 | 1464 | 1464 | 1466 |
| | 719 | 719 | 719 | 721 | 719 | 719 | 721 | 719 | 719 | 719 |
| LDPE | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2917 | 2915 |
| | 2848 | 2851 | 2851 | 2848 | 2851 | 2851 | 2851 | 2848 | 2848 | 2853 |
| | 1464 | 1466 | 1466 | 1468 | 1464 | 1466 | 1466 | 1466 | 1468 | 1466 |
| | 1377 | 1379 | 1379 | 1381 | 1379 | 1383 | 1385 | 1379 | 1381 | 1386 |
| | 719 | 724 | 719 | 724 | 722 | 722 | 722 | 722 | 722 | 724 |

Low-Density Polyethylene (LDPE):

Fig. 6.21 A, B, and C revealed the spectra of the LDPE discs before and after degradation in soil, compost, and leachate in the UK. There were differences in the peaks. Contrasting the intensities of degraded HDPE peaks that reduced with time in all the substrates, the intensities of LDPE peaks increased with time higher than the control LDPE discs in all the substrates. It follows this trend: 24>18>12months>control samples. Degraded peaks after 24 months had the highest reduction of peaks, followed by after 18 months and then 12 months. While the control LDPE had the least peaks, i.e., an increase in the intensities of degraded peaks of LDPE discs also increased the absorbance of the peaks with increased time in the substrates as compared with the control peaks before degradation.

There was little, or no shifting of the peaks of LDPE degraded discs as seen in table 6.11, though the methyl group at 1377cm⁻¹, which differentiated LDPE from HDPE, all experienced shift to higher wavenumber over time in all the substrates used. Weak peaks formed at wavenumber 1710–1715 cm⁻¹, which corresponded to the carbonyl group and was due to the hydrolysis process. There was the formation of a broad peak at wavenumber 3450cm⁻¹ and broad new peaks which became stronger with time in the substrates from wavenumbers: 1710 - 1500cm⁻¹, and 1370 - 1000cm⁻¹ for all the degraded LDPE discs in the substrates in this trend: 24>18>12months>control samples. The observed broad peaks at the hydroxyl group were due to the vibrations in the stretching of the neighbouring intermolecular O-H bond in alcohols (Bhatia et al., 2014). At the same time, the observed wavenumbers: 1710 - 1500, and 1379 -

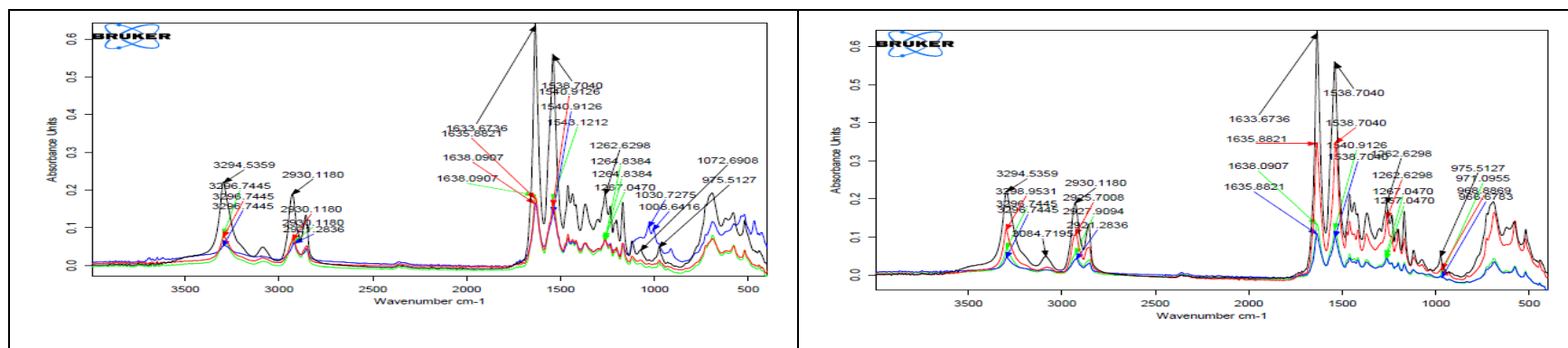
1000 cm^{-1} were attributed to the deformation of C-O and C-H due to the effect of activity microorganisms in the substrates, which caused degradation of these discs.

All the changes observed from the degraded to the peaks of the HDPE and LDPE buried in soil and compost and submerged in leachate are due to hydrolysis/oxidation of their main polymer chain, which is caused by a microbial attack from the substrates (Bhatia et al., 2014).

6.6.6.2 Fourier Transform Infrared (FT-IR) of plastics buried in Nigeria

Polyamide 6 (PA-6).

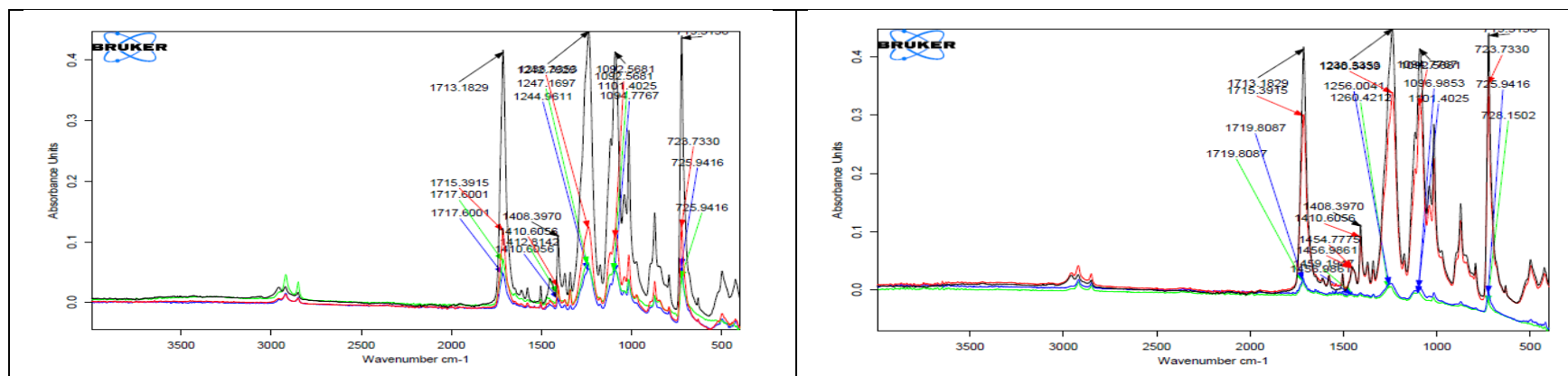
The FT-IR result, as shown in fig. 6.22 A and B displayed combined spectra of PA-6 before and after degradation at 12, 18, and 24 months in soil and compost in Nigeria. While fig. 6.22 A is spectra of control and degraded PA discs in soil, fig. 6.22 B is spectra of control and degraded PA-6 discs in compost as seen in (fig. 6.22 A, and B), the control spectra of PA-6 discs showed some peaks reflecting PA at wavenumbers; 3294, 3080, 2930, 2858, 1633, 1538, 1459, 1262 and 975cm^{-1} .



A

B

Fig. 6.22 FTIR spectra of the degraded PA discs (black peak shows original PA-6, red peak shows PA after 12 months, blue peak shows PA after 18 months, and green peak shows PA after 24 months) buried in media, namely, (A) soil, and (B) compost for 12, 18 and 24 months in Nigeria.



A

B

Fig. 6.23 FTIR spectra of the degraded PET discs (black peak shows original PET, red peak shows PET after 12 months, blue peak shows PET after 18 months, and green peak shows PET after 24 months) buried in media, namely, (A) soil, and (B) compost for 12, 18 and 24 months in Nigeria.

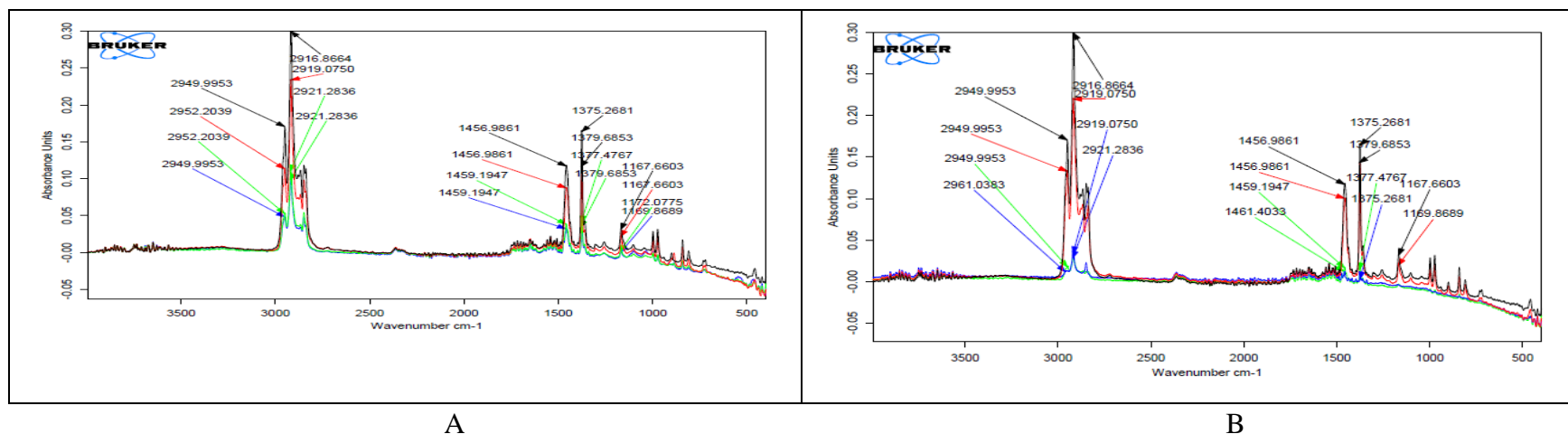


Fig. 6.24 FTIR spectra of the degraded PP discs (black peak shows original PP, red peak shows PP after 12 months, blue peak shows PP after 18 months, and green peak shows PP after 24 months) buried in media, namely, (A) soil, and (B) compost for 12, 18 and 24 months in Nigeria.

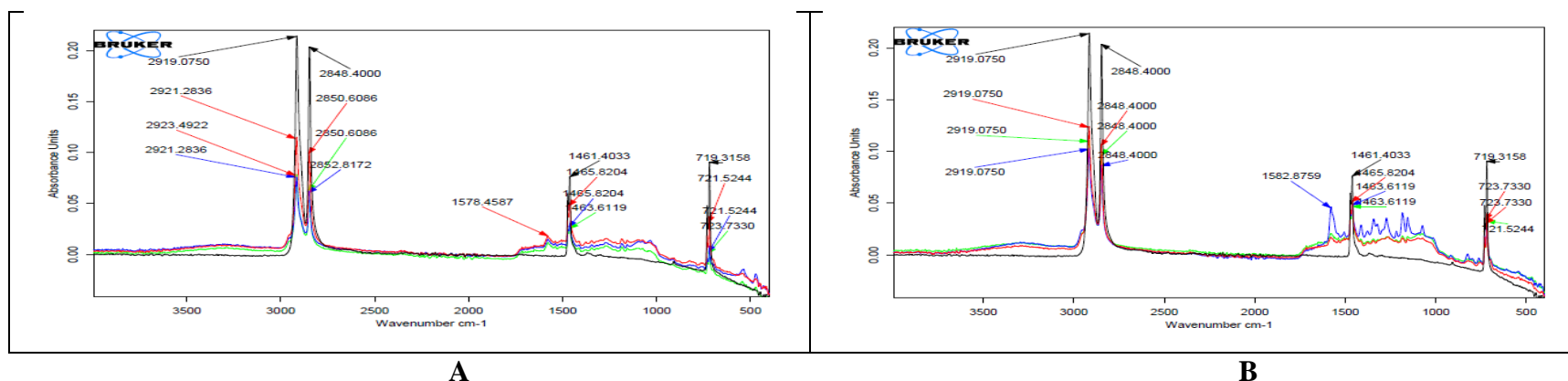


Fig. 6.25 FTIR spectra of the degraded HDPE discs (black peak shows original HDPE, red peak shows HDPE after 12 months, blue peak shows HDPE after 18 months, and green peak shows HDPE after 24 months) buried in media, namely, (A) soil, and (B) compost for 12, 18 and 24 months in Nigeria.

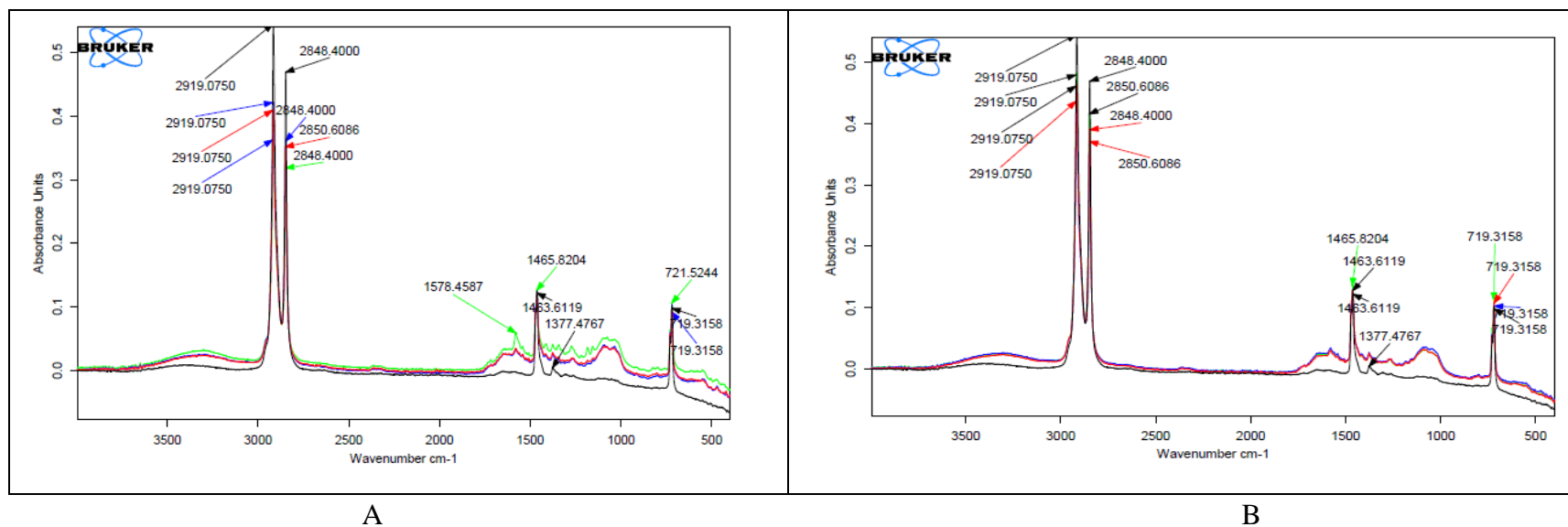


Fig. 6.26 FTIR spectra of the degraded LDPE discs (black peak shows original LDPE, red peak shows LDPE after 12 months, blue peak shows LDPE after 18 months, and green peak shows LDPE after 24 months) buried in media, namely, (A) soil, and (B) compost for 12, 18 and 24 months in Nigeria.

However, the differences noted in the spectra of degraded PA discs when compared to the spectra of the control PA discs are as follows. There were reduction in the peak intensities, as seen in fig. 6.22 A and B as well as reduced absorbances (table 6.12) of their functional groups. The result depicts reduction, broadening, and shifts of all the peaks with a decrease in their functional groups' absorbances and sidechain peaks in both soil and compost.

Table 6. 12 The Absorbance units of peaks of control and degraded PA-6 discs in soil, and compost after 12, 18, and 24 months in Nigeria.

| PA-6 | Peak intensities/ Absorbance units | | | | | | |
|-------------------|------------------------------------|-------------|-------------|-------------|-------------|-------------|------------|
| | 3294 | 3080 | 2930 | 1634 | 1539 | 1459 | 1263 |
| Control | 0.22 | 0.05 | 0.18 | 0.63 | 0.55 | 0.21 | 0.2 |
| Soil 12 | 0.06 | 0.01 | 0.05 | 0.15 | 0.12 | 0.04 | 0.03 |
| Soil 18 | 0.05 | ND | 0.04 | 0.13 | 0.12 | 0.03 | 0.03 |
| Soil 24 | 0.04 | ND | 0.04 | 0.12 | 0.12 | 0.03 | 0.02 |
| Compost 12 | 0.12 | 0.01 | 0.1 | 0.35 | 0.35 | 0.15 | 0.13 |
| Compost 18 | 0.07 | ND | 0.04 | 0.11 | 0.1 | 0.02 | 0.02 |
| Compost 24 | 0.05 | ND | 0.05 | 0.12 | 0.11 | 0.03 | 0.03 |

ND -Not Detected

Table 6.12 revealed the reduction in peaks intensities and the decrease in absorbances of the peaks at all points of interest of the degraded PA discs in soil and compost. In this reduction of the peak intensities, all degraded PA discs followed a trend in soil (control>12 months>18 months>24 months) while compost reduction took this trend: (control>12 months>24 months>18 months). In soil, the peaks reduced after 12 months and had further reduction after 18 months and had the most reduction after 24 months, while in compost, the peaks of PA discs had the most reduction after 18, following at 24 months and then the least reduction at 12 months. Figs. 6.22 A and B and Table 6.13 displayed the disappearance of the peak at wavenumber: 3084cm⁻¹ after 12 months in soil and compost.

Table 6. 13 The shift of FTIR peaks of (control) before degradation and degraded PA-6 discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | |
|-----------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks |
| PA | 3295 | 3297 | 3297 | 3297 | 3299 | 3297 | 3297 |
| | 2930 | 2930 | 2930 | 2921 | 2926 | 2928 | 2921 |
| | 1633 | 1636 | 1638 | 1638 | 1636 | 1638 | 1636 |
| | 1538 | 1541 | 1541 | 1543 | 1538 | 1541 | 1539 |

Table 6.13 revealed one more change observed from the spectra of PA-6 discs after degradation in soil and compost after 12, 18, and 24 months. There was a progressive shift of all degraded peaks to a higher and lower wavenumber than their control spectra. We observed a shift of peaks to a higher or lower wavenumber in soil and compost after 12 months except at wavelength 2930cm^{-1} in soil, which remained constant till after 18 months and at a wavenumber 1538cm^{-1} in compost which remained at 1538cm^{-1} until after 12 months. The reason for the shift in peaks of PA-6 degraded discs was because of the increase in the vibrational frequency caused by hydrolysis and oxidation reaction from the action of microorganisms in these substrates

Polyethylene terephthalate (PET)

Fig. 6.23 A and B displays the FT-IR result of combined spectra of the PET discs before degradation and after degradation at 12, 18, and 24 months in soil and compost in Nigeria. The control spectra of PET wavenumbers identified were at 1713 , 1236 , 1088 , 870 and 724 cm^{-1} which displayed differences in their spectra after degradation when compared to the spectra of the control PET discs in the substrates used. Therefore, after 12, 18, and 24 months of degradation, all the PET peaks directly correlate to the PET discs' peaks before degradation. Except for some peaks of PET that disappeared after 18 and 24 months in soil and compost at wavenumbers between 1236 and 1088cm^{-1} as seen in fig. 6.23 A and B. Also, all peaks between 1713 and 1238cm^{-1} after 18 and 24 months disappeared in compost.

Fig. 6.23A and B reveal the reduction of all peaks of degraded PET discs both in soil and in compost, while table 6.14 shows the reduction in the absorbance at peaks of interest of all degraded PET discs at 12, 18 and 24 months.

Table 6. 14 The Absorbance units of peaks of control and degraded PET discs in soil and compost after 12, 18, and 24 months in Nigeria.

| PET | Peak intensities/ Absorbance units | | | | | |
|-------------------|------------------------------------|-------------|-------------|-------------|-------------|-------------|
| Substrate/year | 1713 | 1453 | 1408 | 1238 | 1093 | 719 |
| Control | 0.42 | 0.04 | 0.12 | 0.46 | 0.41 | 0.45 |
| Soil 12 | 0.12 | 0.02 | 0.03 | 0.13 | 0.12 | 0.13 |
| Soil 18 | 0.05 | 0.01 | 0.01 | 0.06 | 0.05 | 0.06 |
| Soil 24 | 0.07 | 0.02 | 0.02 | 0.08 | 0.07 | 0.08 |
| Compost 12 | 0.29 | 0.04 | 0.1 | 0.34 | 0.32 | 0.35 |
| Compost 18 | 0.03 | ND | ND | 0.04 | 0.03 | 0.02 |
| Compost 24 | 0.02 | ND | ND | 0.03 | 0.02 | 0.01 |

ND -Not Detected.

All PET discs followed a trend in soil (control>12 months>24 months>18 months) and in compost, (control>12 months> 18 months> 24 months). The peaks of PET discs had the most

reduction after 18 months, following at 24 months and then the least reduction at 12 months while in compost, the peaks reduced after 12 months and had further reduction after 18 months and had most reduction after 24 months.

Table 6. 15 The shift of FTIR peaks of (control) before degradation and degraded PET discs in soil, compost, and leachate after 12, 18, and 24 months in the UK.

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | |
|------------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks |
| PET | 1713 | 1715 | 1718 | 1718 | 1715 | 1720 | 1720 |
| | 1453 | 1457 | 1459 | 1461 | 1456 | ND | ND |
| | 1408 | 1411 | 1413 | 1411 | 1411 | ND | ND |
| | 1238 | 1239 | 1245 | 1247 | 1241 | 1256 | 1260 |
| | 1093 | 1093 | 1094 | 1101 | 1093 | 1097 | 1101 |
| | 719 | 724 | 726 | 726 | 724 | 726 | 728 |

ND -Not Detected

Table 6.15 reveals the shift of PET peaks toward a higher wavenumber after degradation at the 12th, 18th, and 24th months in soil and compost. With an exception at wavenumber 1093cm⁻¹ in soil and compost, which remained at 1093cm⁻¹ after 12 months then shifted to a higher wavenumber after 18 months and most after 24 months. All these changes seen from this PET FTIR results include reduction of peaks intensities and absorbances, disappearances of peaks. Finally, we attribute the shift of peaks to the degradation by microorganisms available in soil and compost.

Polypropylene (PP)

The FT-IR result, as shown in fig. 6.24 A and B presented the combined FTIR spectra of the PP before degradation and after degradation at 12, 18, and 24 months in soil and compost in Nigeria, with the control disc displaying its characteristic peaks at wavenumber: 2950-2837, 1745, 1456, 1375, 1167 and 995cm⁻¹.

There were few changes observed from the spectra of the degraded PP discs in soil and compost. One of the changes was a reduction in the intensities of all PP spectra after degradation in soil and compost. Most especially in the soil at wavenumber: 2866cm⁻¹ after 12 months and compost at 2950cm⁻¹ after 18 and 24 months, as seen in fig. 6.24 A, and B. In soil, reduction of peak intensities took this trend, peak at 12th month having the least reduction following a peak at 24th month, 18th months which showed the most reduction. While in compost, peak at 12th month had the least reduction following a peak at 18th month, then at

24th month PP degraded peak showed the most reduction. This reduction of peak intensities also agrees with the reduction of the peak absorbances. For example, the absorbance unit for the control PP peak at 2917cm^{-1} in both soil and compost is 0.3. In soil, that reduced to 0.23 after 12 months, had a further reduction to 0.09 after 18 months, then to 0.11 after 24 months (control>12months>24months>18months) while in compost, the absorbance unit for the control PP peak reduced to 0.22 after 12 months, then further reduced to 0.03 after 18months and finally reduced to 0.02 after 24 months in this format.

Table 6. 16 The FTIR shift of peaks of PP discs in soil and compost after 12, 18, and 24 months in Nigeria.

| Plastic | Control (cm^{-1}) | Soil (cm^{-1}) | | | Compost (cm^{-1}) | | |
|---------|---------------------------------|------------------------------|--------------|--------------|---------------------------------|--------------|-------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks |
| PP | 2950 | 2952 | 2952 | 2950 | 2950 | 2950 | 2961 |
| | 2917 | 2919 | 2921 | 2921 | 2917 | 2919 | 2921 |
| | 2866 | 2866 | ND | ND | 2869 | ND | ND |
| | 2837 | ND | ND | ND | 2839 | ND | ND |
| | New | 2850 | 2853 | 2853 | ND | 2855 | 2855 |
| | 1457 | 1457 | 1459 | 1459 | 1457 | 1459 | 1461 |
| | 1375 | 1380 | 1377 | 1380 | 1380 | 1375 | 1377 |
| | 1168 | 1168 | 1170 | 1172 | 1170 | ND | ND |

Also, from table 6.16, we observed that peaks at wavenumber: 2866cm^{-1} disappeared in both soil and compost after 18 and 24 months. At 2837cm^{-1} after 12, 18 and 24 months in soil and after 18 and 24 months in compost. Not only did some peaks disappear, but we observed new peaks formed at 2850cm^{-1} after 12 months in soil which had a shift to higher wavenumber after 18 and 24 months in both soil and compost. It can be seen from table 6.16 the slight shift of some peaks of the PP spectra after degradation to a higher wavenumber or no shift in soil and compost.

Polyethylene (PE)

Figs. 6.25 and 6.26 reveal the FTIR spectra of HDPE and LDPE plastic discs before degradation and after degradation in Nigeria, respectively. Because HDPE and LDPE share some properties, their control discs also display their characteristic peaks at wavenumbers: 2919, 2848, 1461, 719cm^{-1} with an additional peak at 1377cm^{-1} , which brings about their

differences in their properties for LDPE. (Nishikida and Coates, 2003; Asensio et al., 2009; Brandon et al., 2016).

High-Density Polyethylene (HDPE):

Fig. 6.25 A and B reveal the changes observed in degraded HDPE discs in soil and compost. These changes include reducing peaks and absorbance of peaks, shifts of peaks to a higher wavenumber, and formation of both broad, weak, and prominent peaks.

In soil, peaks reduced after 12 months, and further reduced after 18 months and had most reduction after 24 months, i.e., the reduction of peaks in soil follows this trend: Control > 12 > 18 > 24 months while in compost, HDPE degraded peaks had least reduction of peaks after 18 months, followed degraded discs after 24 months, then after 12 months which had the most reduction in peaks. in this trend: Control > 18 > 24 > 12 months.

Secondly, Table 6.17 displays the slight shift of degraded HDPE discs to peaks to a higher wavenumber region as seen from the spectra of the HDPE degraded discs (Figs. 6.25 A and B). In the soil, there was a shift in all the peaks. While in compost, there were shifts of all peaks except at wavenumbers: 2919 and 2848 cm^{-1} . There was the formation of new broad peaks at wavenumbers 3450 cm^{-1} and 1710-1500 cm^{-1} for all the HDPE discs after 12, 18 and 24 months in soil and compost (fig. 6.25 A, and B). Finally, New peaks formed and shifted accordingly to wavenumbers 1578, 1580 and 1582 cm^{-1} after 12, 18 and 24 months in soil, respectively. At the same time, the new peaks formed and shifted accordingly to wavenumbers 1575, 1584 and 1582 cm^{-1} after 12, 18 and 24 months in compost, respectively, with a peak after 18 months most prominent. The shift of the new peaks to a higher wavenumber in soil and compost over time also agreed with the changes notated on the degraded peaks.

Table 6. 17 The FTIR shift of peaks of HDPE and LDPE discs in soil and compost after 12, 18, and 24 months in Nigeria.

| Plastic | Control (cm ⁻¹) | Soil (cm ⁻¹) | | | Compost (cm ⁻¹) | | |
|-------------|--------------------------------|-----------------------------|--------------|--------------|--------------------------------|--------------|-------------|
| | | 12 months | 18 months | 24 months | 12 months | 18 months | 24 weeks |
| HDPE | 2919 | 2921 | 2923 | 2921 | 2919 | 2919 | 2919 |
| | 2848 | 2851 | 2851 | 2853 | 2848 | 2848 | 2848 |
| | New | 1578 | 1583 | 1586` | 1575 | 1583 | 1584 |
| | 1461 | 1466 | 1466 | 1464 | 1466 | 1464 | 1464 |
| | 719 | 722 | 722 | 724 | 722 | 724 | 724 |
| LDPE | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 | 2919 |
| | 2848 | 2848 | 2848 | 2851 | 2848 | 2851 | 2851 |
| | 1377 | 1379 | 1381 | 1384 | 1377 | 1379 | 1379 |
| | New | 1575 | 1575 | 1578 | 1575 | 1575 | 1575 |
| | 1464 | 1466 | 1466 | 1466 | 1464 | 1464 | 1466 |
| | 719 | 719 | 722 | 722 | 719 | 719 | 719 |

Low-Density Polyethylene (LDPE):

Fig. 6.26 A and B revealed the spectra of LDPE discs before and after degradation in soil and compost in Nigeria. The peaks after degradation revealed some differences compared to before degradation with a slight reduction of the degraded LDPE peaks in soil and compost at their characteristic peaks of interest: 2919, 2848, 1461 and 719cm⁻¹ over time. The trend in the reduction of the LDPE peaks in the soil was control>18months>12months>24months while in compost, the trend goes like control>24months>12months>18months. Degraded peaks after 24 months had the highest reduction of peaks in the soil, while degraded peaks after 18 months had the highest reduction, and the control LDPE peaks had the least peaks.

There was a slight shifting of the peaks of LDPE degraded discs, as seen in table 6.17 in both soil and compost. Most especially at wavenumbers 2848cm⁻¹ after 24 months, 1464 and 1377cm⁻¹ after 12, 18 and 24 months, then at 719cm⁻¹, after 18 and 24 months, all on Nigerian soil. In compost, we observed a slight shift of peaks at wavenumbers 2848cm⁻¹ after 18 and 24 months, 1464cm⁻¹ after 24 months, and 1377cm⁻¹ after 18 and 24 months. Also, there were broad new peaks after 12, 18 and 24 months at wavenumber 3450cm⁻¹ and 1710–1510cm⁻¹ in soil and compost with a peak after 24 months being most prominent in soil and peak after 18 months was most apparent in compost. This formation of new peaks on degraded LDPE discs is caused by hydrolysis and corresponds to hydroxyl and carbonyl groups. Ohtake et al. (1998)

also observed a peak at wavenumber 1640cm^{-1} around degraded LDPE plastics buried in agricultural fields and garden soil. Shovitri et al. (2017) concluded that after burying plastics in beach sand and mangrove sediments for over 16 weeks, there was a reduction of peaks that indicated changes in the functional groups of the plastics. Bhatia et al. (2014) suggested that the broad peaks at the hydroxyl group were due to the vibrations in the stretching of the neighbouring intermolecular O-H bond in alcohols.

All the changes observed from the degraded to the peaks of the HDPE and LDPE buried in soil and compost are caused by hydrolysis/oxidation of their functional groups generated by the microbial attack in the substrates (Bhatia et al., 2014).

6.6.7 Determination of the Carbonyl Index of the plastics

We examined the carbonyl index of plastics as the mean value of different FTIR spectra for each plastic to further understand the effect of degradation on their functional groups, such as the carbonyl groups. The measured carbonyl groups are expressed as a carbonyl index (CI) and were calculated for both the control and the degraded plastics. Figs. 6.27 and 6.28 reveal the CI result obtained after degraded plastics after 12, 18 and 24 months in soil, compost, leachate for the UK and soil, and compost for Nigeria. The results obtained in fig. 6.27 and 6.28 reveal the idea of oxidation and hydrolysis of plastics discs (Ratanakamnuan, & Aht-Ong, 2006; Ojha et al. 2017; Almond et al. 2020). The plots of CI of plastics; PA-6, PET, PP, HDPE, and LDPE buried in soil, and compost, and placed leachate in the UK are revealed in fig. 6.27.

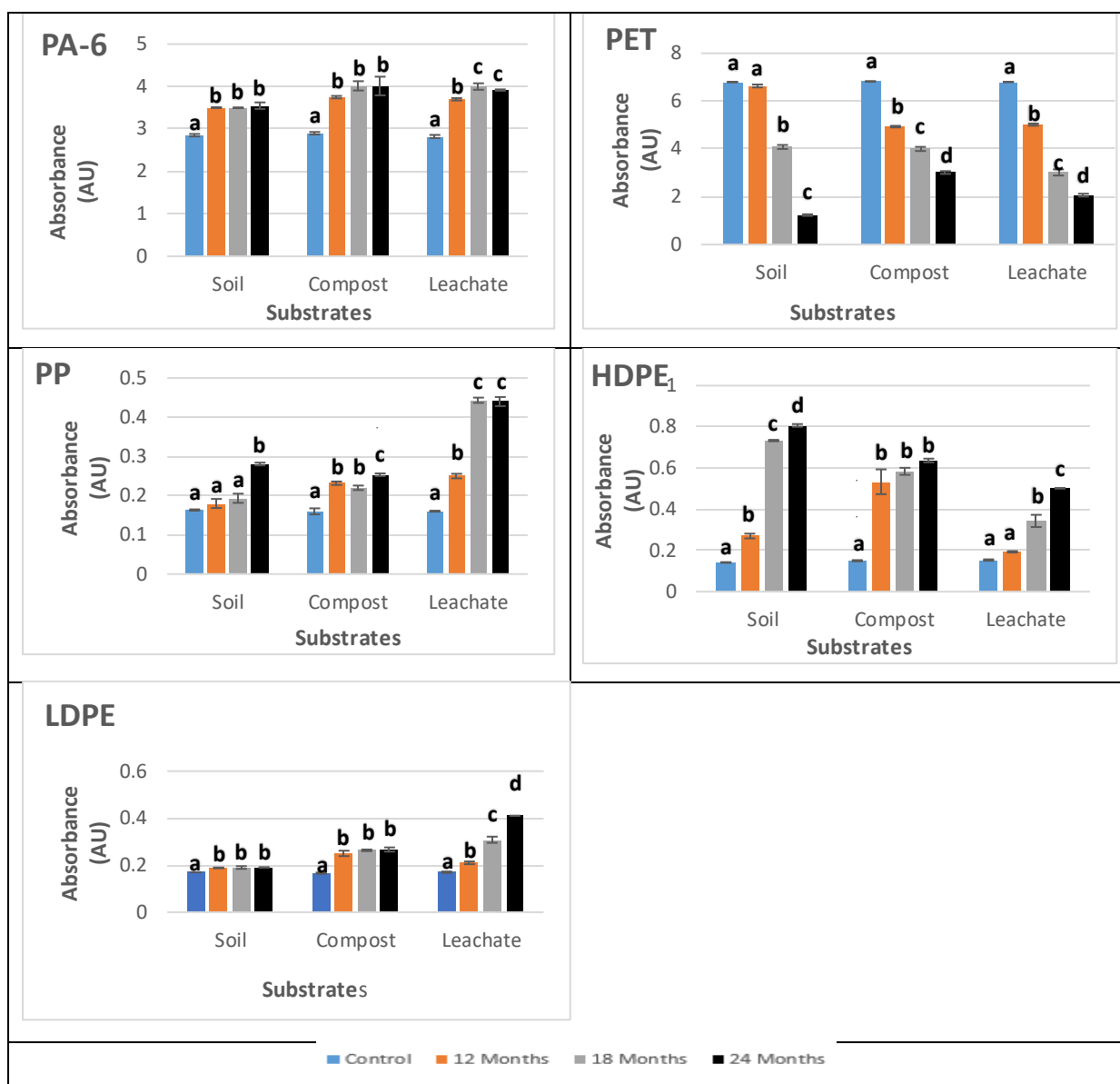


Fig. 6.27 Plots of the carbonyl indices of the plastics discs: PA-6, PET, PP, HDPE, and LDPE after 12, 18 and 24 months in soil, compost, and leachate in the United Kingdom. *Y-Axis values differ. Data represents mean \pm SE (n = 3). Means with the same letter are not significantly different.

Adding PA-6, PET, PP, HDPE, and LDPE plastics in soil, compost, and leachate, respectively, influenced plastics' chemical structure and physical properties. One of the effects of burying plastics in substrates was observed on the carbonyl indices of the plastics.

As shown in fig. 6.27, the average CI values of plastics, PA-6, PP, HDPE, and LDPE before degradation were 2.9, 0.16, 0.15, and 0.17; they increased over time in the substrates. The average CI values of these plastics did not only increase in the substrates over time but are all statistically different ($P < 0.05$). This increase in the average CI took the same trend with PA-6, PP, HDPE, and LDPE. On the contrary, the CI plot of PET displayed an opposite result, suggesting that the average CI values decreased over time in soil, compost, and leachate, respectively. Before degradation, the average CI of PET discs was 6.8 for soil, compost, and

leachate. The average CI of degraded PET discs decreased over time in the substrates. The reduction in CI of PET discs after 24 months was two times less than the CI values of the PET discs before degradation. The reason for the increase and reduction of the average CI of these plastics was due to the oxidation, hydrolysis and reduction of their functional groups over time, probably because of microorganisms and other environmental factors causing chain scission and depletion of their functional groups also leading to more degradation in the plastics (Vague et al., 2019; Canopoli et al., 2020). The more time the plastics stayed in these substrates, the more effect on their CI. Therefore, statistically, the CI of all these plastics were significantly affected with time in substrates. For fig.6.27 statistically, substrates, time and plastic types had significant influence on plastics' CI (substrate: $F= 30.251$, $P<0.05$; time: $F= 522.874$, $P<0.05$; plastic type: $F= 24210.725$, $P<0.05$). Table 6.18 below summarises the ANOVA results of the plastics between groups in the UK.

Table 6. 18 Showing the ANOVA results of the average CI of plastics buried and places in soil, compost, and leachate in the UK.

| PLASTICS | SUBSTRATES | ANOVA RESULT |
|----------|------------|--------------------------|
| PA-6 | Soil | $F= 6.056$, $P<0.05$ |
| | Compost | $F= 18.069$, $P<0.05$ |
| | Leachate | $F= 139.881$, $P<0.05$ |
| PET | Soil | $F= 2330.876$, $P<0.05$ |
| | Compost | $F= 889.557$, $P<0.05$ |
| | Leachate | $F= 811.887$, $P<0.05$ |
| PP | Soil | $F= 38.240$, $P<0.05$ |
| | Compost | $F= 50.348$, $P<0.05$ |
| | Leachate | $F= 377.201$, $P<0.05$ |
| HDPE | Soil | $F= 2231.980$, $P<0.05$ |
| | Compost | $F= 49.970$, $P<0.05$ |
| | Leachate | $F= 111.366$, $P<0.05$ |
| LDPE | Soil | $F= 5.867$, $P<0.05$ |
| | Compost | $F= 39.751$, $P<0.05$ |
| | Leachate | $F= 187.816$, $P<0.05$ |

Fig. 6.28 reveals the Plot of carbonyl indices of plastics before and after degradation in soil and compost in Nigeria. Burying plastics; PA-6, PET, PP, HDPE, and LDPE in soil and compost had effects on the properties of the plastics.

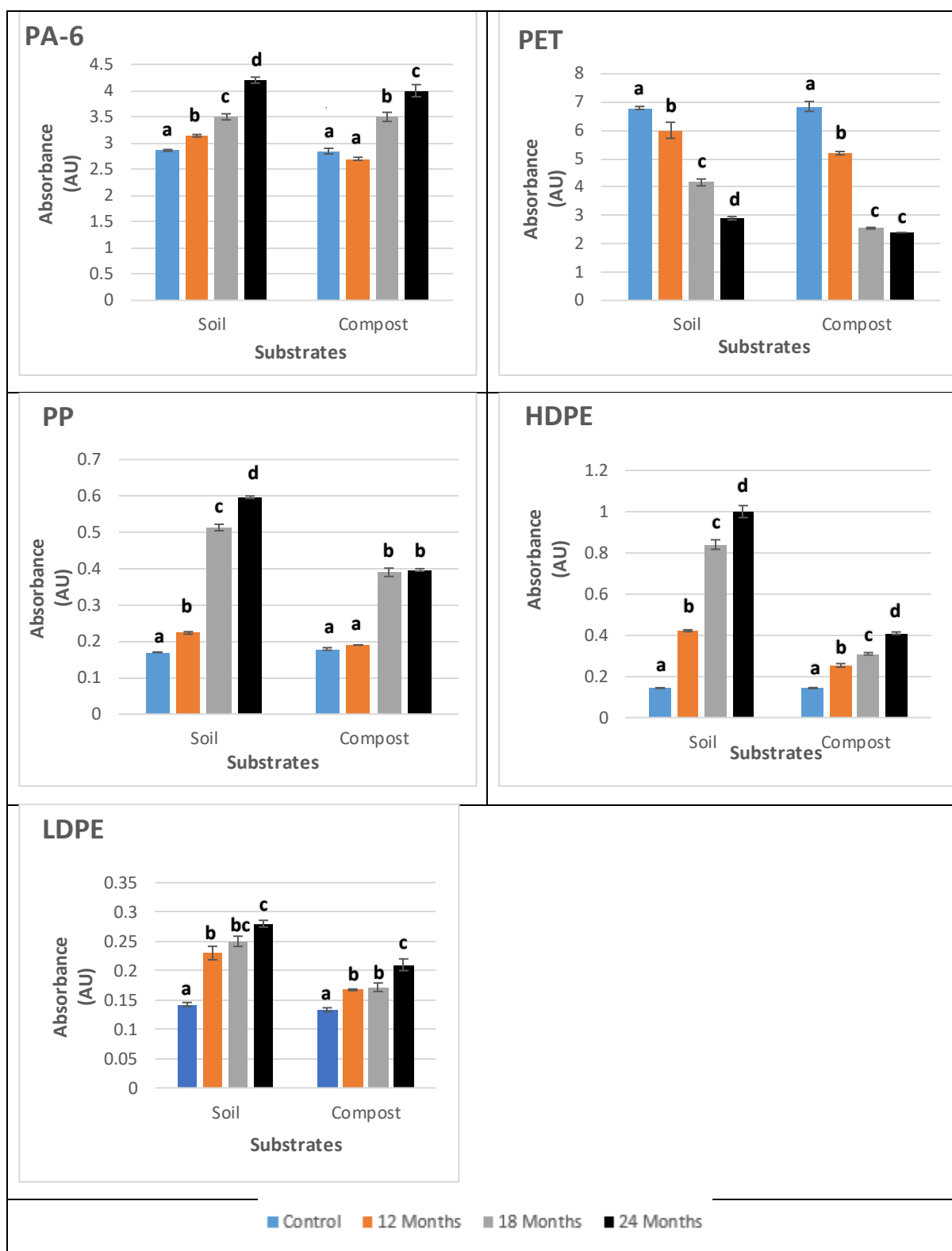


Fig. 6.28 Plots of the carbonyl indices of the plastics discs: PA-6, PET, PP, HDPE, and LDPE after 12, 18 and 24 months in soil, and compost in Nigeria. *Y-Axis values differ. Data represents mean±SE (n=3). Means with the same letter are not significantly different.

The average CI values of plastics, PA-6, PP, HDPE, and LDPE before degradation were 2.9, 0.16, 0.15, and 0.17, respectively, and increased over time in soil and compost. The average CI

values of PA-6, PP, HDPE, and LDPE in all substrates were significantly different ($P < 0.05$). This increase in the average CI of PA-6, PP, HDPE, and LDPE was also similar. Here, the increase in the CI values of PA-6, PP, HDPE, and LDPE was uniform over the years of study in substrates except for PA-6 after 12 months in compost, reduced to 2.7. However, there was still an increase after 24 months compared to PA-6's CI values before degradation. Before degradation, the average CI of HDPE discs was 0.15; this average CI of degraded HDPE discs increased to 0.42 and 0.25 after 12 months of degradation in substrates. It increased to 0.84 and 0.31 after 18 months in the same substrates. It had its highest increase of CI values after 24 months which were 1 and 0.41 in soil, and compost, respectively. After 24 months in soil, the CI got was more than seven times the CI value of HDPE before degradation, while the CI gotten after 24 months in compost was almost four times the CI value of HDPE before degradation. The average CI of HDPE in soil agrees with the result obtained from the weight loss of -5% observed from HDPE plastic in the soil, as seen in table 6.5.

While PET plot in fig 6.28 reveals that the average CI of PET plastics show an opposite result, signifying that the average CI values decreased over time in soil and compost, respectively. Before degradation, the average CI of PET discs was 6.8, as seen in fig. 6.28 B. The average CI of degraded PET discs decreased to 6 and 5.2 after 12 months in the substrates. It further reduced to 4.2 and 2.6 after 18 months and further reduced to 2.9 and 2.4 in all the substrates, respectively. The reduction in CI of PET discs after 24 months was two times less than the CI values of the PET discs before degradation. However, from fig. 6.28, we noticed that the plastics all had higher CI values in soil except PET, which had higher average CI values reduction in compost in Nigeria, i.e., degradation occurred more in soil than in compost except with PET. Also, the increase in average CI values from plastics: PA, PP, HDPE, and LDPE and the reduction in CI values of PET in the UK and Nigeria are caused by the increased oxidation of the functional groups over time, such as the carbonyl bond causing chain scission of the plastic discs (Krehula et al., 2014; Latos-Brozio and Masek, 2020) and also attributed to the depletion of the carbonyl groups (breaking of $C=O$ and $C-O$ bonds of PET during ester-cleavage) (Vague et al., 2019). Thus, the longer the PET discs stay in the substrates, the further reduction we observe, i.e., indicating more depletion of carbonyl groups and degradation of the plastics (Ratanakamnuan & Aht-Ong, 2006).

The variations seen in the oxidation of plastics were due to the microbial activities on the plastics, which need different abilities to oxidize the bonds of these plastics and generate degradation products dependent on the properties of these plastics (Roger et al. 1986; Montazer et al., 2020a). The more time the plastics stayed in these substrates, the more impact their CI.

Therefore, statistically, substrates, time and plastic types had significant influence on plastics' CI buried in Nigeria (media: $F= 171.008$, $P<0.05$; time: $F= 393.101$, $P<0.05$; plastic type: $F= 7935.840$, $P<0.05$).

The CI of all these plastics was significantly affected with time in the UK and Nigeria substrates. Table 6.19 below summarises the ANOVA results of the plastics between groups in Nigeria.

Table 6. 19 Showing the ANOVA results of the average CI of plastics buried and places in soil, and compost in Nigeria.

| PLASTICS | SUBSTRATES | ANOVA RESULT |
|----------|------------|--------------------------|
| PA-6 | Soil | $F= 178.969$, $P<0.05$ |
| | Compost | $F= 59.273$, $P<0.05$ |
| PET | Soil | $F= 123.935$, $P<0.05$ |
| | Compost | $F= 532.682$, $P<0.05$ |
| PP | Soil | $F= 2021.667$, $P<0.05$ |
| | Compost | $F= 391.299$, $P<0.05$ |
| HDPE | Soil | $F= 439.623$, $P<0.05$ |
| | Compost | $F= 330.054$, $P<0.05$ |
| LDPE | Soil | $F= 55.351$, $P<0.05$ |
| | Compost | $F= 23.766$, $P<0.05$ |

6.6.8 Scanning electron microscopy (SEM)

Figs. 6.29, 6.30 and 6.31 show the surface morphologies of PA-6, PET, PP, HDPE, and LDPE plastic discs before and after degradation in soil, compost, and leachate in the UK and soil and compost in Nigeria over two years. We observed holes, cracks, pits, and ridges on the surfaces of discs over time. Results obtained following the same pattern, so I had to pick one image each to represent both before and after degradation. Fig. 6.29 revealed the SEM images of both the control and degraded images of PA-6 and PET plastic discs, fig. 6.30 shows the SEM images of the control and degraded images of PP, HDPE, and LDPE all in the UK, while fig. 6.31 revealed the SEM images of both the control and degraded PA-6, PET, PP, HDPE and LDPE in soil and compost in Nigeria.

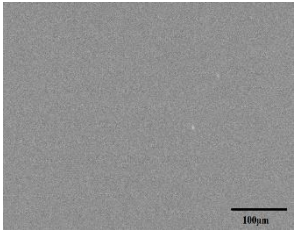
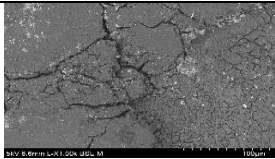
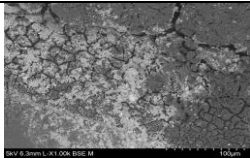
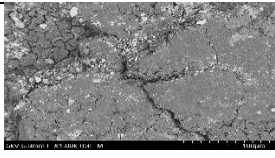
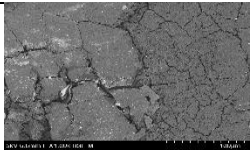
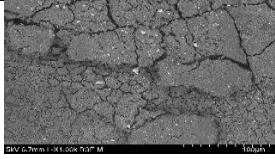
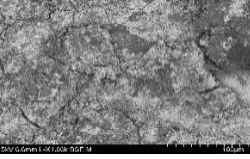
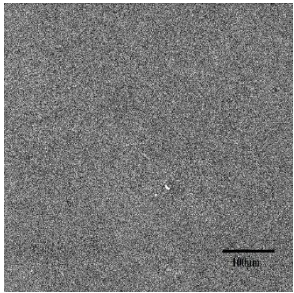
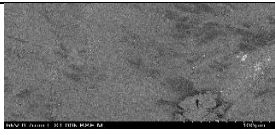


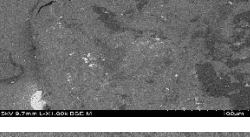
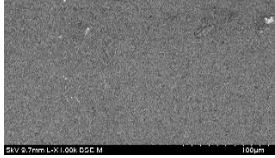
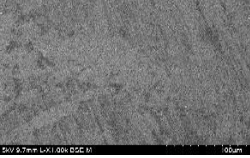
| Control Before Degradation | 12 months After Degradation | 24 months After Degradation | Substrates |
|-----------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------|
|  <p>Polyamide-6</p> |  |  | Soil |
| |  |  | Compost |
| |  |  | Leachate |
|  <p>Polyethylene terephthalate</p> |  |  | Soil |
| |  |  | Compost |
| |  |  | Leachate |

Fig. 6.29 SEM images of plastic discs- PA, and PET, before degradation, after 12 and 24 months in soil, compost, and leachate in the United Kingdom. All images were taken at 1000 -1200x magnification.

Fig. 6.29 displayed the effects on the substrates of all PA and PET plastic discs over time. The microorganisms in these substrates were responsible for the presence of coarse surfaces, cracks, small cavities, and mycelium networks as observed on the surfaces of the discs after 12- and 24 months of degradation. The plastic surface before degradation was smooth and glossy but had changes such as cavities and cracks on the surface of the discs. After 12 weeks, the changes turned to large cavities with pits, holes and cracks with a white powdery substance, as seen with PA discs after 24 months. Though there were changes on PET discs after 12- and 24 months of degradation in the substrates compared to the smooth image seen before degradation. Changes were more observed on PA-6 discs than on PET discs. All these changes suggest microbial degradation of the discs.

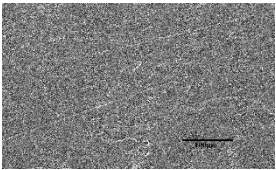
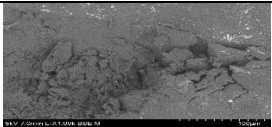

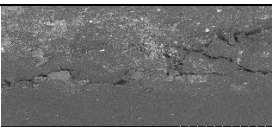
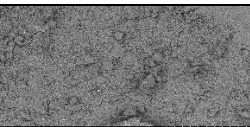
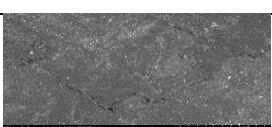
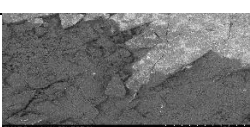
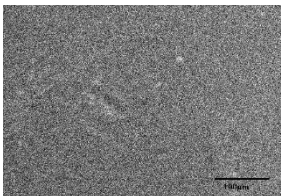
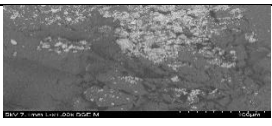
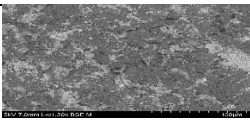
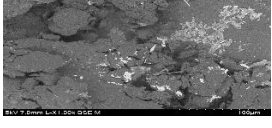
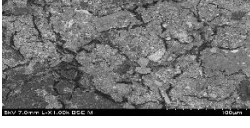
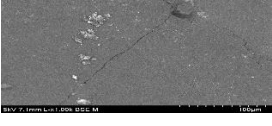
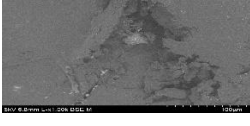
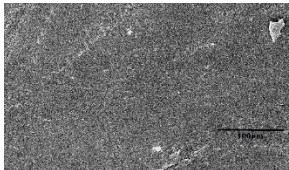
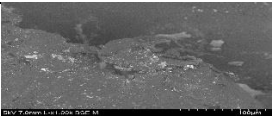
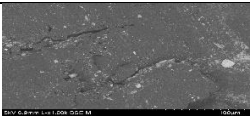
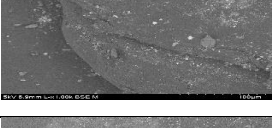
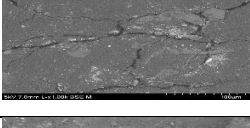
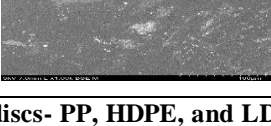
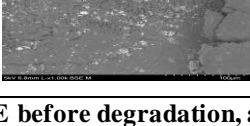
| Control (Before Degradation) | 12 months (After Degradation) | 24 months (After Degradation) | Substrates |
|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------|
|  Polypropylene |  |  | Soil |
| |  |  | Compost |
| |  |  | Leachate |
|  High-density polyethylene |  |  | Soil |
| |  |  | Compost |
| |  |  | Leachate |
|  Low-density polyethylene |  |  | Soil |
| |  |  | Compost |
| |  |  | Leachate |

Fig. 6.30 SEM images of plastic discs- PP, HDPE, and LDPE before degradation, after 12 and 24 months in soil, compost, and leachate in the United Kingdom. All images were taken at 1000 -1200x magnification.

Fig. 6.30 shows the SEM micrographs of PP, HDPE, and LDPE disc surfaces before, after 12- and 24-months degradation in soil, compost, and leachate. There were noticeable changes on the surfaces of the discs after 12 months in the substrates; these changes became more noticeable after 24 months with coarse surfaces, cracks, small cavities, and mycelium networks and white powdery substances like patches on these discs. From fig. 6.30, LDPE had the least surface impact after 12 and 24 months in soil, compost, and leachate compared to PP and HDPE. While comparing the five plastics examined after 12- and 24 months, PET had the least surface impact. The changes and damages observed on the discs increased over the period of

12 – and 24 months due to the oxidation and depletion of the functional groups of the plastic discs leading to degradation of these discs (Ohtake et al., 1995).

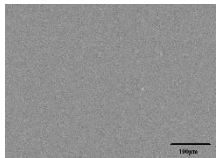
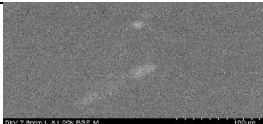
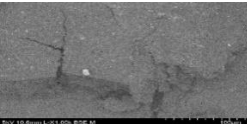
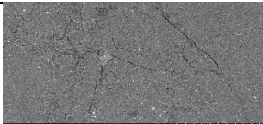
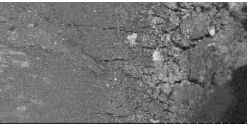
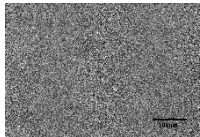
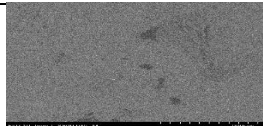
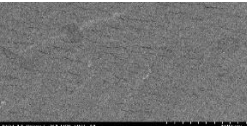
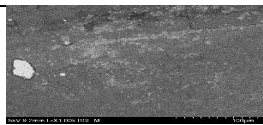
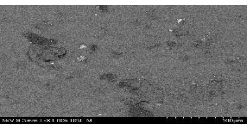
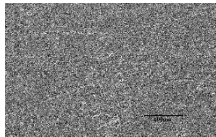
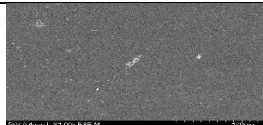
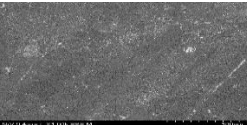
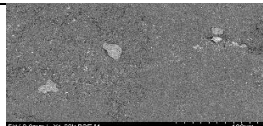
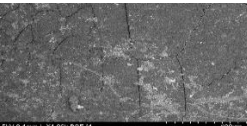
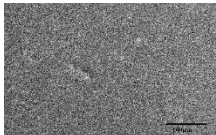
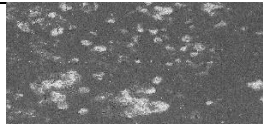


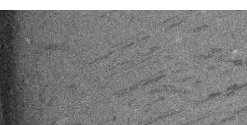
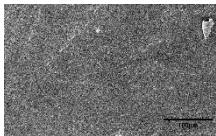
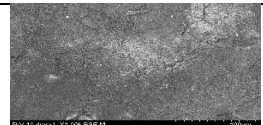
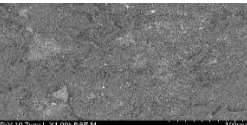
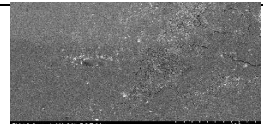
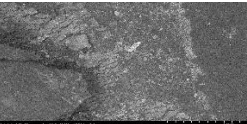
| Control (Before Degradation) | 12 months (After Degradation) | 24 months (After Degradation) | Substrates |
|-------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------|
|  Polyamide-6 |  |  | Soil |
| |  |  | Compost |
|  Polyethene terephthalate |  |  | Soil |
| |  |  | Compost |
|  Polypropylene |  |  | Soil |
| |  |  | Compost |
|  High-density polyethylene |  |  | Soil |
| |  |  | Compost |
|  Low-density polyethylene |  |  | Soil |
| |  |  | Compost |

Fig. 6.31 SEM images of plastic discs- PA-6, PET, PP, HDPE, and LDPE before degradation, after 12 and 24 months in soil, and compost in Nigeria. All images were taken at 1000 -1200x magnification.

Fig. 6.31 revealed the SEM images of PA-6, PET, PP, HDPE, and LDPE plastic discs in soil and compost over time. The microorganisms in these substrates also played roles in the changes observed on the plastic discs. The surfaces of these plastics before degradation were smooth and glossy but changed over time in the substrates. After 12 months in soil, PA-6, PET, and PP had minor impacts, such as round/dotted patches as seen on the discs (fig. 6.31), while after 12 months in compost, tiny cracks and white powdery substances were noticeable on PA-6, PET, and PP discs.

HDPE and LDPE displayed significant changes in soil and compost after 12 months. These changes on the discs include white powdery patches to cracks on the surface of the discs. After 24 months in soil and compost, these changes became more intense on PA-6, PET, PP, HDPE, and LDPE plastic discs. The cavities to giant pits, holes, and cracks with white powdery substance as seen with PA-6, PP, HDPE, and LDPE discs. PET discs had the least surface impact after 12- and 24-months degradation in the substrates compared to the images of other plastic discs examined. The action of microbial activities in the substrates used for the degradation procedure caused these changes observed here. Esmaeilli et al. (2013); Selke et al. (2015); Nauendorf et al. (2016), Adamcova et al. (2018); Reggero et al. (2021) all looked at the SEM images of different plastics after degradation in different environments. They concluded that the longer these plastics stayed in these environments, the more the progressive erosions and surface unevenness on the films examined, changing the surface properties of these plastics.

6.6.9 Tensile strength of plastics

Tensile strength is one of the vital properties for describing the mechanical properties of materials such as plastics. We carried out the tensile Strength testing on dog bone-shaped plastics of PA-6, PET, PP, HDPE, and LDPE before and after degradation in soil, compost and leachate in the UK and soil and compost in Nigeria. The test was carried out before degradation, after 12- and 24-months degradation on PA-6 with a thickness of 2 mm, while PET, PP, HDPE, and LDPE had thicknesses of 1.5mm.

Figs. 6.32 and 6.33 revealed the results from the average tensile strength values of both the (control) before and after degradation of dog bone plastic. While fig. 6.32 shows the tensile strength of the control and degraded dog bone plastics buried in soil, compost and placed in leachate in the UK, fig. 6.33 shows the tensile strength of the dog bone plastics buried in soil and compost in Nigeria. It is observed from plots in fig. 6.32 that the tensile strength of plastics

subjected to degradation in different UK substrates fluctuated with some plastics. While some had increased tensile strength, especially in leachate, they decreased after 24 months of burying them in the UK compared to the tensile strength of control plastics.

The average tensile strength value of PA-6 before degradation was 50.3Nmm^{-2} . It decreased to 44.4, 46.4 and 46.1Nmm^{-2} in soil, compost, and leachate after 12 months, then decreased further to 43.1 and 45.2Nmm^{-2} in soil and compost it increased to 49.2Nmm^{-2} in leachate after 24 months respectively. Here, a decrease in the tensile strength values of PA-6 was uniform over the years of study in substrates except after 24 months in leachate that increased to 54.6Nmm^{-2} . Statistically, the tensile strength of the dog bone PA plastics was only significantly different in soil (TS_{soil}: $F= 6.056$, $P<0.05$), While it was not significantly different in compost and leachate (TS_{compost}: $F= 2.330$, $P>0.05$; TS_{leachate}: $F= 1.962$, $P>0.05$). However, there was still a decrease after 24 months compared to PA's tensile strength values before degradation, which could indicate advanced degradation leading to crosslinking or chain scission of the functional groups.

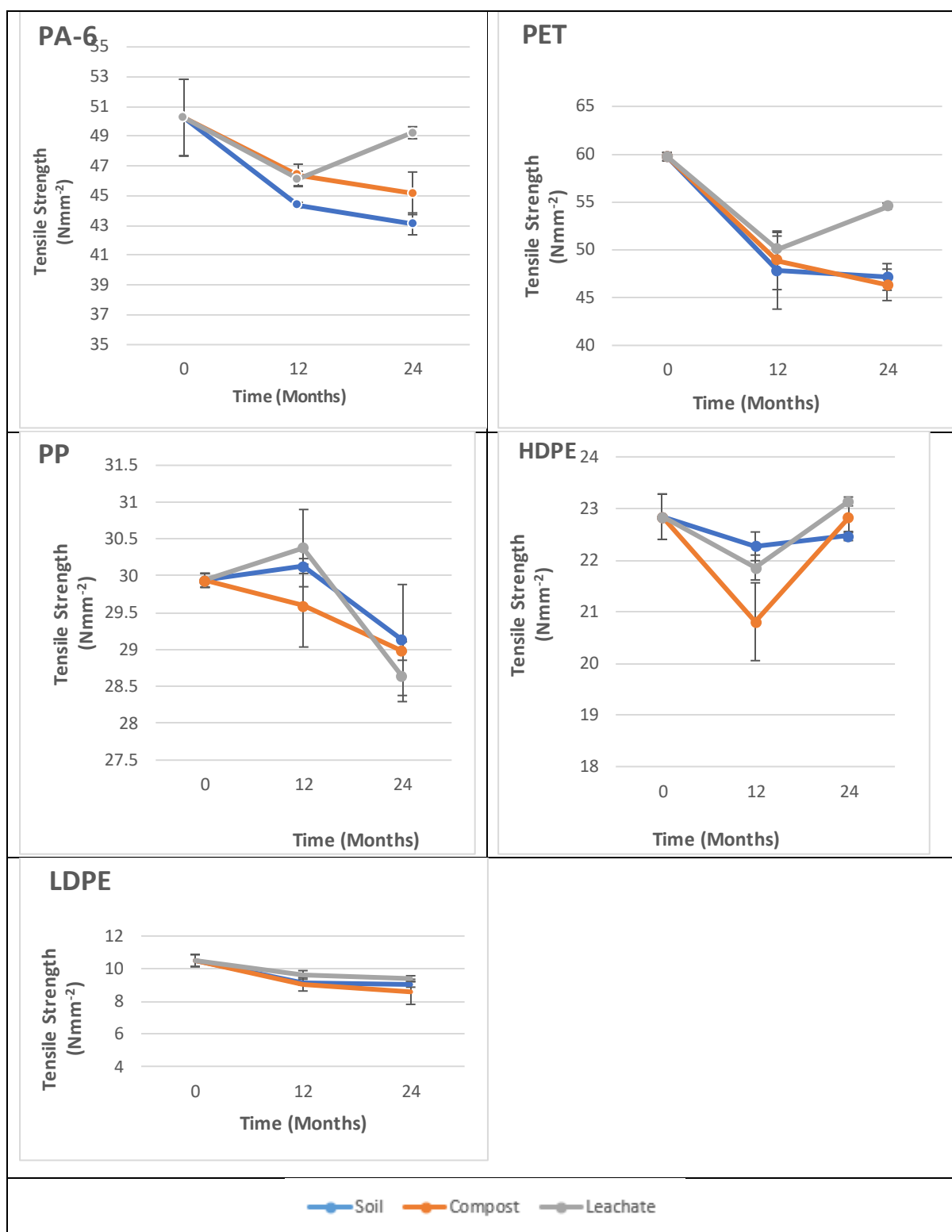


Fig. 6.32 Tensile Strength of plastics discs: PA, PET, PP, HDPE, and LDPE after 12, and 24 months in soil, compost, and leachate in the United Kingdom. *Y-Axis values differ. Data represents mean \pm SE (n=3).

From fig. 6.32, the average tensile strength value of PET dog-bone plastics after degradation decreased over time in the substrates used in this study compared to the values obtained before degradation. PET plastics' average tensile strength value before degradation was 59.7Nmm⁻² is decreased to 47.8, 48.9 and 50Nmm⁻² in soil, compost, and leachate after 12 months. While it

further reduced to 47.2 and 46.3 Nmm⁻² in soil and compost increased to 54.6 Nmm⁻² in leachate after 24 months, respectively. Statistically, the result revealed that the tensile strength of the dog bone PET plastics was all significantly different in soil, compost, and leachate (TS_{soil}: F= 8.271, P<0.05; TS_{compost}: F= 12.393, P<0.05; TS_{leachate}: F= 31.363, P<0.05). Before degradation, the average tensile strength value of PP plastics was 29.9 Nmm⁻²; it decreased to 30.1, 29.6, and 30.4 Nmm⁻² in soil, compost, and leachate after 12 months. The tensile strength of PP plastics had a slight increase in soil and leachate after 12 months, then while it decreased to 29.1, 29, 28.6 Nmm⁻² in soil, compost, and leachate after 24 months, respectively. However, the tensile strength results of PP only presented a statistically significant difference in leachate (TS_{leachate}: F= 6.194, P<0.05), while tensile strength results of PP in soil and compost do not present a statistically significant difference (TS_{soil}: F= 1.451, P>0.05; TS_{compost}: F= 2.087, P>0.05).

The average tensile strength value of HDPE dog bone plastics before degradation was 22.8 Nmm⁻², then decreased to 22.3, 20.8, and 21.9 Nmm⁻² after 12 months of degradation in substrates. After 24 months, the tensile strength of HDPE discs all increased to 22.5, 22.8 and 23.1 Nmm⁻² in soil, compost, and leachate, respectively. Here, also only the tensile strength of HDPE plastics in leachate was significantly different (TS_{leachate}: F= 5.218, P<0.05), while in soil and compost, the tensile strength of HDPE was not significantly different (TS_{soil}: F= 0.915, P>0.05; TS_{compost}: F= 4.855, P>0.05). The decrease in the tensile strength of LDPE dog bone plastics in the UK was uniform. Before degradation, its average tensile strength value was 10.5 Nmm⁻²; it decreased to 9.1, 9, 9.6 Nmm⁻² after 12 months in soil, compost, and leachate, respectively, this further reduced to 9, 8.6, and 9.4 Nmm⁻² after 24 months in the same substrates. In addition, statistically, only the tensile strength of LDPE in soil presented a significant difference (TS_{soil}: F= 12.041, P<0.05). Compost and leachate had no significant effect reducing LDPE's tensile strength (TS_{compost}: F= 3.352, P>0.05; TS_{leachate}: F= 4.345, P>0.05). Fig. 6.32 reveals the tensile strength of PA-6, PET, PP, HDPE, and LDPE dog bone plastics buried in soil and compost over two years in Nigeria.

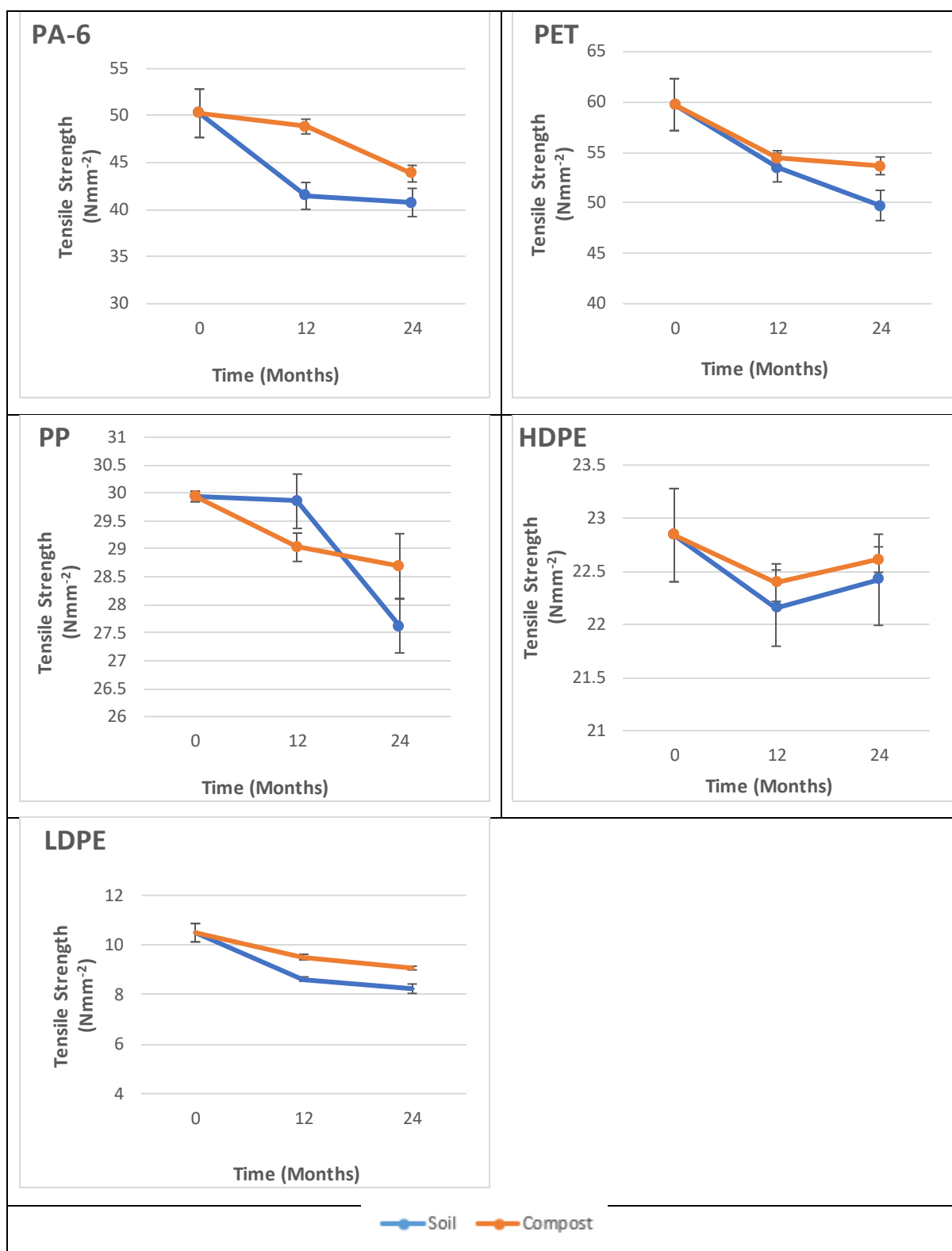


Fig. 6.33 Tensile Strength of plastics discs: PA-3, PET, PP, HDPE, and LDPE after 12, and 24 months in soil, and compost in Nigeria. *Y-Axis values differ. Data represents mean \pm SE (n=3).

Similarly, the tensile strength of these plastics decreased over time in the substrates in Nigeria (fig. 6.33). The average tensile strength value of PA before degradation was 50.3Nmm⁻², decreased to 41.5 and 48.8Nmm⁻² in soil, and compost after 12 months, then further reduced to 40.8 and 43.8Nmm⁻² in soil and compost after 24 months, respectively. Though the decrease

in the tensile strength values of PA was uniform over the years of study in substrates, statistically, only the tensile strength of PA in soil presented a significant difference (TS_{soil}: $F=99.351$, $P<0.05$). Compost had no significant effect tensile strength of LDPE (TS_{compost}: $F=4.265$, $P>0.05$). The average tensile strength of PET before degradation also decreased over time in the substrates used in this study compared to the values obtained before degradation. The average tensile strength value of PET plastics before degradation was 59.7Nmm^{-2} , it decreased to 53.5 and 54.4Nmm^{-2} after 12 months in soil, and compost, then it further reduced to 49.7 and 53.7Nmm^{-2} in soil and compost after 24 months, respectively. Also, the result revealed that the tensile strength of the dog bone PET plastics was significantly different in soil and compost (TS_{soil}: $F=12.507$, $P<0.05$; TS_{compost}: $F=20.384$, $P<0.05$). The average tensile strength value of PP before degradation was 29.9Nmm^{-2} . It slightly decreased to 29.8 and 29Nmm^{-2} after 12 months in soil and compost. After 24 months in soil and compost, the tensile strength of PP plastics further decreased to 27.6 and 28.7Nmm^{-2} . However, the obtained tensile strength results of PP only presented a statistically significant difference in soil (TS_{soil}: $F=10.866$, $P<0.05$), while tensile strength results of PP in compost do not present a significant difference (TS_{compost}: $F=3.046$, $P>0.05$).

The average tensile strength value of HDPE dog bone plastics before degradation was 22.8Nmm^{-2} , then decreased to 22.2 and 22.4Nmm^{-2} after 12 months of degradation in substrates. After 24 months, the tensile strength of HDPE increased slightly to 22.4 and 22.6Nmm^{-2} , respectively. Therefore, for HDPE plastics, their tensile strength in soil and compost was not significantly different (TS_{soil}: $F=0.711$, $P>0.05$; TS_{compost}: $F=0.625$, $P>0.05$). The decrease in the tensile strength of LDPE dog bone plastics in Nigeria was uniform. Before degradation, the average tensile strength value was 10.5Nmm^{-2} ; it decreased to 8.6 and 9.5Nmm^{-2} after 12 months in soil, and compost, respectively, which further reduced to 8.2 and 9.1Nmm^{-2} after 24 months in the same substrates. Finally, statistically, the tensile strength of LDPE plastics presented significant differences in soil and compost (TS_{soil}: $F=24.292$, $P<0.05$; TS_{compost}: $F=23.766$, $P<0.05$).

Generally, the results obtained from the average tensile strength of plastics are presented in figs. 6.32 and 6.33 suggest that a decrease in the tensile strength of plastics increases biodegradation and leads to the loss of the mechanical properties of plastics. The results were obtained from the UK's average tensile strength of plastics, as presented in figs. 6.32 did not follow a uniform trend, though all were reduced after 24 months, especially PET having the highest reduction in compost and soil; 29 and 26%, LDPE had 22 and 17%, and PA had 11 and 17% reduction. Plastics in leachate had the least tensile strength reduction, even where some

of their tensile strengths increased above their control (before degradation) tensile strength. This increase in the tensile strength of plastics relates to degradation because the degradation of plastics is very sensitive to the stress environment. i.e., different environments used for degradation have significantly different effects on the structural components of plastics, which therefore affects the rate of degradation of plastics by re-orientating the functional groups of such plastics (Ohtake et al., 1998; Andrady, 2003; O'Brine and Thompson, 2010; Cai et al., 2018; Han et al., 2020). Another reason for the increase in the tensile strength of plastics could be cross-linking of new functional groups formed by the plastics due to oxidation and hydrolysis, which are routes of degradation that cause an increase in tensile strengths. Guo et al. (2016) noticed an increase in the tensile strength after the first week before a drop during an in vitro degradation of a polymer. While fig. 6.33 presents the consistent trend of plastics buried in Nigeria: Control > 12 months > 24 months, except with HDPE that went this way: control > 24 months > 12 months. PA, PET, and LDPE also had the highest tensile strength reduction in soil, which was 23, 20 and 28%, while in compost, they had 15, 11, and 15%. Mostafa et al. (2010); Czaja-Jagielska et al. (2013); Han et al. (2020); Havstad et al. (2021) all studied the mechanical properties of many biodegradable and agricultural plastics under different soil types. They concluded that the tensile strength of nearly all plastics examined displayed a significant reduction with an increase in time in different substrates.

Therefore, with this experimental result, we can say that the tensile strength of plastics buried and placed in different substrates in the UK and Nigeria for over 24 months varied inconsistently. Some plastics' tensile strength was reduced; others were increased in the same substrates used in the study. The reason may be due to the plastic heterogeneity nature, which are the components used in making the plastics and processing conditions of plastics, environmental and climatic conditions such as heat, light, or exposure to chemicals (Hawkins, 1984), which come together to affect plastics.

The results from burying plastics in soil and compost, submerged in leachate in the UK and soil and compost in Nigeria over 24 months revealed changes in the plastics at the end of each time interval of (0, 6, 12, 18, and 24) checked. It is assumed that the activities of microorganism in the substrates was observed with the formation of biofilms on the plastics' surfaces, which increased the plastic surface's hydrophilicity, thus encouraging more biological activities by microorganisms (Ohtake et al. 1998; Shovitri et al. 2017) to use plastics as alternative carbon and energy source.

From the results obtained in this study, plastics had some form of abrasions, discolouration, biofilm colonisation, lost their glossy nature and became opaque and brittle in the case of PET.

These changes also agreed with the changes observed in plastics subjected to degradation in different environments (Pospisil and Nespurek, 1997; Ohtake et al., 1998; Vasile and Dekker, 2000; Shovitri et al., 2017). Plastics changed to brown, especially PA and PET submerged in the leachate. After the visual inspection, the reasons are the colour and toxic nature of leachate and the heteroatomic nature of PA-6 and PET.

Pits, holes cavities, large longitudinal cracks, mycelium hyphae, biofilm colonisation, grooves and surface irregularities were observed on PA-6, PET, PP, HDPE, and LDPE surfaces using the microscopy and SEM.

Plastics buried in Nigeria lost weight after 24 months in all environments, while some gained weight in the UK during and after 24 months. The weight gain of some plastics in the UK could be because they absorbed water from the environment, knowing that the UK is in the temperate zone, which is always wet around the year. The second reason for the weight gain could be the extra weight of the biofilms formed by microorganisms stuck on the plastics' surfaces that were hard to wash. Therefore, the results from the weight change of plastics buried and placed in different substrates in both the UK and Nigeria for over 24 months differed inconsistently were some plastics' weight was reducing, and others were increasing. The reason may be due to the plastic properties.

The formation, disappearance, increase, and reduction of the peaks (functional groups) and carbonyl indices of plastics during and after 24 months in different environments. We link these changes to depletion, increased hydrolysis, and oxidation on the functional groups, which caused the plastics' main polymer chain scission. Krehula et al. (2014); Shovitri et al. (2017); Latos-Brozio and Masek (2020) also observed changes in peaks of plastics subjected to degradation in different environments over time.

Moreover, substrates properties such as pH, electrical conductivity, moisture content, C content and C/N ratio are good indicators to check for substrates fertility, i.e., substrates with nutrients and accommodating diverse microorganisms. Therefore, an analysis conducted on the properties of substrates used for degradation was revealed in fig. 6.3. An ideal pH that soil microorganisms thrive on is near neutral because naturally, microorganisms in soil and compost thrive well around neutrality (Azim et al., 2018). The UK and Nigerian soil fell into the accepted limit except for Nigerian compost, which had the highest pH of 8.6. The pH value of Nigerian compost could have impacted the microorganisms involved in the degradation of the plastics.

Microorganisms function best at EC levels between (750- 2000 μScm^{-1}), which is the accepted limit for electrical conductivity suitable for soil microorganisms. The EC of UK soil and

compost were within the acceptable range. UK leachate and Nigerian compost had their EC value higher than the accepted range, while Nigerian soil had EC lower than the accepted range. Although high and low EC impact the substrates negatively, microorganisms have been observed thriving in substrates with a low EC of about $100 \mu\text{Scm}^{-1}$ because they accumulate osmolytes (Oren, 1999). Therefore, high EC influences the properties of the substrates, which in turn inhibits the microbial activity and microbial biomass and changes microbial community structure (Rousk et al., 2011; Setia et al., 2011; Andronov et al., 2012).

The leachate from the UK and Nigerian compost had their EC exceed the acceptable limit. The reason could be the nature of the raw materials used in making the compost which may have comprised a very high concentration of water-soluble salts (Dimambro et al., 2006). EC of leachate from the UK was very high because it is the by-product of composting processing. It has a very high concentration of heavy metals and salts from anionic ions present as Cl^- , Br^- , F^- , NO_3^- and SO_4^{2-} (Youcai, 2018). The results obtained from organic carbon from soil and compost in both the UK and Nigeria agreed with the accepted limit value of organic carbon for soil and compost, which must be higher than 1 and 10%, respectively (Batjes, 1996; Khater et al., 2015).

The C/N ratios obtained from soil and compost from the UK and Nigeria were below the acceptable range of 20:1 as recommended by APEX.

The solid substrates' moisture content was checked because substrates' microorganisms solely depend on moisture content, which varies in time and space to transport solutes and gases in nutrient cycling (Adl, 2003). It influences microbial activity, a crucial factor determining mineralisation (Paul et al., 2003). Suppose moisture content in substrates is in excess. In that case, it reduces the oxygen level, which reduces the activities of aerobic microorganisms (Kozolowski, 1984) though it could increase the activity of anaerobic microorganisms. In contrast, a lack of moisture in substrates reduces the activities and growth of microorganisms, C/N values and mineralisation (Kieft, 1987; Sleutel et al., 2008).

Fierer et al. (2003) suggested that drying and rewetting substrates influence the overall functioning of microbial biomass, which affects nutrient cycling. The low moisture content from Nigerian soil and compost could be because water dried out fast enough from substrates before they got to the UK for analysis compared to the UK samples analysed as soon as they were sampled. Other reasons could be the texture or structure of soil because available moisture content depends significantly on the soil texture and structure (Brouwer et al., 1985). Alternatively, mostly topsoil taken from a few metres below the surface was more sandy soil known to have low moisture content (Brandt et al., 2017).

Therefore, low C/N ratios and moisture content will impact soil respiration, number and quality of microorganisms, and nutrient retention and affect the optimal moisture content, thereby influencing the degradation rate of these plastics. These parameters play an essential role in soil and compost because the degradation process depends on the activity of microorganisms in soil and compost, the nature of organic C and its susceptibility towards microbial activity. We assume that this may be why degradation was observed more consistently (with other favourable factors put together) on plastics buried in Nigerian soil and UK soil and compost than in the UK leachate and Nigerian soil.

Leachate, a part of marine environments, gave us inconsistent results. Reasons for our results could be attributed to the type and number of degrading microorganisms that might exist more in some environments than the others used. i.e., the higher number the of plastic degrading microorganisms in an environment, the greater the extent of degradation seen on the plastics (Adhikari et al., 2016).

Rich soils have accommodated many degrading microorganisms in total microbial mass(count) and have been efficient in degrading recalcitrant materials such as plastics. Secondly, Hammer et al. (2012) suggested that reasons for less degradation seen on plastics in leachate may be because of the decreased sun exposure in marine environments, which is due to shading by water and fouling, which might help increase the persistency of plastics (O'Brine and Thompson, 2010). Andrady et al. (2003) exhibited that plastic materials' degradation rates are very slow in marine environments where sunlight is unavailable and there are low temperature and oxygen levels.

The result from the I-buttons used in tracking the temperatures from our experimental sites is displayed in Table 6.4. The UK had the maximum, average and minimum temperatures: of 21.5, 12.5 and 1.5 °C, while Nigeria had the maximum, average and minimum temperatures: of 38, 25.3 and 24 °C from 2018-2019. Because Nigeria is in the tropical zone, always warm round the year, that is the reason she had a higher temperature than the UK. Her minimum temperature was still higher than the UK maximum temperature. We assume that this may be why both surface damages of the discs and the dog bone-shaped plastics buried in Nigeria were more than those buried in the UK, most especially the dog bone-shaped plastics, which all shrunk. Their larger surface area also assisted microbial attacks on the plastics. Ho et al. (1999) found that an increase in temperature and humidity enhanced the degradation rates of plastics. He suggested that the higher the temperature of the environment, the higher the rate of chemical reactions, i.e., the degradation of plastics. Any absorbed UV radiation by the plastics caused

them to release free radicals, triggering photo-oxidation through a free radical reaction known as autooxidation (Rabek and Rånby, 1974; Andradý et al., 2011).

Therefore, it may be that plastics buried in Nigeria went through photolytic or photo-oxidative degradation in the substrates due to the high exposure to UV radiation from the sun. This exposure to UV radiations reduced their half-life. It broke up chemical bonds at the plastics' surface, altering their properties, then encouraging microbial attack from the good properties that Nigeria offered.

6.7 Comparative Study in the Degradation of Plastics in the UK and Nigeria.

This section will carry out a comparative study on the rate of degradation of plastics in both the temperate zone, the UK, and the tropical zone, Nigeria, where the degradation study took place. Also, from the results obtained, we can ascertain the zone that had more impact on the plastics and establish reasons for the results obtained. In this comparative study, it is imperative to know the fate (end of life) of these plastics in the environment since their production, application, usage, and disposal is on the increase (Plastic Europe 2015), ending up in landfills and natural environments and creating waste management challenges around the world (Thompson et al. 2009a).

Figs. 6.34- 6.38 will try to summarise the comparative study of the degradation of plastics: PA-6, PET, PP, HDPE, and LDPE in only soil and compost for over 24 months.

6.7.1 Visual observation




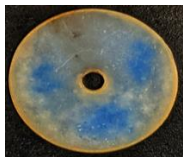




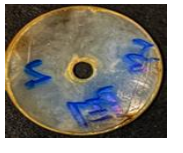


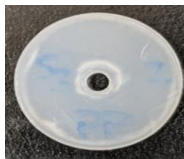
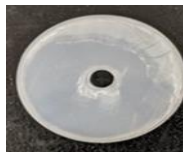
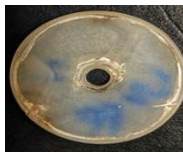





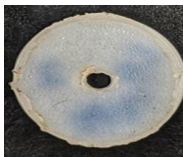





| (Before degradation) | United Kingdom (After 24 months of degradation) | | Nigeria (After 24 months of degradation) | |
|-------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Plastics | Soil | Compost | Soil | Compost |
|  Polyamide-6 |  |  |  |  |
|  Polyethylene terephthalate |  |  |  |  |
|  Polypropylene |  |  |  |  |
|  High-density polyethylene |  |  |  |  |
|  Low-density polyethylene |  |  |  |  |

Fig.6.34 Visual observation of combined plastics discs- PA-6, PET, PP, HDPE, and LDPE before degradation, and after degradation (24 months) in soil, and compost in the UK and Nigeria.

Fig. 6.34 revealed the combined visual observation of the control and degraded PA-6, PET, PP, HDPE and LDPE plastic discs in soil and compost in the temperate, UK, and tropical zones of Nigeria after 24 months. All the plastic discs buried in soil and compost in the UK and

Nigeria displayed some damage on their surfaces, such as discolouration, abrasion, brittleness, biofilm colonisation-like patches and losing their glossy look. All these mentioned damages seen on the plastic surfaces could be degradation from environmental stress. PA-6 discs buried in all substrates in the UK and Nigeria lost their glow, had rough and white small patches on their surfaces, and turned brownish, especially in Nigerian soil and compost. PET in all the substrates in the UK and Nigeria also exhibited some changes on their surfaces. These changes include abrasions, discolouration to brownish colour as seen with PET in Nigerian soil and compost, and a white biofilm on PET disc in the UK soil. Apart from the discolouration of the PET disc from Nigerian compost, we observed that the disc became opaque on half of the surface, while the other half turned brown and brittle to touch. PP discs also showed biofilm colonisation on their surface, losing the glossy nature, and turning brown for the PP disc in Nigerian soil. HDPE and LDPE discs, on the other hand, exhibited roughness of surfaces, slight discolouration and biofilm colonisation which was so notable on HDPE and LDPE discs in Nigeria soil after 24 months.

Therefore, these changes observed on the surfaces of PA-6, PET, PP, HDPE, and LDPE plastic discs were more intense and more robust after 24 months in Nigerian soil are vital signs of degradation.

6.7.2 Light Microscopy

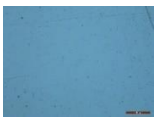
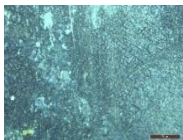
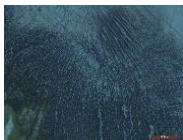
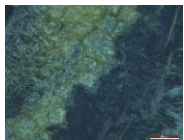
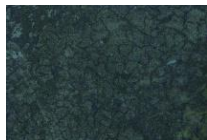





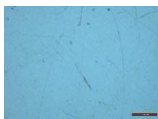


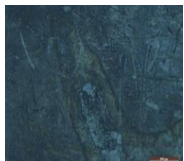
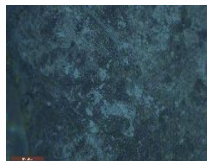



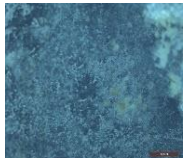


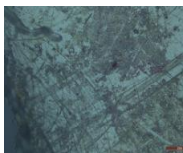



| (Before degradation) | United Kingdom (After 24 months of degradation) | | Nigeria (After 24 months of degradation) | |
|-------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Plastics | soil | compost | soil | compost |
|  Polyamide-6 |  |  |  |  |
|  Polyethylene terephthalate |  |  |  |  |
|  Polypropylene |  |  |  |  |
|  High-density polyethylene |  |  |  |  |
|  Low-density polyethylene |  |  |  |  |

Fig. 6.35 Microscopy images of combined plastic discs PA-6, PET, PP, HDPE, and LDPE before degradation, and after degradation (24 months) in soil, and compost in the UK and Nigeria.

Fig. 6.35 revealed the combined microscopic images of the control and degraded PA-6, PET, PP, HDPE and LDPE plastic discs in soil and compost in the temperate zone, the UK, and the tropical zone, Nigeria, after 24 months. There were significant surface damages seen clearly on all the plastics after 24 degradation studies in the UK and Nigeria with all the plastics used in the study. The plastic discs lost their smooth and glossy surface to degradation after 24 months. With plastic PA-6, we can observe that the discs were all affected in soil and compost in the UK and Nigeria. They displayed abrasions, white and black patches of biofilm

colonisation in the case of PA-6 discs from the UK soil and extensive and thick yellowish biofilm colonisation from Nigerian soil. Though the impact was observed more from discs buried in soils of both zone, discs buried in Nigerian soil exhibited the most surface damage. PET, PP, HDPE, and LDPE discs all had surface damage after 24 months in all the substrates from the UK and Nigeria, as seen in fig. 6.35 with marks, cracks and biofilm colonisation. However, PET, PP, HDPE, and LDPE discs buried in Nigerian soil and compost exhibited more surface damage than discs buried in UK soil and compost. For the PET disc from Nigeria soil, we observed a massive hole on the disc's surface with yellowish biofilm formation around this hole. PP, HDPE, and LDPE discs buried in the soil had more significant surface damage. Also, from fig. 6.35, PA-6 discs had the most surface damage while LDPE had the least surface damage in all the substrates used in the temperate zone, the UK, and the tropical zone, Nigeria, after 24 months.

6.7.3 Weight change in plastic discs

Table 6.20 shows the combined weight change (%) of the plastic discs in the soil and compost after 24 months in the UK and Nigeria.

Table 6. 20 weight change (%) of the plastic discs in the soil, and compost after 24 months in the UK and Nigeria.

| Plastics | SUBSTRATES UK | | SUBSTRATES NIGERIA | |
|-------------|------------------|-------------|-----------------------|-------------|
| | Soil (%) | Compost (%) | Soil (%) | Compost (%) |
| PA-6 | -0.9±0.002 | -1.1±0.001 | -1.7±0.00 | -0.5±0.003 |
| PET | -1.2±0.003 | 0.8±0.001 | -0.7±0.006 | -1.9±0.002 |
| PP | 1.4±0.013 | 2.1±0.002 | -1.4±0. | -0.9±0.004 |
| HDPE | -1.8±0.003 | -1±0.006 | -5±0.009 | -1.7±0.008 |
| LDPE | -1±0.003 | 1±0.004 | -1.3±0.008 | -0.1±0.005 |

Table 6.20 revealed that plastic discs buried in Nigerian substrates showed weight loss after 24 months, especially in Nigerian soil. They all had the highest weight loss except for PET buried in Nigerian compost, which had higher weight loss than the PET buried in Nigerian soil. HDPE discs showed the highest weight loss in Nigerian soil, about 5%, followed by PET discs buried in Nigeria compost, which had about 1.9%.

In contrast, results presented by UK substrates fluctuated. Some lost weight while some gained weight after 24 months in UK substrates. The plastics with weight gain are PET discs buried in UK compost, PP discs buried in UK soil and compost and LDPE in UK compost.

However, these fluctuations were observed in plastics buried in the UK soil and compost than in Nigeria. The weight gain observed by some plastics buried in UK substrates was from the colonisation and activities of microorganisms or/and absorbed water from the substrates.

Statistically, substrates, plastic-type and time had a significant influence on plastics' weight change after 24 months in soil and compost (substrates: $F= 5.203$, $P<0.05$; plastic type: $F= 17648.534$, $P<0.05$; time: $F= 30.956$, $P<0.05$).

6.7.4 Carbonyl indices of the plastics discs

Fig. 6.36 reveals the Plots of combined carbonyl indices of plastics buried in soil and compost in the UK and Nigeria.

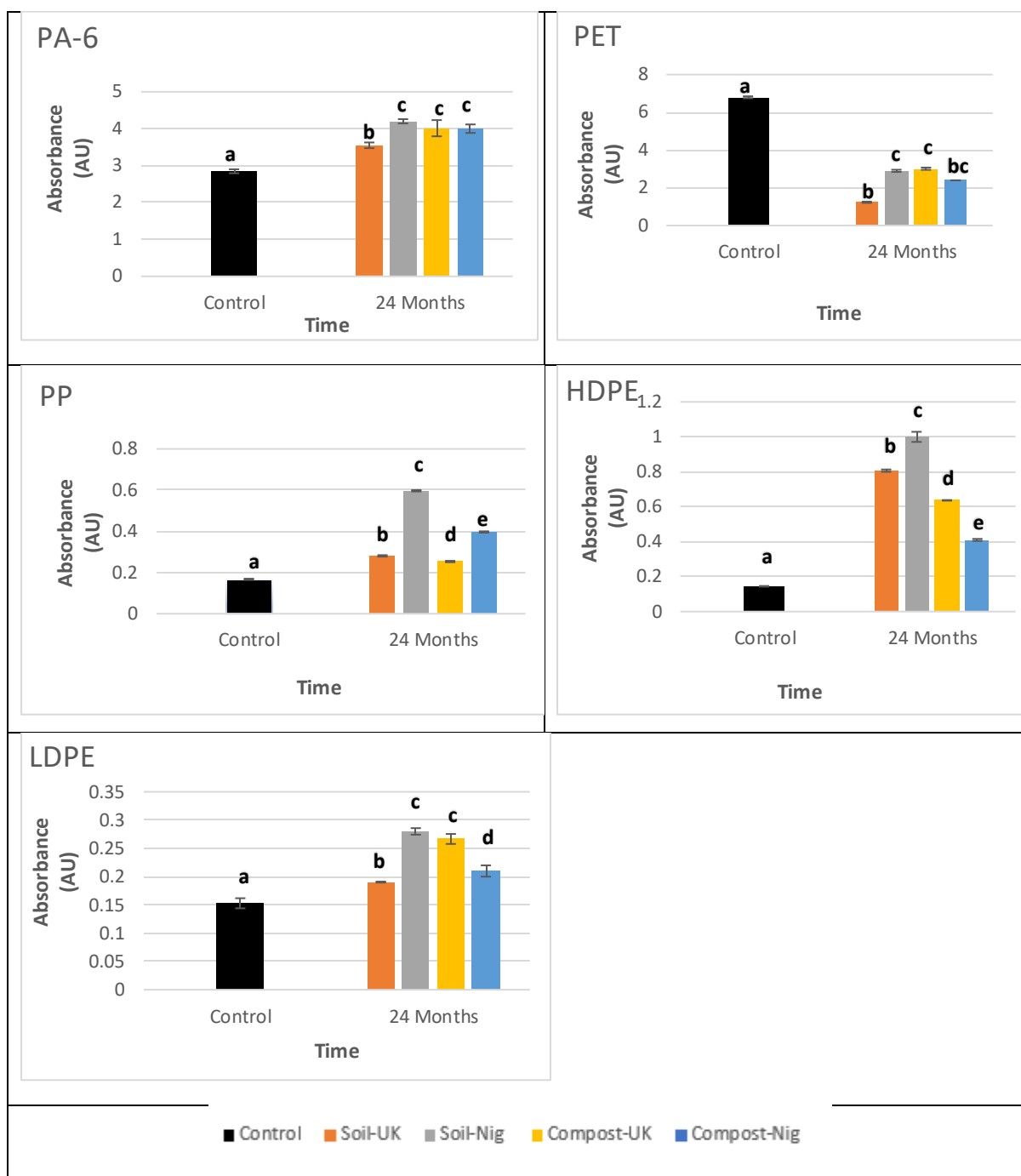


Fig. 6.36 Plots of combined carbonyl indices of the plastics PA-6, PET, PP, HDPE, and LDPE before degradation, and after degradation (24 months) in soil, and compost in the UK and Nigeria. *Y-Axis values differ. Data represents mean \pm SE (n=3).

We observed changes that included an increase in the CI of plastics: PA-6, PP, HDPE, and LDPE and a reduction in the CI of PET in soil and compost in the UK and Nigeria. The carbonyl indices of all the plastics buried in the substrates in the UK and Nigeria increased after 24 months for plastic discs; PA-6, PP, HDPE, and LDPE, and reduced after 24 months for the plastic disc- PET. This section will focus on the bars after 24 months. The average CI value of PA-6 before degradation was 2.8, as seen in fig. 6.36, it increased after 24 months to 3.6, 4.2,

4.0, and 4 in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The PA-6 disc buried in Nigerian soil had the highest CI value, 4.2, while PA-6 buried in UK soil had the least CI of 3.6. The average CI value of PP before degradation was 0.17. It also increased after 24 months to 0.28, 0.6, 0.25 and 0.4 in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The PP disc buried in Nigerian soil also had the highest CI value of 0.6, while PA-6 buried in UK compost had the least CI of 0.25.

The average CI value of HDPE before degradation was 0.14; however, that increased after 24 months to 0.81, 1, 0.64 and 0.41 in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The HDPE disc buried in Nigerian soil had the highest CI value, 1, while HDPE buried in Nigeria compost had the least CI of 0.41. The average CI value of LDPE before degradation was 0.15, as seen in fig. 6.36, it increased after 24 months to 0.19, 0.28, 0.27 and 0.21 in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The HDPE disc buried in Nigerian soil also had the highest CI value, 0.28, while PA-6 buried in UK soil had the least CI of 0.19.

On the other hand, the CI of PET discs results decreased over time in soil and compost, contrasting other plastics with their CI increase over time in substrates. The average CI of PET discs before degradation was 6.8, as seen in fig. 6.36, it decreased after 24 months to 1.2, 2.9, 3 and 2.4 in the substrates; UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The reduction observed in CI of PET discs after 24 months was more than two times less than the CI values of the PET discs before degradation.

Therefore, the CI of plastic discs; PA-6, PP, HDPE, and LDPE all had the highest values in Nigerian soil, apart from PET discs in UK soil, which had the lowest CI value.

Statistically, plastic type, time and country had significant influence on plastics' CI after 24 months in soil and compost (plastic-type: $F= 11601.800$, $P<0.05$; time: $F= 834.116$, $P<0.05$; country: $F= 37.402$, $P<0.05$), while substrates had no significant influence the CI of plastics (substrates: $F= 3.849$, $P>0.05$).

6.7.5 Tensile strength of the plastics discs

Fig. 6.37 displays the combined tensile strength of PA-6, PET, PP, HDPE, and LDPE dog bone plastics buried in soil and compost over two years in the UK and Nigeria.

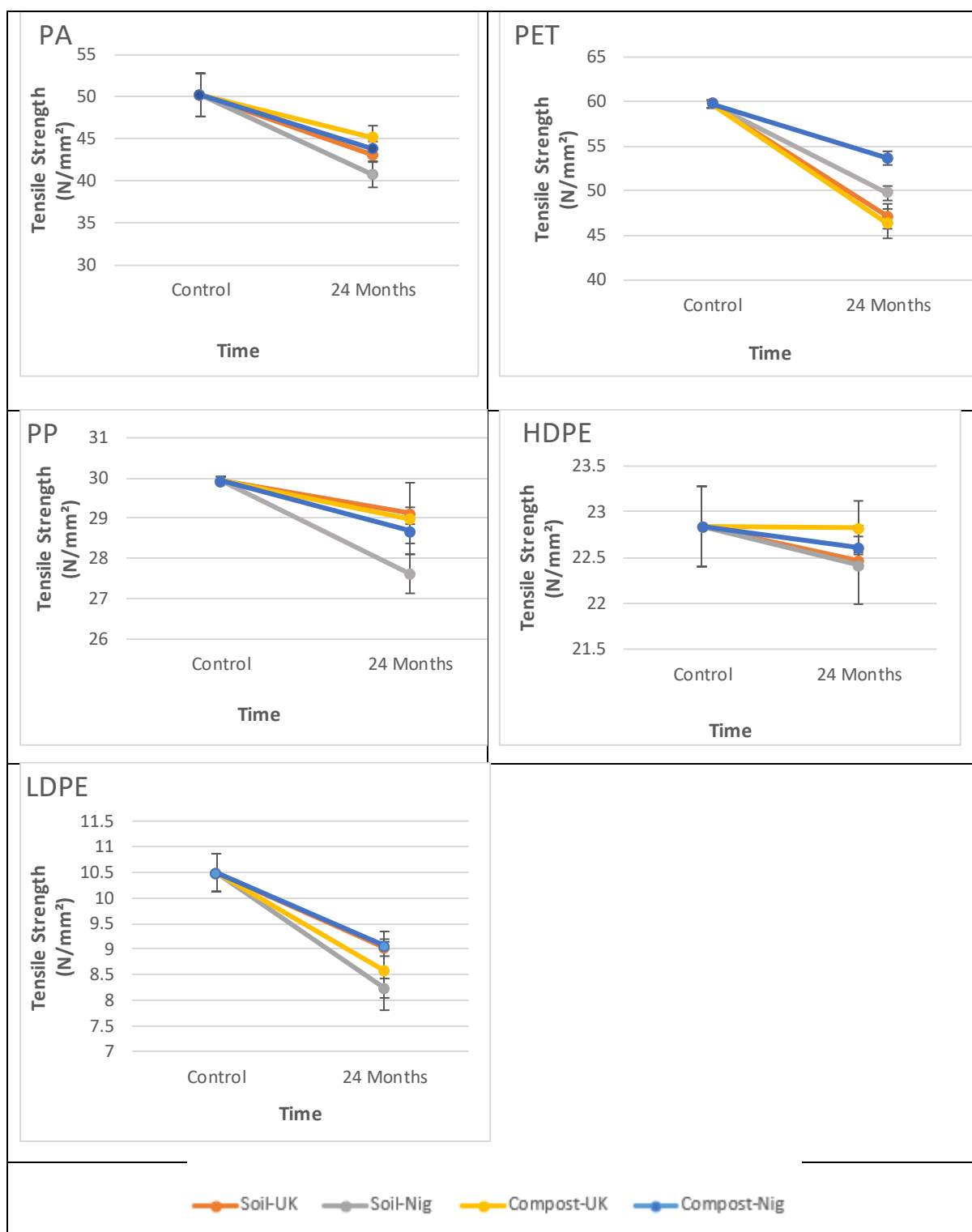


Fig. 6.37 Plots of combined tensile strength of plastics discs PA-6, PET, PP, HDPE, and LDPE before degradation, and after degradation (24 months) in soil, and compost in the UK and Nigeria. *Y-Axis values differ. Data represents mean \pm SE (n=3).

We took the average of the three replicates used for the degradation study of dog bone plastic buried in the substrates over time and will focus on 24 months. There was a reduction in the tensile strength of all these plastics tested after 24 months in all the substrates except HDPE in UK compost that had a significant increase.

The average tensile strength value of PA-6 before degradation was 50.5 Nmm^{-2} , as seen in fig. 6.37, it decreased after 24 months to 43.1, 40.8, 45.2, and 43.8 Nmm^{-2} in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The PA-6 disc buried in Nigerian soil had the most reduced tensile strength value, 40.8 Nmm^{-2} , while PA-6 buried in UK compost had the highest tensile strength value, 45.2 Nmm^{-2} . The average tensile strength value of PET before degradation was 59.7 Nmm^{-2} , it decreased after 24 months to 47.6, 49.7, 46.3 and 53.7 Nmm^{-2} in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The PET discs buried in UK compost had the most reduced tensile strength value, 46.3 Nmm^{-2} , while PET buried in Nigeria compost had the highest tensile strength value, 53.7 Nmm^{-2} .

The average tensile strength value of PP before degradation was 29.9 Nmm^{-2} , but decreased after 24 months to 29.1, 27.6, 29, and 28.7 Nmm^{-2} in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The PP disc buried in Nigerian soil had the most reduced tensile strength value, 27.6 Nmm^{-2} , while PP buried in UK soil had the highest tensile strength value, 29.1 Nmm^{-2} . HDPE discs have their tensile strength before degradation to be 22.8 Nmm^{-2} however, it decreased after 24 months to 22.5, 22.4, 22.8, and 22.6 Nmm^{-2} in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The HDPE discs buried in Nigeria soil had the most reduced tensile strength value, 22.4 Nmm^{-2} , while HDPE buried in UK compost had the highest tensile strength value, 22.8 Nmm^{-2} . Finally, the average tensile strength value of LDPE discs before degradation was 10.5 Nmm^{-2} , it decreased after 24 months to 9, 8.2, 8.6 and 9.1 Nmm^{-2} in UK-soil, Nig-soil, UK-comp, and Nig-comp, respectively. The LDPE discs buried in Nigerian soil had the most reduced tensile strength value, 8.2 Nmm^{-2} , while LDPE discs buried in Nigerian compost had the highest tensile strength value, 9.1 Nmm^{-2} .

Therefore, all the dog bone shaped plastics had a reduction in their tensile strength after 24 months in all the substrates when compared to their control samples before degradation most especially PA, PP, HDPE, and LDPE had the highest reduction in tensile strength in Nigerian soil after 24 months, 18.9, 7.7, 1.8 and 21.5 % respectively. Also, statistically, plastic-type, and time had significant effect on the tensile strength of the plastics after 24 months in soil and compost (plastic-type: $F= 2495.863$, $P<0.05$; time: $F= 165.838$, $P<0.05$) while substrates and

country had no significant effect on the tensile strength of plastics (substrates: $F= 2.410$, $P>0.05$; country: $F= 0.359$, $P>0.05$).

Here, we try to compare studies on the rate of plastic degradation in the temperate zone, the UK, and the tropical zone, Nigeria, where the degradation study took place. From the results obtained, from the visual observation, micrographs from light microscopy and SEM, % weight loss, carbonyl indices and tensile strength revealed that all plastics buried in these substrates were generally affected in the substrates, though at a slow rate. Abrasions, roughness, biofilm colonisation and cracks, and brittleness of plastics were more on plastics buried in Nigerian soils than other substrates.

All the plastics buried in Nigeria soil exhibited colour change to brownish colour though more on PA and PET. Out of all the plastics degraded, PA and PET stood out in terms of being impacted more in the substrates. The reason is the difference in their chemical nature, i.e., they are known as heteroatoms, i.e., they have functional groups such as ester or amide bonds that encourage degradation. The images from microscopy still confirm that most surface damages were observed from plastics buried in Nigeria soil. Again, table 6.18 revealed that plastics; PA-6, PP, HDPE, and LDPE buried in the different substrates, presented the highest weight loss in Nigerian soil, 1.7, 1.4, 5, and 1.3% weight loss respectively, after two years. Fig 6.37 showed us that the carbonyl indices of plastic discs, PA-6, PP, HDPE, and LDPE, all had the highest values in Nigerian soil. fig.6.38 also reveals that PA-6, PP, HDPE, and LDPE had the highest reduction in tensile strength in Nigerian soil after 24 months, 18.9, 7.7, 1.8 and 21.5 %, respectively.

From the results from the comparative studies, plastics were most affected in Nigeria soil except PET plastics results that fluctuated in different substrates used. The results we obtained from Nigeria are assumed, firstly, because of the high exposure to UV radiation from the sun, which caused degradation by photo-oxidation. Photo-oxidation reduced their half-life by fragmenting their chemical bonds present at the plastics' surface, altering their properties, and then enhancing microbial colonisation from the good properties of Nigeria soil.

6.8 Conclusion

This chapter considered the degradation of plastics widely used, PA-6, PET, PP, HDPE, and LDPE, in different environments, as substrates used in the study offered significantly different results observed on the plastics.

Figs. 6.4 – 6.33 reveal these degraded discs' various changes or results. These include visual, weight, physical, structural, and morphological. We attribute the significant differences observed in plastics over time to degradation. Although, this study's degradation rate of PA-6, PET, PP, HDPE, and LDPE plastics was slow after 24 months of degradation in different substrates. However, statistically, this study revealed that plastic types and degradation time significantly affected all the loss of plastics' properties checked as seen in figs. 6.32- 6.38. However, we did not measure the microbial mass in the substrates present. We assume they have affected and encouraged the degradation observed in soil and compost. Secondly, the high UV radiation from sunlight in Nigeria contributed to ionising radiation, which played a significant role in starting the degradation of the surface of plastics (Bergmann et al., 2015; Hakkarainen and Albertsson, 2004; Pritchard, 1998), encouraging microbial colonisation. Also, the microorganisms in the substrates used were able to form a biofilm on the surface of the plastic (figs. 6.4-6.14), using these plastics as both carbon and energy sources. While substrates contributed significantly to affecting the weight change of the plastics, on the other hand, zones (countries) where this experiment occurred significantly affected the CI of plastics checked. Therefore, the degradation rate of plastics in the soil and compost was consistent and faster than in leachate, and plastics had more signs of degradation in Nigerian soil though very slowly. It took 24 months for HDPE to have the highest weight loss of 5% in Nigeria soil, which means this HDPE disc will require roughly 480 months to complete degradation. Therefore, developing new bioplastics with higher degradation rates in different environments and safe for environmental microorganisms should be encouraged for sustainable environmental waste management. The next chapter will employ white rot-Fungi (WRF) in degrading PA-6, PET, PP, HDPE, and LDPE plastics to investigate their effect on them.

CHAPTER 7

DEGRADATION OF SYNTHETIC PLASTICS BY ENDOPHYTIC FUNGI *PHANEROCHAETE CHRYSOSPORIUM*, *CERIPORIOPSIS SUBVERMISPORE*, AND *TRAMETES VERSICOLOR*.

7.1 Introduction

Synthetic plastics, which are mostly petroleum-derived polymers such as polyethylene terephthalate (PET), polyethylene (HDPE and LDPE), polypropylene (PP) and polystyrene (PS) etc are known to be recalcitrant in the natural environment, therefore are seen accumulating in the environment at a rate of 25 million tons/ year (Lee et al., 1991; Mohanan et al., 2020). Webb et al. (2013) suggested that plastics go into the environment through poorly upheld waste disposal approaches and routes such as landfilling. Most of these plastic wastes are resistant to natural biodegradation pathways in the environment, lingering for a long time and moving far from their sources to marine bodies. Barnes et al. (2009); Andrady (2011); Harse (2011); Li et al. (2016); Hurley et al. (2020) looked at the production of plastics and sources, occurrences, and effects of plastic waste in the environment. Such accumulations show the undeniable fact that plastics are now a present component within every ecosystem on earth. Synthetic plastics have some advantages: their cost-effectiveness, relative simplicity of production and wide-range applications in today's world. They also have their downside after their usage, which one of them is contributing to environmental pollution. The reason is because of the ineffective management of the plastic waste generated. Therefore, great concern and attention have been drawn worldwide to find possible ways of managing plastic waste, which is one of the most significant pollution concerns in modern times (Rios et al., 2007; Jambeck et al., 2015).

The concern and attention caused by these plastic wastes have led to more practical and novel ways of managing them which one of them is a less mechanical approach to remediation, such as using microorganisms such as bacteria and fungi to accelerate the degradation of plastics (Gu et al., 2000a; Gu, 2003).

These microorganisms, especially fungi, are used because they produce a rich source of lignin-degrading enzymes, which can survive in all environs with little or no nutrient and moisture situations. These lignin-degrading enzymes have been studied and applied to many sectors such as wastewater treatment, textile, and paper industries, and in the degradation of both natural and synthetic plastics (Abdel-Hamid et al., 2013).

Natural and synthetic plastics are potential substrates for heterotrophic fungi and could spread hyphae which can enter the cracks and clefts of plastics (Jeyakumar et al., 2013, Montazer et al., 2019). Therefore, fungi possess an excellent possibility for the biodegradation of synthetic plastics.

Any alteration in the properties of plastics is referred to as degradation, and it could be due to physicochemical, chemical, or biological methods (fig. 7.1). While photo, thermal and mechanical degradations affect the physicochemical properties of plastics. Chemical and biological degradations are seen, causing hydrolysis and oxidation of plastics.

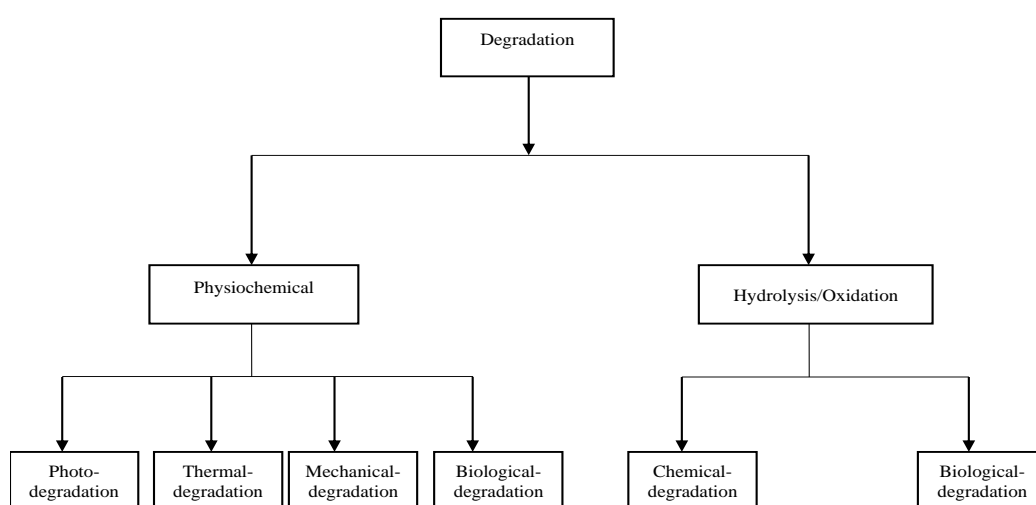


Fig. 7.1 The Pathway to plastic degradation

To improve the degradation of plastics, photo or thermal or chemical initiators could be introduced to the plastic's prior microbial degradation. These initiators produce free radicals on the long plastic chain, triggering a loss of some of the physical properties of the plastics to become oxidized, making the plastics more accessible to microorganisms present for degradation (Chanda and Roy, 1986; Cornell et al., 1984).

Most researchers employed an agar medium for the growth of biological samples, having differences in media with either increased or decreased nutrients and directly affecting plastic degradation (table 7.1). Iiyoshi et al. (1998); Yamada-Onodera et al. (2001); Russel et al. (2011); Shah et al. (2013) also studied the degradation of plastics using different microorganisms followed by FTIR analysis. Loss of peaks, double bonds, and compositional variations in the spectra of plastics indicated that these various plastics degraded.

Table 7. 1 Summary changes found in the literature for plastics after exposure to different biodegradation conditions.

| Plastic | Degradation mode | Analytical method | Changes Observed | References |
|-----------------|-------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| LDPE | a: UV + soil conditions b: <i>B. sphericus</i> | FTIR | Reduced carbonyl index and reduction in ester peaks | Albertsson et al., 1987; Sudhakaret al. 2008 |
| LDPE+12% starch | <i>P. chrysosporium</i> in soils with LDPE with 12% starch. | FTIR | Reduction in the peaks due to biodegradation | Orhan and Buyukgungor 2000 |
| PE with TDPA | <i>Rhodococcus rhodochrous</i> , <i>Cladosporium cladosporioides</i> , and <i>Nocardia asteroides</i> | FTIR, SEM and Molecular weight | Increased carbonyl index, surface physically weak and reduced molecular weight | Bonhomme et al. 2003 |
| PP | Accelerated and outdoor weathering <i>Sporosarcina globispora</i> <i>Bacillus sp</i> in MCW | FTIR, Molecular weight and SEM SEM, FTIR, TGA, weight loss | New carbonyl products formed, reduction in molecular weight and cracks seen on the surface with increased exposure Biofilm on surface, formation of new bonds and decreased thermal stability. | Lv et al., 2015 Jain et al., 2018 |
| PET | <i>Nocardia and Bacillus subtilis</i> . | OM, SEM and XRD | disorientation of PET crystals, microbial colony on PET surface and formation of new peaks | Madhuri and Chetna 2012 |
| PA-6 | <i>P. chrysosporium</i> | DSC and SEM | reducing degree of crystallinity and grooves on surface of PA-6 | Klun et al., 2003 |
| Nylon 6 | <i>T. versicolor</i> | Weight loss, decrease in thickness and FTIR | Reduction in weight and thickness. Decrease in the peaks and formation of new groups. | Chonde et al.,2012 |
| Phenolic resins | <i>P. chrysosporium</i> , | SEM | Rough/cracked surface | Gusse et al., 2006 |

7.1.2 Plastic and microorganisms

The interactions between plastics and microorganisms differ in different substrates leading to the formation of biofilms on the plastics. Hence, the degradation rate of plastics is different with different pathways depending on the environment. Degradation becomes possible when

different factors, including polymer characteristics, type of organism, and nature of pre-treatment, come together. Generally, it results in breaking most chemical bonds, thereby increasing or decreasing carbonyl indices of plastics and forming new functional groups (Fotopoulou and Karapanagioti, 2017).

Microorganisms play several functions in nature; - some are responsible for the degradation of complex and stable lignocellulosic materials such as litters from leaves and wood and remains of dead organisms; - they release nutrients for their metabolic requirements and also contribute to the continuous replenishment of soil quality (Stamets, 2005). Microorganisms can degrade plastic, using their surfaces as a carbon source because of their enzymatic and metabolic potential. Most notably, fungi are considered the main component of degradation because of their ability to drive critical nutrients such as carbon and nitrogen, which is an essential process of life. Fungi are a vastly diverse group of organisms with about 150,000 identified species and 1.5 million unidentified (Hawksworth, 1991). White Rot Fungi (WRF) are essential for nutrient cycling and breaking down fallen leaves and woody materials by excreting extracellular enzymes, especially manganese peroxidase, ligninases and laccase (Kaal et al., 1995). Examples of such WRF are *Phanerochaete chrysosporium*, *Trametes versicolor*, *Lentinula edodes* and *Hypholoma fasciculare*. Utilising fungi to degrade plastics could be an attractive alternative to remediating plastic pollution since they produce very potent enzymes (ligninases) that degrade different parts of the lignocellulosic material and make their nutrients within them readily accessible for metabolic processes (Barr and Aust, 1994). The ligninases formed are free-radical, allowing the fungi to degrade a wide range of persistent organic pollutants used in plastic production. These organic compounds are Dichlorodiphenyltrichloroethane (DDT), Trinitrotoluene (TNT), pyrenes, polychlorinated biphenyls (PCBs), dioxins, etc. (Barr and Aust 1994; Cameron et al., 2000).

In this study, we chose white-rot fungi (WRF) because they are known as the most efficient lignin degrader in nature (Eriksson et al., 1990; Akhtar et al., 1998; de Souza – Cruz et al., 2004; Tanaka et al., 2009). They can degrade all structural components of the polymers. These WRF produce lignin-altering enzymes such as peroxidases, laccases, oxidoreductases and hydrolases, as well as hemicellulases (Guerra et al., 2003; Souza – Cruz et al., 2004), essential for lignin degradation (Eggert et al., 1998) with but phenol groups and non-phenolic lignin groups together with their mediators (Pozdnyakova et al., 2004). This is because of their extracellular oxidative and hydrolytic effect on plastics.

7.2 Aims and Objectives

Studies have shown that strains of many microorganisms such as *Bacillus sp.*, *Pseudomonas sp.*, *Arthrobacter sp.*, *A. flavus*, *T. fusca* have been recognised as having the capacity to degrade several synthetic plastics because of their several metabolic abilities (Singh and Sharma, 2008; Shah et al., 2013). However, three species of White rot fungi (WRF): *Phanerochaete chrysosporium*, *Ceriporiopsis subvermispora* and *Trametes versicolor*, were used in this study to degrade selected synthetic plastics. These species of WRF were chosen because they were readily available in the laboratory when the experiment was set up; their strains are seen in natural isolates, such as Treborth Gardens Bangor, where they were obtained. Finally, their highly effective enzymatic activities are responsible for modifying and degrading lignin and other complex materials such as plastics (Deguchi et al., 1998; Iiyoshi et al., 1998; Baker et al., 2017; Andlar et al., 2018).

This chapter aims to investigate the potential ability of these (WRF)-lignocellulose-degrading fungi to degrade selected plastics- PA, PET, PP, HDPE, and LDPE in pure culture with fungi under controlled laboratory conditions to remediate these plastics across a variety of environments.

Objectives

Checking the rate and effects of microbial degradation of plastic discs; - PA, PET, PP, HDPE, and LDPE using fungi; *P. chrysosporium*, *C. subvermispora*, and *T. versicolor*.

Research Question

RQ: 1. Do microorganisms in a suitable growth medium impact on the degradability of plastics; - PA-6, PET, PP, HDPE, and LDPE?

Hypothesis

White Rot Fungi (WRF) in a suitable growth medium can degrade plastics, - PA, PET, PP, HDPE, and LDPE.

7.3 Materials and Methods

The ability of WRF species to degrade PA-6, PET, PP, HDPE, and LDPE plastic discs was investigated in mixture of nutrient agar culture studies. This study did not consider combining fungi for the degradation of these plastics due to time restraint, however, a follow up microbial measurement was conducted by growing the biofilm that developed in the initial experiment with WRF to determine if any additional microbial species had been encouraged to grow on the plastic discs and may have aided decomposition.

7.3.1 Degradation of plastics by White Rot Fungi

White rot fungi: *P. chrysosporium* (*Pc*), *C. subvermispora*, (*Cs*), and *T. versicolor* (*Tv*) are well known for their lignolytic activity. They were isolated and sourced from the culture collection of Dr Paul Baker, Bangor University. All stock cultures were maintained on malt extract agar at 4°C for 2–12 weeks.

Bacto agar, malt extract agar and glucose were obtained from Sigma Aldrich, U.K. Other chemicals such as glutamine acid, KH_2PO_4 , NaH_2PO_4 , MgSO_4 , ZnSO_4 , CuSO_4 , FeSO_4 and MnSO_4 used for basal medium preparation were obtained from Fischer-Scientific, U.K.

7.3.2 Plastics

HDPE, LDPE, PP, PA, and PET plastic polymers were used in this study. Virgin lightweight plastics (HDPE, LDPE, PP, and PA) in natural sheet form were purchased from Direct plastics, UK. The plastics were: PE300 High-density polyethylene (HDPE), PE300 Low-density polyethylene (LDPE), PPH Polypropylene (PP), and cast Polyamide (nylon 6). The dimension of the natural plastics was 1000 m* 100 m *1.5 mm. (Dimension of height is 1000 m, dimension of width is 100 m while the diameter is 1.5 mm). While Polyethylene terephthalate (PET) sheet used (dimension- 600*600*1.5mm) was purchased from GOOD FELLOW50 (UK). The chosen plastics were used because they are everyday plastics that are used in different applications. Sodium dodecyl sulfate (SDS) was purchased from Sigma Aldrich, UK. Each plastic was cut into discs of 25mm diameter (see fig.7.2) to ensure equal surface exposure and consistency between plastic types. Cutting was performed with cutter and laser machine.

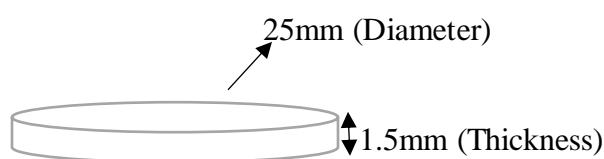


Fig. 7.2 Round disc used for degradation studies.

7.3.3 Sterilisation of materials

All plastic discs (PA, PET, PP, HDPE, and LDPE) used were cut into small discs in triplicates (fig. 7.2) and sterilised overnight by washing in standing 70% (vol/vol) ethanol solution and the knife used in cutting the three fungi was sterilised using heat sterilisation. The impact of ethanol on plastic discs was not considered after cleaning the discs in ethanol. Each disc was

then placed into a pre-weighed sterile petri-dish. The dishes with plastics were placed into an incubator overnight at 25°C to dry, allowed to equilibrate to room temperature, and the weight of the plastic discs was then determined.

7.3.4 Plastic discs culturing and media

The medium contained 15g of Bacto agar and 1.5g of malt extract agar in a nitrogen-free mineral salts solution at pH 7.02 (0.3g of Na₂HPO₄, 1.5g of KH₂PO₄, 1.1g of glutamine acid) and trace element solution was prepared using 0.01g of MgSO₄·7H₂O, 0.01g of ZnSO₄, 0.01g of MnSO₄, 0.1g of CuSO₄ and 0.1g of FeSO₄ in 1 litre of deionised H₂O (pH 7.5) and shaken. 1 ml of the trace element solution was pipetted into the basal medium (Pridham and Gottlieb, 1948; Deguchi et al., 1997). Ninety Beatson-Clark 500ml capacity squat jars were filled with 100 ml of the prepared basal medium (fig.7.3) and were autoclaved for 70 min at 121°C and 1.2 atm to eliminate any form of contamination see fig. 7.3. Each jar was sealed with an aluminium screw-tight lid with a 1.5cm diameter hole, stuffed with cotton wool to act as a filtered air exchange mechanism. Using a ventilation system results in an aerobic environment for each fungal sample.

The basal medium was allowed to stand overnight to cool and solidify in the jars. Each white-rot fungi used was added onto the ninety jars of solidified basal media and left overnight to equilibrate. The pre-weighed sterilised plastic discs were aseptically added to the sterilised culture medium with fungi and incubated at 25°C and 70% humidity. Then degradation was left to progress for 4 and 12 weeks, respectively (fig.7.4), to track the difference in their degradation rates since the pilot experiment conducted after 4 weeks with the WRF revealed changes on the discs. The jars were incubated without shaking for the entire duration of the experimental period. We prepared three replicates of each WRF with a Plastic combination: ninety jars with WRF and Plastics for the study.

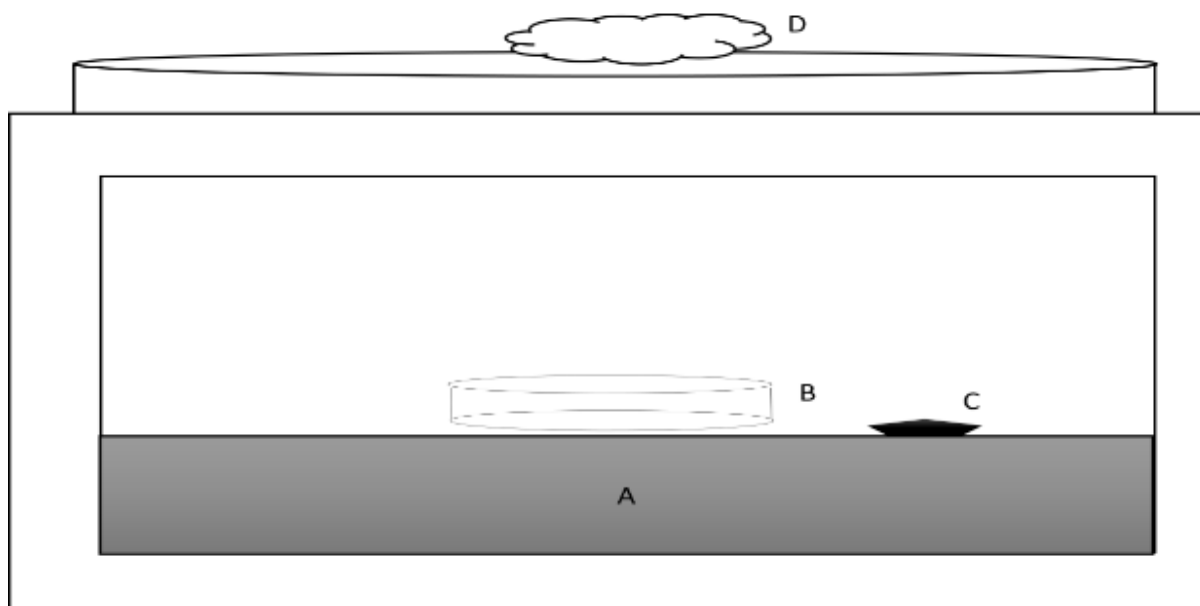


Fig. 7.3 Diagram showing the plastic disc and microorganism on agar: A, growth basal medium (solidified agar), B plastic disc, C the fungi used, D opened lid to allow for oxygen exchange.

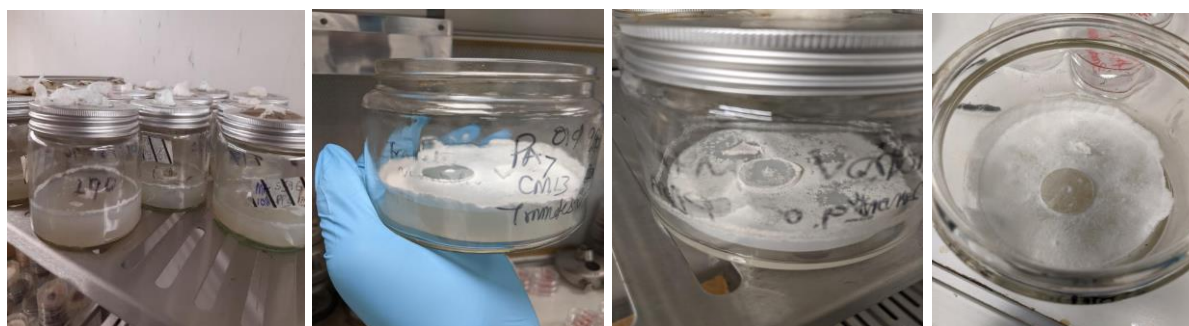


Fig. 7.4 Illustration of incubation for fungi and plastic disc on a growth basal medium

7.3.5 Plastic discs harvest

Plastic discs were taken out after 4 and 12 weeks and washed in water and 70% ethanol to remove as much biofilm from the residual discs as possible. They were dried at 25°C for 24 h. Then their weights were determined after the experiment and kept in a desiccator for 72 hours until the time for analysis. The impact caused during cleaning, such as using ethanol to clean the plastics, was not considered. However, it may have little impact on plastics since chemical factors contribute to the degradation of plastics (Fotopoulou and Karapanagioti, 2017).

7.3.6 Follow-up experiment: Isolating and Identifying other microbes that played a key role in degradation

Isolation and identification of other microbial colonies present from the degradation of plastics with WRF were done using the scraping method (Ibrahim et al., 2009) and spread plate technique on R-2A agar. R-2A agar obtained from Oxoid Ltd Basingstoke, UK, was used to make a media for growing the microbes in the UK. 36.2g of the R2A Agar was added to two empty 1000ml bottle flasks, and then 1 litre of distilled water was added to each flask at a pH of 7.2. Covered with the lids, then shaken and brought to boil in a microwave for 10 minutes with the lids loosely fitted to allow the complete dissolution of the agar. 0.85% of saline solution was made by dissolving 8.5g of NaCl in 1 litre of distilled water in a 1000ml bottle flask with a lid. The flasks with the R-2A agar and the flask with 0.85% saline solution were autoclaved for 15 minutes at 121°C to eliminate contamination and bring it to complete dissolution. Before washing the plastic discs incubated with the WRF, a spore suspension was formed by adding 0.001-0.010g of biofilm seen growing on the discs after 4- and 12-weeks incubation for microbial growth in 2ml Eppendorf plastic of normal saline (0.85% NaCl w/v). Biofilm was scraped into 90 pre-weighed 2ml Eppendorf plastic centrifuge tubes with caps (weight A). The new weight of the tubes with the biofilm was recorded (weight B). 1.5ml of the autoclaved saline solution was added to each tube, and the weight was recorded (weight C). The tubes were put into the mini centrifuge machine for 3 minutes at 5400RPM, 2000 XG to further mix the spore suspension in the 2ml Eppendorf tubes.

The media with the R-2A agar was allowed to cool to 45°C, and 25ml of the prepared media was measured out into ninety Petri-dishes to cover its bottom surface and solidify. The Petri-dishes were covered, labelled, and turned upside down to prevent moisture from condensing on the agar surface until we were ready to introduce the spore suspension formed with biofilm and saline solution. 1ml of the spore suspension was spread plated onto the surface of each plate with R-2A Agar. A sterilized loop was used to spread spore suspension on the Petri-dishes. The Petri-dishes were sealed with parafilm to prevent excessive evaporation during incubation. There were three replicates of Petri-dishes with R-2A Agar, and spore suspension with the biofilm from the plastic discs was incubated for seven days at 25°C and counts were recorded at the end of the seventh day. Then the remainder of the spore suspension (0.5ml) was allowed to dry for seven days at 50°C in an incubator and weighed again (Weight D).

The difference between weights A and D gives the microbes' total biomass.

The total biomass of the microbes/contaminants involved in the degradation of the discs was calculated as follows.

Total biomass = weight D - weight A (Equ.7.1)

Weight A is weight of empty tubes

Weight D is weight after drying the spore suspension

Amount of each microbial colonies = microbial count/ total biomass(Equ.7.2)

We identified the microorganisms present on the petri-dishes at the end of each experiment through visual observation and microscopic analysis for the ones we couldn't see with our bare eyes, then came to conclusion after a discussion with Paul Baker.

7.3.7 Analytical method

Biodegradability was evaluated by visible observation, weight loss, FTIR, microscopic imaging, and SEM.

7.3.7.1 Visual Observation

The observation of visible changes in plastics can be carried out in almost all tests. The following are used to describe degradation, scratches on the surface, presence of holes or cracks, disintegration, discoloration, or formation of hyphae on the surface. These changes observed visually can be used as a first suggestion of any microbial attack. The plastic discs were checked visually after 4 and 12 weeks of incubation in culture medium with fungi to note changes on the discs prior to cleaning. More modern technical observations can be performed on the plastic discs to obtain detailed information about microbial degradation (Ikada, 1999).

7.3.7.2 Light microscopy

Light microscopy is a non-destructive analysis. The degraded discs from the culture media with the fungus were examined after 4 and 12 weeks of incubation under a Leica microscope (model is DM6000 M) with an attached camera at magnification of 200 μ m. This analysis is carried out before and after washing and disinfecting the discs with 70% ethanol. It checks fractures and colonies of possible microorganisms on the surface of the discs which were responsible for degradation. Micrographs of the three replicates of plastics subjected to degradation with the WRF were taken and the best one that portrayed significant effect was used chosen.

7.3.7.3 Determination of Weight Change plastics

This was to determine the loss or gain in weight of plastic discs caused by biodegradation process. The loss in weight of plastics such as in films is generally seen in degradation tests however, no direct proof of degradation is gotten because issues can rise with accurate cleaning of the plastics, or if the plastics fragments excessively. Plastic discs were weighed three times before and after incubation with fungi prior to further analysis. The change in the weights of these discs was determined through the subtraction of values for both pre-incubation and post-incubation, the difference between the two values signify the weight gain/loss. Plastic weight loss or gain will display substrate affinity for organism growth linking to biodegradation of the plastics and with combination of the weight loss and other analytical tests will reveal detailed information regarding the degradation process (Witt et al., 2001; Ojha et al., 2017)

The difference in their weights between initial and final weight shows the extent of plastic utilization by the fungi. (Ojha et al., 2017)

The weight change will be calculated as follows:

$$\text{Weight (g)} = \frac{W_0 - W_m}{W_0} \dots\dots\dots (\text{Equ.7.3})$$

W_0 is the original weight of plastic discs before incubation

W_m is the measured plastic discs weight after incubation in basal growth medium.

7.3.7.4. Decrease in thickness

The thickness of plastic discs was measured by micrometre to track microbial degradation process. Plastic discs will be checked the end of 4- and 12-weeks incubation in fungi to evaluate degradation.

7.3.7.5 Fourier Transform Infrared (FT-IR)

FT-IR is a non-destructive analysis which studies the changes in the structural features of discs in the culture medium for 4 and 12 weeks. It makes use of PerkinElmer precisely spectrum 100 FTIR spectrometer (USA) to identify the composition of plastic samples. FTIR spectra by attenuated total reflectance (ATR) will be obtained at room temperature. Background and sample spectra were obtained using 16 scans at a spectral resolution of 4 cm^{-1} and 64 cm^{-1} , in the wavenumber range of 4000 to 400 cm^{-1} (Ter-Halle et al., 2017). A minimum of 3 replicates of infrared spectra were recorded for both the control and degraded plastic samples.

The structural features cover the changes which appear mostly on the carbonyl regions functional groups on the discs during degradation which is responsible for a drop/gain in weight of the plastics (Yamada-Onodera et al., 2001; Russel et al., 2011; Shah et al., 2013).

After both incubation periods, plastics were cleaned, dried, and put in the desiccator for 72 hours before analyses on the FT-IR machine. The background spectrum was recorded before each sample was measured, and each spectrum was obtained by scanning over a range of 4000 – 650 cm^{-1} at a resolution of 8 cm^{-1} , with fifteen scans for each measurement. OPUS 7.5 software was used to obtain the measurements and baseline correction was applied to each spectrum.

7.3.7.6 Carbonyl Index

Carbonyl index (CI) was used to measure the degree of biodegradation mostly on carbonyl groups ($\text{C}=\text{O}$) and methylene groups ($-\text{CH}_3$) as its value depends on the degraded carbonyl bond. CI is obtained by the formula given in

$$\text{Carbonyl Index (CI)} = \frac{\text{Absorbance at } 1740\text{cm}^{-1}(\text{the maximum carbonyl peak})}{\text{Absorbance at } 1460\text{cm}^{-1}(\text{the maximum carbonyl peak})} \dots \text{(Equ.7.4)}$$

7.3.7.7 Scanning electron microscopy

SEM is also a non-destructive analysis which makes use of high beam of electrons from a Phenom desk-top SEM (Phenom, FEI, USA), with samples affixed to aluminium stubs using conductive carbon pads, with gold coating at an accelerating voltage of 5 kV in a magnification range of 500-20,000x at a resolution of 30 nm.

The topography and morphology of the plastics which includes surface roughness, grooves, cracking, porosity, and notches was determined using the Phenom pro-suite surface analysis software. Measurements were taken at a replication level of 3 measurements from each plastic sample.

The plastic samples discs were pasted onto the SEM sampler (10 μm -25mm diameter) on a stub using carbon tube and sputtered coated with gold (Klun et al., 2003; Madhuri and Chetna 2012). Then morphology of plastic discs was checked for changes.

7.3.8 Data and statistical analysis

SPSS version 25.0 (SPSS Inc., CHICAGO, IL) was used to statistically analyse data. 1-way ANOVA was used to check the differences in from the weight changes of plastic types, the

comparison of means based on Tukey's HSD post Hoc tests were carried out on the data for a confidence level of 95 %, (significant difference ($P < 0.05$)). The graphs and diagrams were processed using Excel software. Errors bars reveal the standard error of three replicates for each experimental point.

7.4 Results and Discussion

Studies conducted on plastics with *P. chrysosporium*, *C. subvermispora*, and *T. versicolor* in basal medium culture conditions revealed the effect of fungi on plastic discs. We hypothesised that these results revealed plastic degradation because of the observed changes, supporting this chapter's aim and objectives.

7.4.1 Visual Observation

Visual inspection of the plastic discs after being placed on the agar with *P. chrysosporium*, *C. subvermispora*, and *T. versicolor* for 4 and 12 weeks, respectively, were carried out. As shown in figs. 7.5 and 7.6 below. Fig. 7.5 are the microscopy images of the discs captured before cleaning and disinfecting them, while fig. 7.6 are images of discs captured after cleaning and disinfecting them. There were apparent differences between the degraded discs. Also, discolouration was observed. Powdery residue around their edges and abrasive marks on some of the discs was also visible in the culture medium (Fig. 7.5) (Klun et al., 2003; Madhuri and Chetna, 2012).

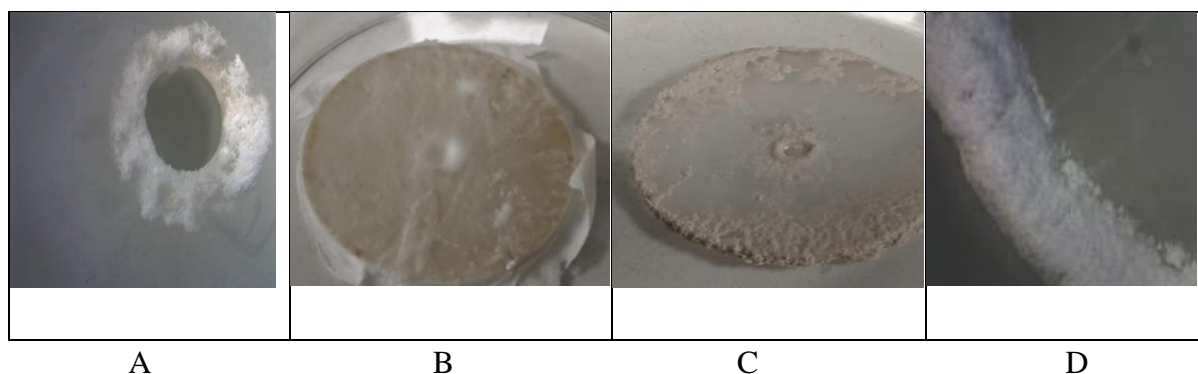


Fig. 7.5 Microscopy images of some uncleaned plastic discs (A is PP, B is PA-6, C is LDPE and D is HDPE) after incubation in a culture medium with fungus: *T. versicolor* after 4 and 12 weeks respectively.






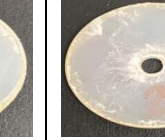




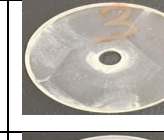

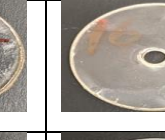


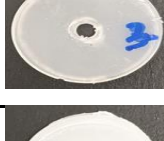
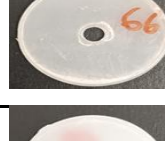

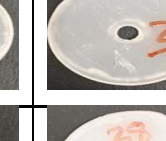
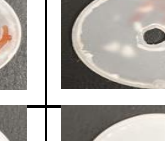








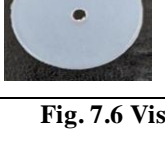
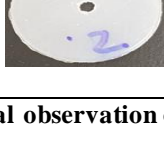

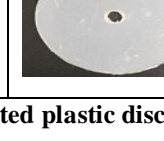

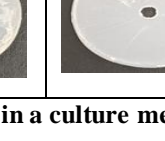
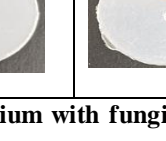
| Plastic types | Original plastic | <i>P. chrysosporium</i> (Pc) | | <i>C. subvermispora</i> (Cs) | | <i>T. versicolor</i> (Tv) | |
|---------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| | | 4 weeks | 12 weeks | 4 weeks | 12 weeks | 4 weeks | 12 weeks |
| PA |  |  |  |  |  |  |  |
| PET |  |  |  |  |  |  |  |
| PP |  |  |  |  |  |  |  |
| HDPE |  |  |  |  |  |  |  |
| LDPE |  |  |  |  |  |  |  |

Fig. 7.6 Visual observation of cleaned/disinfected plastic discs after incubation in a culture medium with fungi after 4 and 12 weeks.

From the visual observation, the white powdery substance and mycelium network were evident on the plastic discs after 4- and 12-weeks incubation with the fungi, as seen in fig. 7.5. There were slight changes on discs after being cleaned, especially PET and PA-6 discs that exhibited slight brownish discolouration and slightly damaged surface after 4 and 12 weeks in culture media (fig. 7.6).

PA-6 exhibited signs of biofilm formation on some parts at four weeks with fungi: *P. chrysosporium*, *C. subvermispora*, and *T. versicolor*. This biofilm became evident with a white-like structure on the discs at 12 weeks. The discs' surfaces and sides/edges became rough to touch with slight discolouration at 12 weeks. PET also demonstrated surface damage at 4 weeks with white patches, which was noticed more on PET discs with fungi: *P. chrysosporium* and *C. subvermispora*. However, at 12 weeks, all the discs presented biofilm colonisation with all the fungi used in the study.

PP discs showed some biofilm colonisation with *C. subvermispora* and *T. versicolor* at 4 and 12 weeks, in contrast with minor visible changes observed on HPDE discs with all the fungi. All LDPE discs displayed little changes on their surfaces at 12 weeks with *C. subvermispora* and *T. versicolor*. Generally, the changes observed from the visual check-in in both figs. 7.5 and 7.6 were biofilm colonisation, the roughness of the discs' surfaces and edges, and slight colour change. These observed changes became more evident with the plastic in the media with fungi after 12 weeks.

7.4.2 Light microscopy

The plastic discs were also closely studied using optical light microscopy before degradation and after 4 and 12-weeks incubation with fungi, *P. chrysosporium*, *C. subvermispora*, and *T. versicolor*. Changes and comparisons were noted in figs. 7.7 and 7.8 This enabled us to observe larger superficial changes in plastic surfaces. In this part, the three images of the plastic discs used for the experiments followed the same pattern in changes observed, so one representative image is chosen for each plastic-type and WRF combination.

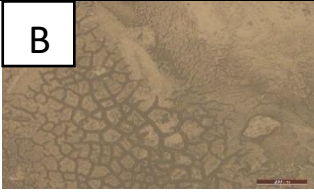
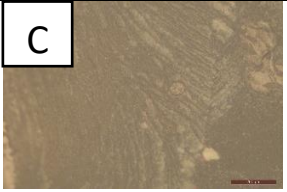
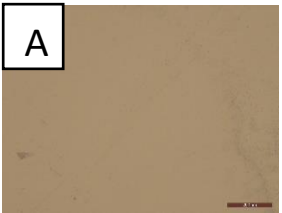

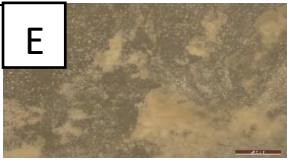


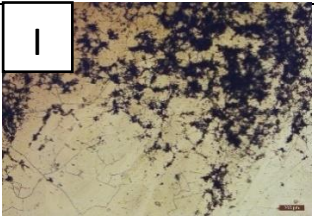
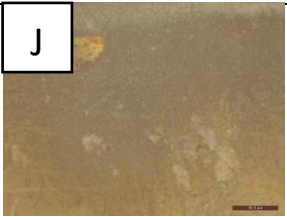



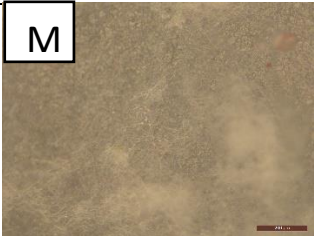
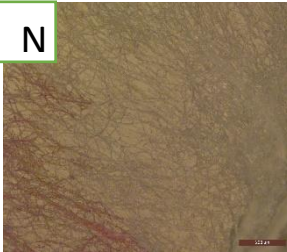
| Plastic Disc and fungus | Control | After 4 Weeks | After 12 Weeks |
|-----------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PA <i>Phanerochaete chrysosporium</i> | |  |  |
| PA <i>Ceriporiopsis subvermispora</i> |  |  |  |
| PA <i>Trametes versicolor</i> | |  |  |
| PET <i>Phanerochaete chrysosporium</i> | |  |  |
| PET <i>Ceriporiopsis subvermispora</i> |  |  |  |
| PET <i>Trametes versicolor</i> | |  |  |

Fig. 7.7 Microscopy images of plastic discs- PA and PET before degradation (A, and H), after 4 weeks (B, D, F, I, K and M) and after 12 weeks (C, E, G, J, L and N) fungal degradation in *P. chrysosporium* , *C. subvermispora* and *T. versicolor*. Magnification 200µm

Fig. 7.8 reveal the micrographs from microscopy analysis on plastics, PP, HDPE, and LDPE with *P. chrysosporium*, *C. subvermispora*, and *T. versicolor* in 4 and 12 weeks used for this study. Changes and comparisons were noted.


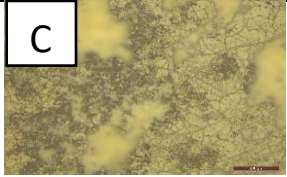
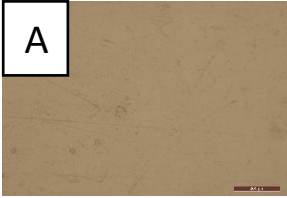
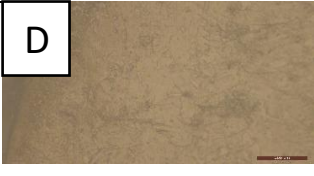









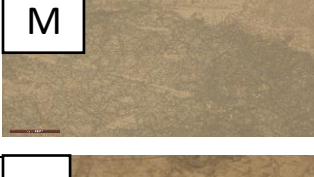
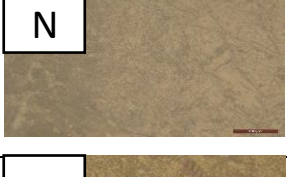
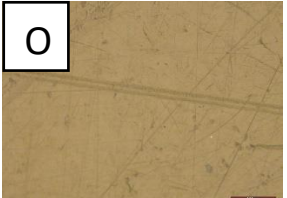

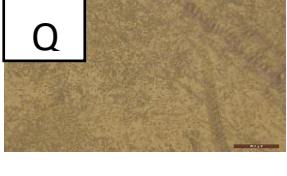
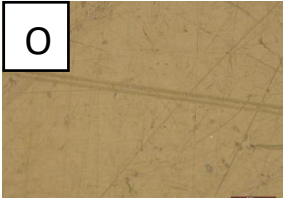
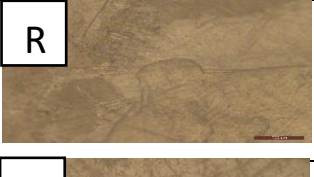



| Plastic Disc and fungus | Control | After 4 Weeks | After 12 Weeks |
|--------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PP <i>Phanerochaete chrysosporium</i> | |  |  |
| PP <i>Ceriporiopsis subvermispora</i> |  |  |  |
| PP <i>Trametes versicolor</i> | |  |  |
| HDPE <i>Phanerochaete chrysosporium</i> |  |  |  |
| HDPE <i>Ceriporiopsis subvermispora</i> |  |  |  |
| HDPE <i>Trametes versicolor</i> | |  |  |
| LDPE <i>Phanerochaete chrysosporium</i> |  |  |  |
| LDPE <i>Ceriporiopsis subvermispora</i> |  |  |  |
| LDPE <i>Trametes versicolor</i> | |  |  |

Fig. 7.8 Microscopy images of plastic discs- PP, HDPE, and LDPE before degradation (A, H and O), after 4 weeks (B, D, F, I, K, M, P, R and T) and after 12 weeks (C, E, G, J, L, N, Q, S and U) fungal degradation in *P. chrysosporium*, *C. subvermispora* and *T. versicolor*. Magnification of 200µm

Fig. 7.7 displayed both the control and degraded microscopic images of PA-6 and PET plastic discs. While fig. 7.7 A and H revealed the control microscopy images of PA-6 and PET, fig. 7.7 B, D, F, I, K and M showed the microscopy images of PA-a and PET plastic discs degraded after 4 weeks and fig. 7.7 C, E, G, J L and N revealed PA-6 and PET plastic discs after 12 weeks of incubation with fungi: *P. chrysosporium*, *C. subvermispora* and *T. versicolor*. The surfaces of these plastic discs on which the biofilm was seen growing directly were degraded by all the fungi employed. These plastic surfaces had biofilm compared to the controlled plastic discs, which maintained smooth surfaces even after 12 weeks of incubation without fungi. There were notable differences between control images of PA-6 and PET plastic discs (fig. 7.7 A and H) when compared to images after 4 weeks of incubation with fungi (fig. 7.7 B, D, F, I, K and M). There were hyphae (thread-like networks) that were growing on the surface of the discs after 4 weeks of making a network on the discs. This thread-like network growing on the surface of PA-6 and PET discs became more evident after 12 weeks of incubation with all the fungi, especially with fungus *T. versicolor*. (fig. 7.7 G and N). Degradation on PA-6 and PET discs became more evident after 12 weeks of incubation, while the thread-like network seen on PA-6 after 4 weeks turned mycelium with spores on the PA-6 discs, PET discs turned to a more branched thread-like network. This is assumed to be the fungi growing on discs and consuming them (Klun et al., 2003; Madhuri and Chetna, 2012).

PET and PA-6 discs had more biofilm growing on them, which agrees with the results obtained from the weight change and discolouration, FTIR, and other results of the PET and PA-6 discs. Their functional groups encouraged this change mainly because their active sites aided these changes observed on the discs.

On the other hand, fig.7.8 displayed the microscopic images of the control and degraded images of PP, HDPE, and LDPE in the three fungi. Figs. 7.8 A, H and O revealed the control microscopy images of PP, HDPE and LDPE, while fig. 7.8 B, D, F, I, K, M, P, R and T showed the images of PP, HDPE and LDPE plastic discs degraded after 4 weeks. Fig. 8 C, E, G, J, L, N, Q, S and U revealed PP, HDPE and LDPE plastic discs after 12 weeks of incubation with fungi: *P. chrysosporium*, *C. subvermispora* and *T. versicolor*, respectively.

Also, degradation took the same trend on PP, HDPE, and LDPE. The hyphae were seen growing on the surfaces of these discs, and we could see several hyphae on the discs after 4 weeks, as shown in Fig. 7.8. A white fungal network was seen on discs after 12 weeks of incubation with fungi, as seen in fig. 7.8 C, L and S: PP in *P. chrysosporium*, HDPE in *C.*

subvermispora and LDPE, respectively. All the changes observed through the microscopy of the discs are an indication of a surface degradation of these plastics, which became more apparent over time with the fungi.

7.4.3 The change in weight

Weight change with the combination of other techniques was employed to track microbial degradation in plastics. The fungi used for the degradation process secreted enzymes which attached themselves to the surface of the plastic discs, initiating degradation through oxidation or hydrolysis. Thereby altering the properties of the plastics, which may lead to the weight change.

The plastic discs incubated in a culture medium with fungi for 4 and 12 weeks observed the gain or loss in weight. Fig. 7.9 shows the initial and final weights, while fig 7.10 shows the decrease in the thickness of the plastic discs over time. There were fluctuations in the weight change of discs while there was a decrease in the thickness of the discs over time. Fig. 7.9 presents us with the results from the average of the three replicates used for the degradation study of plastic discs added to culture media with fungi for 12 weeks in the UK. Table 7.2 below summarises the weight change (%) observed after 12 weeks of degradation of plastic discs with fungi, *P. chrysosporium*, *C. subvermispora* and *T. versicolor*.

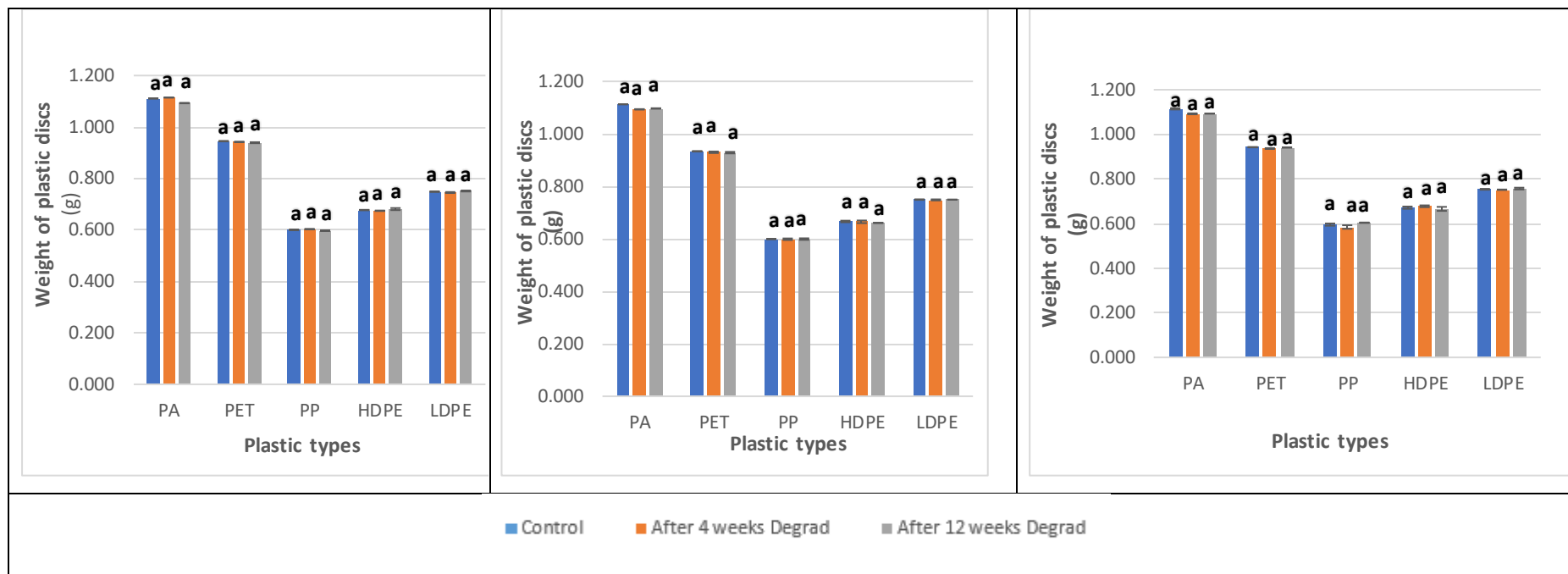


Fig. 7.9 Measurement of the weight changes (in g) of the degraded PA, PET, PP, HDPE, and LDPE discs by the potential fungi, namely, in a culture medium with fungi (A) *P. chrysosporium*, (B) *C. subvermispora* and (C) *T. versicolor* after 4 and 12 weeks of incubation. *Y-Axis values differ. Data represents mean \pm SE (n = 3). Means with the same letter are not significantly different.

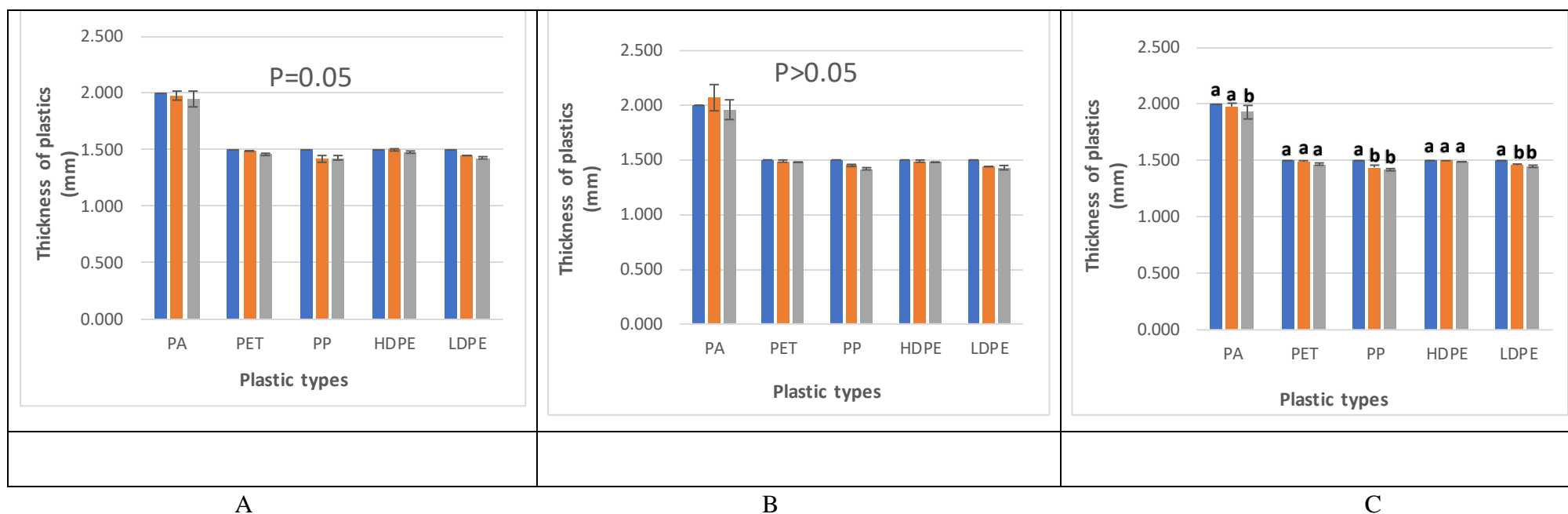


Fig. 7.10 Measurement of the changes in the thickness (in mm) of the degraded PA, PET, PP, HDPE, and LDPE discs by the potential fungi, namely, in a culture medium with fungi (A) *P. chrysosporium*, (B) *C. subvermispora* and (C) *T. versicolor* after 4 and 12 weeks of incubation.*Y-Axis values differ. Data represents mean \pm SE (n = 3). Means with the same letter are not significantly different.

Table 7. 2 The combined weight change (%) of the plastic discs with fungi, *P. chrysosporium*, *C. subvermispora* and *T. versicolor* after 12 weeks in the UK.

| Plastics | Fungi | | |
|-----------------------------------|--------------------------------|--------------------------------|-----------------------------|
| | <i>P. chrysosporium</i> (%) | <i>C. subvermispora</i> (%) | <i>T. versicolor</i> (%) |
| Polyamide-6 | -1.6±0.001 | -1.4±0.001 | -2±0.000 |
| Polyethylene terephthalate | -0.6±0.002 | -0.6±0.003 | -0.2±0.001 |
| Polypropylene | -0.5±0.001 | 0 | 1.3±0.001 |
| High-density polyethylene | 0.6±0.004 | -0.8±0.001 | -0.8±0.009 |
| Low-density polyethylene | 0.3±0.002 | 0 | 0.4±0.004 |

Fig. 7.9 and table 7.2 revealed the average of the three replicates used for the degradation study in this chapter with their small standard error. PA-6 and PET discs had weight losses in all the three fungi studied, with PA-6 discs having the highest weight loss in *T. versicolor* after 12 weeks which was about -2%. PP discs had a weight loss of -0.5% in *P. chrysosporium*, 0 in *C. subvermispora*, while PP discs gained weight (1.3%) in *T. versicolor* after 12 weeks. HDPE discs also had a weight loss in both *C. subvermispora* and *T. versicolor* (-0.8 and -0.8%), respectively, while the discs gained weight (0.6%) in *P. chrysosporium* after 12 weeks. LDPE discs did not lose weight; instead, they were zero in *C. subvermispora* and gained weight (0.3 and 0.4%) with *P. chrysosporium* and *T. versicolor*, respectively.

The reasons for the weight gain observed by the PP discs with *T. versicolor*, HDPE discs with *P. chrysosporium* and LDPE discs in *P. chrysosporium* and *T. versicolor* could be by activities of microorganisms directly on the discs. They secrete enzymes and form biofilms that increased over time in the jars with the media and attached themselves to the surface of the plastic discs. El-Shafei et al., (1998); Taghavi et al. (2021) attributed the increase in the weight of films subjected to degradation to the colonisation of microorganisms. Although, some plastics lost weight with the fungi used.

Statistically, time had no significant influence on plastics' weight change (Time *P. chrysosporium*: $F=2.115$, $P>0.05$; Time *C. subvermispora*: $F=2.459$, $P>0.05$; Time *T. versicolor*: $F=2.367$, $P>0.05$) with the 3 fungi.

Nowak et al. (2011) suggested that the fungus *Penicillium funiculosum* influenced the weight of polyethylene terephthalate after 84-day incubation. Klun et al. (2003) examined the effect of *P. chrysosporium* on Polyamide discs when exposed as the only nitrogen source to the

fungus in submerged environments. Their results revealed that the fungus attached itself to the polymer films, slowly degrading them and reducing their molar mass by 50% after three months. The results obtained in weight changes of the discs were lower compared to the results obtained by Klun et al. (2003); Nanda and Sahu (2010); Nowak et al. (2011).

The increased weights of plastic discs higher than their initial weights as observed in PA-6 with *C. subvermispora* suggests that plastic discs gained more weight after four weeks of incubation with the fungi or absorbed water from the surrounding with the help of its functional group. This may indicate an increase in the fungal growth biofilm accumulating on the discs as seen in fig. 7.6 with PA-6 in *T. versicolor* at 12 weeks. However, there was no weight loss or gain by PP and LPDE in *C. subvermispora*. The lack of weight gain or loss for discs incubated with fungi depicts less microbial activity or not as fast as in other plastics with other fungi.

7.4.4 Decrease in thickness

The thickness of the plastic discs incubated in a culture medium with fungi for 4 and 12 weeks, were observed in micrometre and shown in Fig. 7.10. There was decrease in the thickness of all the plastic discs in the three media with fungi after 4 weeks except PA in fungus; *C. subvermispora* and HDPE that remained constant after 4 weeks in fungi *P. chrysosporium* and *T. versicolor*. The thickness of all the plastic discs further reduced in the three fungi media with fungi except PP in fungus *P. chrysosporium* after 12 weeks. The thickness and access area of plastics will also determine the extent at which the microorganisms will penetrate the plastic discs (Montazer et al. 2020). Chonde et al. (2012), also treated nylon sheets with fungus *T. versicolor*. The observed that there was not just a decrease in the weight of the nylon sheets but also a decrease in the thickness of these sheets within 75 days of treatment with fungus. Statistically, time had no significant influence on plastics' decrease in thickness with fungi: Pc and Cs (Time *P. chrysosporium*: $F=3.436$, $P=0.05$; Time *C. subvermispora*: $F=1.875$, $P>0.05$) however, time had a significant influence on plastics' decrease in thickness with fungus *T. versicolor* (Time *T. versicolor*: $F=6.365$, $P<0.05$).

Also, the type of plastic discs used significantly influenced the decrease in the thickness of plastics ($P<0.05$). Table 7.3 summarised the significant effect of thickness based on plastic type.

Table 7. 3 Post Hoc tests (Tukey Ba) and significance levels for the means of thickness based on plastic type.

| Thickness | | | | | |
|-------------------------|----|-------|-------|-------|-------|
| Tukey B ^a | | | | | |
| Subset for alpha = 0.05 | | | | | |
| Plastics | N | 1 | 2 | 3 | 4 |
| PP | 27 | 1.455 | | | |
| LDPE | 27 | | 1.463 | | |
| PET | 27 | | 1.486 | | |
| HDPE | 27 | | | 1.493 | |
| PA | 27 | | | | 1.994 |

Means for groups in homogeneous subsets are displayed.

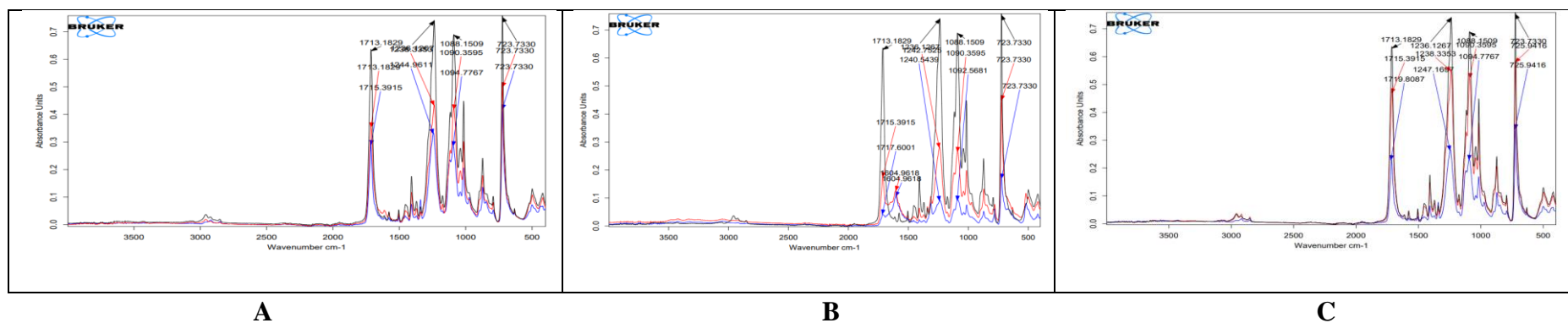
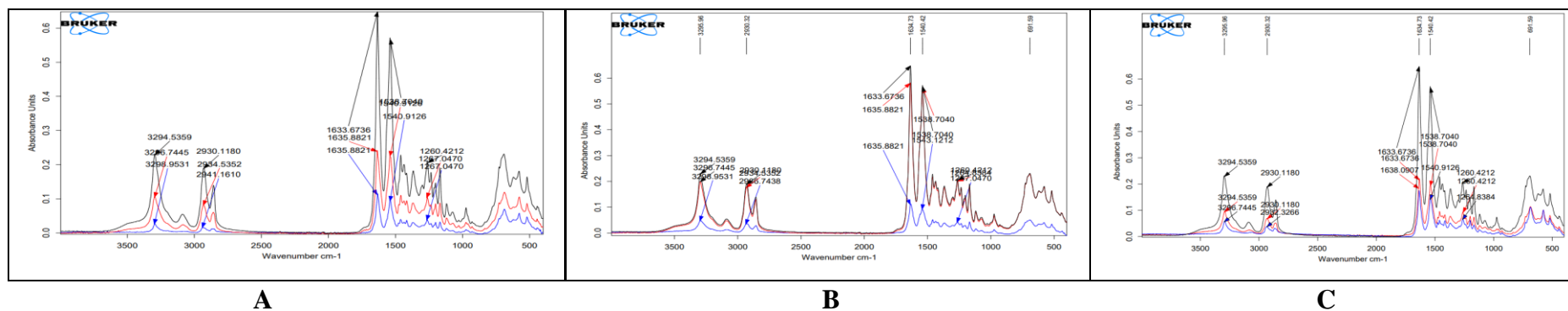
Based on observed means.

a. Uses Harmonic Mean Sample Size = 27.000

Statistically, (2-way ANOVA) used revealed that the type of plastic discs, and time significantly influenced their thickness after 12 weeks of incubation study. (plastic type: $F=567.550$, $P<0.05$; time: $F=7.799$, $P<0.05$) .

7.4.5 Fourier Transform Infrared (FT-IR)

FTIR spectroscopy offers vital about the interaction of those chemical bonds with Infrared radiation. Figs. 7.11-7.15 and table 7.5 reveal the reduction, shift and formation of peaks of the plastics discs incubated in fungi; (*P. chrysosporium* , *C. Subvermispora* and *T. Versicolor*) after 4 and 12 weeks. A decrease in absorbance (AU) is caused by decreased absorbency of infrared radiation. This is due to decrease or lack of bonds within the expected wavelength region (Figs. 7.11-7.15).



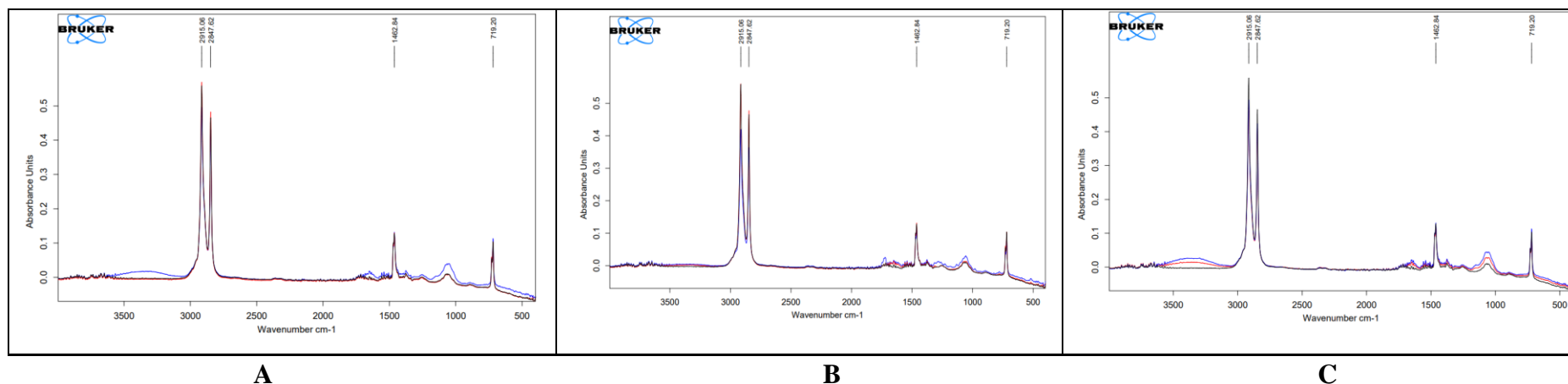


Fig. 7.15 FTIR spectra of the degraded LDPE discs (black peak shows original LDPE, red peak shows LDPE after 4 weeks incubation and blue peak shows LDPE after 12 weeks incubation) by the potential fungi (A) *P. chrysosporium*, (B) *C. subvermispora* and (C) *T. versicolor* after 4 and 12 weeks of incubation.

Table 7.4 The shift of FTIR peaks of (control) before degradation and degraded PA, PET and PP discs with *P. chrysosporium*, *C. subvermispora* and *T. versicolor* after 4 and 12 weeks of incubation.

| Plastic | Control (cm ⁻¹) | <i>Phanerochaete chrysosporium</i> (cm ⁻¹) | | <i>Ceriporiopsis Subvermispora</i> (cm ⁻¹) | | <i>Trametes versicolor</i> (cm ⁻¹) | |
|-------------|--------------------------------|---------------------------------------------------------------|----------|---------------------------------------------------------------|----------|---------------------------------------------------|----------|
| | | 4 weeks | 12 weeks | 4 weeks | 12 weeks | 4 weeks | 12 weeks |
| PA-6 | 3295 | 3297 | 3299 | 3297 | 3299 | 3295 | 3297 |
| | 2930 | 2935 | 2937 | 2935 | 2941 | 2930 | 2932 |
| | 1633 | 1636 | 1636 | 1636 | 1636 | 1633 | 1638 |
| | 1538 | 1539 | 1543 | 1541 | 1541 | 1538 | 1540 |
| PET | 1713 | 1713 | 1715 | 1715 | 1718 | 1715 | 1720 |
| | 1236 | 1238 | 1245 | 1243 | 1241 | 1238 | 1247 |
| PP | 2946 | 2950 | 2948 | 2950 | 2950 | 2950 | 2950 |
| | 2835 | 2840 | 2837 | 2840 | 2840 | 2840 | 2837 |
| | 1455 | 1455 | 1455 | 1455 | 1455 | 1455 | 1459 |
| | 1375 | 1375 | 1375 | 1375 | 1375 | 1375 | 1377 |

Poly amide 6 (PA-6)

The functional groups of PA-6 played an important role in the fungi degrading the plastics. The spectra of PA-6 discs after degradation differed from those of the original PA-6 discs (fig. 7.11). The result displayed little difference after 4 weeks of incubation with three fungi but exhibited noticeable changes after 12 weeks with the three fungi. The control spectra of PA-6 discs, as seen in (fig. 7.11 A B and C), displayed a number of peaks reflecting the nature of PA-6 at wave numbers; 3294, 3080, 2930, 2858, 1633, 1538, 1459, 1262 and 975 cm⁻¹. Three main changes were observed from the spectra of PA-6 after incubation with the three fungi.

Firstly, there was a reduction in the peak intensity in all the areas of interest of PA-6 discs compared to their peaks before degradation. There were reductions of the weak peaks of PA-6 discs after 4- and 12-weeks incubation with the three fungi at wavenumber 1751cm⁻¹ as compared to the original PA-6 peaks. This is because the C-H bond of the methylene group next to the nitrogen is very weak and therefore is readily oxidized during degradation (Dong and Gijsman, 2010). Also, the peaks of PA-6 between wavenumbers 3294-2858 cm⁻¹ in the three fungi became broader after 12 weeks. This reduction of the peak intensities of all PA-6 discs was less after incubation for 4 weeks but became apparent after 12 weeks with the three fungi.

Table 7.4 revealed another change observed from the spectra of PA-6 after incubation with the three fungi, which was the progressive shifts of the peaks to higher wavenumber. Any shift of peaks of plastics causes an increase in vibrational frequency. There were shifts of the PA-6 peaks to higher wavenumber after 4 weeks in all the fungi, *P. chrysosporium* and *C. subvermispora*, except for fungus *T. versicolor*, while all PA-6 peaks observed further shifted toward higher wavenumber after 12 weeks with all the fungi. The more time the PA-6 discs were with the fungi, the more vibrational frequency increases (shifting of the peaks toward higher wavenumber), depicting degradation of these PA-6 discs.

Not only was there a reduction and shift in the peaks, but the third change observed was also the disappearance of peaks at wavenumber 3080cm^{-1} between wavenumbers 3294.5 and 2930.1cm^{-1} after 12 weeks with all the fungi used, as seen in fig. 7.11 A, B and C. According to Cannon (1960) and Gonçalves et al. (2007), after trying to degrade polyamides also observed the disappearance of the peak at 3080cm^{-1} and attributed it to an oxidation reaction of the stretching of C-N bonds and deformation of N-H bonds which causes the degradation of the PA-6 discs. i.e., the transformation of (CO-NH-CH_2) mono substituted amide groups to (CO-NH_2) non-substituted amide groups (Gonçalves et al., 2007).

These changes observed after the microbial degradation of PA-6 at the different wavenumbers were due to the hydrolysis and oxidation reaction from the action of fungi used in this study (Chonde et al., 2012). They proved the change of the amides ($-\text{CONH}-$) functional groups of PA-6 chains. See fig. 7.16 and observe the microbial degradation of polyimides forming hydrolysis products.

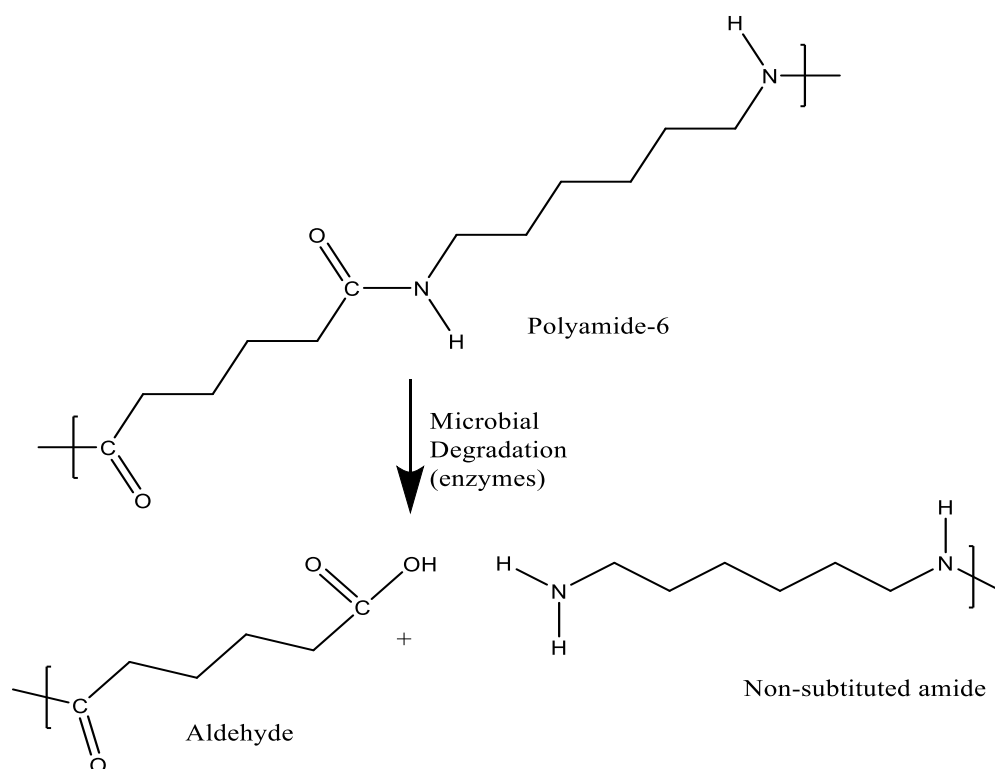


Fig. 7.16 Microbial hydrolysis of polyamide-6

Polyethylene terephthalate (PET)

Fig. 7.12 reveals the characteristic FTIR peaks of the functional groups of PET discs before and after 4- and 12-weeks incubation with 3 fungi. The main wavenumbers identified were: 1713, 1236, 1088, 870 and 724 cm^{-1} corresponding to ketones ($\text{C}=\text{O}$), ether aromatic ($\text{C}-\text{O}$), ether aliphatic ($\text{C}-\text{O}$), aromatic ($\text{C}-\text{H}$) and aromatic ($\text{C}-\text{H}$) bond. The occurrence of all the peaks after 4 and 12 weeks of incubation directly correlates to the peaks of discs before incubation except some peaks of PET that disappeared, and new ones were formed at wavenumber 1604 cm^{-1} in all the spectra which was more distinct with fungus *Ceriporiopsis Subvermispora* (fig 7.12 B).

Their peak intensities and absorbance units were reduced in all the PET discs checked after the period of incubation. Fig. 7.17 suggests possible mechanisms of microbial degradation of Polyethylene terephthalate forming hydrolysis products.

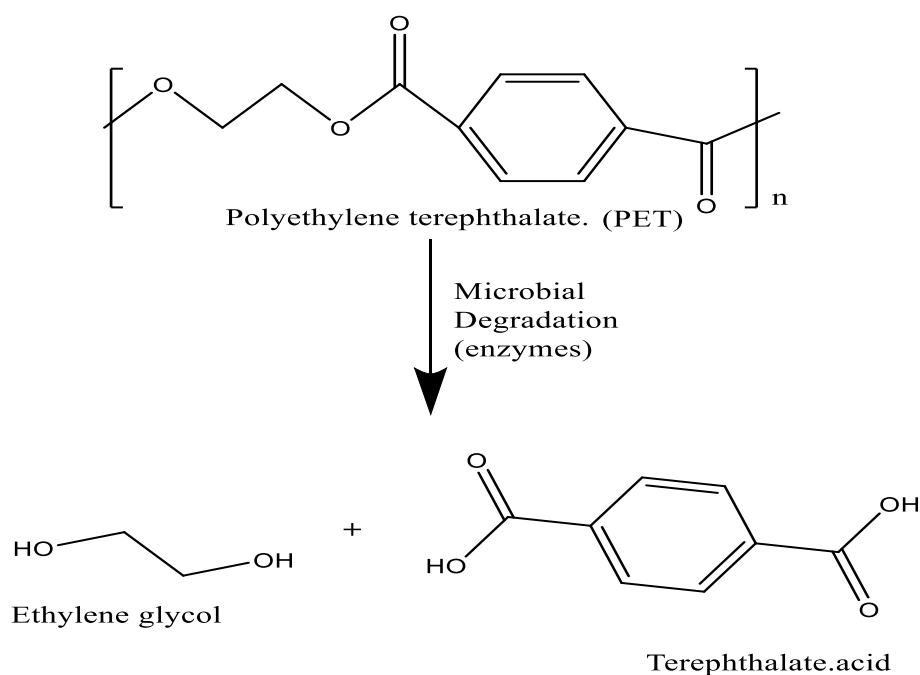


Fig. 7.17 Microbial hydrolysis of polyethylene terephthalate (PET)

There was reduction, shift, disappearance, and formation of new peaks as seen in fig 7.12 Which were all attributed to the effect of the enzymes on its functional groups leading to degradation. Prominent peak intensities of PET spectra reduced after 4 weeks incubation with the 3 fungi, and a further reduction of these peaks after 12 weeks in all the fungi depicting fungal degradation.

Also, there was a shift of the peaks to higher wavenumber of all the peaks after the 4 weeks of incubation and further shift after 12 weeks with the all the fungi as seen in table 7.5, most especially at wavenumber: 1713 and 1238cm^{-1} which corresponds to the ketones bearing the carbonyl group ($\text{C}=\text{O}$) and the ether aromatic group ($\text{C}-\text{O}$). While a peak between wavenumbers 1236 and 1088cm^{-1} disappeared from all the spectra after 4- and 12-weeks incubation but most especially after 12 weeks.

Finally, the peaks after degradation at wavenumber $3060, \text{cm}^{-1}$ were seen becoming flatter and broader. The shifts, and reduction in the peaks and the appearance of new peaks of degraded discs is because of the change in the chemical and structural properties caused by microbial degradation (Zhang et al. 2004). The microorganisms play important role in utilizing diethylene glycol terephthalate (DTP) a product of PET as a sole carbon and energy source (Zhang et al. 2004; Chonde et al. 2012)

Polypropylene (PP)

Figs. 7.13 A, B and C reveal both the control and degraded spectra of the PP discs incubated with fungi. They show a number of peaks at wavenumber: 2915, 1745, 1454, 1375, 1175 and 1084 cm^{-1} which corresponds to C-H stretching, C=O stretching, CH_3 bending, CH_2 wagging, C-O-C symmetric stretching and asymmetric CH_3 bonds respectively.

A few observations were made which all point to the alteration of the discs properties and was due to the microbial degradation. There was reduction in the intensities of the peaks of the PP spectra after incubation with the fungi, however, it was a slight reduction. Also, there were shifts in some peaks of the PP spectra as observed after incubation from table 7.5 at wavenumbers; 2946, 2835, 1455 and 1375. The peaks at 1455 and 1375 cm^{-1} were constant and did not shift after 4- and 12-weeks incubation in *P. chrysosporium* and *C. subvermispora* and after 4 weeks in *T. versicolor* and further shifted after 12 weeks in *T. versicolor*.

The peak at wavenumber 1080 cm^{-1} became more intense and prominent in fungi *P. chrysosporium* and *T. versicolor* after 12 weeks. Also, while there was appearance of peaks after 4 weeks and more intense after 12 weeks in fungi *P. chrysosporium* and *T. versicolor* in the hydroxyl region at wavenumber 3450 cm^{-1} of PP, the peak in the carbonyl region at wavenumber 1720 cm^{-1} of PP discs became more intense with time in all the fungi as seen in fig. 7.13.

The increase in the intensities of the broad peaks of PP at hydroxyl group was due to the surrounding intermolecular hydrogen bonded hydroperoxides and alcohols while the increase in the intensities of peaks at the carbonyl regions of ketones which is often used to monitor the oxidation process, leading to oxidative degradation of PP discs (Moldovan et al. 2012).

It is observed in fig. 7.13, that these intensities of these groups increased with time in all fungi at 12 weeks incubation. The formation and prominence of these new peaks after incubation with fungi suggested the fungi attack on the polar groups of PP making the discs more susceptible to microbial degradation with time.

Polyethylene (PE)

Figs. 7.14 and 7.15 reveal the spectra of the FTIR spectra of LDPE and HDPE plastic discs respectively. While LDPE and HDPE share several properties due to the same methyl group (C-H bonding) linked together, their basically different internal compositions give rise to many differences too. Figs. 7.14 and 7.15 therefore reveal their characteristic peaks before and after incubation with 3 fungi at wavenumbers: 2914, 2846, 1467, 1461, 730 and 718 cm^{-1} . The only difference between the characteristic peaks of HDPE and LDPE is the additional small peak at 1377 cm^{-1} this is because of the more abundant methyl group in very branched LDPE. This

difference in polymer chains leads to distinct properties in each plastic (Nishikida and Coates, 2003; Asensio et al. 2009; Brandon et al. 2016).

High-Density Polyethylene (HDPE):

There were 2 main changes seen occurring as seen in (fig. 7.14 A, B and C). Firstly, all the intensities of peaks of HDPE discs reduced with a decrease in absorbance of the peaks after incubation as compared with the control peaks before incubation with all fungi. They peak slightly reduced at 4 weeks and further reduction was observed at 12 weeks in the 3 fungi.

Also, the HDPE control disc without fungus showed a peak at 2914, 2846, 1467, 1461, 730 and 718 cm^{-1} while HDPE with fungi *P. chrysosporium*, *C. subvermispora* and *T. versicolor* indicated a shift peak intensity after 4 weeks at wavenumbers 2914, 2846, 1467, 1461, 730 and 718 cm^{-1} , 2914, 2846, 1467, 1461, 730 and 718 cm^{-1} and 2916, 2848, 1467, 1463, 732 and 719 cm^{-1} respectively and indicated a shift peak intensities after 12 weeks at wavenumbers 2919, 2852, 1467, 1461, 732 and 719 cm^{-1} , 2919, 2852, 1467, 1461, 730 and 718 cm^{-1} and 2920, 2852, 1473, 14635, 735 and 723 cm^{-1} respectively (Fig. 7.14). While there was no shift after the first 4 weeks of incubation with fungi *P. chrysosporium* and *C. subvermispora* there was noticeable shifts after 4 weeks and further shift to a higher wavenumber after 12 weeks of incubation in *T. versicolor*.

Low-Density Polyethylene (LDPE):

Fig. 7.15 revealed the spectra of the LDPE discs before and after incubation with fungi. There were variations in the peaks. Unlike the intensity of HDPE peaks that reduced with time in all the fungi, the intensity of LDPE peaks increased with time in all the fungi. Peaks after 12 weeks had the highest peaks, followed by peaks of HDPE after 4 weeks. The control HDPE had the least peaks. Also, as all the intensities of peaks of LDPE discs was increasing, the absorbance of the peaks increased after incubation as compared with the control peaks before incubation with all fungi.

There was little or no shifting of the peaks of LDPE discs but there was a formation of weak peaks at wavenumber 1710–1715 cm^{-1} which corresponds to carbonyl group and was due to hydrolysis process. There was also a formation of a broad peak at wavenumber 3450 cm^{-1} for all the LDPE discs with the fungi most especially with *P. chrysosporium* and *T. versicolor* and after 12 weeks of incubation. These peaks were observed at hydroxyl group due to the vibrations in the stretching of the neighbouring intermolecular O-H bond in alcohols. (Bhatia et al. 2014). the peaks at wavenumber 1107 cm^{-1} became stronger over the period with fungi. The reason for this was due to microbial activity which caused degradation of this discs. Das and Kumar (2014) observed that the peaks of LDPE were altered after incubation with 2

microbial isolates. Additional peaks were observed after LDPE was treated with fungal consortia in vitro study for 10 days and 3 months (Negi et al. 2011; Sha et al. 2011). All the changes associated to the peaks of LDPE is due to hydrolysis of the functional groups which is caused by microbial attack (Bhatia et al., 2014).

Ibiene et al. (2013); Ojha et al. (2017) conducted microbial degradation of HDPE and LDPE sheets. They observed shifts and alteration in the peak intensities of the polymers. There is a broad peak showing in the Hydroxyl groups ($3650\text{--}3200\text{ cm}^{-1}$) to distinguish the degraded discs from the control discs of both PE and PP spectra (Figs. 14-16). This agrees with the report of Guadagno et al. (2001) and Gardette et al. (2013) who observed an increase in the -OH stretching peak of hydroxyl group due to formation of alcohols and hydroperoxides (degradation products) during oxidation (Moldovan et al. 2012). The broad peak in hydroxyl region is more intense in PP discs than PE (Alariqi et al 2006).

Therefore, using microbes to degrade plastics causes various changes in their functional groups thus affecting their properties. Generally, FTIR results revealed the degradation of all plastic using fungi as seen in this study (Figs. 7.11-7.15). The result depicts reduction, broadening and shift of all the peaks with a decrease in the absorbance of their functional groups and sidechain peaks also.

While the reduction of some peaks of plastics may be small, others are big. Small reductions can be from incomplete consumption of their major functional groups by enzymes activities. Therefore, may continue with oxidation/hydrolysis/hydroxylation of these functional groups resulting to cleavage/shortening of polymer chains and converting them into small groups such as monomers and oligomers thus, altering of the original properties of the plastics.

7.4.6 Determination of the Carbonyl Index of the plastics

The carbonyl index is a parameter used to identify the effect of FTIR on the functional groups of plastics such as the carbonyl groups, i.e., tracking degradation of plastics. The measured carbonyl groups are usually expressed as a carbonyl index (CI) The carbonyl index (CI) is presented as the average value of different FTIR spectra for each plastic and were calculated for both the control and the degraded plastics. The result obtained revealed the effects of microbial attack on the degraded plastics after 4 and 12 weeks of incubation and therefore, supports the idea of oxidation of plastics which eventually have been utilized by the microorganisms (Ratanakamnuan, & Aht-ong, 2006; Ojha et al. 2016; Almond et al. 2020). The carbonyl indices of plastics used for this study were calculated and displayed in fig. 7.18. The incubation of PA-6, PET, PP, HDPE, and LDPE using fungi; fungi *P. chrysosporium*, *C.*

subvermispora and *T. versicolor* respectively caused significant alterations in not only the chemical structure of the plastics but also on the physical properties of the plastics also. Which one of the alterations was on the carbonyl indices of the plastics as shown in fig. 7.18.

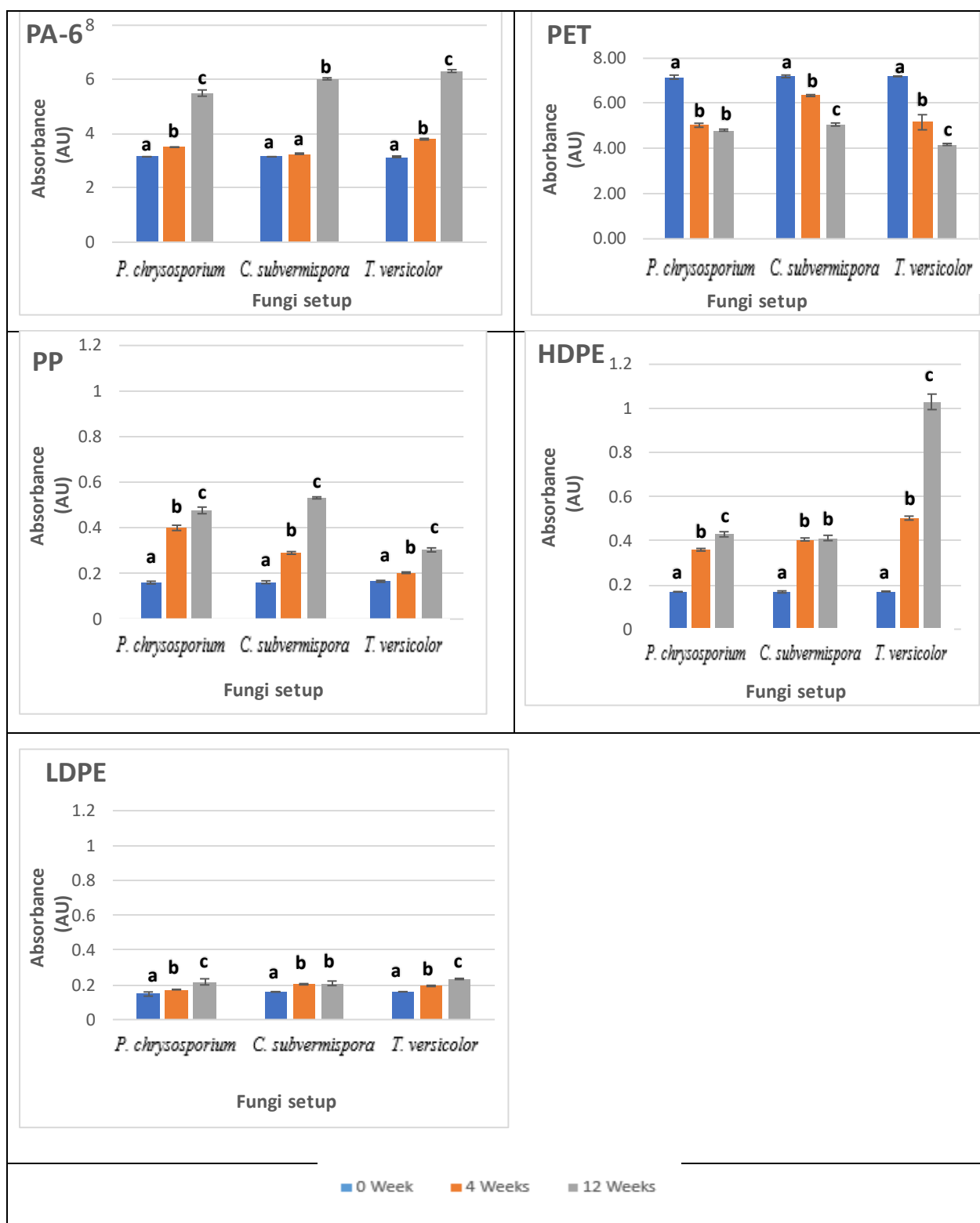


Fig. 7.18 Plots of the carbonyl indices of the plastics discs PA-6, PET, PP, HDPE, and LDPE after 4 and 12 weeks of incubation in a culture medium with fungi *P. chrysosporium*, *C. subvermispora* and *T. versicolor* respectively

Fig. 7.18 PA-6 revealed the average carbonyl index before and after degradation. The CI average values of PA-6 before degradation were 3.15, it increased slightly after 4 weeks incubation, and further increased after 12 weeks incubation with all the fungal species used. This is due to oxidation of their functional groups over time with fungi causing main chain scission. The results after 12 weeks incubation with fungi were 5.5, 6 and 6.3 respectively, twice the obtained result from before degradation. This confirms increase in degradation over time with fungi. The CI of PP also increased overtime with all fungal species used in this study when compared to the values obtained before degradation. The average CI value of PP discs before degradation was 0.16 in fungi *P. chrysosporium*, *C. subvermispora* and *T. versicolor* respectively. The increased to 0.4, 0.29 and 0.2 after 4 weeks incubation and further increased to 0.48, 0.53 and 0.3 respectively after 12 weeks incubation with all the fungi. This was due to the increased oxidation of the weak carbonyl bond of the PP discs after incubation with the 3 fungi.

The average CI values of degraded PE (HDPE and LDPE) followed the same trend of PA-6 and PP. The discs had their CI values increase over time after incubation with the 3 fungi. The average CI values of HDPE discs before degradation was 0.16 and increased to 0.17, 0.20 and 0.19 after 4 weeks incubation and further increased to 0.21, 0.21 and 0.23 respectively after 12 weeks incubation with all the fungi. While LDPE discs before degradation was 0.17. It increased to 0.36, 0.40 and 0.5 after 4 weeks incubation in fungi *P. chrysosporium*, *C. subvermispora* and *T. versicolor* respectively and further increased to 0.43, 0.41 and 1 after 12 weeks incubation with all the fungi. The difference in the obtained CI values of degraded HDPE and LDPE discs is that LDPE had the obtained CI values after 12 weeks almost 3 times the values of CI before degradation which was 0.16 with all the fungi while HDPE had small increase of CI values after 12 weeks incubation. Therefore, the higher the degree of CI of polyethylene plastics, indicates a higher degree of plastic degradation (Krehula et al. 2014). This difference in the CI values of HDPE and LDPE could be attributed to the difference in their molecular structures. (Sudhakar et al. 2008; Fontanella et al. 2010; Devi et al. 2015 and Montazer et al. 2020) used different microorganisms to degrade both HDPE and LDPE, they concluded that LDPE degrades faster than HDPE, perhaps because the polymer chains of LDPE are (branched) more closely packed than those of HDPE and that LDPE has a lower content of vinylidene defects, which have been shown to be directly linked with oxidization of the polymer.

Increase in CI values of PA-6, PP, HDPE, and LDPE in fig.7.18 depicts fast oxidation on the carbonyl bonds which is attributed to an increase in the activities of fungal enzymes causing degradation. The fast oxidation on the carbonyl bonds increases the rate of the formation of new carbonyl bonds in the degradation products formed. it is hoped that the CI values will keep increasing as degradation progresses (Latos-Brozio and Masek 2020).

On the contrary, PET in fig.7.18 presents an opposite trend which suggests that the average CI values decrease overtime with fungi *P. chrysosporium*, *C. subvermispora* and *T. versicolor* respectively. The reduction in the CI values of PET confirms the idea that carbonyl groups of the plastic were depleted because plastics have been utilized by the fungi (Ratanakamnuan, U. & Aht-Ong 2006). PET discs before degradation were 7.20 in all the fungi used here. The decreased to 5.03, 6.35, and 5.2 after 4 weeks incubation and further decreased to 4.82, 5.07, and 4.2 respectively after 12 weeks incubation with all the fungi. Here, reduction in CI values is attributed to carbonyl group been depleted (breaking of C=O and C-O bonds of PET during ester-cleavage) (Vague et al. 2019). Thus, further reduction indicates more depletion of carbonyl groups leading to more degradation of the PET discs.

The differences observed in the oxidation of plastics used here is due to the fungal activities on the plastics which require different abilities to oxidize their bonds and generate degradation products depending on the properties of these plastics (Roger et al. 1986; Montazer et al. 2020).

Furthermore, the fungus fungi *T. versicolor* significantly had the greatest impact on all plastics from fig. 7.18 except in PP where fungus *C. subvermispora* had the greatest impact and *T. versicolor* had the least impact.

Canopol et al. (2020), suggested that the (CI) of degraded PE plastic samples buried for 10 years was between 1.5 and 2 times higher than before 10 years and the control materials i.e., that degradation of the plastics samples increased with time. Contrary, to the result obtained, Dolezel, (1967); Albertsson, (1987); Weiland, (1995); Ratanakamnuan, & Aht-Ong, (2006); and Ojha et al. (2017) conducted on degradation of plastics in exposure to the environment and different microbial culture. They all concluded that the CI of plastics reduced overtime after various route of degradation was employed.

Statistically, time and plastic type had significant influence on plastics' CI with fungi: *P. chrysosporium*, *C. subvermispora*, and *T. versicolor* (Time *P. chrysosporium*: F= 71.949, P<0.05; Time *C. subvermispora*: F= 227.942, P<0.05; Time *T. versicolor*: F= 238.491, P<0.05) and (plastic type

P. chrysosporium: $F=7297.424$, $P<0.05$; plastic type *C. subvermispora*: $F=30680.894$, $P<0.05$; plastic type *T. versicolor*: $F=19583.323$, $P<0.05$).

Therefore, time and the type of plastic used significantly influenced the CI of plastics ($P<0.05$).

7.4.7 Scanning electron microscopy (SEM)

PA, PET, PP, HDPE, and LDPE plastics discs exposed to *P. chrysosporium*, *C. subvermispora* and *T. versicolor* were also investigated by SEM to check their surface morphologies by allowing electron microscopes to provide higher resolution images of the discs. Incubation resulting from fungal growth shows surface grooves seen on the discs (figs. 7.19-7.20).

Fig. 7.19 revealed the SEM images of both the control and degraded images of PA and PET plastic discs. Figs. 7.19 A and H are the control SEM images of PA and PET, fig. 7.19 B, D, F, I, K and M are the SEM images of PA-6 and PET plastic discs degraded after 4 weeks while fig. 7.18 C, E, G, J, L and N are the SEM images of PA and PET plastic discs after 12 weeks only of incubation with fungi: *P. chrysosporium*, *C. subvermispora* and *T. versicolor*.

The morphology of all PA and PET plastic discs were affected by all the fungal species studied. The presence of coarse surfaces, small cavities and mycelium network were observed after 4 weeks (figs. 20 B, D, F, I, K and M) incubation with all the fungi. This can be attributed to the actions of fungi on the surface of the discs. The small cavities and mycelium network on the surface of the discs after 12 weeks soon turned to large cavities now with pits, holes and cracks as seen in figs.20 C, E, G, J, L and N. Suggesting further microbial degradation of the discs. Nauendorf et al. (2016) demonstrated that formation of biofilm/hyphae on the surface of plastic can be influenced by some factors which are surface unevenness, plastic hydrophilic surface features, and the properties of the medium used as well as on cell surface properties.

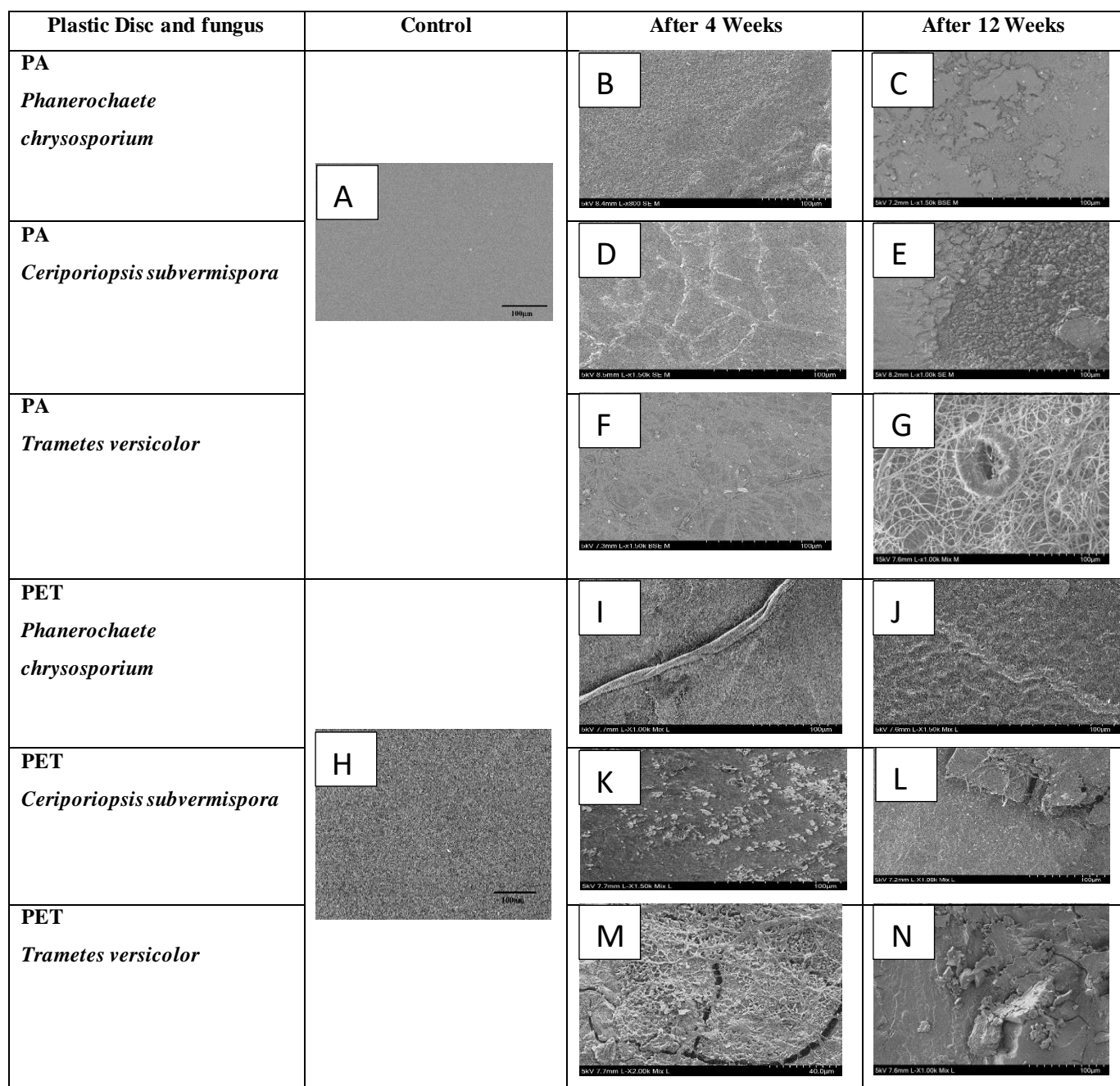


Fig. 7.19 SEM images of plastic discs- PA-6 and PET before degradation (A, and H), after 4 weeks (B, D, F, I, K and M) and after 12 weeks (C, E, G, J, L and N) fungal degradation in *P. chrysosporium*, *C. Subvermispora* and *T. Versicolor*. The solid bar in A and H = 100 µm, all images were taken at 1000 - 1200x magnification.

Fig. 7.20 shows the SEM micrographs of PP, HDPE, and LDPE disc surfaces before, after 4 weeks and after 12 weeks incubation with fungi. Figs. 7.20 A, H and O displayed the smooth surfaces of microscopy images of PP, HDPE and LDPE, Figs. 7.20 B, D, F, I, K, M, P, R and T showed the images of the plastic discs after 4 weeks and Figs. 7.20 C, E, G, J, L, N, Q, S and U revealed the plastic discs after 12 weeks of incubation with fungi: *P. chrysosporium*, *C. Subvermispora* and *T. Versicolor* respectively.

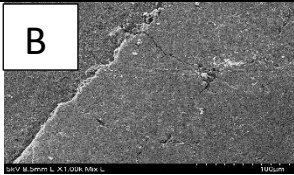
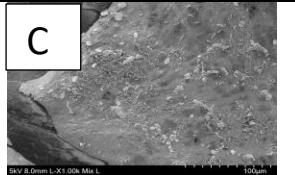
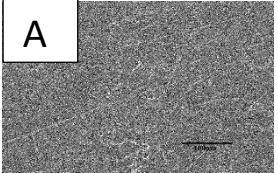
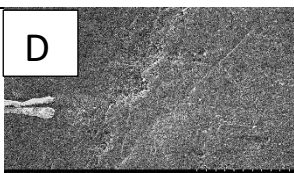
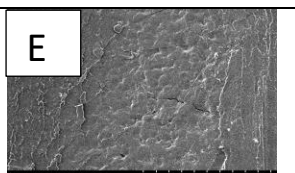
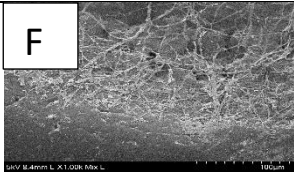
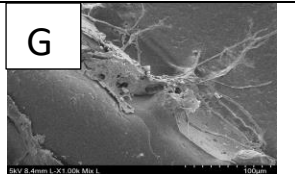
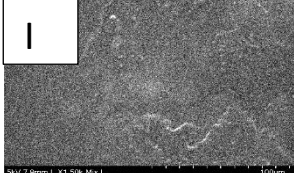
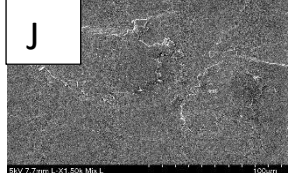
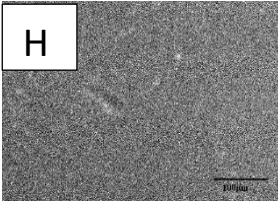
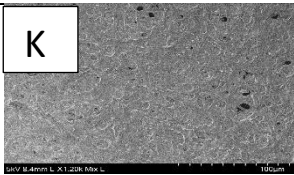
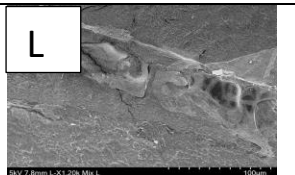
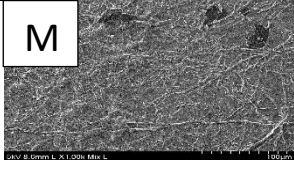
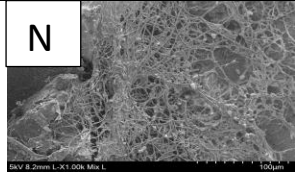
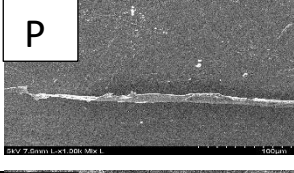
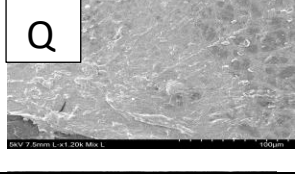
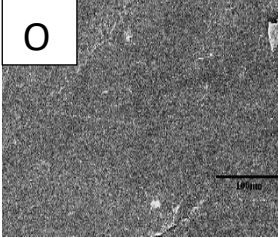
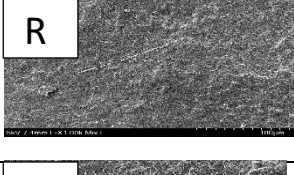
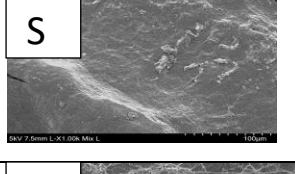
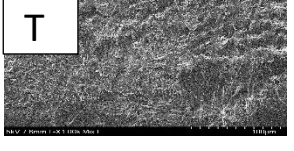
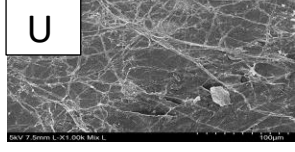
| Plastic Disc and fungus | Control | After 4 Weeks | After 12 Weeks |
|--------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| PP <i>Phanerochaete chrysosporium</i> | |  |  |
| PP <i>Ceriporiopsis subvermispora</i> |  |  |  |
| PP <i>Trametes versicolor</i> | |  |  |
| HDPE <i>Phanerochaete chrysosporium</i> | |  |  |
| HDPE <i>Ceriporiopsis subvermispora</i> |  |  |  |
| HDPE <i>Trametes versicolor</i> | |  |  |
| LDPE <i>Phanerochaete chrysosporium</i> | |  |  |
| LDPE <i>Ceriporiopsis subvermispora</i> |  |  |  |
| LDPE <i>Trametes versicolor</i> | |  |  |

Fig. 7.20 SEM images of plastic discs- PP, HDPE and LDPE before degradation (A, H and O), after 4 weeks (B, D, F, I, K, M, P, R and T) and after 12 weeks (C, E, G, J, L, N, Q, S and U) fungal degradation in *P. chrysosporium*, *C. subvermispora* and *T. versicolor*. The solid bar in A, H and O = 100 µm and all images were taken at 1000 -1200x magnification.

The effects of degradation were seen after 4 weeks of incubation compared to the smooth surfaces of the discs shown before incubation. Further damages were seen on the discs after 12 weeks of incubation with the fungi with holes, pits, ridges, cracks, and the presence of mycelium networks. The growth of the fungi used was mainly in the form of biofilm/ white powdered substances on the surface of the plastic discs, as seen in fig.7.6 The result obtained is consistent, agreeing with the results of visual observation, microscope images, weight loss and FTIR. Deguchi et al. (1997) and (1998); Gusse et al. (2006); Klun et al. (2003); Manzur et al. (2004); Madhuri and Chetna (2012); Odusanya et al. (2013) all looked at the impacts done on different plastic material after incubated with different microorganisms, and the concluded that their SEM images all had physical changes on their surfaces. This is because of degradation caused by different microorganisms employed.

Klun et al. (2003) stressed the need for time if apparent degradation should be observed in plastics. They revealed that after 3 weeks of incubating nylon-6 with fungus, minor changes were observed on nylon sheets. However, after 3 months of exposure, to fungus, nylon plastics displayed noticeable profound hollows on their surfaces. The growth of mycelium, cavities and damage to the discs increased over the 4 – and 12 weeks. It was a function of the oxidation level of plastic discs leading to the degradation of these discs (Ohtake et al., 1995). The degraded surfaces of all the plastic discs checked revealed a general surface alteration of the discs compared to the control discs that retained their gloss/ smoothness (Fig. 7.21), which is characteristic of the control discs (Rouillon et al., 2016; Gijsman, 2008).

From the SEM results in figs. 7.19 and 7.20), *C. subvermispora* had the least impact on all plastic discs while *T. versicolor* had the most notable impact on all the discs after 4 and 12 weeks. No notable morphological changes were found on control discs, though they were also incubated under the same conditions. In the case of the discs incubated with the fungi, morphological changes were observed after 4 weeks, which continued to increase after 12 weeks.

Therefore, comparing the SEM images obtained in figs. 7.19 and 7.20, it can be concluded that *P. chrysosporium*, *C. subvermispora* and *T. versicolor* can degrade plastics under suitable conditions (Jaya et al., 2020).

7.5 Follow-up experiment: Measurement of other Microbial Communities present in the degradation study with WRF.

Microbial degradation of plastics is driven mainly by microorganisms such as white-rot fungi because they are involved in the degradation of wood and complex carbon compounds such as lignin. However, these fungi have enzymes which naturally coexist with other fungi and bacteria and could degrade complex materials such as plastics. From the results obtained in this chapter, it is established that *P. chrysosporium*, *C. subvermispora* and *T. versicolor* all took part in the degradation of plastic, PA, PET, PP, HDPE, and LDPE. Degradation caused a significant impact on the physical, structural, and morphological properties of these plastic discs. WRF is often accompanied by a succession of bacteria and other fungi in forming mycelium network/biofilm on the plastic discs. The biofilm formed decreases the plastics' hydrophobicity, improving the degradation rate (Kiatkamjornwong. et al., 2001). However, the hydrophobicity of the bacteria would be enhanced in the absence of a carbon source which in turn leads to an increase in attachment properties of the bacteria (Sanin et al., 2003). Bacterial–fungal interactions (BFI) significantly impact all the materials employed, ranging from aggressive to beneficial relationships (Embacher et al., 2021). Fig. 7.21 shows the photo images and microscopy images of the microbial communities seen on the agar plates with the plastic discs, while fig. 7.21 shows the microbial count in grams per dry mass of hyphae seen on the agar plates with the plastic discs.

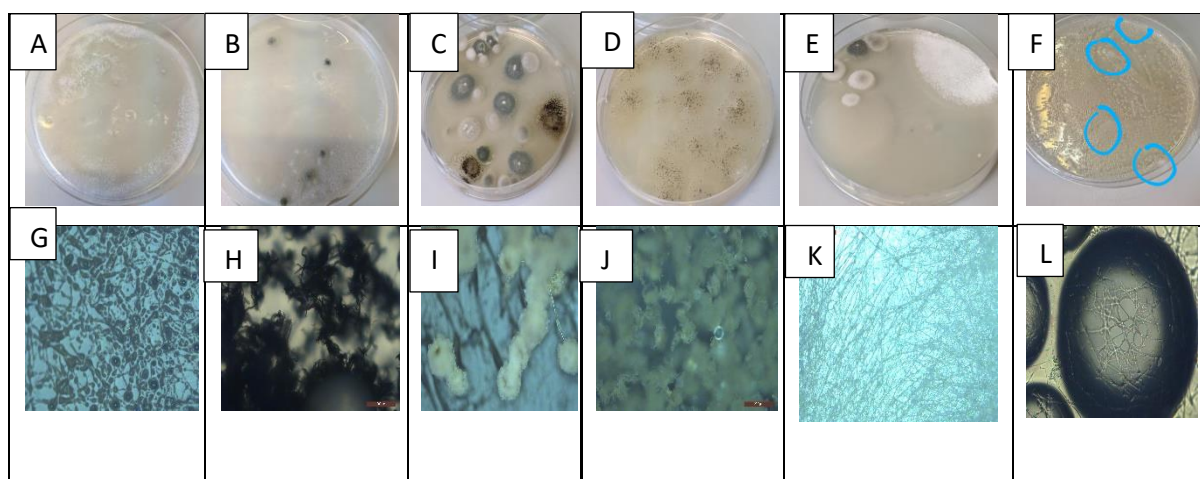


Fig. 7.21 Photo images (A-F) and microscopy images (G-L) of microbial activities on the agar plates (A and G; C and I; E and K after 4 weeks and B and H; D and J; F and L after 12weeks) with fungi; *P. chrysosporium*, *C. subvermispora* and *T. versicolor* respectively.

Fig. 7.21 A-F displays camera images of plates (A and B- after 4 and 12 weeks) with *P. chrysosporium*; (C and D- after 4 and 12 weeks) with *C. subvermispora* and (E and F- after 4 and 12 weeks) with *T. versicolor*. Showing the different colonies of microbial organisms that

took part in the degradation of these plastics. And fig. 7.21 G-L displays the microscopic images of plates (G and H- after 4 and 12 weeks) with *P. chrysosporium*; (I and J- after 4 and 12 weeks) with *C. subvermispora* and (K and L- after 4 and 12 weeks) with *T. versicolor* showing the colonies of diverse hyphae/mycelia network of the microbial organisms that took part in the degradation of these plastics.

The results seen from the contamination of the fungi setup fig. 7.21, followed the same trend in showing diverse colonies of microbes present on plates with most of the plastics and fungi, *P. chrysosporium*, *C. Subvermispora* and *T. versicolor* respectively. We had to select the ones that with the best images to present the result.

Fig. 7.21 also revealed many microbial activities that encouraged degradation of the plastic discs. These (both fungi and bacteria) ranged from different coloured and shaped structures such as filamentous, spherical, spiral, and cob-web network. Table 7.5 will further characterise the microbial colonies as seen visually and with microscope.

Table 7.5 Characteristics of microbial communities associated in plastic degradation. + represents little colony-forming units (CFU), while ++ shows more colony-forming units (CFU) and +++ represents most abundant colony-forming units (CFU) observed.

| Plates Fungi isolates | Fungi | Bacteria | Colour | Description |
|--------------------------|-------|----------|--------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>P. chrysosporium</i> | + | + | Green, grey, brown, White-like powdery colonies. | Completely covered with diverse colonies of fungi, powdery, filamentous, velvety, irregular cob-web structure which are mostly, <i>Penicillium sp.</i> , <i>Mucor sp.</i> and yeast and yellow regular rounded-bacteria. |
| <i>C. subvermispora</i> | +++ | + | Green, brown, White powdery colonies. | Spreading fungi, wavy surface, filamentous, cottony, whitish centre with greenish edge which are mostly, <i>Penicillium sp.</i> , <i>Mucor sp.</i> , mold, yeast and <i>Fassarrim sp.</i> Had irregular bushy structure with different yellow rounded regular bacteria. |
| <i>T. versicolor</i> | ++ | +++ | Green, grey, white, transparent swelling patches with powdery substance. | Entirely covered with varied coloured colonies of fungi which are filamentous, cottony and bushy, greenish centre with whitish edge which are mostly, <i>Penicillium sp.</i> and yeast regular rounded pale-yellow clustered bacteria with irregular cobweb like structure fungus on its surface. |

Most of the fungal communities observed in addition to *P. chrysosporium*, *C. subvermispora* and *T. versicolor* as used in the degradation of the plastic discs are *Penicillium sp.*, *Mucor sp.*, *Fassarrim sp.* mold and yeast while the bacteria community observed are mostly motile bacteria which were seen spreading over the plates and are probably *Pseudomonas sp.* Images obtained from fig. 7.21 by the individual fungus used showed similar results over all the replicates.

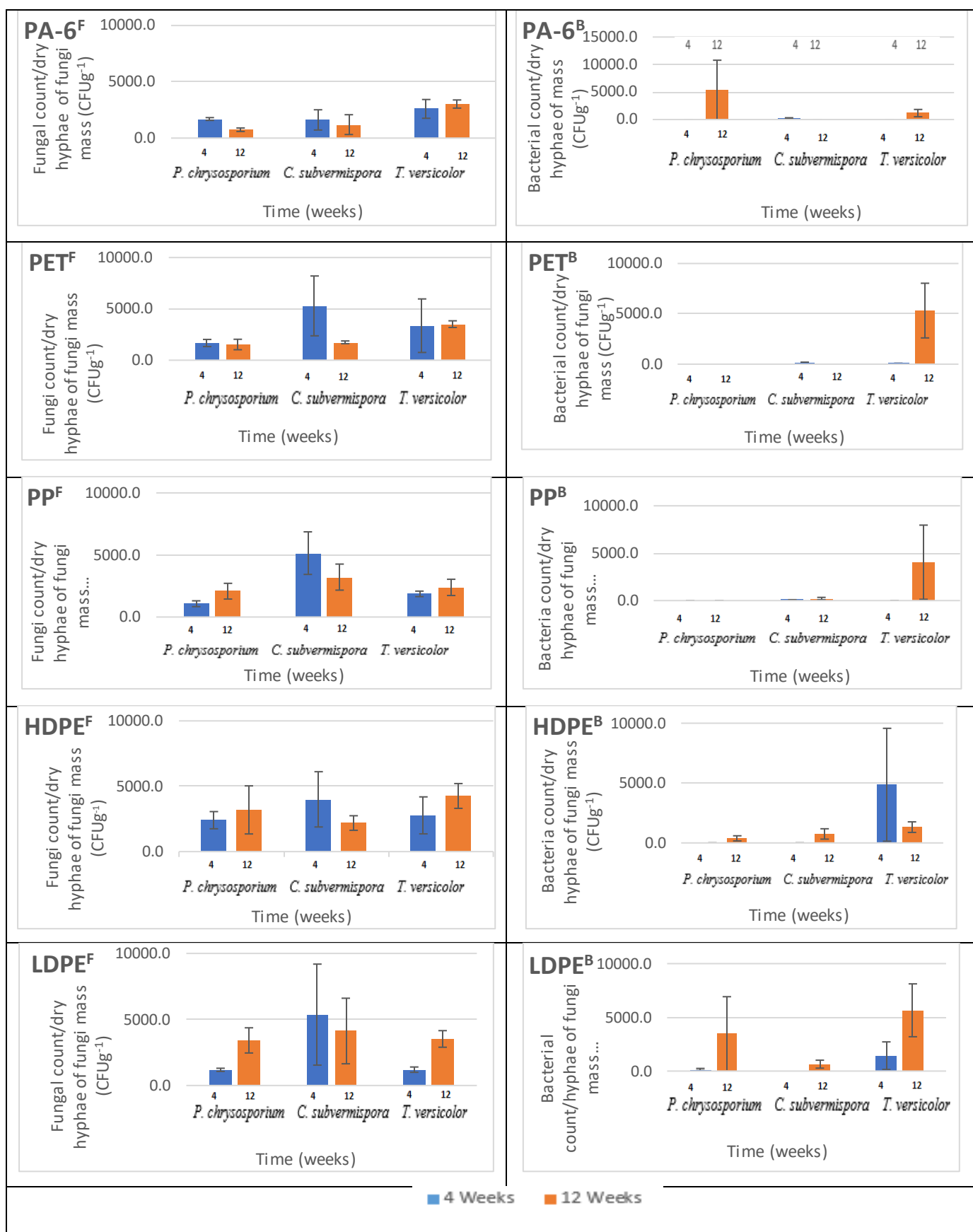


Fig. 7.22 Microbial count/ colony-forming units per gram (CFUg⁻¹) from PA-6^F, PET^F, PP^F, HDPE^F and LDPE^F with fungal count while from PA-6^B, PET^B, PP^B, HDPE^B and LDPE^B with bacterial count on the agar plates after 4- and 12-weeks incubation of plastics with fungi, *P. chrysosporium*, *C. subvermispora*, and *T. versicolor* respectively (mean counts \pm SEM).

The microbial count was compared on the agar plates with plastic discs and known fungal inoculants. Fig.7.22 (PA-6^F and PA-6^B), (PET^F and PET^B), (PP^F and PP^B), (HDPE^F and HDPE^B) and (LDPE^F and LDPE^B) are the averages of the fungal and bacterial count with plates with PA-6, PET, PP, HDPE, and LDPE respectively. The total number of other fungal biomass present varied in the initial fungal inoculum setups used over time. There was an increase in the fungal count with fungus: *T. versicolor* set up between 4 and 12 weeks, while the fungal count decreased between 4 and 12 weeks with fungus: *C. subvermispora* with all the plastics. Fig 7.22 revealed that apart from PA-6^F and HDPE^F, which had a more fungal count of 3024 and 4256 CFU g⁻¹ with fungus: *T. versicolor* setup, the highest counts derived were from fungus: *C. subvermispora* after 4 weeks for PET^F, PP^F and LDPE^F- 5288, 5148 and 5365 CFU g⁻¹ respectively followed by *T. versicolor* and the least *P. chrysosporium* (fig. 7.22 PET^F, PP^F, HDPE^F and LDPE^F). Other fungi setups had higher loads after 12 weeks of incubation.

On the other hand, the average total number of bacteria biomasses also revealed variation in the initial fungal inoculum setups used over time. Bacteria contamination had the highest loads with fungus: *T.versicolor* (fig. 7.22 PET^B, PP^B, HDPE^B and LDPE^B) apart from fig.7.22 (PA-6^B), which had a more bacterial count of 5392 CFU g⁻¹ with fungus: *P. chrysosporium* setup. Also, the highest bacterial contamination was observed after 12 weeks of incubation in fungi: *P. chrysosporium*, *C. subvermispora* and *T. versicolor* apart from fig. 7.22 (PET^B) had a more bacterial count of 99.5 CFU g⁻¹ after 4 weeks with fungus *C. subvermispora* setup.

Generally, time of incubation also played a major role in the contamination done by microbes. Microbial loads of fungi and bacteria were higher after 12 weeks of incubation with the original inoculum. The reason is that as the activity of the white-rot fungus declines, other microorganisms that might be present on the plastic after sterilizing with ethanol or microorganisms associated with the fungus have an opportunity to flourish.

Thus, the competition between bacteria and fungi may impact the bacterial community's formation and activities (Embacher et al., 2021). Fungi are considered better degraders because of their larger size and mobility through hyphal formation, unlike most immobile bacteria spreading over the petri dish with agar with plastic discs. Finally, their unique enzymatic and non-enzymatic capability to degrade the main structure materials (Clausen, 1996; Eastwood et al., 2011; Noll and Jirjis, 2012). It can be explained that the reduced number of bacterial loads observed from our obtained result in fig. 7.22 could be from the toxic fungal secondary metabolites (De Boer and Van der Wal, 2008) and the reduction in pH because of oxalic acid produced by the enzymes involved in the degradation process (Arantes et al., 2014).

Statistically, the number of microbial loads (both fungi and bacteria) was significantly influenced over time in the fungi set up with different plastics ($P < 0.05$).

7.6 Comparison of White-Rot Fungi Performances towards Plastic Discs: PA, PET, PP, HDPE, and LDPE.

P. chrysosporium, *C. subvermispora* and *T. versicolor*, were tested for their degradative capabilities against selected plastics for 4 and 12 weeks. This experiment aimed to determine if WRF would aid the degradation of plastics in a shorter time under controlled laboratory conditions. Encouraging results were obtained from the experiments conducted on the plastic discs. The fungi degraded these plastics in 4 weeks and further degraded the plastics after 12 weeks. The fungi grew in the jars containing the culture broth with the plastic disc over time, making hyphae/ mycelium network on these discs, displaying different degradation rates. Using the decomposition rates observed and assuming conditions similar to those in this experiment, it took 12 weeks for PA-6 to have the highest weight loss of 2% fungus: *T. versicolor*.

From all the results obtained from the experiments in this chapter, apart from the weight loss and thickness, which fluctuated, one could conclude that *P. chrysosporium*, *C. subvermispora* and *T. versicolor* degraded the plastic discs after 4 and 12 weeks of incubation in this way: *T. versicolor* > *C. subvermispora* > *P. chrysosporium*. It can be concluded that plastics degrade due to the capability of the fungal inoculum to produce ligninolytic extracellular oxidative enzymes, which aided the degradation of these discs. The extracellular oxidative enzymes cleave to the discs' polymer chains, reducing the chains to smaller units known as oligomers and monomers and are later assimilated by the fungi. *T. versicolor* had the most impact on the plastic discs because of their broad range of biosorption capabilities (Fomina and Gadd, 2014), their ability to thrive under stressful conditions, such as the absence of nutrients (Pezzella et al., 2017) and their ability to produce uncontrolled free radicals such as (superoxide anion ($O_2^{\cdot-}$), hydroxyl radical ($\cdot OH$) and hydrogen peroxide (H_2O_2)) that damage cellular components (Giardina et al., 2010; Nguyen et al., 2014). Soares et al. (2005) concluded their research that upon fungal treatment, the EDC concentrations reach a point of triggering fungus response through the expression of enzymes that aided the degradation of EDC. Reassuring results were also established in the complete elimination of parabens on treatment with both *T. versicolor* and *P. chrysosporium* (Mizuno et al., 2009).

Pezzella et al. (2017), on the other hand, employed the use of *T. versicolor* for the remediation of endocrine-disrupting chemicals (EDCs) for one week in bioreactors and came to the

conclusion that *T. versicolor* efficiently removes EDCs without any needs of other nutrients over the investigated time for repeated cycles. Most white-rot fungi act differently in colonising any material's surface, eventually causing erosion of that material's surface. This type of WRF is known as non-selective or simultaneous WRF (Hatakka et al., 2002). An example of such WRF is *T. versicolor*, while some will be selective in degrading some parts and leaving out some part of that material. This reason will also explain why the WRF acted differently on the plastic discs from our obtained results, with *T. versicolor* having the most impact than the other WRF employed in the study.

7.7 Conclusion

This study investigated a comparative analysis of the degradation of selected plastics PA, PET, PP, HDPE, and LDPE by different species of WRF, namely, *P. chrysosporium*, *C. subvermispora* and *T. versicolor*. Changes were observed on the discs after 4 and 12 weeks, as seen in figs. 7.4 - 7.20. These changes seen from these incubated discs include visual, weight, physical, structural, and morphological. They were notable over time and could be attributed to microbial degradation, i.e., the breakdown of the additives used in plastic production and the carbon-carbon backbone which makes up the plastics. The fungi secreted extracellular enzymes, which assisted in the degradation process. Also, one of the reasons for the changes observed in the incubated plastic discs could be because of the ability of fungi to form a biofilm on the surface of the plastic, reducing the hydrophobicity of plastics, thereby utilizing these plastics as part of their nutrients and energy. The first step of degradation is the cleavage of the main polymer chains leading to the formation of low molecular components such as oligomers, dimers, or monomers (Vasile and Seymour, 1993), which are further utilized by the fungi.

From the results obtained in this study, we can conclude that there is an indication to support the reduction in plastic integrity caused by some endophytic microorganisms, especially white-rot fungi (WRF). The WRF play a vital role in the biological oxidation, degradation, and reclamation of lignocellulosic waste in the environment (Asther et al., 1988; Kumar and Chandra, 2020). There was a reduction in the pH value from 7.1 to 6 after 4 weeks and to 4.88 after 12 weeks of incubation with fungus *T. versicolor*. The reduction is due to the microorganisms' secretion of enzymes and oxalic acids (Gu, 2003). The reduction further confirms that the fungal media is metabolically active and will utilize the discs for its growth and as a carbon source.

These results encourage increased biomass accumulation on plastics by endophytic fungi during incubation, suggesting the increased surface area for degradation through extracellular

enzyme expression. There were apparent changes in the properties of plastic discs incubated after 4 and 12 weeks with *P. chrysosporium*, *C. subvermispora* and *T. versicolor* in a basal medium. The changes include colour change (fig. 7.6), weight change, formation and reduction of functional groups, disorientation, biofilm formation on the surfaces of plastics and finally, the cracks, holes and grooves as observed (Figs.7.5-7.8, 7.19 - 7.20). These changes can be attributed to the degradation of the PA, PET, PP, HDPE and LDPE discs. However, the weight loss of discs fluctuated for the 4 and 12 weeks in the medium and was lower than the results obtained by some researchers (Klun et al., 2003; Nanda and Sahu, 2010; Nowak et al., 2011). From the results of this analysis, one could establish that the weight loss of the plastic discs was not significantly different from one another (P-value >0.05). PET and PA degraded more than HDPE, LDPE, and PP in all the analyses carried out; this is because of the difference in their chemical nature, i.e., the presence of functional groups with polar covalent bonds, such as ester or amide bonds (aromatic and amides) which encouraged degradation. It is hence necessary to employ these groups of microorganisms that occur in nature and have enormous ecological significance in the degradation of the world's most significant pollutant, plastics (Russel et al., 2011). This course of research also provides novel ways of implementing individual microorganisms for degradation purposes over the long run. This may be applicable for other microorganisms through exhibiting hydrolase enzyme activity to reduce/impact other landfill constituents and environmental pollutants such as plastic waste. However, this cost-benefit analysis is vital before any in-situ trial is considered.

CHAPTER 8

OVERALL DISCUSSION

8.1 Introduction

1. As the volume of mixed waste generated keeps increasing, especially in the developing countries such as Nigeria, it becomes increasingly vital to evaluate the decomposition characteristics of the individual components of the waste stream, trying to find ways to efficiently and effectively manage and control solid waste practices from their generation to disposal.
2. It is overwhelming to know that many of these mixed wastes from different sectors are either in solid or liquid form and could be biodegradable or non-biodegradable. They are sent all together without sorting to dumpsites or landfills to date with minimal control towards their disposal. There is little or no form of material and energy recovery, which leads to loss of resources, environmental decay, pollution, and, most times, causing health complications by generating leachate and GHGs (Heyer et al., 2005; Verma et al., 2016). The biodegradable fractions of the waste stream degrade slowly, while the non-biodegradable fractions remain unchanged at the dumpsites. High concentrations of heavy metals, water-soluble salts, and anionic ions are seen in leachates from dumpsites contaminated with mixed wastes (Dimambro et al., 2006; Youcai, 2018).
3. However, most degradation studies are based on one component of this waste in a particular medium or policies and regulations governing these components of the waste stream. Against this background, this research has attempted to build on the existing knowledge to investigate the individual components of these waste streams. This research work can be divided into three parts. The first was the seasonal assessment of compost made in Nigeria, a product from the decomposition of the biodegradation fraction of the dumpsites. The second tried identifying plastic wastes from Nigeria's dumpsites using FTIR spectroscopy. And finally, evaluating the degradation of plastics: PA-6, PET, PP, HDPE, and LDPE in soil, compost and leachate in an open field condition and using white rot-fungi (WRF) under controlled laboratory conditions. The results from each study were discussed individually in their respective chapters. We will summarise the results, linking the findings to answer the original research questions, which were:
4. Does seasonal variability influence the chemical properties of compost?

5. Does the seasonal variability of feedstock have an impact on compost?
6. Does the prevalence and weight of plastic polymers influence plastic mobility in and around the dumpsites?
7. What are the most prevalent plastic types in Nigerian dumpsites?
8. Does the degradation rate of PET, LDPE, HDPE, PP and PA-6 differ significantly among plastics in soil, compost, and leachate?
9. Does the rate of degradation of plastics differ from temperate to tropical regions?
10. Do microorganisms in a suitable growth medium degrade plastics?

8.2 Seasonal differences in the Physico-chemical properties of the end product of organic waste, “compost”.

After studying the seasonal differences in the chemical properties of MSW compost made in Nigeria, it can be concluded that wet and dry seasons significantly affected the composts' chemical properties, except for nitrogen content, which did not show any significant differences seasonally. The reason may be that poultry manure, a source of nitrogen content, may have been obtained from the same poultry farm in both wet and dry seasons, therefore, not having a significant effect on the compost made seasonally.

Also, as seen in fig. 4.2, results revealed that the quantity and type of feedstock used in making compost in Nigeria significantly differed between the three years checked. Reasons for the differences in the feedstock are simply from different sources in these three years. Also, Bary et al. (2005); Boldrin and Christensen (2010) all suggested that the type and composition of feedstock were the main reason for differences noted seasonally through the years of sampling. Means of pH, EC, organic matter, carbon (C), and C/N ratios displayed seasonal dependence and were significantly higher in the wet season than in the dry season. Though the mean EC of composts made in the wet season was higher than those made in the dry season, the means from the two seasons were 4534.17 and 2631.58 μScm^{-1} , above the Apex EC limit (750 to 2000 μScm^{-1}). At the same time, the means of C/N ratios for both wet and dry seasons were 14.7 and 13.1% lower than the Apex EC limit of 15-20. Rawat et al. (2013) suggested that more feedstock of high carbon sources should be added to enhance the C/N ratios for such composts. The means of nutrients and heavy metal concentrations of composts investigated revealed higher concentrations in the dry seasons than in the wet season, except for higher sodium and magnesium in the wet seasons. Reasons may be attributed to leaching in the wet seasons during composting, and magnesium is known to be held more tightly in composts; this may be why it was not reduced in the wet season (Hardy, 2013). Therefore, seasonal conditions, feedstock,

which is also seasonal and locations where the feedstock is sourced are likely to have influenced the high concentrations of nutrients and iron and zinc, which is linked to the high EC obtained from our results (Richard & Woodbury, 1992; Ciavatta et al. 1993; Montejo et al. 2015). However, Benito et al. (2006) concluded that no significant differences were found in the chemical properties of composts sampled from four seasons except for EC values from the composts. He suggested that the differences in the results were from seasonal changes in components entering the facility.

8.3 The distribution of plastic wastes away from the active dumping areas of the dumpsites.

FT-IR spectroscopy is commonly used to identify plastic wastes (Rotter and Ishida, 1992; Beltrán and Marcilla, 1997; Verleye et al., 2001; Nishikida and Coates, 2003; Noda et al., 2007; Asensio et al., 2009; Jung et al., 2018). Here, we also used FT-IR to analyse plastics from Irete, Orogwe and Nekede dumpsites. The results revealed that the composition of these plastic wastes in Irete, Orogwe and Nekede dumpsites was significantly different, with polypropylene, polyethylene terephthalate and polyethylene being significantly dominant and higher in number than other plastics seen at these dumpsites. PP consists of over 36%; PET had 27%, LDPE had 12%, HDPE had 13%, PS had 4%, EVA had 2%, and PA had 1%. The result revealed that their distribution away from the active sites of the dumpsites significantly decreased with the lighter ones seen moving further away. However, the plastic wastes in the dumpsites were significantly higher in abundance than those seen at distances away from the dumpsites. Therefore, three plastics, namely, PP, PE, and PET, were the most dominant in the dumpsites because they are light, used for many applications and were the same plastics that moved further away from the active dumping areas of the dumpsites and are likely to be most often observed in the surrounding environments. (Zhang et al. (2016); Canopoli et al. (2016); Nicholson, (2017); Thompson, (2017)) revealed that PE and PP plastics were most dominant from different sites. The reason is that they are single-use plastics used in many applications and are discarded immediately after use, but their lightweights make them possible to be transferred from one place to another (Browne et al., 2010; Nor and Obbard, 2014; Thiel et al., 2003).

Finally, as seen in fig. 5.10, Shannon diversity index and equability plots for different plastic waste distribution and abundance in Irete, Orogwe and Nekede dumpsites revealed that the number of plastic wastes in Nekede and Orogwe dumpsites had the most diversity than Irete dumpsite.

8.4 Plastic degradation routes

Plastic degradation was investigated in field conditions, soil, compost and leachates in the temperate zone, the UK and tropical zone, Nigeria, and then in controlled laboratory conditions with chosen microorganisms. The different analyses revealed changes in the plastics over time in the different media investigated. The changes observed on the discs include visual, weight, physical, structural, and morphological. They were notable over time in /with these substrates used, i.e., surface damages on the plastics, discolouration of the plastics, and loss of shape for the dog bone plastics (as seen in figs. 6.4-6.7 and 7.5-7.6, respectively), weight changes (6.15-6.16, and 7.9), SEM and micrographs (as seen in figs. 6.12-6.14, 6.29-6.31, and 7.8-7.10) respectively) of the plastics revealed colonisation of biofilm, dotted white patches, cracks, cavities, and pits on the plastics. FTIR displayed shifts, reduction, appearance and disappearance of peaks (figs. 6.17-6.26 and 7.11-7.15) respectively, CI of the plastics were not left out; also, the added and reduced according to the plastics' properties (6.27-6.28 and 7.18) respectively, and tensile strength on the dog bone reduced over time (6.32 and 6.33). These notable changes indicate advanced degradation, leading to crosslinking, chain scission, or breaking of the functional groups.

For field experiments, Two-way ANOVA revealed that substrates, plastic-type, and time significantly influenced weight change, carbonyl indexes, and the tensile strength of plastics, and country only significantly influenced the plastic's CI. In contrast, the countries (the UK and Nigeria) where the study took place had no significant influence on plastics' weight change and tensile strength.

Further surface damage was observed on the plastic discs for plastics degraded with the WRF. Statistical results from two-way ANOVA revealed that plastic-type significantly influenced the plastics' thickness and CI after 12 weeks of incubation. Also, time significantly affected plastics' CI and thickness after 12 weeks of incubation. Finally, the weight change of the plastics was not significantly influenced by WRF after 12 weeks.

The degradation of plastics in these media investigated significantly varied. However, degradation progressed primarily by microorganisms in the substrates cleaving on the main polymer chains, secreting enzymes, and producing biofilms on the surfaces of the plastics leading to the formation of low molecular components such as oligomers dimers or monomers (Vasile and Seymour, 1993). More microorganisms further utilise these low molecular components. The weakness and damage to the surfaces of the plastics are attributed to

degradation. They will continue with the help of microorganisms until the newly formed low molecular components have degraded.

CHAPTER 9

CONCLUSION AND RECOMMENDATION

9.1 General Conclusions

After studying the decomposition characteristics of 2 rising components of the waste stream in Nigeria, the organic wastes and plastics results concluded that seasonal variability influences the feedstock used in compost making in Nigeria (figs.4.5 – 4.9). This is because most feedstock used for composting is highly seasonal and will drive the type of compost made. Also, seasonal differences significantly influenced the properties of compost samples, taken from 12 batches made in each season in Nigeria except for nitrogen content. EC values obtained in wet and dry seasons were above the Apex EC limit; It is attributed to the high EC content of food waste, which is used as feedstock and is known to contain very high water-soluble salts, as seen in fig. 4.6. C/N ratios of compost made in the wet and dry seasons were below the Apex C/N limit; Dilution caused by the wet season was the main reason for the differences observed in the values of nutrients and heavy metal contents of composts. However, the feedstock of high carbon sources should be added to the composts to compensate for the low C/N ratios.

FTIR spectroscopy identified various plastic wastes in and around the three dumpsites with no destruction to the collected samples (fig. 5.7- 5.9). This study discloses reliable information on the quantity and polymer types of dispersed plastic wastes at Nigerian dumpsites, as seen in fig. 5.11. The outcomes also revealed that the accumulation of these plastic wastes at the dumpsites was significantly different, with 36% PP, 27% PET, and 25% PE being significantly dominant and higher in number than other plastics at these dumpsites.

At the same time, synthetic plastics, which also make up the waste at dumpsites, were subjected to degradation in an open field and with chosen white-rot fungi (WRF). There were significant positive results with these plastic surfaces being altered after 24 months and 12 weeks in different substrates/WRF (figs. 6.4 – 6.14, 6.26 - 6.31, 7.5 – 7.8 and 7.19 -7.20). In this study, biofilm colonisation encouraged biodegradation of the different plastic materials in substrates and WRF. The degradation study was slow, with varying results, in substrates and WRF. However, all the plastics showed loss of their properties, as seen visually, as shown in SEM, and light microscopy, weight change of plastics, reduction, shifting, disappearance, and appearance of peaks of plastics functional groups as revealed by FTIR and reduction of the tensile strength of the plastics. Our results confirmed that the impact of degradation was more

on PET and PA discs than on HDPE, LDPE, and PP discs in the analyses conducted. The reason is the differences in their chemical nature, i.e., the presence of functional groups with polar covalent bonds, such as ester or amide bonds (aromatic and amides), which enhanced degradation. The study did not consider the half-life of the plastic polymers subjected to degradation in substrates and with WRF because of the fluctuating weight changes, as seen with some plastic discs buried in the UK and plastics with some WRF gaining weight after degradation.

Therefore, this research has tried to consider how seasonal differences will affect the compost made from organic fractions and the degradation of plastics in the soil, compost, and leachate, and with WRF. Results proved that compost properties differed in wet and dry seasons, and plastic surface properties were impacted after 24 months in substrates and 12 weeks with WRF. However, there were some limitations encountered in this research, and they are as follows.

1. The first limitation is incomplete sampling and analyses of the composts. Compost samples were collected only for three months each season, leaving out the other three months of each season. This action may have influenced the results obtained. Therefore, future work should be repeated for the seasonal chemical properties experiments at all months of each season (wet and dry seasons) to account for the other seasonal variances in the repeatability investigation. That is to accurately understand these composts and choose the suitable compost for the proposed use and the ideal application approach.
2. The second limitation was in the sampling of waste plastics from the dumpsites. Scavengers visit dumpsites very early in the morning to pick plastic wastes up before sampling was carried out at these dumpsites for this study. These actions may have influenced the obtained results from the quantity to the polymer types of the accumulated plastic wastes. Perhaps, a repeat experiment of this study should be carried out in a future study focusing on the complete and robust sampling of these plastic wastes, removing bias of any sort to establish the results obtained. The second limitation in this study was the lack of the previous study focused on the dumpsites.
3. The weight gain is another limitation of the degradation study. Further research may be needed to consider the degradation study of plastics in these substrates/WRF tracking the temperature and humidity in the real-life open field conditions and drying the discs at suitable temperature before weighing as moisture could influence the final

weight of the plastics. In contrast, two or more fungi should be combined to see if degradation would be aided or faster than using only one fungus in laboratory conditions.

9.2 Recommendations

Though this thesis offers/offered vital information through the obtained results regarding the locally made Nigerian compost and the degradation of plastics in substrates, soil compost and leachate and using white-rot fungi, further research will continuously improve its performance and efficiency. Thus, further research goals identified include,

1. More intensive Physico-chemical investigation should be carried out on the compost and the feedstock used for effective comparisons. Experiments should be repeated at other times of the year (wet and dry seasons) to account for the other seasonal variances in the repeatability investigation.
2. Feedstock should be sourced directly from households and mixed dumpsites for compost making for an improved understanding of nutrient amendments of compost made in Nigeria. Afterwards, proper evaluation should be carried out on their properties from these two sources to check if their properties will differ.
3. It is recommended to conduct the degradation investigations in open environments tracking temperature and humidity under controlled conditions using WRF. Thorough cleaning of the plastics subjected to degradation should be encouraged with suitable drying of the plastics to assist in measuring the half-life of these plastics in the environment
4. Integration of other natural materials into plastics or include other degradation routes (initiators) that will introduce new functional groups and free radicals to the plastics that will modify and break up their long chains before trying biodegradation in any substrate (Onodera et al., 2001).
5. Extending the time of plastics in media with the fungi and combining two or more fungi in the degradation study to see if there would be effects on the plastics.

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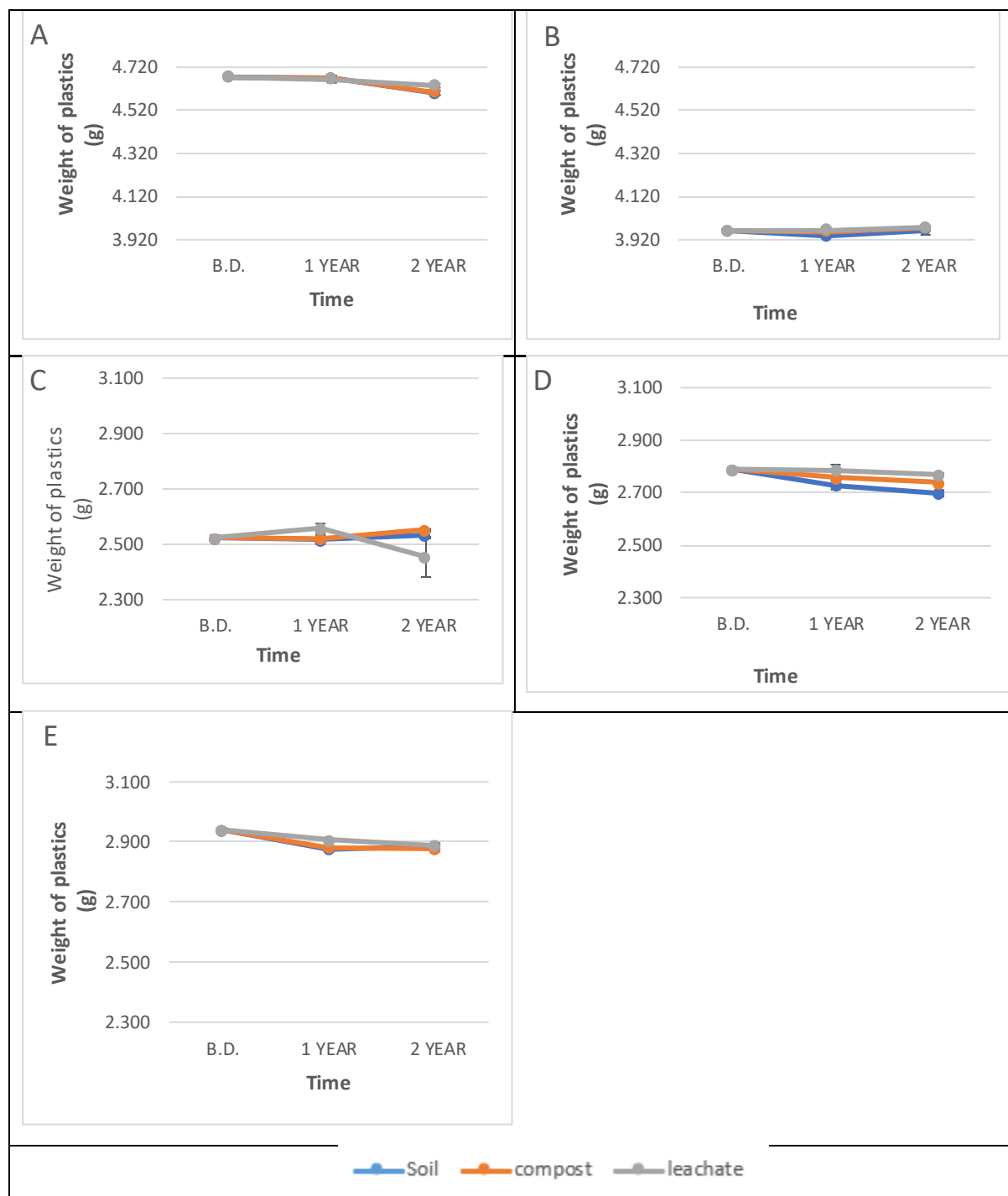
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11 APPENDICES

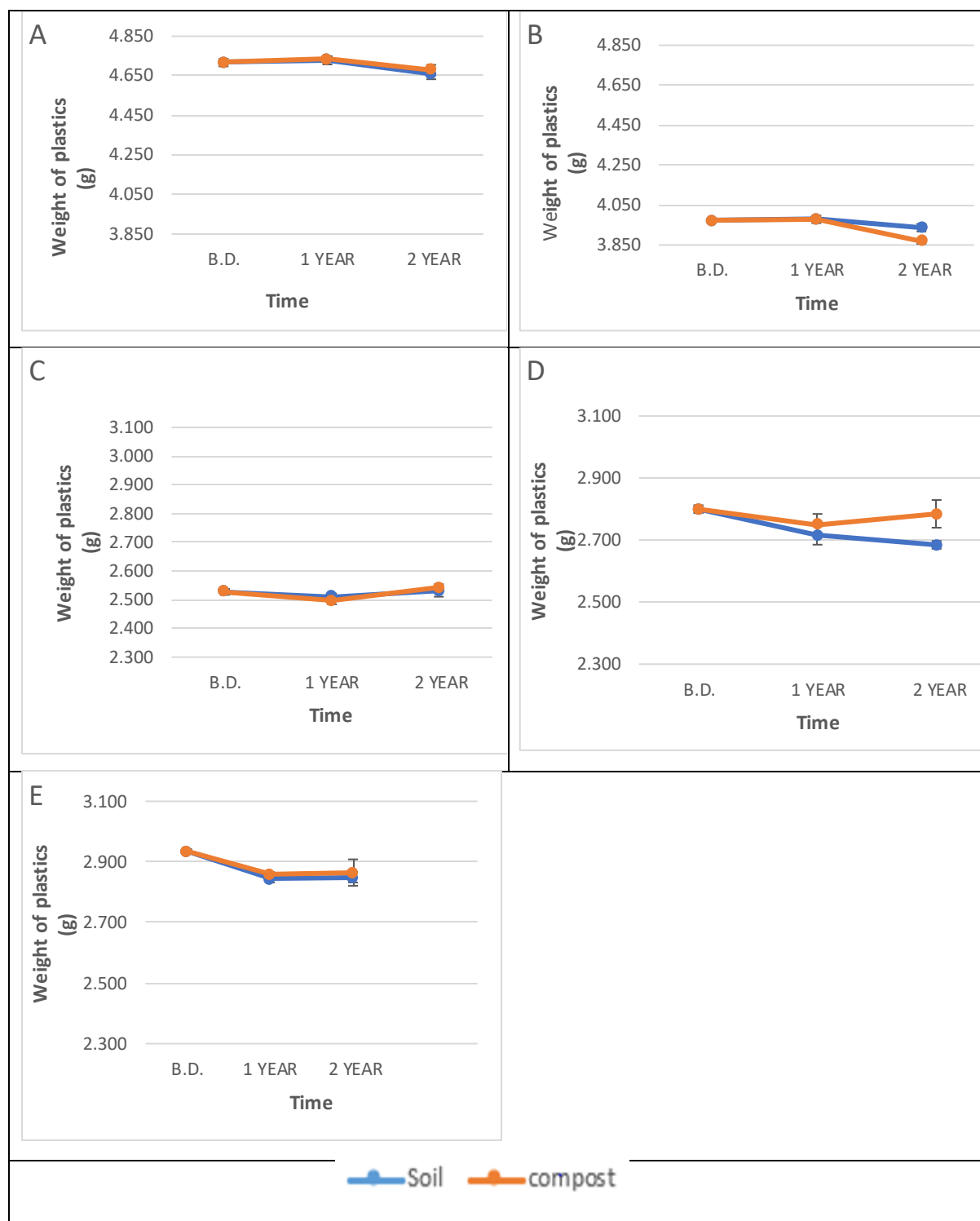
(Additional results related to chapter 6).

Appendix 10.1 Weight change of dog bone-shaped plastics



The weight change of dog bone plastics - A is PA, B is PET, C is PP, D is HDPE, and E is LDPE after degradation (12, and 24 months) in soil, compost, and leachate in the UK. Data represents mean \pm SE, (n = 3). *Y-axis A and B are same while *Y-axis C, D, and E are the same.

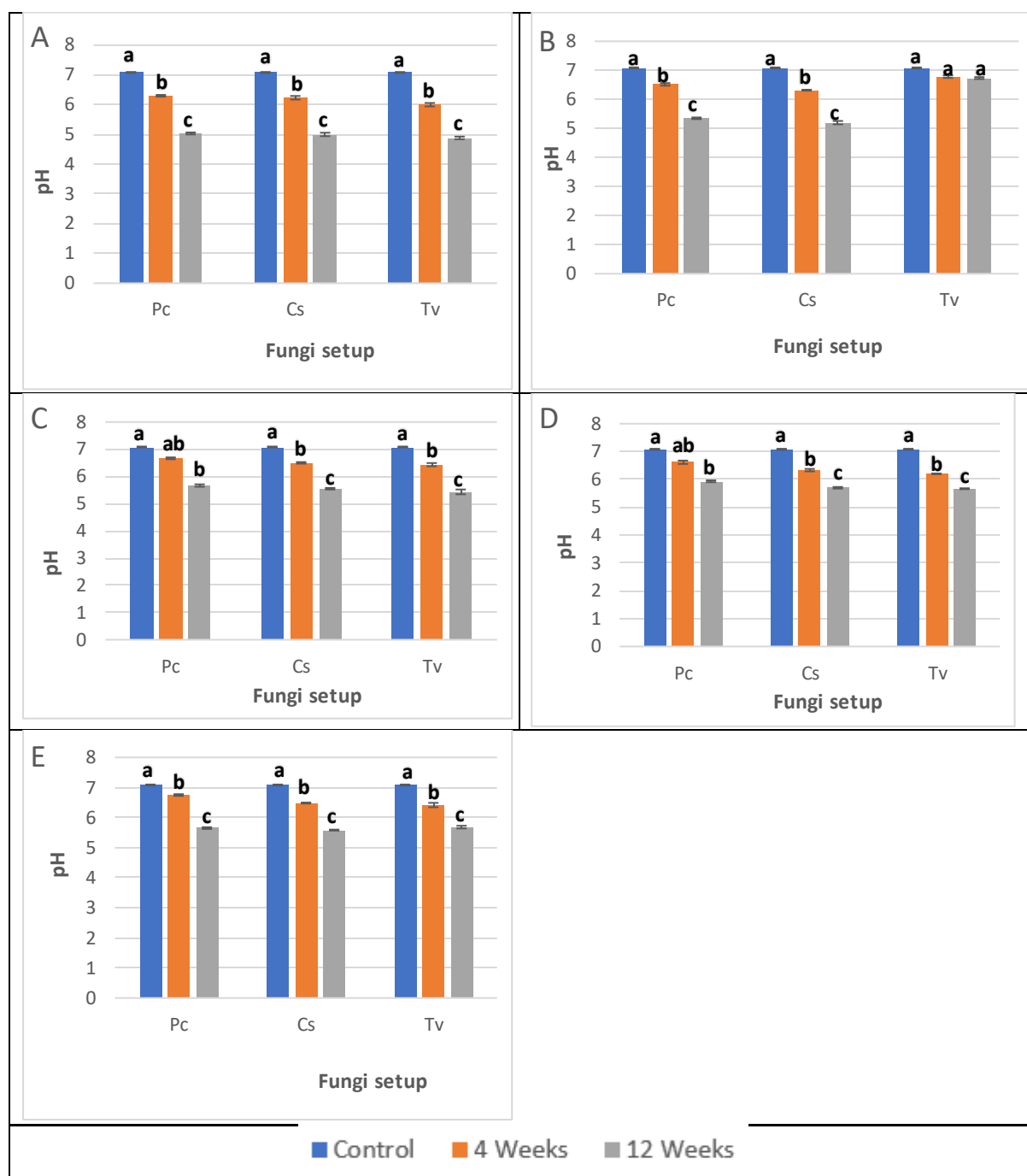
Appendix 10.2 Weight change of dog bone-shaped plastics



The weight change of dog bone plastics - A is PA, B is PET, C is PP, D is HDPE, and E is LDPE after degradation (12, and 24 months) in soil, and compost in Nigeria. Data represents mean \pm SE, (n = 3). *Y-axis A and B are same while *Y-axis C, D, and E are the same.

(Additional results related to chapter 7).

Appendix 10.3 Change in the pH of the fungi setup



Plots of change in the pH of the fungi setup with the plastics discs: A is PA, B is PET, C is PP, D is HDPE, and E is LDPE after 4 and 12 weeks of incubation by the potential fungi, namely, in a culture medium with fungi *P. chrysosporium* (Pc), *C. subvermispora* (Cs) and *T. versicolor* (Tv) respectively. Measurements with the same letter do not differ significantly according to the Tukey's HSD test at $P < 0.05$.

