An Investigation of Synthetic Body Covering Materials in Soil Burials for Forensic Application

by

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A thesis submitted for the degree of

Doctor of Philosophy (Science)

University of Technology Sydney

2016

Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text. I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Clare Sullivan

18/04/2016

Acknowledgements

Firstly, I would like to thank my supervisors, Associate Professor Barbara Stuart and Dr Paul Thomas for their valuable guidance and advice throughout this project. I would especially would like to thank them for all the help with editing this thesis, I would have been completely lost without their help in writing a document on this scale for the first time. They made it easy for me to ask questions when I was unsure about aspects of the project and when I felt a bit out of depth due to my lack of experience in the various aspects of conducting research. Their help made it possible for me to complete this project and I can't thank Barbara and Paul enough for it. Thank you very much Barbara and Paul.

I would like to express my sincere gratitude to Jean-Pierre Guerbois, Linda Xiao, Katie McBean and Ronald Shimmon for their continual technical and administrative support throughout this project. The advice that was given to me by these people helped me greatly in completing this project and was invaluable.

A huge thank you to Mr. Mark Berkahn for running my polymer samples on the AFM especially with the complicated setup required in order to run the polymer samples properly as well as helping me find the best way to clean the samples up. I'm sure I would be still running the samples now without his help.

A big thank you to Dr Brian Reedy and Johanna Howes for all the statistical expertise especially with using the Unscrambler software. I had a lot of trouble with how to use multivariate analysis in my project and they assisted me with utilizing this technique as a way to explain trends in the data.

I would also like to thank Mr. Nishath Geekiyanage for helping me with the UV Visible spectrophotometer and for lending his quartz cuvettes to me when I wasn't able to find them anywhere else.

I would also like to thank my fellow PhD students who kept me sane as we were all going through the process of completing our projects.

Lastly, I would like to like to say a huge thank you to my family and friends who supported me throughout this project. This project would not be possible without my parents, Ray and Maree, who both financially and emotionally supported me when I was completing the project. The financial support that they gave me allowed me to focus on my project without the worry about looking for a job capable of covering my expenses. I would also like to thank them for dealing with my changing moods when something wasn't going to plan and for being there when I needed help. I would like to thank my sister Rhea and my brother in law Damien who would give me encouragement to keep going with this project and to not give up on it even when was I down as well taking me to the many yumchas, which helped to keep me sane. Thank you also to my friend Dianne for being able to distract me from thinking about the project all the time and giving me something else to talk about.

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Abbreviations

AFM – Atomic Force Microscopy

ATR – Attenuated Total Reflectance

DSC – Differential Scanning Calorimetry

DEHP- Bis(2-ethylhexyl) phthalate

DTG – Derivative Thermogravimetry

FTIR – Fourier Transform Infrared

HFW – Horizontal Field Width

HDPE – High Density Polyethylene

LDPE – Low Density Polyethylene

LLDPE – Linear Low Density Polyethylene

PCA – Principal Component Analysis

PCR – Principal Component Regression

PE – Polyethylene

PET – Poly(ethylene terephthalate)

PLS-R – Partial Least Squares Regression

PP – Polypropylene

PVC – Poly Vinyl Chloride

SEM – Scanning Electron Microscopy

STD Error – Standard Error

TGA – Thermogravimetric Analysis

UTS – University of Technology Sydney

UV-VIS – Ultraviolet - Visible

Abstract

During the forensic investigation of grave sites artefacts are often located and have the potential to provide valuable information about the victim or the perpetrator. Such artefacts may include body coverings used by the perpetrator to interfere with the crime scene. Polymer materials are now frequently encountered at crime scenes and given their use in bag and carpet manufacture, there was an increased likelihood that this class of materials will form part of a clandestine grave. Understanding the degradation of these materials in potential crime scene soils will provide insight into the age and nature of the burial. Previous forensic research on polymers at the crime scene has mostly focused on identifying polymer materials such as fibres and the studies that have investigated polymer degradation, examined the effect degradation had on identifying the polymer rather than the information the polymer can provide about the burial. This thesis provides a comprehensive examination of the degradation of five commonly encountered polymers with potential to be used as body coverings in a variety of soil t types. A comparison of the suitability of a range of analytical techniques to understand polymer degradation associated with burial has also been made in this thesis.

The five polymers -polyethylene (PE), polypropylene (PP), poly vinyl chloride (PVC), polyethylene terephthalate (PET) and nylon- in the form of films and carpets were buried in a series of laboratory controlled environments that varied by soil type, moisture content, soil pH and temperature for a burial period of 24 months. Scanning electron microscopy and atomic force microscopy were utilised for the examination of changes to the morphology of polymer surface. Spectroscopic analyses, including infrared, Raman and ultraviolet-visible spectroscopies, were applied to monitor changes to the chemical structure of the polymers and their additives. Thermal analysis was also investigated as an approach to monitoring the subtle changes associated with the degradation processes. This study determined that certain soil environments enhanced the degradation of the polymers in soil, while other environments were shown to preserve the polymers. The degradation of these polymers often included the interaction of polymer additives with the soil environment. The factors that were shown to enhance polymer degradation included the availability of water and the ability of the soil environment to encourage microbial growth. In this thesis, a combination of morphological changes determined by scanning electron microscopy and the microstructural changes determined using infrared spectroscopy, and to a lesser extent, thermal changes monitored using thermogravimetric analysis, were determined to be the most powerful methods for monitoring degradation processes in the polymer systems investigated.

This thesis provides new knowledge about the impact different soil variations have on the degradation of polymers that are more and more likely to be found at clandestine grave sites.

Chapter 1

Introduction

1.1 Introduction

In certain types of death, including murder or manslaughter, a clandestine burial is used to hide the victim. This is in order to reduce the likelihood of the victim being found, leading to an investigation to determine the identity of the victim and the perpetrator. Body covering materials can be observed in clandestine burials for many reasons including the perpetrator's attempt to interfere with the crime scene. These materials are able to hide remains or modify the decomposition process of the body. Valuable information about the nature and condition of materials that have being collected from a crime scene could assist the investigators in determining the circumstances behind the death.

Body coverings, including clothing and other wrappings, have previously provided a valuable source of information in forensic and archaeological contexts (Bier and Dusenbury, 2008; Taupin and Cwiklik, 2011). Most studies have focused on natural materials, such as cotton and linen as these materials have been available for many centuries. In the 20th, modern plastic materials were introduced and since then many household goods are now polymer-based. This increases the likelihood that such materials will be also found at a gravesite. Cases where polymer materials have played a role in the evidence collected from a gravesite have been publicised in the media over a number of years. For example, the high profile murder case of Leanne Tiernan in the United Kingdom involved synthetic carpet fibres and plastic bags (*John Taylor: Killer in the Woods*). Due to the information gained from the analysis of the polymer materials, authorities were able to convict her murderer in 2001.

The nature of a burial environment will affect the rate at which any grave good with deteriorate. Such materials may be exposed to a variety of conditions, such as different soil types. The environment to which these materials are exposed is largely responsible for the rate at which the buried materials will degrade in a burial environment. The acceleration or inhibition of the materials degradation processes will affect the interpretation of a burial site.

There are many cases where the body or potential evidence has been encased within a polymer. These polymers could potentially provide information about the burial such as the age or the environment to which the polymer has been exposed via analysis of the degradation that the polymer has undergone. Many forensic studies that examine the degradation of polymers buried with the body in a burial, investigate such a process to determine the viability of the identification of the polymer fibres after degradation (Walter, 1996). There are many studies investigating the degradation of the polymers outside the forensic field, but these studies have not focused on the influence of environmental conditions. Instead the focus has been on the impact of either photochemical, thermal or specific microbial strains on the polymers. This represents a gap in the understanding in the degradation of these artefacts and how the environment influences the degradation process.

1.2 Burial Environments

1.2.1 Soil Chemistry

Soil is a complex environment and it is characterised by its biological, chemical and physical properties (Conklin, 2005a). It is comprised of many organic and inorganic materials that are in a solid form (e.g. sand), in an aqueous solution (e.g. iron and carbon) and in a gaseous form (e.g. oxygen and methane) (Sposito, 2008). Soil also contains a large amount of biological life that can be either microbial life, plants or larger animals. There are many soil types each containing varying amounts of the different materials that make up soil. Generally, the solid portion of soil is made up of four principal components: sand, silt, clay and organic matter (Osman, 2013; Yong et al., 2012). Loam soil contains all of these materials in varying amounts and modification to the quantities of these materials will affect the properties of the loam soil (Osman, 2013). For example, more sand present in the loam soil will produce a more aerated soil than the average loam soil, while the presence of more clay will produce a soil that is less aerated and will hold water more easily. Sand is comprised of large particles (particle size between 0.05 – 2 mm of mostly Silicon Oxide, and is common around beaches and rivers (Skopp, 2011). Clay soils contain fine particles (less than 2µm) are the result of a silica and alumina mix due to the chemical or physical breakdown of rocks (Rycroft and Amer, 1995; Vaculíkovà and Plevovà, 2005;Skopp, 2011). There are also lime deposits that can occur from the breakdown of chalk (calcium carbonate) but these are not considered to be true soil as there are not many of the critical soils components present (Sébaïbi et al., 2003; Conklin, 2005a).

There are also differences between soils due to the chemical properties rather than the physical properties (Conklin, 2005a). The moisture content of the soil is an important parameter (Schnürer et al., 1986; Shukla, 2011; Stolp, 1988). Excessive water tends to give the soil a weak structure not allowing larger plant and animal life. Too little water affects the ability of animals and plants to survive in the environment since water is needed to hydrate as well as deliver the nutrients needed from soluble elements and minerals. The ability of the soil to retain water is also essential to the promotion of microbial growth as soils with greater moisture retaining capacities tended to have greater levels of microbial life (Dalal and Mayer, 1987; Conklin, 2005b). The pH of the soil greatly affects the variety of biological life present in the soil (Killham, 1994; Matthies et al., 1997; Pandey et al., 2015; Xue et al., 2010). All biological life forms have a pH threshold that can be handled by the species. Certain plants and animals thrive better in acidic soil types while others survive better in basic soils (Spiegelberger et al., 2006). However, too far from the optimum pH will reduce the availability of biological life as well as possibly changing any soil chemical reactions that would occur. Another property of the soil that is to be considered is the temperature of the soil environment (Chavant et al., 2002; Pietikäinen et al., 2005; Janaway, 2008). Colder environments tend to have reduced animal and plant life as well as slow down any chemical reactions occurring in the soil, while warmer soils tend to be the opposite with increased animal and plant life and faster soil chemical reactions.

1.2.2 Degradation of Buried Objects in Soil

Different soil types and the associated chemical and biological properties are known to influence the rate of degradation of the materials that are buried within the soil environment. It has been found in previous studies that materials that are buried in soils that are damp and aerated have faster rates of degradation as opposed to materials that are buried in dry, cold and compact soils, which have slower rates of degradation (Janaway, 2008). The most prominent reason for the increased rate of degradation in damp and aerated soils is due to the greater abundance of biological life present as these soils tend to promote microbial growth (Yao et al., 2011). This is a generalisation however, as certain compact soils such as clay soil have been observed to increase the degradation of buried objects when compared to more aerated soil types (Mitchell et al., 2012). Since the availability of biological life in the soil is a major contribution to the degradation of buried objects, soil types like clay that have an increased availability of nutrients present will have a positive effect on biological growth (Brennan et al., 2014). Soils with a small average particle size such as clay, also have a greater ability to retain water around the buried objects when compared to the aerated soils (Nguyen and Marschner, 2014). Studies that investigated the movement of water through soil noted that soils that retain water tend to have less mobility in the microbes present (Abu-Ashour et al., 1994). This occurs as the movement of water through the soil carries microbes along with the water. Since biological life such as microbes are mainly responsible for the degradation of buried objects, the movement of the microbes through the soil would help preserve the buried artefacts. Since aerated soils tend to have a greater movement of water compared to the compact soils, this would lead to preservation of the buried objects.

It has also been found that the depth at which the object is buried will also affect the degradation rate. The deeper the object is buried, the slower the degradation process. This is due to the higher levels of microbes present in the top soil, as well as possible access to other methods of degradation such as photochemical degradation (Deschesne et al., 2007; Hebert and Miller, 1990). Since most clandestine burials are at fairly shallow depths (approximately 60cm) this would mean that the degradation of the deceased as well as any objects buried with them will tend to degrade faster than in a non-clandestine burial situation such as where the depth of burial is much deeper (Pokines and Baker, 2013).

1.2.3 Soil Burial Method

The soil burial method is one of the most common methods used to study the degradation of polymers in soil (Singh and Sharma, 2008). This method mainly examines the effect of biodegradation on the polymers however other methods of degradation can be taken into account (Innocenti, 2005; Singh and Sharma, 2008). This method can be carried out in either a laboratory controlled environment or under outdoor burial conditions (Hiroshi, 2002; Morse and Dailey, 1985). A polymer sample with known dimensions and mass (the mass of the sample is not usually considered for forensic purposes; it is usually only for environmental reasons) are buried in the soil at a specific depth. These polymers are exhumed from the environment at different time intervals and cleaned using distilled water. The samples are left to dry either at room temperature or in an oven. This method is considered a feasible way of studying the effects of a particular soil environment has on the degradation rate of a polymer buried in the soil (Müller, 2005). This is because this method sets up an environment that closely resembles the soil environments of interest. However, this method is also not considered easily reproducible since slight changes in the soil environment can affect the results. There is also some difficulty in controlling any climate factors. There are other methods of looking at the degradation of synthetic polymers in a soil environment however these methods are not useful from a forensic point of view. These methods usually involve isolating specific microbial strains and placing the microbes on the polymer (pure cell culture) or using compost or sewer sludge (Flemming, 1998; Singh and Sharma, 2008). These methods focus more on the biological impacts of the soil (such as microbes present) on the polymer and do not take into account the physical and chemical properties of the soil. In a clandestine burial, the entirety of the environment impacts the degradation of the polymer artefacts indicating that the soil burial method is the most appropriate method to use to analyse the polymers.

1.3 Degradation Mechanisms

There are a number of ways that materials can degrade in the environment. These include photochemical, thermal, chemical and biological degradation (Brueckner et al., 2008; Gardette and Lemaire, 1991; Restrepo-Flórez et al., 2014). The main degradations mechanisms for materials buried in the soil environments are chemical or biological in nature. Thermal and photochemical degradation are unlikely in a soil environment. The burial of these artefacts would reduce the amount of photochemical radiation reaching the polymer as UV radiation does not penetrate far into soil (Johnson, 2003). Photochemical degradation of polymer artefacts would likely only occur in very shallow clandestine burials. Thermal degradation of the polymers is unlikely since the temperatures required to initiate thermal degradation of many artefacts are unlikely occur in a soil environment. For example, the temperature required for thermal degradation of polymer is dependent on the polymer with some like nylon, PET, PP and PE being resistant to thermal degradation up to 400°C while PVC is stable up to approximately 200°C (Kutz, 2012).

1.3.1 Chemical Degradation

Chemical degradation of polymers usually involves oxidation or hydrolysis. Oxidative degradation occurs when the polymer is in contact with molecular oxygen. This could be in the form of components in the atmosphere such as O_2 or O_3, certain enzymes produced by microbes or by photochemical means (Dilara and Briassoulis, 2000; Gardette and Lemaire, 1991; Restrepo-Flórez et al., 2014). At ambient temperatures oxidation degradation follows five general steps as illustrated in Figure 1.1. Initiation is the reaction of the polymer chains where molecular oxygen forms an alkyl radical (Singh and Sharma, 2008; Gijsman et al., 1993). This is followed by radical conversion where the alkyl radical reacts with oxygen forming an alkylperoxy radical. Chain propagation occurs next as the alkylperoxy radical undergoes a hydrogen abstraction reaction forming a hydroperoxide molecule followed by the degradation of these hydroperoxides to free radicals. After the free radicals are formed, they are terminated leaving the oxidised polymer, as well as other products such as water, ketones and alcohols.

The oxidation of buried artefacts is usually initiated by the presence of either light or heat (Restrepo-Flórez et al., 2014). However, since the required levels of both light and heat needed to oxidise artefacts is unlikely to occur in a clandestine burial situation, the main methods of initiating oxidation in the soil environment would occur due to either enzyme from microbes or chemicals present in the soil (such as water, acids or bases) (Sudhakar et al., 2008). Both of these methods of oxidising buried artefacts is very slow when compared to the rate of oxidation when these artefacts are exposed to either light or heat indicating that the degradation of these objects are very slow in soil (Auerbach, 1989; Thanki and Singh, 1998).

Initiation: $R \xrightarrow{\text{Initiator}} R\cdot$

Propagation: $R\cdot + O_2 \longrightarrow RO_2\cdot$

$RO_2\cdot + RH \longrightarrow R\cdot + RO_2H$

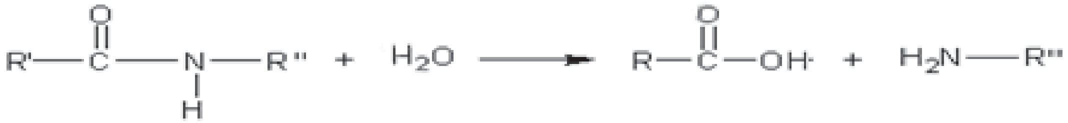
Chain-branching: $RO_2H \longrightarrow RO\cdot + OH\cdot$

$RO\cdot + RH \longrightarrow ROH + R\cdot$

Termination: $2RO_2\cdot \longrightarrow RO_2R + O_2$

Figure 1.1 General mechanism for the degradation of the polymers via oxidation as observed in Gijsman et al., (1993)

Hydrolysis is the process where the polymer chains are degraded by the reaction of certain covalent bond groups (such as the amides present in nylon) with water (Lucas et al., 2008). The water used for the hydrolysis of the buried artefacts can be either from the environment or through the enzymes produced by microbes (Singh and Sharma, 2008). This causes the bonds in the polymer chain at the point of these groups to break allowing degradation of the polymer to occur. Only specific polymers can undergo hydrolysis as this process can only occur when a hydrolysable covalent bond groups, such as the amides present in nylon, are present. The basic hydrolysis mechanisms can be observed for nylon in Figure 1.2 and PET in Figure 1.3.



$$R'\text{—}C(=O)\text{—}NH\text{—}R'' + H_2O \longrightarrow R\text{—}C(=O)\text{—}OH + H_2N\text{—}R''$$

Figure 1.2 General mechanism for the hydrolysis of nylon

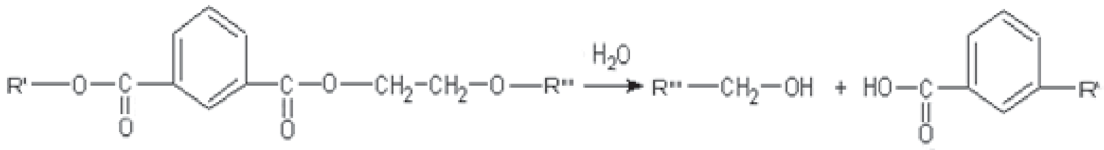


Figure 1.3 General mechanism for the hydrolysis of PET

1.3.2 Biodegradation

Biodegradation is the degradation of material due to the attack from microorganisms such as fungi and bacteria (Kirbas et al., 1999; Klun et al., 2003; Nowak et al., 2011). This can occur in a number of ways including enzymatic degradation or by physical degradation. Enzymatic degradation occurs when the microorganisms produce enzymes that break down the polymer chains into smaller molecules such as oligomers, dimers and monomers (depolymerisation) and allows the microorganisms to utilise the energy and the carbon within the polymer as a food source (Gu, 2003; Singh and Sharma, 2008). There are two types of enzyme groups that start the degradation of polymers. These are hydrolytic and oxidative enzymes (Lucas et al., 2008). Although the end result is the same, both of these groups of enzyme start the degradation process in different ways. Hydrolytic enzymes degrade the polymer by attacking certain types of carboxylic linkages that occur in a variety of polymers (e.g. poly(ethylene terephthalate)) or by attacking an amide (e.g. nylon), which causes hydrolytic cleavage (Guebitz and Cavaco-Paulo, 2008). The other group of enzymes oxidise the polymer and this leads to the cleavage of the polymer chains (Kumar Sen and Raut, 2015). The way that the polymer is oxidised is dependent on how the polymer is structured and the type of enzymes that are been produced by the microorganisms. Although the oxidation processes for both the anaerobic and aerobic microorganisms are very similar, the products produced by the mineralisation (the last step of the oxidation process that occurs once the microorganisms have utilised the energy available from the polymer) will be different (Shah et al., 2007). Anaerobic microorganisms that occur in either sulfur or methane rich environments will eventually lead to the production of CH_4 and H_2S, while aerobic microorganisms will eventually produce water and carbon dioxide. Microbes can also degrade polymers physically by secreting a glue-like substance made up of a variety of natural polymers such as proteins (Lucas et al., 2008). This works particularly well on porous materials as the 'glue' alters the size as well as the distribution of pores present in the material causing the structure of the material to break down.

1.4 Polymer Materials

Synthetic polymers are used for a large variety of purposes. There are many different polymers available that may potentially be discovered during an investigation of a clandestine burial. This study focuses on polymers that are used in domestic environments that have potential to be used as a body covering, including bags, sheets or carpets. The polymers that fit the criteria for this study are polyethylene (PE), polypropylene (PP), poly vinyl chloride (PVC), nylon and poly(ethylene terephthalate) (PET). These polymers are among the most common mass produced polymers in the market, with these polymers comprising of approximately 70% of the polymer production in Western Europe (Azapagic et al., 2007).

1.4.1 Polyethylene

Polyethylene (PE) is a popular general purpose thermoplastic that is used for a large variety of reasons due to its low cost and ability to be produced on a large scale. The structural repeat unit of PE is illustrated in Figure 1.4. PE has a good chemical resistance to many solvents, acids and bases (Maraschin, 2005). There is a number of commercially important grades of PE based density and amount of branching that occurs in the polymer chain.

$$(\text{-CH}_2\text{-CH}_2\text{-})_n$$

Figure 1.4 Structural repeat unit of polyethylene

The most common grades of PE are low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) (Edward, 1986; Benham and McDaniel, 2005; Maraschin, 2005). LDPE has a branched chain structure and is generally used for purposes that required more flexible materials such as bags and packaging. This polymer is manufactured by a high pressure process involving a film blowing process at a temperature between 150-210°C. LLDPE has very similar properties and is manufactured in a similar process to LDPE, but LLDPE has improved mechanical properties such as a higher strength over LDPE (Vasile and Pascu, 2005; Schmitz and Janocha, 2012). This greater strength in the polymer film is due to the more linear chain structure of LLDPE (Prasad, 1998). HDPE has a more linear structure and is mostly used when a more rigid material is required, such as in bottles or containers. The presence of PE bags material has been reported in a number forensic cases.

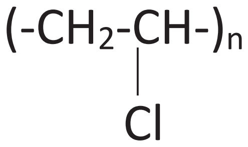
PE is known to be resistant to microbial degradation that is predicted to occur in a burial situation. This is due to its high hydrophobicity that increases the difficulty in microbes being able to sustain themselves on the polymer due to the lack of water. The high molecular weight of PE also makes it harder for microbes to find a way to break down the long carbon chains that make up PE (Shah et al., 2007). It has been found that the degradation of PE generally requires either photo degradation or chemical degradation to break down the C-C bonds in the carbon chains (Shah et al., 2007). This can be followed up by biodegradation due to microbes, which are then able to degrade the polymer due to the effects of the photo or chemical degradation.

The main way that chemical degradation occurs in soil is via oxidative degradation. How the oxidative degradation occurs in a soil environment is dependent on the nature of the soil environment. For example, in the case of an environment with higher amounts of sulfur present, the sulfur can also act as an oxidative agent that allows for biodegradation of the material after the sulfur has oxidised the PE chains (Dilara and Briassoulis, 2000). It is also likely that any oxygen present in the soil will act as an oxidising agent and degrade the PE buried in the soil, allowing aerobic bacteria to start the biodegradation process (Singh et al., 2008). Once the polymer has been oxidised, microorganisms can then degrade the polymer further using enzymatic degradation. It is believed that this occurs by bacteria generating peroxidase enzymes that oxidises the PE further due to the enzymes reacting with the carbon chains, turning them into smaller more manageable molecules that allow the microbes to use the carbon as an energy source (Mumtaz et al., 2010a).

There are a number of ways to investigate the changes to PE due to degradation. This process can be visibly seen by cracks or pits (due to the oxidation process) that form on the surface of PE, which become the centres of noticeable microbial activity (usually either bacteria or fungi) (Feuilloley et al., 2005; Mumtaz et al., 2010a; Mumtaz et al., 2010b). Changes to crystallinity of the polymer also indicates changes to the polymer structure. Many studies investigated the crystallinity of PE and how degradation impacted this polymer feature. An increase to the crystallinity of PE has been previously associated with the absorption of water (Albertsson et al., 1987). This absorption occurs to the normally hydrophobic PE due to the formation of carbonyl bonds that occur during the oxidation of the polymer. This occurrence has been well established in previous literature (Dothée et al., 1988; Dilara and Briassoulis, 2000). While rarer in previous studies, decreases to the crystallinity of PE have been noted to occur. It has been put forward that a decrease to the crystallinity occurs due to biotic rather than abiotic degradation of the polymer (Albertsson et al., 1995; Balasubramanian et al., 2010). While increases to the crystallinity of PE were observed in diffent ways of degrading the polymer, a decrease has only been associated with microbial degradation showing that investigating the crystallinity of the polymer is useful in determining the intiator of the degradation process in PE.

1.4.2 Poly Vinyl Chloride

Poly vinyl chloride (PVC) is a common thermoplastic polymer that is used in both plasticised and unplasticised forms. The PVC structure is illustrated in Figure 1.5. (Summers, 2006).



$$(\text{-CH}_2\text{-}\underset{\underset{\text{Cl}}{|}}{\text{CH}}\text{-})_n$$

Figure 1.5 Structural repeat unit of PVC

Flexible PVC applications require the addition of plasticiser, usually phthalates, to make the polymer less rigid and easier to process (Patrick, 2004, 2005). Plasticisers create this flexibility in PVC by binding to the amorphous regions of the polymer and then weakening the van der Waal's forces (Krauskoff and Godwin, 2005; Summers, 2006). Some of the most common phthalate plasticisers used in PVC are DEHP (Figure 1.6), dioctyl phthalate (DOP) and di-isononyl phthalate (Howick, 1997).

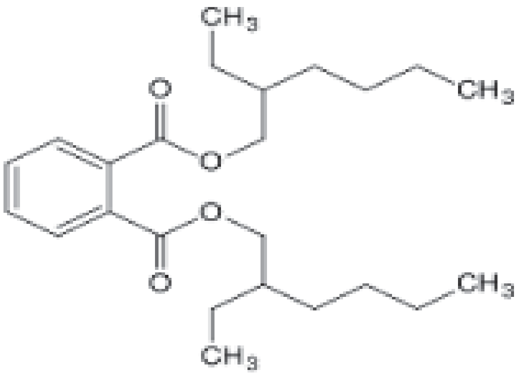


Figure 1.6 Chemical structure of DEHP

PVC can be degraded by chemical, thermal, photochemical methods of degradation (Bowley et al., 1988). The degradation process is started when hydrochloric acid is removed from the polymer (Bowley et al., 1988; Hillemans et al., 1993). This eventually leads to formation of polyenes occurring within the polymer (Bowley et al., 1988; Williams and Gerrard, 1990). These polyenes are extremely reactive and lead to cross linking occurring between the polymer chains (Bowley et al., 1988). The presence of the plasticiser within the PVC sheeting has being previously observed to accelerate this process. It has been put forward by Hollande that this occurs due to the formation of free radicals when the plasticiser degrades along with the PVC, which in turn speeds up the dehydrochlorination of the polymer (Hollande and Laurent, 1997). Since the plasticisers are incompatible with the polyene structure, this causes the plasticiser to leach out of the polymer allowing further cracking in the polymer structure to occur (Bowley et al., 1988; Gumargalieva et al., 1996).

Since plasticised PVC is resistant to chemical degradation and has a low moisture absorption (making it harder for microbes to degrade PVC), this makes it a difficult polymer to degrade in a soil environment (Titow, 1984; Louie, 2005; Shah et al., 2007). Most previous studies that have investigated the degradation of PVC have tended to look at either thermal or photo degradation (Shah et al., 2007). It has been found PVC with a low molecular weight can be biodegraded directly by white rot fungi, but this was tested within an aqueous environment rather than a soil environment and it is unknown whether this would affect how efficiently the fungi degrades PVC (Kirbas et al., 1999). It has been found that when chemical degradation occurs in PVC it follows the same mechanisms to those that occur when PVC is degraded thermally or photo chemically (Bowley et al., 1988). An example of the chemical degradation of PVC has been found when the polymer is in contact with polyurethane foam and the chemical degradation that results from this contact eventually leads to the PVC stiffening and cracking (Bowley et al., 1988). This process could be similar to what occurs when PVC is chemically degraded in a soil environment. It is most likely that in a soil burial situation (dependent on the soil environment itself) degradation will occur in PVC due to a combination of chemical and biodegradation similar to that which occurs in PE.

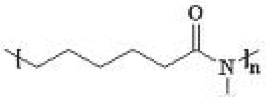
Another important factor to consider with the degradation of PVC, is the interaction of the additives, particularly the plasticiser with the soil environment. This is due to the effect the removal of the plasticiser has on the degradation of the polymer. The ability of these plasticisers to migrate from the PVC to another medium such as water or soil, has been widely studied (Kastner et al., 2012; Magdouli et al., 2013; Monney et al., 2001). Kastner found that DEHP and other similar plasticisers were able leach into water from PVC (Kastner et al., 2012). These observations showed that phthalate plasticisers including DEHP were able to leach into water at a higher rate than some other plasticiser groups found in PVC. This was not repeated when investigating the migration of plasticiser into other polymers as Marcilla observed that phthalate plasticisers tended to have a low ability to migrate into another polymer compared to plasticiser like the adipates (Marcilla et al., 2008). This was possible with the relatively hydrophobic phthalates due to the there been a polar component within the plasticiser molecule that was needed in order for it to interact with PVC (Senichev and Tereshativ, 2013). In a basic environment, it was noted to increase the rate of removal of the plasticiser into the environment when compared to a neutral or acidic one (Hammad Khan and Jung, 2008). This would be an important factor to consider in the removal of plasticiser from the polymer as the pH has been observed to have a large impact on the rate of removal.

Phthalate plasticisers have generally been observed to be resistant to microbial degradation, but there are bacteria strains that are able to use the phthalate plasticisers as an energy source

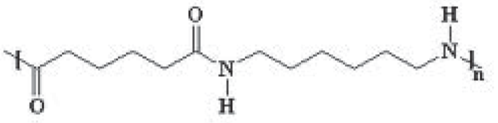
(Coulthwaite et al., 2005; Xu et al., 2008; Latorre et al., 2012; Nakamiya et al., 2005; Pradeep and Benjamin, 2012). These microbial strains were observed to be able to remove DEHP from PVC.

1.4.3 Nylons

Nylons are polyamides that contain an amide linkage group within the structure of the repeating unit (Weber, 2011). There are many different types of nylons with each type differing by the number of carbons present in the repeating unit as well as how the repeating unit itself is structured. In nylon carpets, the nylon fibres used are either nylon 6 or nylon 6,6 (Moody and Needles, 2004). Examples of both of these nylons can be observed in Figure 1.7.



nylon 6



nylon 6,6

Figure 1.7 Structural repeat units of Nylon 6 and Nylon 6,6

There are a number of different ways that nylon fibres are manufactured in industry. The method of the fibre production used is dependent on which nylon product is desired at the end of the process. Nylon 6 which is commonly used in carpeting, can be manufactured using a number of techniques. These include using perpendicular flow through tubes at a temperature between 240-270°C with small additions of water throughout the process, using pressure autoclaves to produce batches of the polymer (Bianchi et al., 2002; Estes and Schweizer, 2011). The polymer is then purified by washing with boiling water and vacuum dried. The polymer can also be purified by passing the polymer through a thin film evaporator, which then feeds into a spinning machine to create the fibres. There are many different additives that can be included in the polymer melt in order to improve some properties of nylon. Common additives that are used with nylon carpets includes stain blockers and acid dyes. Stains blockers are used in nylon in order to improve the resistance of nylon to water absorption (Cooke and Weigmann, 1990). These are commonly used in nylon carpets in order to prevent staining of the carpets when various liquids are spilled on the carpet. The most common stain blockers used in nylon are formaldehyde polycondensates of sulfonated substituted naphthols, phenols and dihydroxydiphenyls as known as syntans (Burkinshaw and Son, 2008). There are also non-aromatic sulfonic acids that have be utilised as a stain blocker in nylon, but these are not as commonly used as the syntans (Cooke and Weigmann, 1990). It has been proposed that the stain blockers help protect nylon against water by the negatively charged group of the syntans, which form a surface layer on the nylon fibre. These stain blockers are often use in conjunction with the acid dyes as the stain blockers also help to hold the dye to the fibre and prevent the dyes from being washed out of the fibres. Acid dyes are the most common dyes used to colour nylon carpet although other dyes such as basic dyes and metallised dyes can also be used (Burkinshaw and Son, 2010; Chakraborty, 2014). The acid dyes bind to the nylon fibres by reacting with the amino end groups present in the nylon polymer chain (Estes and Schweizer, 2011). These dyes have been previously noted to interact with the surrounding environment easily especially in the presence of water (Burkinshaw and Son, 2010)

Generally, the nylons are a tough and flexible material with good wear and frictional properties (Weber, 2011; Yang, 2006). Nylon is also resistant to microbial degradation and is not attacked by insects (Janaway, 2008). Nylon is considered hydrophobic even though there is a tendency to absorb water (Janaway, 2008; Weber, 2011). This is due to nylon been less likely to absorb water over a short period of time when compared to other polymers like poly(ethylene terephthalate) (Weber, 2011). This would occur due to water forming hydrogen bonds with the amide sections of the polymer chain (Iwamoto and Murase, 2003).

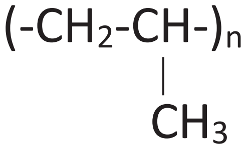
Nylon has been observed to be resistant to microbial and enzymatic degradation due to the structure of the repeating unit (Friedrich et al., 2007; Klun et al., 2003). Although nylon has an amide linkage group similar to the peptide bonds that occur in proteins, this polymer is less polar than these proteins, microbes are not able to easily attach to the polymer (Klun et al., 2003). Due to this, microbes cannot easily access the carbon or nitrogen present within this polymer and so are not able to easily cause degradation (Klun et al., 2003). The main degradation mechanism of nylon involves hydrolysis. The hydrolysis of nylon has been observed to be accelerated in an acidic or wet environment while an alkaline environment decreased the rate of hydrolysis (Burkinshaw, 2013; Lyu and Untereker, 2009; Scheirs, 2000). The hydrolysis of nylon is also accelerated by increasing temperatures (Chen et al., 2010). While hydrolysis of nylon would be the most likely method of degrading nylon due to the abundance of water in the environment, oxidation of the nylon fibres could also occur. Like hydrolysis, oxidation would break down the nylon chains in order to allow microbes to futher degrade the polymer. Without the presence of water , however, the only method of degradation would be oxidation. The oxidation of nylon is a very slow process at room temperature compared to the hydrolysis of nylon and would not degrade nylon easily in the environment (Auerbach, 1989; Thanki and Singh, 1998).

There have been a number of studies that have reported the biodegradation of different types of nylon. It has been found that there are certain types of bacteria and fungi that can degrade nylon (especially the lower molecular weight nylons) in the environment. Enzymes from the white rot fungus were found to be able to degrade various nylon types (Eubeler et al., 2010; Friedrich et al., 2007; Klun et al., 2003; Tachibana et al., 2010). These fungi are presumed to be able to degrade nylon due to the nonspecific oxidative action from the enzymes these fungi produce (Friedrich et al., 2007; Sonal. et al., 2010). This would mean that nylon is degraded by the oxidising action of the enzyme, which allows the fungus to partially solubilise and metabolize the polymer degrading it even further (Friedrich et al., 2007). There have also been bacteria strains found that can degrade nylon in a similar way the fungi do (Andreoni et al., 1993; Sudhakar et al., 2007). Nylon is also able to be degraded by hydrolysis from the presence of water especially over a longer time period which breaks down the nylon chains allowing microbes to degrade it further (Weber, 2011).

The degradation of nylon can be investigated in many different ways. Physical changes to the polymer surface such as fibre fraying or surface stripping indicate that the hydrolysis of nylon has occurred (Parvinzadeh et al., 2009). The area of the nylon chains that is likely to be degraded are the amide sections of the polymer (Gashti et al., 2013; Kiumarsi and Parvinzadeh, 2010; Wang et al., 2014). While these sections are harder for microbes to attack when compared to other amide containing chains (such as proteins), these amide regions would provide the best energy to the microbes and warrant investigation (Klun et al., 2003). Examining the changes to the crystallinity of the polymer over time also gives an indication of whether degradation is occuring as observed with most polymers, an increase to the crystallinty indicates a reduction to the amorphous regions of the polymer (Hanna, 1984)

1.4.4 Polypropylene

Polypropylene (PP) is a thermoplastic that is within the same polymer group (polyolefins) as PE. The structure of PP is very similar to PE except for the replacement of one of the hydrogen atoms for a methyl group on the alternating carbon (Figure 1.8). The location of the methyl group on the polymer chain determine the tacticity of PP with isotactic PP being the most common commercial type (Sundell et al., 1996). The addition of the methyl group makes PP a more rigid and stronger material then PE (Lieberman et al., 2000). PP is known to be resistant to both acids and bases, has low moisture absorption as well as being inexpensive to produce on a large scale (Wust and Landoll, 2000). It is most commonly used in items such as furniture, piping, packaging and carpets (Gu, 2003).



$$(\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-})_n$$

Figure 1.8 Structural repeat unit of polypropylene

PP fibres are manufactured using melt spinning, where the molten polymer is extruded through a spinneret forming the fibres (Pellegrini et al., 2000). The conditions set during the spinning process also can determine the mechanical properties of the fibres. Included in the polymer fibres during manufacturing are also many additives that are added to the polymer in order to improve some of the polymer properties. Additives that are usually added to PP carpet fibres include flame retardants, light stabilisers, and pigments (Wolf and Kaul, 2012). Flame retardants are used in PP carpets since PP is considered to be fairly flammable and can still burn with the flame removed from the polymer (Pellegrini et al., 2000). The flame retardants reduce many of the hazards that occur when PP burns such as the formation of toxic gases and the production of smoke as well as reduce the general flammability of the polymer (Wolf and Kaul, 2012). PP has previously been noted to be susceptible to UV radiation (Wust and Landoll, 2000). The addition of light stabilisers such as the hindered amine stabilisers (HALS) scavenge the free radicals produced by UV radiation reducing the effect the UV light has on the polymer (Tolinski, 2015). These are commonly added to PP carpet since this polymer is often used as an outdoor carpet and in other area with high levels of light (Ghosal, 2008). Pigments are used to colour PP instead of dyes since this polymer has low water absorption, which does not allow the dyes to easily penetrate the polymer to dye it (Pellegrini et al., 2000).

The main method for PP degradation involves photochemical radiation as PP is not very resistant to UV radiation without the use of additives designed to reduce the susceptibility of PP to degrade under these conditions (Andreassen, 2012; Maier and Calafut, 2008). Degradation can also occur by chemical means similar to that of PE. This process is then accelerated by other factors such as temperature, mechanical strain applied either internally or externally or how the polymer was moulded (Rosa et al., 2005). The pH of the surrounding environment, however, was not found to impact on the rate of degradation of PP (Salvador et al., 2003). There are also additives that can be included in the polymer which will speed up the degradation process. The mechanism by which PP degrades is believed to involve the formation of hydroperoxides (Gu, 2003). The hydroperoxides oxidise the polymer chains and results in the formation of carbonyl groups (Cacciari et al., 1993). This process can be seen by a decrease in both the tensile strength and the molecular weight of the polymer (Gu, 2003).

It has been found in a soil burial situation that PP degrades in a similar way to PE. This occurs first by oxidation, which weakens PP enough so microbes can then further degrade the polymer (Arkatkar et al., 2009). This can be observed by the formation of carbonyl and ester groups within the polymer (Arkatkar et al., 2010). Previous studies have found that when oxidation degradation is occurring the amount of carbonyl and ester groups increase within PP followed by a decrease in these groups and resulting in microbial degradation. The oxidation of PP can be caused by a variety of factors in the soils environment such as chemicals present in the soil (e.g. sulfur) or by the formation of enzymes similar to that which occurs for PE. As with PE the microbes degrade PP from the cracks formed in the polymer by the oxidation degradation.

1.4.5 Polyethylene terephthalate

Polyethylene terephthalate (PET) is an aromatic polyester commonly used in the textile industry and carpeting (East, 2004; Hansen and Atwood, 2005; Militky, 2009). The structural repeat unit of PET is shown in Figure 1.9. PET polymer fibres are manufactured using melt spinning, where the polymer is extruded through a spinneret (Sattler and Schweizer, 2011).

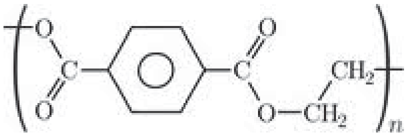


Figure 1.9 Structural repeat unit of PET

PET fibres have been used in carpeting due to various properties of the fibres. PET fibres have a short term low water absorption rate, giving PET carpet stain resistance properties (Edge et al., 1991). It is also a strong material reducing the effects of wear and tear on the carpets as well as being a cheap material to manufacture (Eubeler et al., 2010). PET as fibres are susceptible to static build up and are often hard to clean due to the stain resistance properties. PET fibres used in carpeting are pre-treated before dying in order to remove these properties (Bendak and Raslan, 2011; Zimmermann and Billig, 2011).

The main mechanism for PET to degrade is via hydrolysis whether by chemical or biological means (Janaway, 2008; Badia et al., 2012; Turnbull et al., 2012). Water degrades PET by causing the chain degradation of the polymer, which leads to the ester bond of the PET to break apart (Edge et al., 1991). PET is considered resistant to degradation in the environment particularly biodegradation (Eubeler et al., 2010; Janaway 2008; Szostak-Kotowa, 2004). It has been found, however, that PET can become more sensitive to degradation in the presence of either heat or water and this can be accelerated by any impurities in or around the PET fibres (Edge et al., 1991).

The crystallinity of the fibres has previously been observed to have a large impact on the rate of degradation of the polymer (Pirzadeh et al., 2007). It has been put forward that the crystalline regions of the polymer act as a barrier to water reaching the degradable amorphous regions, stopping hydrolysis of the polymer from occurring. Temperature is another factor that has being observed to impact the rate of degradation of PET with higher temperatures accelerating the hydrolysis process (Demirel et al., 2011; Turnbull et al., 2012). Most soil environments tend to be at temperatures too low to enable chemical hydrolysis to occur. This is due to hydrolysis only readily occurring in PET above the glass transition temperature at approximately 70-80°C (Badía et al., 2009; Pirzadeh et al., 2007). This would lead to the polymer being preserved rather than degraded. The length of the polymer chain also has an impact on the rate of degradation, with shorter PET polymer chains being more likely to degrade than longer chains (Edge et al., 1991). The carbonyl end groups at the end of the chain are particularly susceptible to water, higher concentrations of these carbonyl groups accelerate the rate of degradation.

Various studies have observed the impact the environment has on PET. Previous observations have found that PET is resistant to hydrolysis without the intervention of a strong alkali solution (Brueckner et al., 2008; Sammon et al., 2000). Weathering from outdoor exposure was also observed to have little impact on the polymer (Arrieta et al., 2013). However, it has been noted that various enzymes from microbes, such as the cutinase enzyme from *Fusarium solani pisi* were able to successfully hydrolysis the polymer, although to a lesser extent than an alkali solution (Brueckner et al., 2008; Donelli et al., 2010). Fungi in various media (such as soil and sewage) were also observed to degrade PET, with the environment type having a large impact on the degradation of the polymer (Umamaheswari and Murali, 2013). These studies show that the degradation of PET at lower than the glass transition temperature is possible under the right conditions.

1.4.6 Burial of polymer artefacts in a forensic context

Many studies that investigate the degradation of polymers, examine the polymers in an environmental context such as examining the effect specific microbes have on the polymers degradation. There have been relatively few studies that examine the degradation of polymers in a forensic context. Many of the studies that do examine the polymers in a forensic context investigate the degradation of textiles made from synthetic fibres such as polyester and nylon rather than other polymer types (Lowe et al., 2013; Mitchell et al., 2012; Morse and Dailey, 1985; Walter, 1996). These studies reported the degradation of the polymers in model environments either in the field or in a laboratory.

The degradation of polyester blended with cotton shirts were investigated using model soil environments that were also exposed to the weather (Mitchell et al., 2012). The soil types that were investigated in this study was clay and sand soils. This is due to these soils representing two extremes of potential soils that could be encountered in a forensic investigation. This study found that there are several factors affecting the degradation of the shirts. These include the soil type, time in burial and fabric condition before burial. It was observed in this study that the clay soil was noted to have a greater impact on the degradation of the shirts while the sand soil had less of an impact. This is possibly due to either the alkaline nature of the soil or the bacteria contained in it. The burial length was noted to impact both the strength and colour of the polymer fibres with longer burial times giving a weaker and more stained textile while poorer fabric condition before burial enhanced the degradation process. Another study investigating similar polyester and cotton blends examined the impact the decomposing body has on the degradation of the polymer blends along with the different soil types (Lowe et al., 2013). This study found that that the polyester blends were resistant to degradation in all soil types and the decomposing body did not impact the preserving effect these soils had on the polyester blends.

The degradation of a number of different fibres including polyester blends and nylon were investigated in order to determine the degradation of these fibres in a variety of different soils (Morse and Dailey, 1985). Unlike the Lowe study, it was observed that the polyester cotton blends showed signs of degradation in all of the soil environments after 7-10 months of soil burial while nylon was noted to be resistant to degradation except in acidic environments with poor water drainage. It was determined from this study that the analysis of the degradation of these fibres could be used as an independent method of determining the age of the burial. However, using fibres to find the burial age is complicated by the varying properties of the different soil environments worldwide. In order to use polymer fibres to accurately determine the age of the burial, studies would need to be carried out in a number of different soil types.

As shown by the above studies, the investigation of polymer degradation in regards to the use in forensic situations is relatively minor when compared to the body of study into polymer science. These studies are limited by the polymer type and the types of soils that are investigated. The studies are limited to polymers that could be used as clothing found on the victim. While clothing is a common way that some polymers such as nylon and polyester could be found in a forensic case, clothing is not the only means of polymers being observed in a clandestine burial. Another common method of polymers appearing in a soil burial would be as body coverings such as garbage bags and carpet, which would be used to disguise the burial. The variety of polymers that could be used in this way are greater than what is commonly used in clothing. This indicates a gap in the forensic study of many common polymers such as PE and PVC, which are considered to be the most common polymers in the market.

The analysis of different soil types is fairly limited in the forensic study of polymer degradation, with the focus of the soil studies being either limited to extreme environments (such as the comparison between clay and sand in the Mitchell study) or the soils in specific areas. In a forensic situation, many different soil types may be encountered indicating a lack of study in this aspect of polymer degradation.

These polymers have been studied extensively in other fields of science, however, many of these studies focus on other aspects of polymer degradation that are not considered as important to a forensic investigator. These include many degradation studies on accelerated degradation studies, thermal and ultraviolet degradation and the use of microbial degradation in order to enhance polymer degradation (Arutchelvi et al., 2008; Gu, 2003; Restrepo-Flórez et al., 2014; Singh and Sharma, 2008). While these studies would provide important information about the degradation of the polymers, these studies are less likely to focus on aspects important to forensic investigators such as length of burial time. This indicates a large gap in the forensic understanding of polymer artefacts and the impact burial has on these artefacts.

1.5 Analytical Methods

There is a number of established analytical methods used in the identification and the degradation of polymers. Each of the analytical techniques reveal different aspects of degradation. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are microscopic techniques that show morphological changes to the polymer surface. These can include the development of surface features such as pits and cracks and changes to the surface properties such as roughness. Infrared, Raman and UV-visible spectroscopies are the spectroscopic techniques that reveal information about changes to the structure of the polymer such as the formation of new chemical bonds and the loss of polymer additives. Thermal analysis techniques, including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) provide details about changes to the thermal properties of the polymer due to degradation such as changes to the thermal stability. These techniques can also provide information about the polymer composition including the formation of degradation products and the loss of additives.

1.5.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a technique used to characterise the topography of specimen surface. The technique examines the sample surface by firing a beam of electrons. These electrons are then either emitted or backscattered from the surface, which are then collected by a relevant detector. The backscattered electrons are collected by a backscatter detector (BSE). There are number of detectors for the emitted electrons including a gaseous secondary electron detector (GSE) and a variable pressure secondary electron detector (VPSE).

This technique is widely used due to the improved field of depth and higher magnification when compared to techniques such as optical microscopy (Goldstein et al., 2003). Conventional SEM however, does require samples that are either electrically conducting or are coated with a material (such as gold) that can conduct electricity (Reimer, 2013). This is a common problem encountered when using SEM to analyse polymers. This is due to polymers been an insulating material, which cause excessive charging (a build-up of electrons in the sample) when analysed by SEM. While this can be overcome by coating the polymer with a conducting material like gold, this coating could potentially hide surface features (Reimer, 2013). The use of ESEM allows samples like polymers to be analysed without the need for a conducting coat.

Since many of the early changes due that occur in polymers due to degradation are quite small, SEM with a higher maximum magnification limit compared to optical microscopy is easily able to detect these changes (Goodhew et al., 2000).

ESEM is a method of easily analysing insulating materials such as polymers with SEM. This SEM technique uses a relatively low vacuum (compared to the conventional SEM vacuum that has a pressure of less than 1.3×10^{-4} Pa). It reduces charging in polymers as the positive ions from the gas in the SEM chamber interact with the electrons, greatly reducing the build-up of electrons in the polymer sample (Reimer, 2013). This technique can be run in a number of different gases including air or water vapour. The use of water vapour in ESEM allows greater control of the sample environment within the SEM chamber, as water vapour allows control of the humidity that then sample is analysed under (Haberland et al., 2013).

Since polymers degrade very slowly, any visible changes that occur over a reasonable time period are expected to be small. SEM has been used in order to see what visible indication of polymer degradation has occurred as well as giving an indication to the possible degradation process. Previous studies have found using SEM that when polymer films in soil degrade surface erosion occurs, which thins out the polymer as well as pits and cracks appearing on the polymer surface (Aslanzadeh and Kish, 2005; Kijchavengkul et al., 2010; Kijenska et al., 2010; Liu et al., 2005b; Longo et al., 2011; Mumtaz et al., 2010b; Rosa et al., 2009; Škvarla et al., 2010;). This technique has also previously been utilised in order to detect defects in the polymer film (Mackley et al., 1998). Since these defects are possible intiation sites for degradation, the use of SEM allows these areas in the polymers allows for a greater understanding of the degradation process.

When investigating polymer fibres, there are some similarities to the observations that have previously being noted in the degradation of the polymer films. These include the formation of cracks and thinning of the polymer surface (Rahman, 2012). In polymer fibres, the formation of cracks was observed to all occur perpendicular to the fibre as opposed to cracks forming along the length of the fibre (Friedrich et al., 2007; Rahman, 2012) Other signs of degradation that has been observed in polymer fibres using SEM includes the removal of the outer fibre layers and fibre fractures and breakage (Klun et al., 2003; Rahman, 2012).

SEM is a technique that has being used extensively for the qualitative analysis of polymer degradation. This is due to the capacity of this technique to reveal small surface changes that can be easily identifiable to be due to degradation. There are issues when using this technique in the analysis of polymers, however, these are easy to overcome with the right instrument settings and sample preparation.

1.5.2 Atomic Force Microscopy

Atomic force microscopy(AFM) is a technique also used to analyse the surface topography of a material. Unlike techniques like SEM, AFM does not rely on an incident beam made of electron or light. Instead AFM relies utilises the force due to a sharp tip probe's contact with the surface as it moves across the specimen (Dufrêne, 2002). These changes are measured by the amount of bending that the cantilever that the probe is connected to shows. The greater the bend, the higher the force acting on the probe. Unlike SEM AFM can provide quantitative measurements of the specimen surface (such as surface roughness and specimen height) (Khulbe et al., 2007). However, unlike SEM, this technique cannot show large areas of a specimen, with a maximum area of 125 μm^2 that can be analysed.

There are two main ways that the probe scans the surface in AFM. Contact mode is where the probe has constant contact with the specimen surface, while tapping mode is where the probe has intermittent contact with the surface (Hobbs et al., 2009). Contact mode is often used on specimens with a hard surface that does not scar easily and the advantage of using this mode is that it can be operated in any medium such as water or air (Yourek et al., 2006). This makes this useful for studying a specimen that needs to be kept within a particular environment. This scanning mode, however, applies high levels of force to the specimen, potentially creating damage. In tapping mode, the cantilever that the probe is connected to is oscillated at or near the resonant frequency of the cantilever (Hobbs et al., 2009). This scanning mode puts less force on the specimen, which makes it suitable for investigating the surfaces of softer material such as polymers. However, this scanning mode can be less accurate when investigating the surface topography. This is because the changes to the probes are determined by the frequency rather than height variations on the specimen surface (Yourek et al., 2006).

This technique has not been used as commonly in the analysis of polymers compared to the widespread application of SEM to polymers. This is due to the difficulty of analysing the soft polymer materials with a probe. The probe can easily cause specimen deformation which alters the surface of the polymer and introduces artefacts (Nakajima and Nishi, 2011). However, work is currently being done to investigate the best AFM methods to use when analysing polymers.

AFM has been used previously in a number of different studies looking into the surfaces of polymers, many to investigate the degradation of different polymers under different conditions (Arkatkar et al., 2009; Gu et al., 2001; Hurley and Leggett, 2009; Szép et al., 2004). Most studies, however, investigate polymer films as opposed to polymer fibres (Gu et al., 2001; Risnes et al., 2003). This is most likely due to the small surface area available because of the cylindrical nature of fibres as opposed to films which have a much greater surface area available to examine, making it more difficult to get an overall view of the sample (Allahkarami et al., 2010). In addition, soft samples such as polymers are particularly hard to analyse the surface due to movement of the sample when the probe contacts the surface (Schönherr and Vancso, 2010)

Since AFM is a technique that allows for three dimensional imaging as well as high magnification of the polymer surface, it has been used as a technique to examine changes in the morphology of polymers due to degradation (Freure et al., 1999; Gu et al., 2001; Hurley and Leggett, 2009; Sudhakar et al., 2008). Most of these studies reported the change to the morphology of polymer surfaces via examination of the average roughness of the surface and how it changed over time, as well as being used to investigate general changes in the morphology of the polymers (Gu et al., 2001; Hurley and Leggett, 2009; Sudhakar et al., 2008; Szép et al., 2004). Most of these studies found a change in the roughness and the morphology over time, although one study demonstrated little change to PET after exposure to UV light (Hurley and Leggett, 2009). Another study investigated changes to the polymer due to degradation using the AFM to examine the changes to the surface energy over time, finding an increase in the surface energy of PP occurred as the sample degraded (Arkatkar et al., 2009). Most of these studies used AFM to examine the degradation of the polymers water-based or light environments rather than in soil (Freure et al., 1999; Gu et al., 2001; Hurley and Leggett, 2009; Szép et al., 2004). A study that examined thermally treated PP examined the degradation of the polymer in soil, but this study was used to examine only the effect of the bacteria in the soil rather than observing other aspects such as the soil chemistry (Arkatkar et al., 2009). AFM has also been utilised to investigate the interactions of PVC and several plasticisers in regards to how the surface interaction affect the removal of soil particles from the polymer surface (Määttä et al., 2007).

AFM has been under-utilised for the analysis of polymers particularly in the analysis of polymer degradation due to the environment. This represents a significant field for investigation into using this technique into the analysis of polymer degradation.

1.5.3 Fourier Transform Infrared Spectroscopy

Infrared spectroscopy is a technique based on the vibrations within a molecule. This technique has often been utilised in the analysis of polymer degradation due to the ease of use and the wide variety of changes due to degradation that can be detected by this technique (Nishikida and Coates, 2003; Suëtaka and Yates, 2013).

FTIR spectroscopy has been used extensively in the analysis of polymers. Along with other instrumental techniques to clarify the result, FTIR spectroscopy is useful as an identification tool (Koenig, 2001). This technique can be used to distinguish between different polymers of the same group, such as the various PE grades or different classes of polyamides (Gulmine et al., 2002; Vasanthan and Salem, 2000, 2001). This technique has also previously been utilised to identify the additives present within the polymer (ASTM Standard D2124, 2011). This can be performed either by separating the additives from the polymer or by analysis of the polymer spectrum.

Many studies have utilised FTIR spectroscopy in order to examine the degradation mechanisms of polymers (Arutchelvi et al., 2008; Restrepo-Flórez et al., 2014). There are a number of different ways that polymers can degrade such as PE and PP that have been observed to degrade via oxidation, while nylon and PET can degrade via hydrolysis (Colin et al., 1981). FTIR spectroscopy allows for the analysis of the degradation mechanisms by investigating specific bands that would occur due to the degradation of the polymer. An example of a study investigating the oxidation of a polymer examined the biodegradation of HDPE when degraded by marine bacteria (Balasubramanian et al., 2010). This study examined the degree of oxidation that occurred to the

HDPE by investigating the ester and keto carbonyl bands and the terminal and internal double bond bands. This is a common method often used by many studies in order to study the oxidation of many polymers as these bands appear due to oxidation of the polymers (Chawla et al., 2006; He et al., 2005; Kijchavengkul et al., 2010; Sudhakar et al., 2008). Another study that investigated the degradation of PET, used FTIR spectroscopy to analyse PET after alkali hydrolysis (Donelli et al., 2010). As with the study examining the polymer for oxidation, hydrolysis can be observed in the spectra by examining changes to the carbonyl band along with other bands that change during hydrolysis. From these studies, it can be observed that FTIR spectroscopy has the potential to show the changes to the polymer due to degradation as well as determine the degradation mechanism.

Changes to the crystallinity of the polymer also occur when the polymer undergoes degradation. There are many studies that examine the changes to the crystallinity in order to determine if degradation is occurring (Balasubramanian et al., 2010; Freure et al., 1999; Nam et al., 2011; Sudhakar et al., 2008). Increases to the crystallinity of many polymers are commonly observed during degradation indicating the reduction of the amorphous regions of the polymer. Since the amorphous regions are easier to degrade than the crystalline regions, this is a strong indication of degradation (Achim, 1996).

Another aspect of polymers are additives and polymer blends. Previous studies have used FTIR spectroscopy to analyse the leaching of polymer additives due to the degradation of the polymer. One such study examined the migration of plasticisers from PVC used FTIR spectroscopy in an investigation of the differences in the migration of various plasticisers from PVC to other polymer types (Marcilla et al., 2008). Another technique investigated the interactions between a polymer blend with a plasticiser, using FTIR spectroscopy to determine the blends that were optimal for the two polymers for a specific use (Ramesh et al., 2007). The use of FTIR spectroscopy allowed for easy analysis of the changes to the additive content over time, with the plasticisers and PVC having some distinct bands. However, FTIR spectroscopy may not be as useful when investigating additives that have similar bonds to the polymer being analysed as this technique cannot distinguish between the same bands from different molecules.

FTIR spectroscopy is a versatile technique able to analyse many properties of the polymers that may be affected by degradation. This technique is sensitive enough to detect minor changes in the polymer structure due to degradation. Due to the non-destructibility, fast run times and adaptability of FTIR spectroscopy makes this technique ideal to utilise to examine the degradation of polymers in soil.

1.5.4 Raman Spectroscopy

Raman spectroscopy is a technique that uses the interactions of photons from a laser source interacting with the molecule of interest. This impact of the photons with the molecule causes inelastic scattering of the light, causing either a gain or loss of energy in the photons (Grasselli et al., 1980). Raman spectroscopy unlike IR, is more likely to detect homonuclear bonds such as C-C, as opposed to the polar bonds that are favoured by IR (Xue, 1994). This allows Raman especially when used in conjunction with IR spectroscopy, to give a complete image of the structure of the specimen.

Raman spectroscopy can be a useful technique in the analysis of polymers. It requires very little sample preparation and is mostly non-destructive (Xue, 1997). The biggest issue when analysing polymers with Raman is fluorescence, which produces a signal much stronger than the Raman effect signal (Xue, 1994). There are methods to overcome fluorescence, such as the use of a near IR laser or using Fourier transform Raman spectroscopy (Xue, 1997). Due to problems with fluorescing in polymers, Raman spectroscopy has not been used to its full potential in the analysis of polymers. Raman spectroscopy can potentially give important information about the structure of the polymers particularly in the non-polar regions of the polymer.

Raman spectroscopy has previously been investigated in order to analyse the degradation of polymers. One study examined the crystalline and amorphous phases of LDPE using Raman spectroscopy (Szép et al., 2004). This was in order to determine the effects of natural ageing on the polymer structure. It was noted that the bands associated with the crystalline phase of the polymer increased due to ageing while the amorphous bands decreased. Other studies have also used Raman spectroscopy to determine the crystallinity of PE using different initiators for the degradation of the polymer such as photo-chemical radiation and friction (Dothée et al., 1988; Rull et al., 1995). These studies agree with the observations from Szép. It was put forward that the increase in the crystallinity occurred to degradation only impacting the amorphous phase of the polymer, causing the crystalline portion to increase in relation to the rest of the polymer. While it is possible to determine the changes to the crystalline phase of PE using FTIR spectroscopy only, this technique does not provide easily accessible information about the amorphous phase of the polymer. Raman spectroscopy has also been investigated for the analysis of the crystallinity of PE and PP (Dothée et al., 1988; Minogianni et al., 2005; Rull et al., 1995).

The other polymer that has being commonly investigated using Raman spectroscopy is PVC. These studies observed that Raman spectroscopy can detect the formation and length of polyenes (Hillemans et al., 1993). Often Raman spectroscopy is used either as a comparison tool or in conjunction with UV/Vis spectroscopy (Gilbert et al., 2013; Hillemans et al., 1993). One study found that Raman spectroscopy was able to detect an increase in the degradation of PVC, that was not observed by one of the other techniques used in this study (Gilbert et al., 2013). However, another study determined that Raman spectroscopy is not enough to analyse the formation of polyenes in PVC and that another technique such as UV/Vis spectroscopy must be used together in order to give the most information about the polymer degradation (Hillemans et al., 1993). This is due to the fact that Raman spectroscopy is only able to analyse small sections of the polymer due to the laser size and must be compared to a bulk technique like UV/Vis spectroscopy in order to determine whether the results are representative of the whole.

Raman spectroscopy has been under-utilised in the analysis of polymers when compared to a technique like FTIR spectroscopy. This is mainly due to the problem of polymers fluorescing when analysed by Raman spectroscopy. However, if the polymer can be investigated by Raman spectroscopy, this technique is capable of providing extra information about the changes to the polymer structure as it can provide more selective information about the polymer structure than other similar techniques (Kim et al., 2009).

1.5.5 Thermal Analysis

There are a number of thermal techniques that can be used in the study of polymers, but the techniques that are applicable to the study of the degradation of polymers are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

1.5.5.1 Thermogravimetric Analysis

TGA is a technique that investigates the changes to the mass of a specimen while heated in a controlled environment (Gooch, 2006; Sepe, 1997; Sidwell, 2008). The measurements obtained from analysis of the specimen by TGA can provide information about aspects of the specimen such as thermal stability and composition (Burlett et al., 2002). This technique can be used as the only method of analysis or can be used in conjunction with other techniques such as TG-FTIR, TG-gas chromatography (GC) and TG-mass spectrometry (MS) (Sepe, 1997). This allows for further identification details about the specimens to be determined.

The standard configuration used in TGA involves a balance suspending a crucible into a furnace (Kelsey and Foreman, 2000; Gabbott, 2008). This allows the crucible to be indirectly heated up by the furnace, due to the furnace heating the area around the crucible (Kelsey and Foreman, 2000). This method of heating the crucible does allow for inaccuracies to occur as the temperature recorded for the crucible is an approximation, as there is no direct way to measure the temperature of the specimen in the crucible.

The gas used in the controlled environment of the furnace can be either reactive such as air or inert such as N_2. Inert gases delay the onset of decomposition due to the heating process (Sepe, 1997). It is also possible that the shape of the trace will be different for the same specimen depending on the gas used. This can include the thermal decomposition of the specimen been a single step process under N_2 gas while under air is more complex (Prime et al., 2014). This makes the choice of gas for the study important as only specimens run under similar gases can easily be compared. It is also important to consider the weight of the sample measured as a small sample size increases the error in the data and can affect the information obtained (Stawski, 2009).

TGA can be used to show the formation of degradation products as well as the absorption of volatile products (such as the water absorption that occurs with nylon) (Brown, 2001). Both the degradation and volatile products are detected by TGA using the mass losses that occur (Martelli et al., 2009; Schlemmer et al., 2009; Wong and Lam., 2002). TGA has also been used for the study of the degradation of polymers by utilising the shift that occurs in the decomposition temperature (T_g) (Krupa and Luyt, 2001; Martelli et al., 2009; Schlemmer et al., 2009; Slapak et al., 2000; Wong and Lam., 2002). This shift occurs while the structure of the polymer changes during the degradation process (Schlemmer et al., 2009).

The derivative of the TG trace (DTG) can provide more information about the polymers. Observing any changes that occur to the DTG trace is a possible indication of the polymer degrading over time. Previous studies have used DTG to investigate degradation of different polymers by observing changes to the height and width of the DTG peak or changes to the T_{max} (Broda et al., 2007; Dimitrov et al., 2013; Karayildirim et al., 2006; Kim, 2001; Latorre et al., 2012; Shi et al., 2008). Changes to the T_{max} in the DTG trace shows a change in the thermal stability of the polymer (Chrissafis et al., 2007; Jha and Bhowmick, 1998). Shifts to a lower T_{max} have been previously observed to indicate degradation of the polymer, which generally lowers the thermal stability (Martelli et al., 2009; Nam et al., 2011). Changes to the width or height of the DTG trace also indicates degradation of the polymer. A decrease to the height and a wider peak has generally been noted to indicate the addition of impurities (such as formation of degradation products), which decreases the overall purity of the polymer. This was observed in Canetti et al., who showed that the addition of lignin to PP had this effect (Canetti et al., 2006). An increase to the height and decrease to the width however, indicates possible leaching of additives into the environment.

TGA traces have previously being utilised in the analysis of polymer degradation particularly in relation the effect degradation has on the thermal properties of the polymer.

1.5.5.2 DSC

DSC is a technique that measures the energy required to have no temperature difference between the sample and the reference material (Brown, 2001). DSC is mainly used to study the melting and crystallisation behaviour of the polymers as well as the heat loss or gain that occurs during the phase transitions (Arkatkar et al., 2009).

DSC is often used as an identification tool particularly in identifying the different polymers that are under the same group (e.g. nylons or PE). This is achieved by comparing either the melting temperature (T_m) or through examination of the appearance of the melting endotherms (Dobkowski, 2006; Kijchavengkul et al., 2010; Marten et al., 2005). This allows this technique to be used as a complimentary technique to other analytical techniques such as FTIR in identification of the polymer due to DSC being able to accurately determine the m.p. of the polymers.

DSC has been used as a technique to investigate the degradation of the polymers as degradation affects both the crystallinity and the T_m. A previous study showed that the type of degradation will change the DSC curve in different ways (biotic as opposed to abiotic) (Klun et al., 2003). This means that the degradation mechanisms of the polymers can be studied as these changes that occur could be compared to either previous studies or a set of references that have been set up and allow the study to see which degradation process is affecting the material.

Previous studies have shown the capacity of DSC to analyse many features of the polymers such as the m.p, which is can be used to assist in the identification of the polymers and the crystallinity, which helps in understanding the degradation mechanisms for the polymers. This makes it a useful technique in the analysis of polymer degradation.

1.5.6 Ultraviolet and Visible Spectroscopy

Ultraviolet and visible spectroscopy (UV-Vis spectroscopy) is a technique that investigates the wavelengths of the electromagnetic radiation that a specimen will absorb at (Clark et al., 1993). This technique is useful in determining the concentrations of a molecule of interest in a specimen.

The analysis of PVC using UV-Vis spectroscopy mostly involves the analysis of the formation of the polyenes in the polymer chain. Many studies that investigate the thermal degradation of PVC, use UV-Vis spectroscopy as the formation of polyenes in PVC is easily detectable by UV-Vis spectroscopy (Behnisch and Zimmermann, 1989; Daniels and Rees, 1974; Kip et al., 1992; Martinez et al., 1979; Szakács and Iván, 2004). These studies also used UV-Vis spectroscopy to determine the length and distribution of the polyene chains in PVC.

Although there UV-Vis has been used for the analysis of the formation of polyenes in PVC, less work has been done on using UV-Vis for the analysis of PVC additives. UV/Vis spectroscopy has previously been used to analyse the effect that different additives have on the degradation of PVC (Gilbert et al., 2013). It has also previously been used to compliment other techniques in the characterisation of different PVC additives (Li et al., 2014). The changes that occur over time to common PVC additives like plasticisers, can give an indication of the degradation of the polymer. Plasticisers in particular, are known to leach out of PVC due to the formation of polyenes as well as environmental factors such as water (Kastner et al., 2012). While the movement of plasticisers out of PVC have been analysed by previous studies using techniques such as IR and gas chromatography, UV-Vis is a useful technique to investigate as it allows for quantitative analysis of the plasticiser loss (Marcilla et al., 2008; Monney et al., 2001).

1.6 Aims and Objectives of Project

This thesis is an investigation of how different burial environments affect the degradation of the five polymers of interest in a forensic burial context. The primary aim was to determine the impact the soil environments had on the polymers, that is, whether the soils preserved or degraded the polymers. The secondary aim was to investigate the most appropriate analytical techniques to investigate the degradation of specific polymers.

It has been identified that more research is required on the impact the soil within the burial site has on potential polymer artefacts. This is in order to understand the impact the soil environment has on the polymers and the information that can be gained from the polymer artefacts to build up a forensic case. While previous studies have investigated the degradation of polymers in the environment, very few examine the impact the soil environment as a whole has on the polymer. Many of the previous studies focus on the impact of thermal or photochemical degradation on the polymers, which is unlikely to be the primary degradation mechanism within a soil environment. Other studies examine only the impact of microbial life without taking into account the role the rest of the environment has on the polymer. In this study, burial environments that vary in soils types, moisture content, pH and temperature will be investigated in order to understand how the different soils impact the polymers.

The principal analytical techniques used in this study to analyse the polymers were SEM, FTIR spectroscopy and TGA. These three techniques allow surface properties, structural and thermal properties to be characterised. These techniques were used to analyse all five of the polymers of interest in this study. The other techniques were utilised as complementary techniques where. AFM was used in conjunction with SEM for the polymer films (PE and PVC) as this technique provided additional information about the changes to the polymer surface. Raman spectroscopy was utilised as a complementary technique to FTIR spectroscopy in order to examine changes to the crystallinity of PE. While FTIR spectroscopy is capable of analysing the crystallinity of PE, Raman spectroscopy provided details about changes to the amorphous phase of the polymer as well confirming the FTIR spectroscopy data. UV/Vis spectroscopy was found to be able to analyse the changes to the plasticiser content of PVC and provide quantitative data of the observations noted in FTIR spectroscopy.

1.6.1 Primary Aim

The primary aim of the current study was to determine the impact possible soil environments that may be encountered in a forensic case, had on the five polymers. This was carried out by burying the polymers in various laboratory controlled environments and then analysing the polymers with various analytical techniques. In order to achieve this aim, several objectives were established in order to achieve this aim. This included soil environment preparation, polymer burial and polymer analysis.

1.6.1.1 Objectives

i. The first objective involved preparation of the soil burial environments. The burial environments are to be laboratory controlled and vary from the loam soil reference by one variable such as temperature, pH, moisture content or soil type.
ii. The second objective involved the burial of the polymers in the soil and subsequent removal of the polymers from the soil in set time intervals
iii. The third objective involved the analysis of the polymers. The techniques used to analyse the degradation of the polymers after soil burial includes infrared, Raman and UV/Vis spectroscopy, scanning electron and atomic force microscopy and the thermal analysis techniques, TGA and DSC.

1.6.2 Secondary Aim

The secondary aim of this project was to determine the most suitable analytical techniques for the analysis of the degradation of polymers in a soil matrix. This was carried out in conjunction with the primary aim during objective iii, as various analytical techniques were determined to not reveal new information about the degradation of the polymers. There are various changes to the polymers that were investigated in order to determine the extent of the degradation in the polymers. These included the impact degradation has to the polymer surface, changes to the chemical bonds due to degradation, changes to the thermal properties and the impact the soil environments had on the polymer additives. The techniques utilised for the various polymers in order to investigate these aspects of polymer degradation are listed in the objectives.

1.6.2.1 Objectives

i. Investigation of the polymer surface involves the use of SEM and AFM microscopic techniques. Both of these techniques provides information about the polymer surface. Both of these techniques have known problems in regards to analysing polymers. These include charging of the polymer surface (SEM) and the soft nature of polymer materials interfering with analysis (AFM).
ii. The changes to the chemical bonds in the polymer were investigated using FTIR, Raman and UV-Vis spectroscopy. FTIR spectroscopy is commonly used in regards to the analysis of polymer degradation partially due to the flexibility of this technique in regards to sample preparation. Raman spectroscopy is less utilised for polymer analysis since polymers are

susceptible to fluorescing mostly due to the additives contained within the polymer. UV-Vis spectroscopy would not be suitable for analysis of the degradation of most polymers unless a factor of the polymer (such as additives) have a measureable absorbance in the UV Visible light range.

iii. The techniques utilised in order to investigate changes to the thermal stability of the polymers are TGA and DSC. Both of these techniques investigate various aspects of the thermal stability of polymers.

1.7 Thesis Structure

This thesis investigated the effects that various soil environments that could be encountered in a forensic case, have on common polymers. Chapter 1 discussed the relevant background information as a literature review. This review included a discussion of the degradation of polymers including potential degradation mechanisms and the analytical methods that detected these changes. This chapter also included an investigation into previous forensic research on polymer degradation and the shortcomings observed. Chapter 2 discusses the experimental design of this study as well as justifications for the use of particular techniques. Chapters 3-7 show the results and discussion for the effect that the soil environments have on each of the five polymers with each chapter corresponding to one polymer. These chapters are broadly divided into three sections based on analytical techniques: microscopic, spectroscopic and thermal analysis techniques. There is also a fourth section that discussed and summarised the information obtained from the analytical techniques for each polymer. The final chapter presents an overview of the impact of the soil environments on the polymers. This included a brief discussion on the environments that were generally noted to be more damaging to the polymers over other environment types.

Chapter 2

Development of Methods

2.1 Materials

The following details the materials and burial environments used in this project as well as an explanation for their inclusion in this project.

2.1.1 Polymer Materials

There are many different polymers available today that are in common use. In order to determine which polymers would be the most common and therefore most likely to be found as an artefact in a soil burial situation, factors such as availability and common uses were investigated (Hansen and Atwood, 2005; Patrick, 2005; Vasile and Pascu, 2005; Yang, 2006). The polymers chosen for this study needed to be manufactured in a form that could encase a human body in a soil burial situation. The polymers obtained for use in this project are discussed in detail in Table 2-1

Table 2-1 Polymer samples used in this project

Polymer	Description	Purchase Origin
Polyethylene	Polymer sheeting as taken from garbage bags	Multix brand from Coles Supermarket
Polypropylene	Brown loop pile PP carpet with jute backing[1]	Carpet Court
Poly Vinyl Chloride	Polymer sheeting as take from shower curtains	Homebrand from Kmart
Poly(ethylene terephthalate)	Cream cut pile PET carpet with PET fibre backing[2]	Carpet Court
Nylon	Light brown cut pile nylon carpet with jute backing	Carpet Court

[1] PP Carpet was loop pile due to the availability of PP carpet styles present at the burial time in Carpet Court

[2] PET carpet with jute backing was not available at Carpet Court when polymers were buried in the soils

2.2 Burial Environments

In order to simulate a soil burial situation as close as possible, many factors need to be included in the burial environments. These include the different variable of the soils as well as the method of the polymer burial in the soil environments.

2.2.1 Soil Burial Method

A soil burial method was a common method used when investigating the effect, a soil environment has on the degradation of a polymer (Singh and Sharma, 2008). This involves burial of the polymer for a set time period in a soil medium, followed by washing with distilled water and drying. This method allows for an approximate simulation of a natural environment within the laboratory. However, when using this method with laboratory controlled conditions as opposed to natural environmental condition, many factors cannot be taken in account such as the effect of flora, fauna and weather.

The samples in this study, were removed from the original source in 20 x 5 cm rectangles. One of these for each polymer were buried at a depth of 5 cm (total soil was 10 cm, samples buried at a depth with 5 cm above and 5 cm below) in polyethylene boxes filled with a soil type. These boxes had fourteen holes drilled in the sides, this was in order to allow air circulation through the soil environment. An example of the environment that the samples were kept in can be observed in Figure 2.1. These boxes were left to sit at room temperature in a dark room (the exception was the cold box which was left in a refrigerator at 4°C).

Figure 2.1 Example of prepared soil environment

The sample were exhumed from the box every 3 months and a 2 x 5cm subsection of the buried sample was removed. Figure 2.2 shows the polymer samples before and after soil burial. The exception to this was for the 1st and 2nd months where 1 x 5cm was removed. This was to check to see if any early rapid changes occurred.

Figure 2.2 Samples before (top) and after burial (bottom)

The removed subsection was washed twice in distilled water. Specimens were then left to dry overnight in the air and then placed inside a PE slip lock bag labelled with the date the sample was exhumed, the number of months the sample was buried, the sample type and the soil type. Prior to analysis these samples were stored in a dark drawer in a larger PE bag labelled with the number of months buried and sample type.

2.2.2 Soil Environments

It was decided for this project to investigate common variables that are found in the environment within Australia for these laboratory control soil environments. These variables include soil type, pH, temperature and moisture content. The burial period of the polymers investigated was 0-24 months. The soil variables that were investigated are detailed in Table 2-2, which shows the soil type, pH, moisture content and temperature of the 9 soil environments. These environments were checked regularly (refer to appendix for variations to moisture content and pH) to maintain the soil environments properties observed before the burial of the polymers.

Table 2-2 Summary of the soil properties of the environments used in this study

Environment Type	**Soil Type**	**pH**	**Moisture Content Scale**	**Temperature**
Loam	Loam	7	4	Room
Sand	Sydney Sand	7	2	Room
Clay	50:50 Clay: Loam	6.5	3	Room
Lime	Lime	8	2	Room
Cold	Loam	7	4	4°C
Dry	Loam	7	1	Room
Wet	Loam	7	10	Room
Acidic	Loam	4	5	Room
Basic	Loam	8	5	Room

2.2.2.1 Soil environment packaging

Environments were placed in HDPE boxes (Keji, Officeworks) that has a volume of 21 Li with spatial dimensions of 46.7 (width) x 32.3 (Height) x 30.0cm (Length)

Boxes were prepared for burial environments using a drill bit (size – 6,5) to drill 4 holes on the long edges of the box (spaced 7cm apart) and 3 holes on the short edge (spaced 8cm apart) to allow for air circulation within the soil environments. These boxes were then cleaned with distilled water and left to air dry overnight

2.2.2.2 Reference Environment

The reference soil environment (or control) contained polymers buried in loam soil at received pH, moisture content and left at room temperature (varied from 20-23^{o}C). At the start of this project it was observed that the loam soil had a pH of 7 and had a mid-range amount of moisture contained within the environment. The loam soil had the brand name Naturalgrow potting mix and was purchased from Bunnings Warehouse in Sydney. Potting mix soils are loamy soils that also contain other features such as tree bark, fertiliser, perlite and vermiculite (Parker, 2009). This particular potting mix was described to be a general purpose potting mix and did not contain features from the specialised mixes such as an acidic pH. This makes this potting mix similar to the loam soils present in many developed parts of Australia and was therefore chosen to represent the loam environment. This environment required distilled water to be added approximately every three months in order to maintain the mid-range moisture reading.

2.2.2.3 Soil Types

For this study a variety of different soil types were investigated. These were the sand, clay and lime environments, which were then compared to the reference environment. All of these environments were used with as received pH, moisture content and were maintained at room temperature. The sand environment was produced using Greenlife Sydney River Sand, and had a low moisture content and a neutral pH. The lime environment was produced using Richgro Garden Lime that had low levels of moisture and a pH of 8. Due to clay commonly been found mixed with other soil types particularly loam soil, it was decided to mix the builder's clay (brand name Boral Builders Clay) with loam soil in a 50:50 ratio in order to take this environmental aspect into account. This environment was found to also have a low moisture content and a neutral pH. All material for these environments were purchased from Bunnings Warehouse in Sydney.

2.2.2.4 Moisture Content

As the reference environment was found to have a mid-range level of moisture, it was decided for this study to compare the two extremes of a very dry and very wet loam soil environment to the reference environment. The wet environment was prepared by adding distilled water to the loam soil environment until it was visibly saturated with water. This environment was monitored weekly using a moisture meter during the initial stages of the experiment to determine how long was needed until the environment would show signs of drying. Observations show that the environment could be monitored every 3 months with little change in the soil environment. If the soil started drying distilled water was added to the environment until it was saturated again. The dry environment was prepared by baking loam soil in a vacuum oven at 60°C overnight.

2.2.2.5 Soil pH

In order to compare the effect that a change in pH would have on the polymer samples, basic and acidic soil environments were prepared. The acidic environment was made by first adding corrective element sulfur fine granules (Manutec Garden Care) to the loam soil environment, which was then watered with distilled water. It was observed that this method only lowered the pH to 6 so it was decided to add small amounts of 18M sulfuric acid to the environment in order to lower the pH to a more acidic environment that can occur in soil (pH was found to be 4). In order to maintain the pH at 4, small amounts of 18M sulfuric acid were added to this environment over the burial period when the pH of the soil reached 5 keeping the acidic soil within a pH of 3.5-5. The basic environment was made by adding lime to the soil environment which was then watered in with distilled water. This was found to have raised the pH to 8 which was considered to be the high end of basicity for a soil environment. This environment had the pH of 8 maintained by adding more lime to the environment when the pH approached 7 keeping the basic soil within a pH of 7-9.

2.2.2.6 Soil Temperature

This environment was prepared by placing loam soil in a refrigerator that was set to 4°C and was digitally controlled in order to simulate a cold environment. This was compared to the reference environment that was left at room temperature (22 °C). It was observed that over time condensation would appear on top of the soil potentially increasing the moisture content of this environment. The refrigerator containing the soil environment was monitored using a thermometer placed on top of the box containing the soil environment. This was checked weekly in order to determine that the temperature did not rise above 5°C.

2.3 Analytical Methods

The methods outlined in this chapter were used to conduct the experiments that are detailed in later chapters.

2.3.1 Scanning Electron Microscopy

In this study, SEM was used in order to examine the changes that occurred to the polymer surface after burial in the soil environments. There were 2 instruments used to complete this examination. From 0-12 months a FEI Quanta 200 ESM with Gatan MONOCL3 was utilised in order to examine the polymer surface. This was changed to the Zeiss Evo L15 SEM for the remaining polymer samples due to instrument availability. Both instruments are capable of analysing samples under a number of different conditions such as high vacuum, low vacuum and ESEM vacuum. Low vacuum and ESEM vacuum for both instruments can be run using air or water vapour.

The polymer samples were placed onto the mounting stage using double sided conducting stickers. In the FEI Quanta, 8 samples were able to be mounted onto the stage, while on the Zeiss Evo, 9 samples were mounted and analysed in a session. In both instruments the vacuum mode used was low vacuum using water vapour as the chamber gas. The pressure of the chamber was 130 Pa on the Quanta and 105 Pa on the Evo. The samples were run under a 20 kV electron beam with a spot size of 4.0 for the FEI Quanta and 5.0 for the Evo and a working distance of approximately 10 mm. The 20 kV electron beam was used as a higher kV caused excessive charging in the polymer samples. A lower kV beam, however, had a much lower resolution, leading to the 20 kV compromise to be used. Although the FEI quanta setting were investigated on the Zeiss Evo, it was found that these were not the optimal conditions (as determined experimentally by examining polymers) for analysis of the samples in this instrument. The settings used for the Zeiss Evo were optimised for the instrument and were as close as possible to the original FEI Quanta settings.

To account for differences between the magnifications of the two instruments the horizontal field width (HFW) was used instead of magnification. The following HFW settings were investigated – 2970 µm, 1490 µm, 745µm, 298µm, 149µm, 74.6µm, 29.8µm. The sample were examined to note any signs of degradation. Each sample had a three number areas checked to both find any unusual features as well as checking the polymer sections for consistency. Any unusual features that could be indicative of sample degradation were also noted. The detector found to be optimal for analysis of the polymer samples in the FEI Quanta large field gaseous secondary electron detector (LFD-GSE) as this provided the best image to examine the polymers. An example micrograph taken from this instrument, can be observed in Figure 2.3.

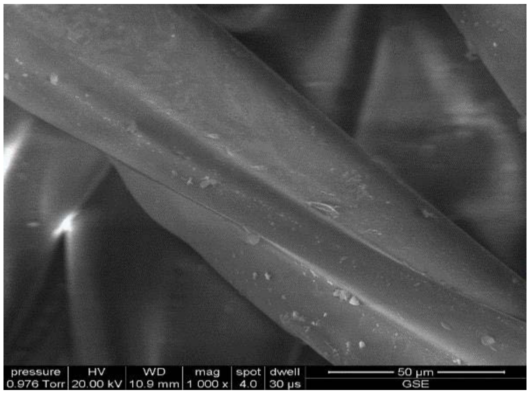


Figure 2.3 SEM Micrograph of PET from the FEI Quanta

The detector used on the Zeiss EVO was a two-part detector using both VPSE along with a BSE as a secondary detector. Figure 2.4 shows a comparison between the VPSE with BSE and BSE as the only detector. It can be observed from Figure 2.4 that the VPSE with BSE detector shows greater detail on the polymer surface than the BSE detector. The BSE detector, however, was observed to be able to more easily distinguish between foreign particles and the polymer compared to the VPSE with BSE detector. Since the VPSE with BSE detector produced the clearest images of the surface, this detector was used in the analysis of the polymer. However, if unusual features were found during the examination of the polymer, the BSE detector was used in order to help distinguish which areas were due to the polymer and the area due to another factor microbial life or soil.

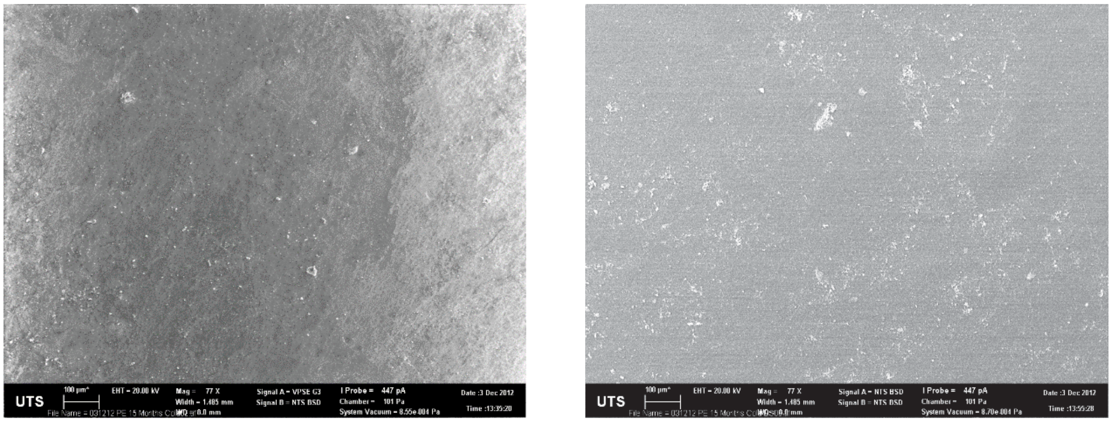


Figure 2.4 SEM micrographs of PE from the Zeiss EVO, using VPSE with BSE (left) and BSE only (right)

The SEM micrographs were investigated over the 24 months of soil burial. Analysis of the polymer samples was performed every 3 months. These micrographs were examined to see if any trends were emerging that could be associated with the degradation of the polymer. Features that were investigated include the formation of pits and cracks as well as the appearance of possible microbial life.

2.3.2 Atomic Force Microscopy

2.3.2.1 Experimental Details

In this study, AFM was used to investigate the topography of the polymer surface, particularly changes to the surface roughness over the burial period. A Veeco Dimension 3100 SPM instrument was employed. This instrument was capable of analysing an area of up to 100μm^2 of the specimen and changes in the polymer surface of less than a few nanometres.

In order to remove as much as the soil residue as possible from the polymer surface, the sample was washed with detergent and distilled water three times followed by drying with N_2 gas. Alternate methods were investigated, such as the use of solvents including ethanol, however, this appeared to cause modification to the polymer surface.

Since the polymer materials are soft, this makes it difficult to analyse the surface using AFM. Mounting the samples on a flat surface did not allow the probe to make suitable contact with the polymer surface and greatly distorted the image. In order to give the AFM a more suitable surface for analysis, the polymer samples after washing were mounted on a cylindrical glass rod by pulling the sample over the rod. This rod was attached using adhesive to microscope slides to give stability while analysing the sample. Using this method of mounting the samples gave a small area at the top of the rod which could act as a hard surface allowing better analysis of the polymers.

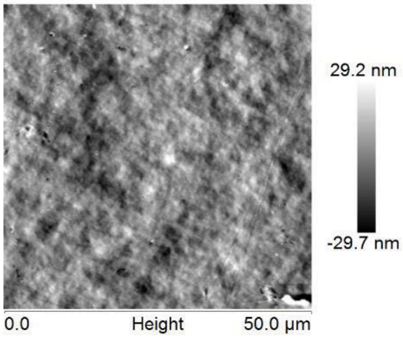


Figure 2.5 AFM micrograph of PVC as analysed by AFM

The polymer samples were analysed using a soft tip in tapping mode instead of contact mode to avoid damage to the polymer surface. This was carried out at a constant force as set by the instrumentation. Three 50 μm^2 images of each sample were collected. An example of an image collected using the AFM can be observed in Figure 2.5.

The film polymers PE and PVC, that were been investigated in this study, were found to be ideal to examine using the above method with AFM. However, the fibre polymers, PET, nylon and PP were not able to be analysed with AFM. This due to both the difficulty in mounting the fibres as well as the small width of the fibres. This made it difficult to get the probe to contact with the polymer.

2.3.2.2 Data Analysis

The images recorded on the AFM were examined the Nanoscope Analysis (Bruker, USA). This software was used to both manipulate and analyse the images. Manipulation of the images included 2nd order plane fitting of the image. This was required due to the method of mounting the polymer samples as the unprocessed images produced have a slope to the image where the sample on the glass rod curved down. This slope impacted many features of the polymer such as the height. This can be observed in Figure 2.6, which shows an AFM micrograph as taken from the instrument and after image manipulation. It can be observed from these micrographs that there was a curve to the surface in the firstmircograph, while the second image appears flat. Also, the maximum height can be observed to be smaller in the micrograph on the right of Figure 2.6 when compared to that on the on the left of the figure.

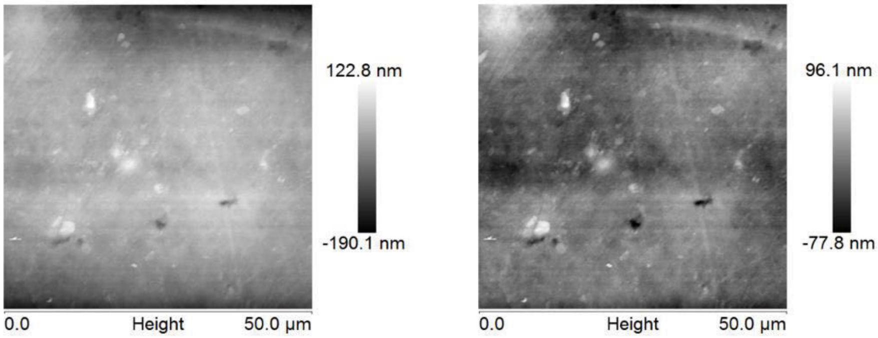


Figure 2.6 AFM micrograph of PVC as analysed by AFM before image manipulation (left) and after (right)

In order to account for the variability due to factors such as residual soil that was strongly attached to the polymer surface or imaging artefacts due to the instrumentation, 6 sections of each of the 3 50 µm images were collected and had the roughness (rms) value determined for each. This was used instead of a R_a mean for the whole image as any instrumentation artefacts could easily affect the roughness mean. These sections were also compared to each other to see if any changes within the wave structure occurs over the course of the burial process.

2.3.3 Vibrational Spectroscopic Techniques

2.3.3.1 Fourier Transform Infrared Spectroscopy Experimental Details

There were a number of different IR spectroscopic methods were determined to provide the most information about the different polymers. All IR spectra obtained in this project were analysed by the Omnic software suite (Thermo Scientific, USA).

2.3.3.1.1. Micro ATR

The PVC specimens were analysed using a Nicolet Magna IR 6700 Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector. The specimens were examined using an attenuated total reflectance (ATR) diamond sampling accessory. The spectra were recorded over a range of 4000-500 cm^{-1} with 128 scans that were collected with a resolution of 4 cm^{-1}. Samples were repeated in duplicate with each duplicate having the mean of 3 scans used.

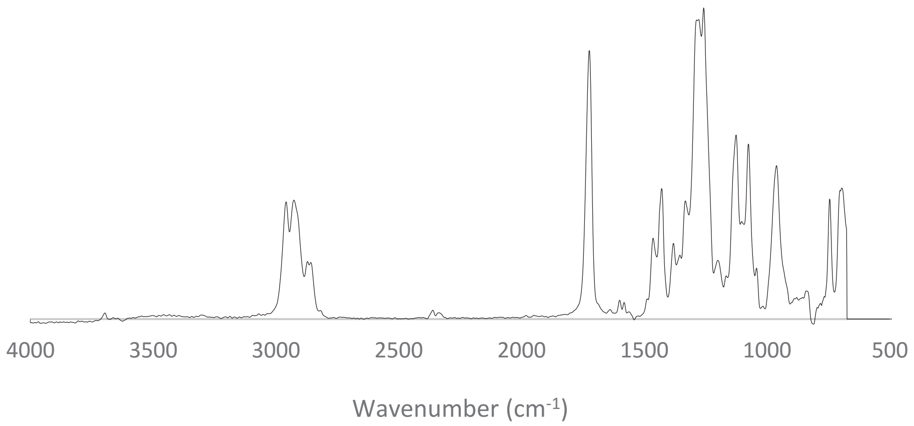


Figure 2.7 An example IR spectra of PVC as obtained from micro-ATR

2.3.3.1.2 Marco ATR

Nylon, PET and PP samples were analysed using a Cary 630 Fourier transform infrared spectrometer and sampled using a diamond ATR accessory. The spectra were recorded over a range of 4000-600 cm^{-1} and 64 scans were collected with a resolution of 4 cm^{-1}. The samples were repeated in duplicate, with each duplicate having the mean of 3 separate scans that were used.

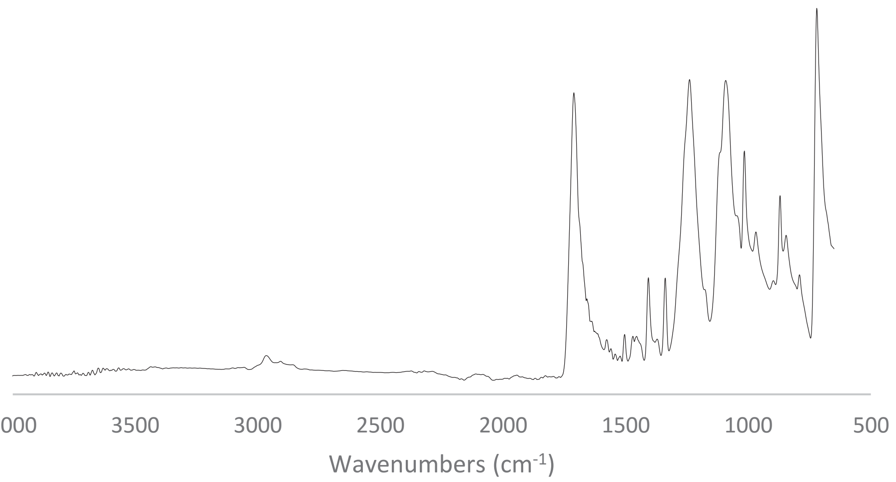


Figure 2.8 Example IR spectrum of a PET fibres as obtained using macro-ATR

This method of collecting the IR spectra was utilised for the fibre polymers due to difficulty in using other method to obtain consistent data. While other methods such as fibre transmission and micro ATR were attempted, this method did not fulfil the requirements needed for this study. Micro ATR produced a poor signal for the fibres since the ATR crystal was unable to make a viable contact with the fibres. Fibre transmission did produce IR spectra for the fibres, but there was very little consistency over the 24 months' polymer burial with unusually large variations occurring to the spectra of the fibres. Since this large change was not observed in any of the other techniques used to analyse the fibres, this change over time was believed to be due to other factors and not to degradation of the fibres. It was possible that this variation occurred since fibre transmission IR only investigates single fibre. Macro ATR spectroscopy, which was the method used for analysing the fibres under IR, can sample a bundle of fibres in one spectra. This reduced the issues associated with using a single fibre as a representative of the whole polymer.

2.3.3.1.3 Transmission IR

PE specimens were analysed using a Nicolet Magna IR 6700 Fourier transform infrared spectrometer. The PE samples were placed into the instrument by attaching the samples to a metal insert with magnetic strips. The sample was maintained in a nitrogen purged sampling chamber for 30 min to minimize atmospheric contributions. The spectra were recorded over a range of 4000-600 cm^{-1} with 100 scans and a resolution of 4 cm^{-1}. These samples were repeated in duplicate.

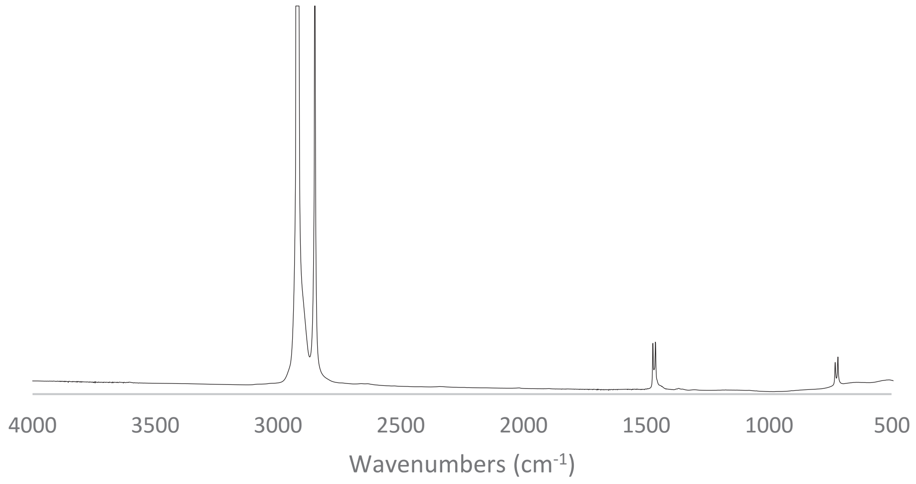


Figure 2.9 An example of the IR spectra obtained from the analysis of PE using transmission IR

2.2.3.2 Raman Spectroscopy Experimental Details

2.2.3.2.1 Experimental Details

Raman spectra were recorded using a Renishaw inVia Raman microscope equipped with a 785 nm red laser. This laser was chosen in order to control fluorescence that was common within polymers due to the potential additives present. The laser was set to 50% power in order receive the best signal without overloading the detector.

The Raman shift range of analysis was from 4000-400 cm^{-1}. Each sample was examined in duplicate with each duplicate having 3 different scans. The Omnic software suite (Thermo Scientific, USA) was used to analyse the Raman spectra.

This technique was found to be useful in the analysis of PE as this polymer gave a clear signal with Raman.

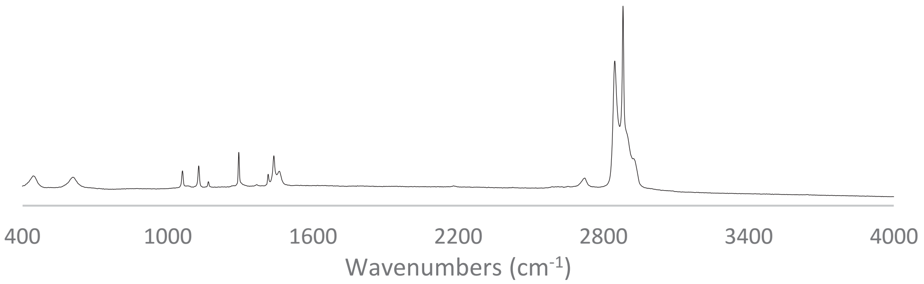


Figure 2.10 An example of a Raman spectra of PE

This technique was found to be not viable for use in analysing PVC, PET, Nylon and PP. PET and nylon are dyed fibres. It has been observed previously that dyes in polymers are well known for inducing fluorescence in Raman spectroscopic studies (Bart, 2006). While it was possible to remove the fluorescence due to dyes in the polymers with Fourier transform Raman spectroscopy, this technique was not available at the time of analysis. PVC unlike PET and nylon did show a signal. However, while this signal was viable in the use of characterising the polymer, it was not possible to use the Raman spectra from PVC to study changes over time due to degradation because only a weak Raman signal to be detected. Most likely the fluorescence was due to the different additives that are present within PVC. PP unlike the other polymers did not fluoresce and a viable signal was detected. However, bands that were important to the analysis of the polymer were very unstable with large and inconsistent shifts occurring to the ratios of these bands. While the cause of this variation was unknown, it was possibly due to interactions of the Raman laser with different sections of the fibres. An example of this can be observed in Figure 2.11, comparing 2 different Raman spectra of PP from the same environment and burial time.

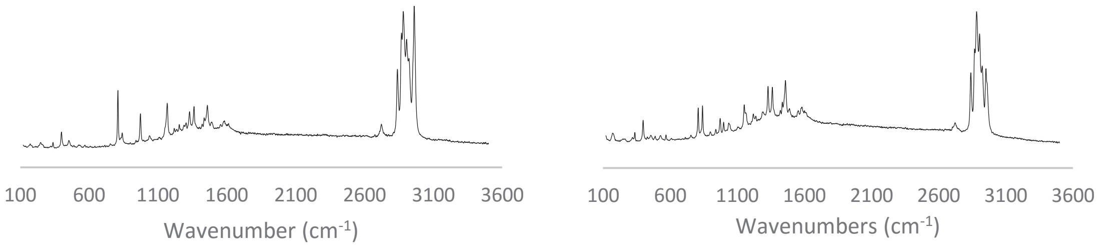


Figure 2.11 Comparison of two PP Raman spectra from the basic environment after 6 months

2.3.3.3 Multivariate analysis

2.3.3.3.1 Pre-processing of Data

Spectra were analysed using the Unscrambler X software (Camo, Norway). It was converted to a 2^{nd} derivative spectra using a Savitzky-Golay filter. In order to remove as much variation within the data, a standard normal variate transformation was applied. This auto scales the absorbance values of the spectra in order to provide an easy comparison of easily compare the data (Varmuza and Filzmoser, 2009b). This data was then normalised to a specific band for each polymer (refer to Chapters 3,4,5,6 and 7 for further details).

2.3.3.3.2 Principal component analysis of polymers

PCA was a technique used to simplify large quantities of data into a point on a x,y axis (Jolliffe, 2013). This allows for trends to be easily identified in the data as well as compare groups of different data points. This technique was used in this study to compare the trends found in the PCA analysis of data with the ratio analysis of the bands in the Raman and IR spectra. PCA however, only investigates one independent variable and does not show any changes due to other dependent variables.

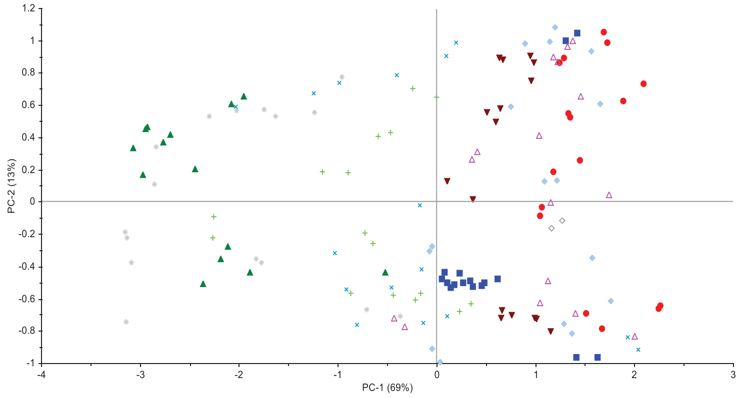


Figure 2.12 PCA graph of the IR data obtained from PVC

2.3.3.3.3 Comparison of PCR and PLS-R

PCR and PLS-R are types of linear regression analysis method that allow for models to be generated based on the data. Unlike PCA which only investigate independent variables, linear regression also takes into account dependent variables in the generation of a model (Varmuza and Filzmoser, 2009a). Linear regression analysis was used to analyse the retention times, absolute intensities and post-burial times of polymer specimens buried in the different environments. In order to determine the most suitable method of linear regression analysis to use in this study, the models obtained from PCR and PLS-R were compared for the polymers using the polymers buried in the loam soil environment as a reference. Figure 2.13 shows the model obtained from PVC buried in the loam soil environment from PCR, while Figure 2.14 show the model from PLS-R. The figures show the correlation between the actual time since burial of polymers and the predicted post-burial time as determined by the models generated by the Unscrambler software.

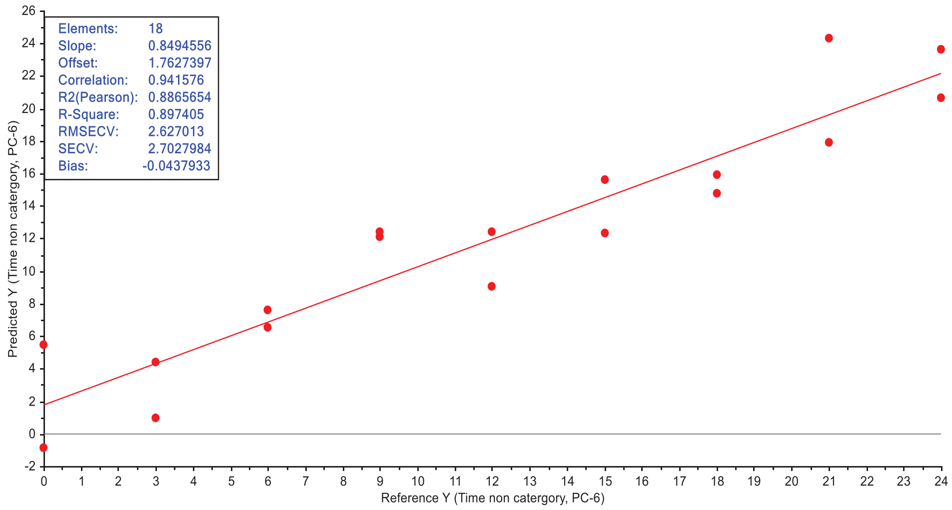


Figure 2.13 PCR model of PVC after burial in the loam soil environment

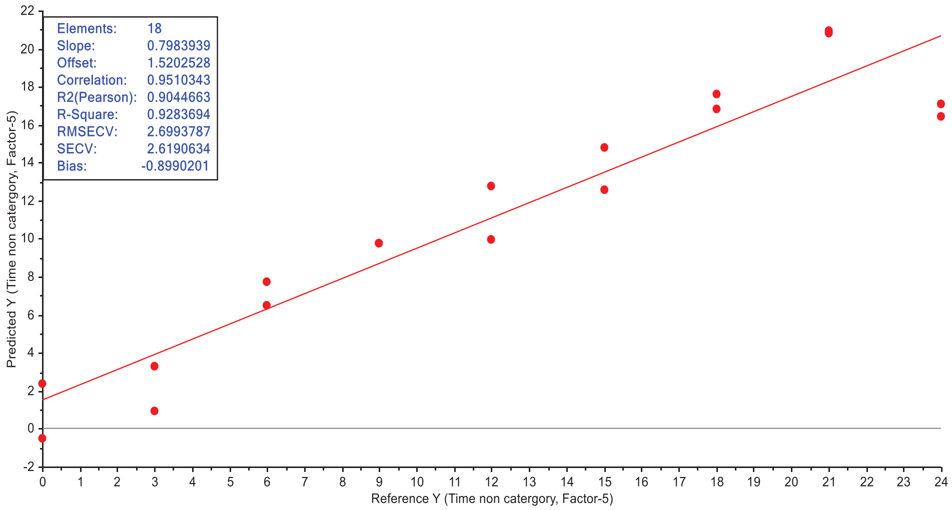


Figure 2.14 PLS-R model of PVC after burial in the loam soil environment

A comparison of the models obtained from PCR and PLS-R indicated that PLS-R was the more suitable model for use in this study. This was indicated by the R^2 values, which are 0.88 for PCR and 0.92 for PLS-R. The PLS-R model also show the duplicates for the polymer are closer than the PCR model. The PCR model, however, did predict the later months better than the PLS-R model. However, the majority of the burial time periods were predicted more precisely in the PLS-R model.

2.3.4 Thermogravimetric Analysis

In order to prepare the polymer specimens for analysis by TGA, the polymers were placed in a desiccator in order to remove any residual water. TGA and DSC was carried out on the polymer specimens using a SDT Q600 simultaneous thermogravimetric analyser and differential scanning calorimeter (TA Instruments, USA).

5± 0.5mg specimen were placed in platinum crucibles. This crucible was previously zeroed against a reference crucible of the same material. The sample was run from 30° to 700°C at a rate of 10°C/min in N_2 gas. The gas was set at the flow rate of 50 cm^3 /min.

The data was analysed using Universal analysis 2000 (TA Instruments, USA). The TG curves are smoothed to a region width of 25°C while the DTG curve are smoothed to 10°C. These curves are exported from the software into Microsoft excel.

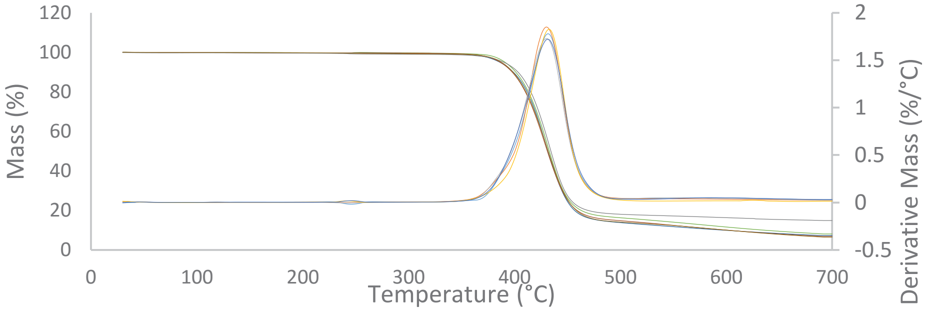


Figure 2.15 An example of the PET data obtained by TG

2.3.5 UV-Vis Spectrophotometry

UV-visible spectroscopy was used for qualitative and quantitative analysis of the plasticiser additive used in the PVC specimens. The PVC specimens were dissolved in tetrahydrofuran (THF) (inhibitor free HPLC grade from Sigma Aldrich, USA) at a concentration of 0.26 g/L. (Daniels and Rees, 1974; Kip et al., 1992; Szakács and Iván, 2004). This concentration was determined to be optimal in regards to the absorbance of the plasticisers at the wavelength of interest. This was due to this concentration of PVC in THF keeping the absorbance of the peak of interest under 1 to allow for easier measurement. Samples were run in duplicate on a Cary number 100 UV/Vis spectrophotometer over a range of 200-800 nm using a 1 cm^2 quartz cuvette.

In order to determine the molar absorptivity (ε) of the plasticiser present in the PVC samples, a sample of the pure plasticiser was extracted from the PVC. The plasticiser was extracted using the method listed in Section 2.3.6.1. It was determined that the ε of the DEHP plasticiser at 275 nm was 1200 L mol^{-1} cm^{-1}.

The UV-Vis absorbance spectra were analysed using Spek32 win spectroscopy software (Dr Friedrich Menges, Germany). The duplicate specimen spectra were smoothed and the mean was found in order to determine the absorbance of the plasticiser at 275 nm. The changes to the concentration of the plasticiser in the polymer were studied every 6 months over the 24 months of burial.

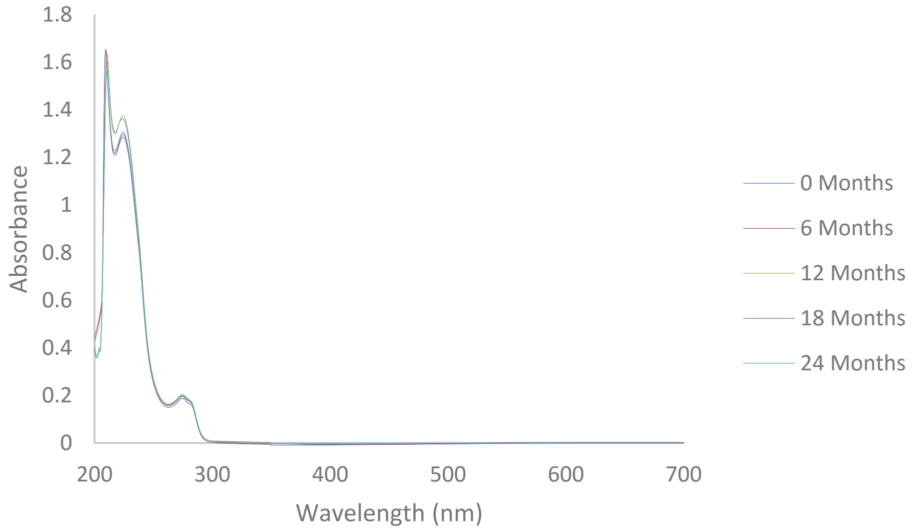


Figure 2.16 An example of the UV-Vis spectra as obtained from the analysis of DEHP

2.3.6 Miscellaneous Methods

These techniques were not used for the ongoing analysis of the polymer rather were used for characterisation of either the polymer or an aspect of the polymer such as any additives.

2.3.6.1 Determination of plasticiser in PVC samples

In order to determine to identity of the plasticiser present in the PVC specimens, the plasticiser was extracted from the PVC specimen. The plasticiser removed from the PVC using this method was also used to determine the ε of DEHP in UV-Vis spectroscopy allowing the changes in the plasticiser content to be quantitatively determined.

The plasticiser was extracted from the PVC by dissolving the PVC in THF and heating the polymer solution to near boiling. Once the polymer was completely dissolved in the THF, methanol was added to the solution in order to precipitate the PVC. The solution was filtered in order to remove the solid PVC and the remaining solution was heated at a low temperature to evaporate the THF, leaving the plasticiser behind. The plasticiser extract was collected and was identified using IR and a NaCl plate. The spectra obtained from this can be observed in Figure 2.17.

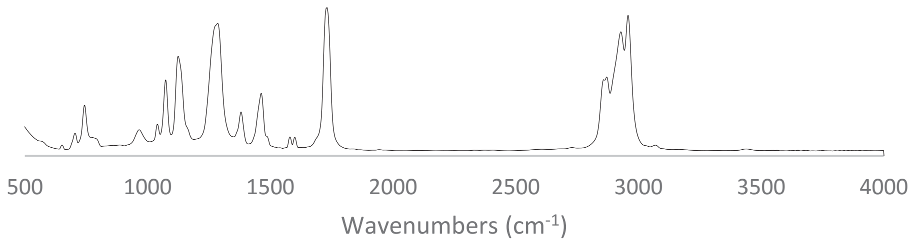


Figure 2.17 IR spectrum of the plasticiser obtained from PVC

2.3.6.2 Differential Scanning Calorimetry

DSC was used as a characterisation tool in this study. 2.5± 0.5 mg of polymer specimen removed from the original buried sample was then placed in a tzero sealed aluminium pan. This was placed in the DSC with an empty pan acting as a reference. All the polymers that were analysed by DSC were run at a rate of 5°C/min. Due to the different melting points of the polymers, each of the polymers were run to a different maximum temperature. These temperature programs are listed in Table 2-3. The data was then collected and analysed using Universal analysis 2000 (TA Instruments, USA).

Table 2-3 DSC temperature programs used to determine the m.p. of the polymers

Polymer	Temperature range of DSC program
PE	20 to 180°C
Nylon	20 to 300°C
PET	20 to 300°C
PP	20 to 200°C

2.4 Limitations of Study

A main limitation of the study was in the lack of replicates in the initial burial of the polymers. This would require additional replicate burial environments to contain the polymer replicates. Due to availability of space, this was not possible and should be considered when the results of this study are examined.

Chapter 3

Polyethylene Film Analysis

3.1 Introduction

PE was the most common polymer in the world and its primary application was in packaging. Due to their ready availability, PE plastic bags or films are a likely source of material to be used by a perpetrator attempting to hide remains. In this chapter, a commercial PE plastic bag has been used to model how soil burial will influence the properties of this polymer in a burial context. In order to study the effect that the laboratory controlled burial environments have on the polymer, a variety of different techniques were used.

The techniques that were found to give the most information about the degradation of PE were SEM, AFM, IR spectroscopy, Raman spectroscopy and TGA. SEM and AFM were used to examine the polymer surface in order to observe any surface changes that can be attributed to degradation. IR spectroscopy was utilised in order to examine various changes to the polymer structure due to degradation such as the formation of carbonyl bonds and changes to the crystallinity of PE. Raman spectroscopy also examined the crystallinity of the polymer, allowing confirmation of the changes to the crystalline phase observed in IR spectroscopy to occur. TGA used in a preliminary study that examines the bulk changes to the polymer and whether these changes could be detected in PE by TGA.

3.2 Characterisation

PE was one of many polymers that can be used as a film. Infrared spectroscopy has been used in order to confirm that the polymer material used in LDPE. Figure 3.1 shows the IR spectra of the polymer before burial in the soil environments and confirms that this material was PE. The bands at 2919 and 2851 cm^{-1} are associated with C-H stretching while the doublet band at 1473 and 1463 cm^{-1} was due to a CH_2 bending deformation and the doublet at 731 and 720 cm^{-1} was due to the CH_2 rocking deformation (Gulmine et al., 2002). There was also a weak group of bands located at 1377, 1369 and 1352 cm^{-1}associated with CH_2 deformation.

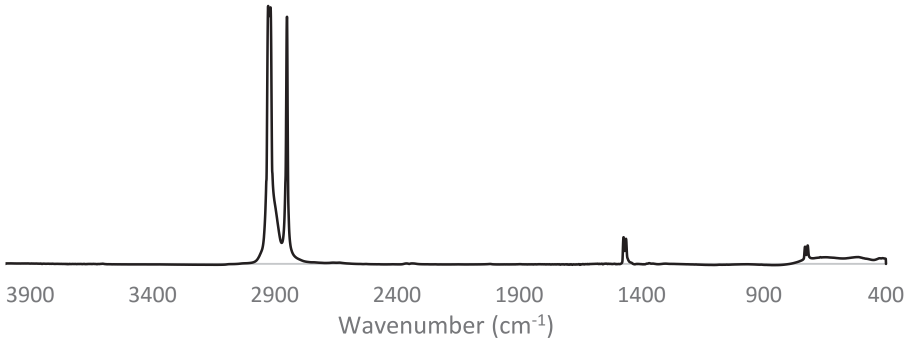


Figure 3.1 IR spectrum of PE before soil burial

There are many different variations of PE many which look similar in appearance, may have vastly different properties. These properties affect how the polymer degrades, with HDPE degrading slower than LDPE (Vasile and Pascu, 2005). Since the properties can have a large impact on the degradation of the polymer, it was important to characterise the polymer further. It has been observed that it was possible to distinguish between the different PE type by the band at 1377 cm^{-1} (Gulmine et al., 2002). Figure 3.2 shows the IR spectrum of PE between 1330 and 1390 cm^{-1}. It has been previously noted that the band at 1377 cm^{-1} increases in relation the other bands as the PE becomes more branched. In LDPE, the bands at 1377 and 1369 cm^{-1} are approximately the same height while in LLDPE, the bands at 1377 and 1352 cm^{-1} are closer. It can be observed from

Figure 3.2, that the band at 1377 cm^{-1} was closer to 1352 cm^{-1}, which indicates the identity of polymer as LLDPE.

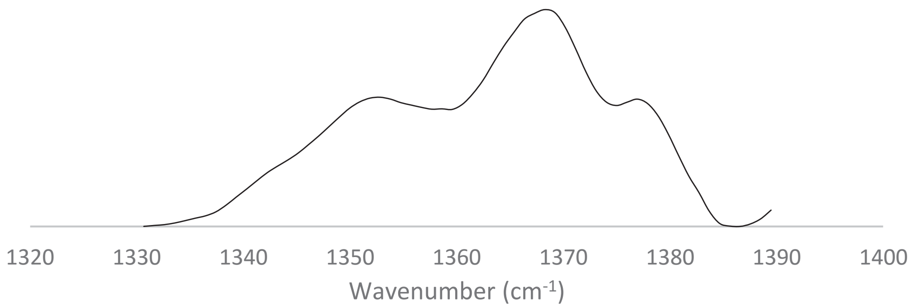


Figure 3.2 IR spectrum of PE before soil burial between wavenumber 1330 to 1390 cm^{-1}

In order to confirm the identity of the polymer as LLDPE, another analytical technique was required that gives further information about the polymer. DSC was used as it can give the melting point of the polymer, allowing it to be distinguished from other similar PE types such as LLDPE and LDPE. Figure 3.3 shows the DSC curve of PE before burial in the soil environments. From Figure 3.3, it was observed that the m.p. as seen in DSC was 127°C. The melting range of LDPE has previously been found to approximately 106-112°C while the melting range for LLDPE was found to around 120-124°C. Since the m.p. identified using DSC was found to be 127°C, which was closer to the melting range associated with LLDPE, this confirms the identity of the PE sample been investigated as LLDPE (Prasad, 1998).

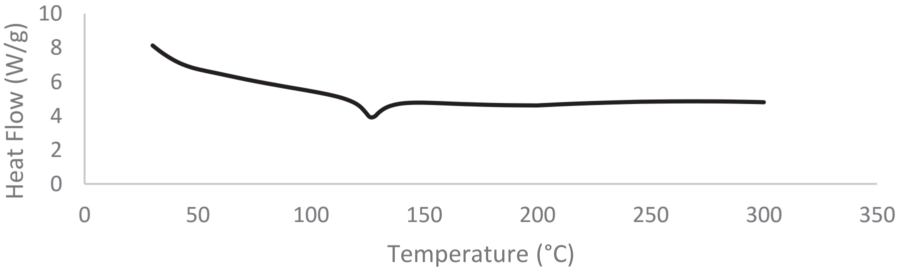


Figure 3.3 DSC trace of PE before soil indicating the m.p. of the polymer

3.3 Scanning Electron Microscopy

3.3.1 Results

Changes to the surface morphology of the polymer surface over the 24 months' period were examined using SEM. It has been previously noted that the degradation of PE film can be observed by changes to the film surface. The first stages of degradation can be observed by peeling and the formation of pits in the film structure, this was followed by peeling of parts of the film and finally fracture of the film itself (Mumtaz et al., 2010b). The morphology of the surface of PE was examined every 3 months to look for these signs of degradation.

Typical SEM micrographs of the PE surface prior to burial are shown in Figure 3.4. The surface does not appear to be completely smooth, with varying texture noticeable on the surface of the polymer as well as the presence of what appear to be small particles. When examining the polymer under a smaller HFW (as also seen in Figure 3.4), it can be observed on further inspection that the surface was generally quite smooth except for the small particles present. This variation in the surface of the polymer was most likely due to the manufacturing process. This was commonly seen in LLDPE where variations during the manufacture of the film can cause the surface texture to change (Mackley et al., 1998).

There was very little noticeable change occurring to the surface of PE until 9 months of burial as illustrated in the example in Figure 3.5 that shows the micrograph of the lime environment at 6 months. By 9 months the lime, clay, wet and sand environments start to produce some changes to the surface of the polymer. The specimens buried in the lime and wet environments show evidence of pit formation scattered over the surface of the polymer, as seen in the wet environment example given in Figure 3.6. While the clay environment does not show this pit formation, it does show a different surface texture to the surface before burial PE, as illustrated Figure 3.7. The polymer in the sand environment also has a different surface texture, however this was to a much lesser extent than the specimens buried in the clay environment. The rest of the environments show little to no change. The dry environment specimen was shown in Figure 3.7 and provides an example.

After 12 months of soil burial, all the environments show some change occurring to the surface of the polymer with the clay, lime, basic, wet and sand environments showing greater changes than the other environments. The pits that were noticeable in the polymer in the lime environment have transformed into areas of scarring occurring on the polymer surface, while the basic environment specimens also show similar scar formation but to a lesser extent, as seen in Figure 3.8, which depicts the surface of the polymer extracted from the basic environment after 12 months. The PE from the clay and sand environments now show pits forming on the polymer surface along with surface texture changes that occurred by 9 months giving the PE surface a rougher appearance as seen in Figure 3.9 (depicts the surface of the polymer after extraction from the clay environment at 12 months), with the sand environment showing the similar changes but to a lesser extent than the clay. The specimens from the wet environment (rather than scarring like the polymer specimens from the basic and lime environments) developed more widespread pit formations with mostly small pits been observed occurred the polymer surface as opposed to been concentrated in one area as seen in Figure 3.10, which depicts the PE surface after removal from the wet environment. The rest of the environments show some evidence of pit formation. This can be observed in the example given in Figure 3.11, which shows the polymer surface after extraction from the dry environment at 12 months. However, unlike the wet environment this pit formation was not widespread and only occurs in small areas.

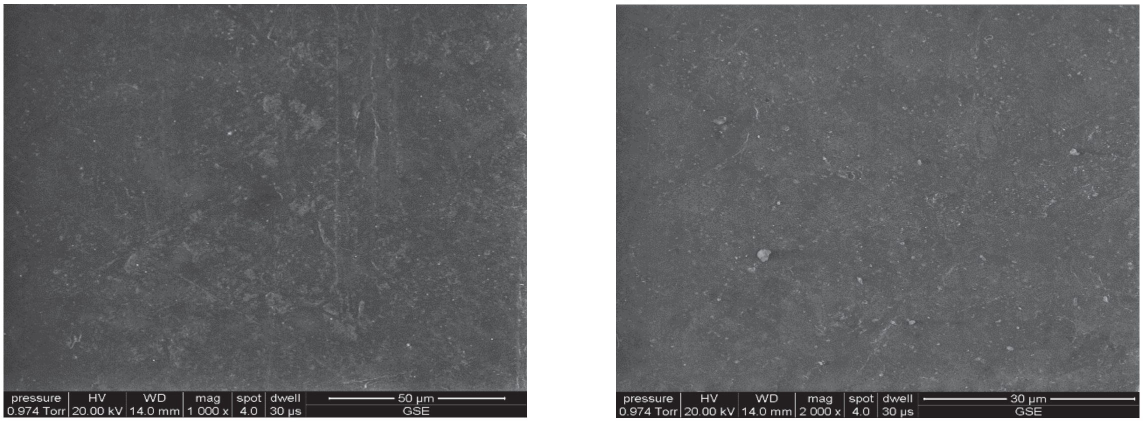


Figure 3.4 SEM micrograph of PE before burial with HFW of 149.1 µm (left) and 79 µm (right)

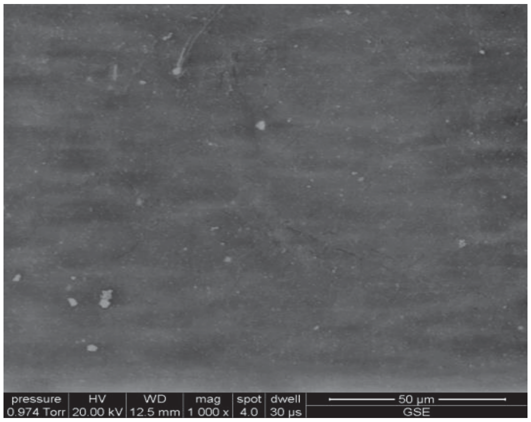


Figure 3.5 SEM micrograph of PE extracted from the lime environment at 6 months

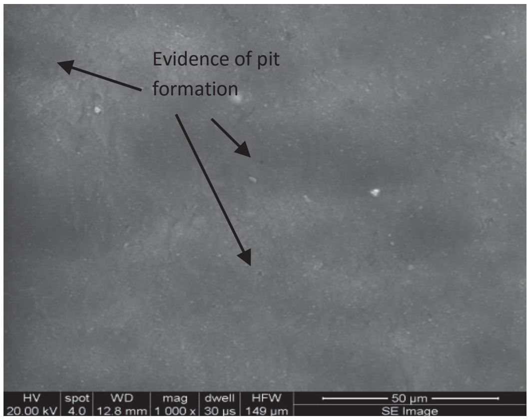


Figure 3.6 SEM micrograph of PE extracted from the wet environment at 9 months

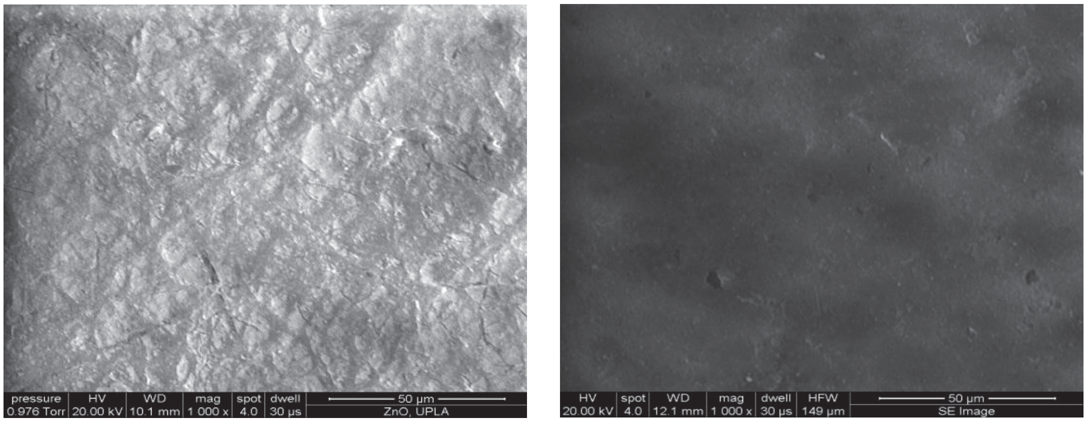


Figure 3.7 SEM micrograph of PE extracted from the clay environment (left) and dry (right) at 9 months

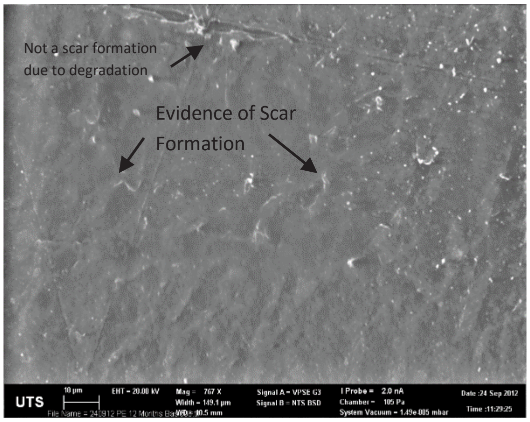


Figure 3.8 SEM Micrograph of PE after burial in the basic environment for 12 months

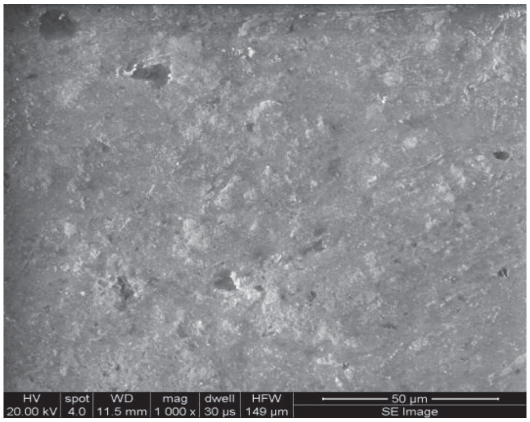


Figure 3.9 SEM Micrograph of PE after burial in the clay environment for 12 months

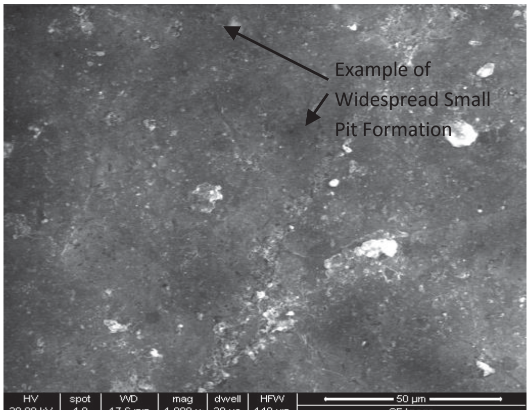


Figure 3.10 SEM micrograph of PE after burial in the wet environment for 12 months

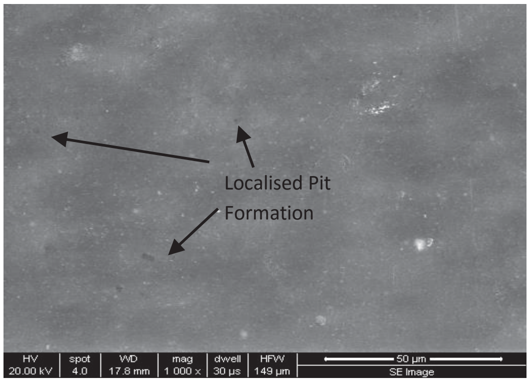


Figure 3.11 SEM Micrograph of PE after burial in the dry environment for 12 months

From 15 months to 18 months, PE in most of the 9 soil environments shows no more evidence of pit formation occurring. Instead there seems to be minor cracks appearing on the surface of the polymer for most of the environments in varying degrees as seen in the example provided by the sand environment example shown in Figure 3.12. The exceptions to this behaviour are the clay, lime and acidic environments. The clay and lime environments still show evidence of pit formation on the specimens occurring, as well as comparatively large scale cracking when compared to the less reactive environments, as seen in the clay environment example shown in Figure 3.13. The clay environment specimen appears to have pit and crack formation occurring on a larger scale then the lime environment. The acidic environment specimen shows an unusual surface texture formation that appears at 15 months and has mostly disappeared by 18 months. Instead by 18 months it was observed that there are long straight cracks as well as areas of pits forming on the surface of the polymer, as seen in Figure 3.14. The most likely reason for this occurrence would appear to be due to the variations with the pH that occurred during this project. It was noted that while the pH of the soil was kept within 3-4, there could be a large difference in the microbial life present when comparing a pH of 3 to a pH of 4 (Nowak et al., 2011). The Nowak study observed that biodegradation of the PE was slowed in a more acidic environment. This was due to the strains of microbes that are able to sustain themselves on PE such as bacteria from the Bacillus genus, been less able to produce more bacteria due to the acid inhibiting outgrowth (Pandey et al., 2015)

Between 18-24 months, the polymer buried in the dry, cold, sand, and loam environments show no change from 18 months to 24 months, with only some minor scarring present on the polymer surface*,* as seen in the example given of the polymer after 24 months' burial in the sand environment in Figure 3.15. The wet, lime and clay specimens also have not changed since 18 months, however, these environments show greater changes overall on the polymer surface as illustrated by the example of the wet environment specimen after 24 months as shown in Figure 3.16. In these specimens there were more cracks noticeable on the polymer surface than when compared to the specimens from the dry, cold, sand and loam environments. The specimens from the acidic and basic environments both show large cracks and surface texture changes on the polymer surface. The acidic environment looks very similar to how it appeared at 18 months indicating that there have been no further changes to the polymer surface during this period. However, the basic environment does show change between the 18 to 24 months with larger cracks noticeable on the polymer surface by 24 months as shown in Figure 3.17.

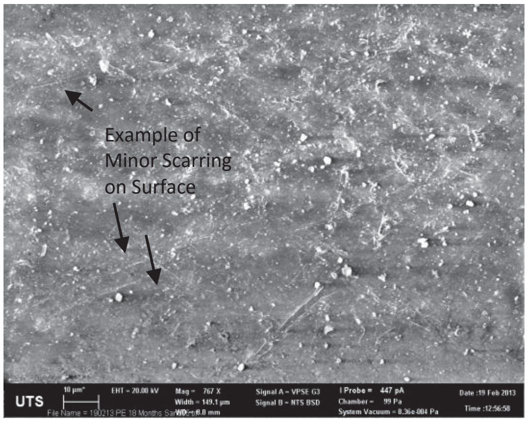


Figure 3.12 SEM micrograph of PE after burial in the sand environment for 18 months

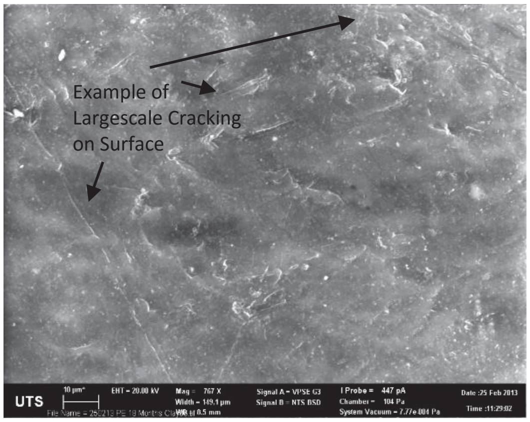


Figure 3.13 SEM micrograph of PE after burial in the clay environment for 18 months

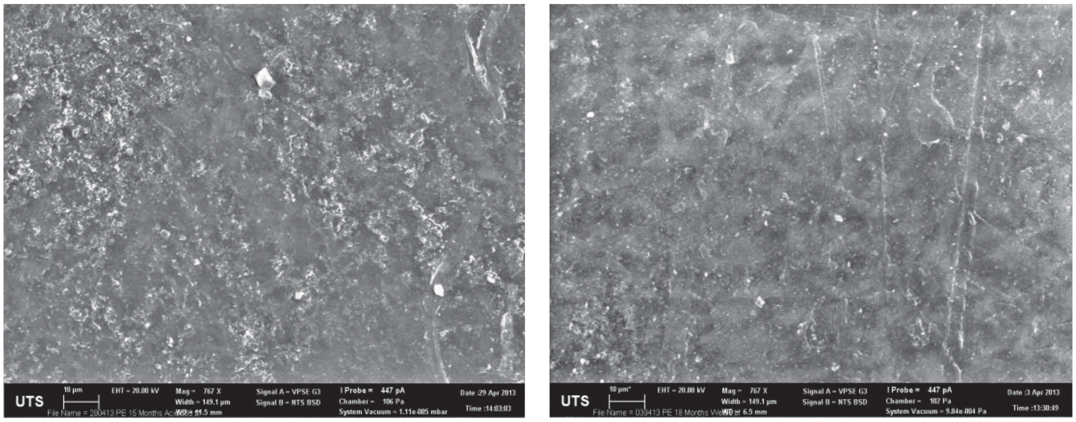


Figure 3.14 SEM micrographs of PE after burial in the acidic environment for 15 (top) and 18 (bottom) months

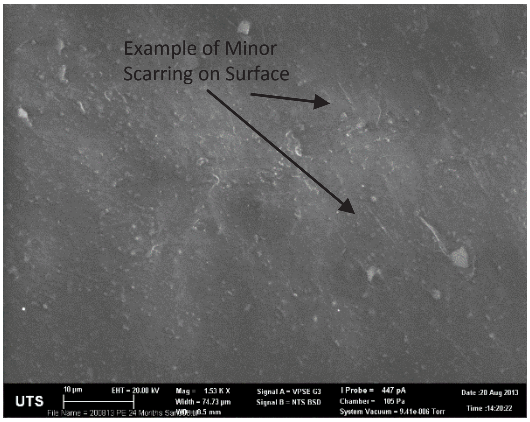


Figure 3.15 SEM micrograph of PE after burial in the sand environment for 24 months

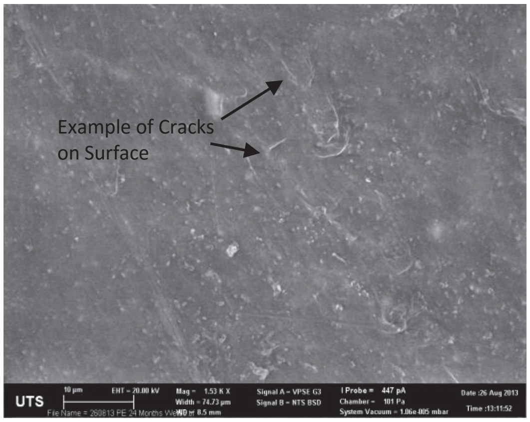


Figure 3.16 SEM micrograph of PE after burial in the wet environment for 24 months

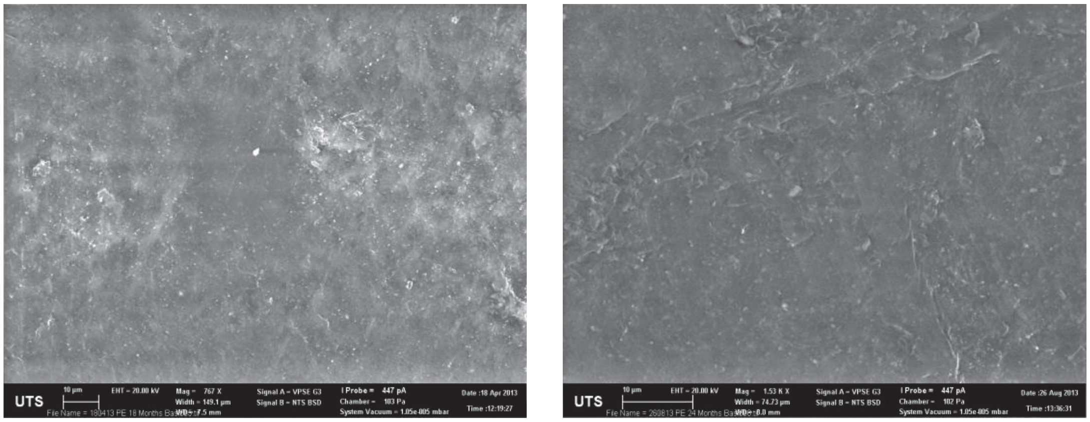


Figure 3.17 SEM micrographs of PE after burial in the basic environment for 18 (top) and 24 (bottom) months

3.3.2 Discussion

From an examination of the micrographs obtained from the SEM, the environments varied in how much change they caused to the polymer surface. The environments were observed to affect the polymer the greatest were the sand, lime, clay and wet soils while the cold, dry and loam soils had the least impact. The sand, acidic and basic environments were observed to affect the polymer specimens however, not to the same extent as the more reactive environments.

The lime, clay and wet environments showed greater signs of degradation occurring throughout the project, however, these changes were not consistent throughout the burial time and had mostly disappeared after 24 months. The most probable reason for this would be due to manufacturing processes rather than solely the effect of the environment itself. It has been noted that slight changes during the manufacture of LLDPE such as changing temperature and shear stresses, can result in defects on the polymer surface (Mackley et al., 1998). The original use for the PE used in this study was as garbage bags meaning that small surface defects resulting during manufacture on the polymer surface are acceptable as long as the defects do not affect the function of the bag. These small defects, however, acts as weak points in polymer potentially allowing for more degradation to occur than in other regions of the polymer surface (Mackley et al., 1998). It was possible that the time periods that show greater levels of degradation may have had more of these surface weaknesses and in combination with the effect the environment had more observable pit and crack formation.

3.4 Atomic Force Microscopy

3.4.1 Roughness Analysis of PE Surface

The changes to the microstructure of the PE film as a result of burial in the different environments were investigated using AFM. Figure 3.18 depicts the AFM micrograph of the surface of PE before soil burial. It can be seen from Figure 3.18 that the topography of the surface of the PE film has a fairly textured structure with some peaks and pits been observed. This surface variation could be due to the manufacturing process with such variations has been proven to introduce imperfections to the otherwise flat surface of PE (Mackley et al., 1998). The peaks and valleys that can be seen in Figure 3.18 correspond to a black to white scale with the darker areas being pits found on the surface. It has been demonstrated in previous studies of various polymers that an indication of degradation occurring can be seen by an increase in the roughness of the film, changes in the appearance of more and deeper pits as well as smoother peaks and waves appearing in the sections taken from the image (Gu et al., 2001; Sudhakar et al., 2008; Szép et al., 2004).

Most of the environments produced some variation in pit size and distribution to the specimens over the 24-month period when compared to the before burial polymer, as seen in the example in Figure 3.19. Most of the environments produced specimens with a larger number of pits when compared to the polymer before burial, although there does not seem to be much visual difference when comparing the reactive and less reactive environments. The wet and the acidic environments by 24 months also show an unusual region visible in some of the images, as seen in the top left region of Figure 3.20. It was unknown what these growths may be, however, it was most likely that these growths are either due to fine soil particles attached to the polymer surface or microbial growth.

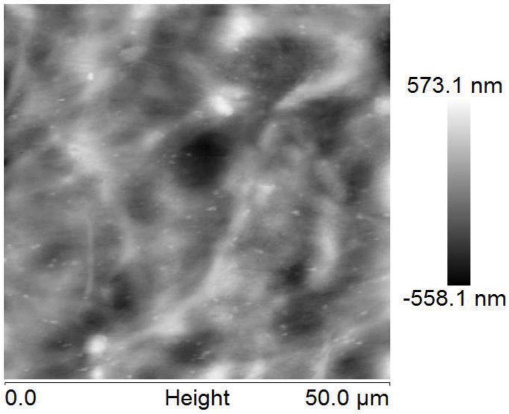


Figure 3.18 AFM micrograph of PE before soil burial

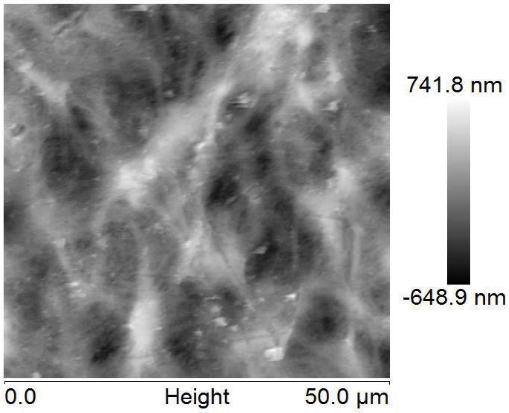


Figure 3.19 AFM micrograph of PE after burial in the clay environment for 24 months

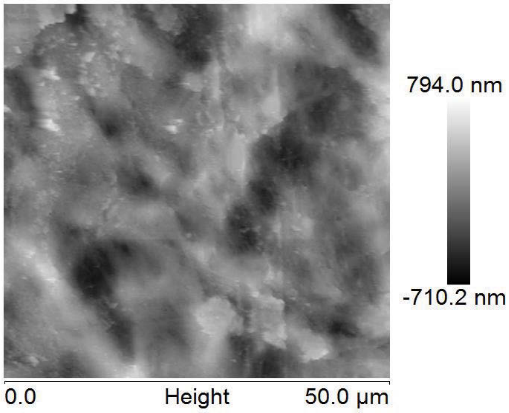


Figure 3.20 AFM micrograph of PE after burial in the wet environment for 24 months

The roughness of the PE film in the soil environments was analysed by taking 6 sections from each image and finding the mean value of the roughness using the standard deviation of the Z values (rms) (Gu et al., 2001). Figure 3.21 shows the variation in the roughness of the PE surface over 24 months. It can be observed from Figure 3.21 that the roughness of the polymer surface showed variations in the impact that the soil environment had on the specimen. From Figure 3.21, it can be observed that the clay, lime, wet and basic environments showing the most change to the surface roughness over time. The dry, cold, acidic, sand and loam environments were observed to have little impact on the roughness of the polymer surface. It was noted from the observations of Figure 3.21 that the greatest change in roughness occurs between the burial and removal of the polymer at 12 months for the more reactive environments. The less reactive environments did not show much change occurring to the roughness of the polymer surface, with the mean of the RMS values being found to be approximately the same as the polymer before burial. The standard deviation of the 6 sections analysed also varied with different environments in the different time periods. At 12 months all of the environments show a small standard deviation indicating that the surface was fairly similar throughout the 3 images. At 24 months all of the environments show an observable increase in the variation present on the surface of the polymer. The much larger variation in the standard deviation at 24 months was most likely due to a change in pit size distribution occurring across the polymer surface between 12 and 24 months (Gu et al., 2001).

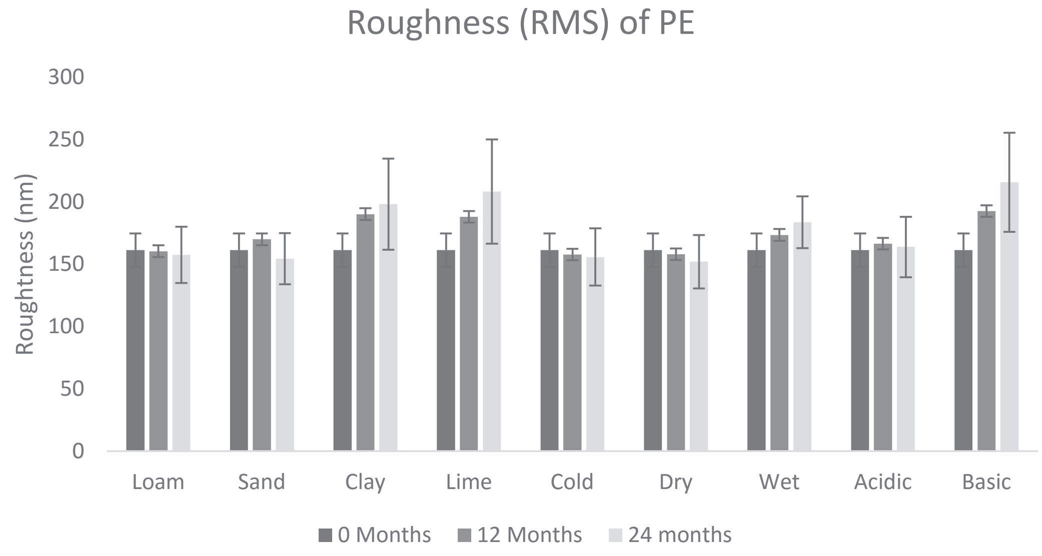


Figure 3.21 Mean roughness changes to the surface as observed using AFM of PE after soil burial with standard error (error bars)

3.4.2 Section Analysis of PE Surface

Another method that has been used by previous studies to investigate degradation on the surface of the polymers was by the examination of the changes that occur to section waves. It has been noted that degradation can be seen using this method by observation of the changes to both the heights and the smoothness of the section curves (Szép et al., 2004). In Figure 3.22, an example of the section analysis from the PE before burial can be seen. It shows variations occurring on the surface of PE that are within 300nm of the centre line on a wavy surface with a wavelength of approximately 50µm. This 'wavy' characteristic of the surface was most likely to due to the manufacturing process (Szép et al., 2004).

By comparison, Figure 3.23 shows an example of 2 different environments, the specimens in the clay and dry, which showed different levels of changes to the roughness of the surface with the clay environment specimens demonstrating the greater amount of change compared to the dry environment, as was observed in Figure 3.23. The amplitude of peaks and pits in the reactive environments show a slight increase on the surface of PE. By contrast, for the dry, loam, cold, acidic and sand environments, there was minimal increase in the corresponding peaks and pits in the section analysis data. There appears to be a change in the wavelength in both example environments showing an average wavelength of approximately 5µm. As noted earlier, the degradation of the samples was not consistent across the whole sample and that can be also seen here where in both environments there was a degree of variability in wavelength. There are some areas in both the clay and dry environments that show the longer wavelength present in the polymer before burial as opposed to the shorter wavelength mostly seen after degradation.

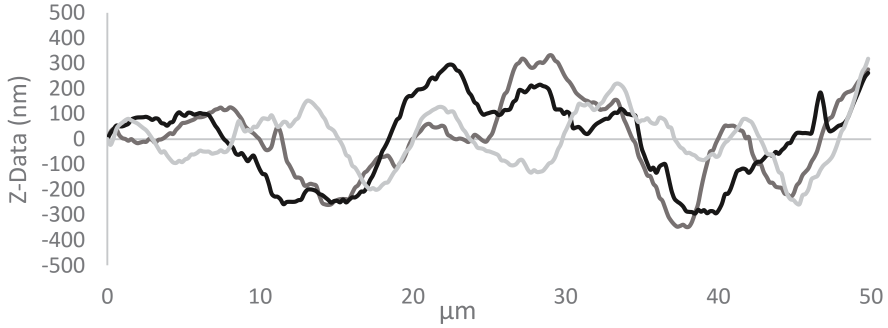
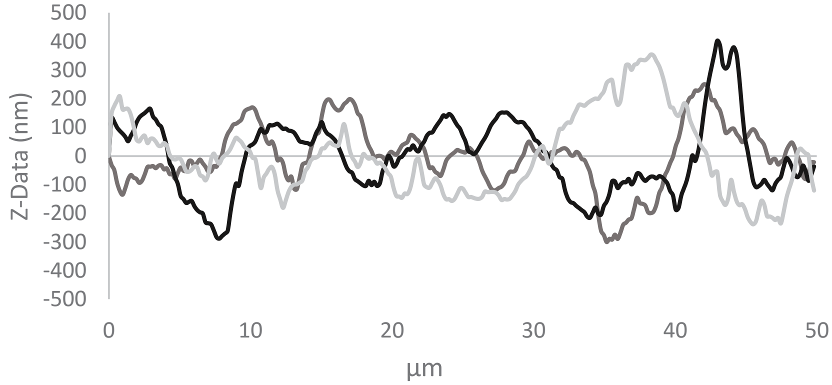


Figure 3.22 Section analysis for the before burial PE



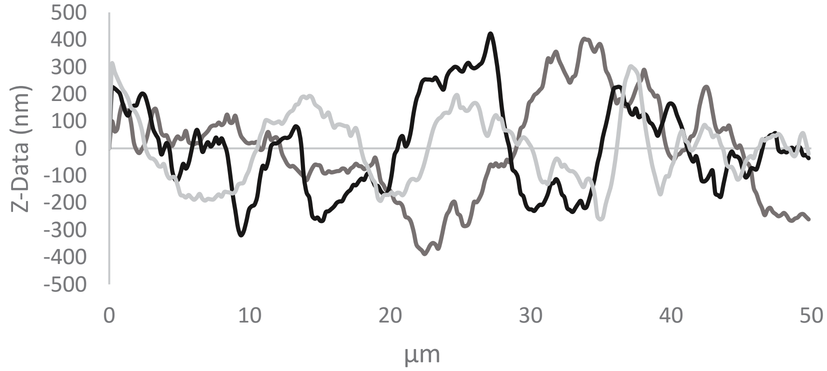


Figure 3.23 Section analysis of PE after burial in the dry (top) and clay (bottom) environments for 24 months

3.4.4 Summary of Changes Observed to PE by AFM

It can be observed from the data obtained that there have been some changes that have occurred in PE. Visually there was very little change that occurred in the different environments, except for some extra pit formation that did not seem to follow a particular trend as all of the environments show this change. The more reactive environments, however, do show a slight increase in the depth of the peaks and pits on the polymer surface when compared to the less reactive environments. Additionally, slight changes over time to the mean roughness of the surface of the PE and to the wavy feature of the surface also indicated some degradation occurring to PE in the 9 environments. Most of the changes that were observed to have occurred during the 24 months process seem to be similar across all the environments. This indicates that most of the soil environments have very little impact on the polymer as the different properties of the environments did not influence changes to the polymer surface. This was with the exception of the changes to the mean roughness of the polymer surface as well as the pit depths which have shown to be environment specific with some environments showing greater changes than others.

3.5 Vibrational Spectroscopy

Both IR and Raman spectroscopy has commonly used to analyse the degradation of PE. One of the most common uses of vibrational spectroscopy with respect to the degradation of PE, was to investigate the changes in the crystallinity of the polymer due to degradation (Balasubramanian et al., 2010; Nowak et al., 2011). Both IR and Raman spectroscopy are able to detect changes to the crystallinity of the polymer, allowing for comparison of the data obtained from these two techniques. Investigation of the IR spectra can also reveal information about the formation of bonds (such as the carbonyl bond) due to degradation that can be found in the polymer's chemical structure.

3.5.1 Fourier Transform Infrared Spectroscopy

3.5.1.1 Analysis of IR Band Ratios - Method

FTIR spectroscopy was utilised to analyse the changes to the PE specimens over time in the nine soil environments. Figure 3.1 shows the IR spectrum of PE prior to burial in the soil environments. The assignment of the bands observed in Figure 3.1 was discussed in Section 3.2. Unique to the clay environment was also some peaks that appear at 1113, 1031 and 1007 cm^{-1} and these are associated with residual clay soil particles that were resistant to the cleaning process (Vaculíkovà and Plevovà, 2005)

There are two main ways of investigating the degradation of PE using IR spectroscopy. The first was to look for an indication of the oxidation of PE by examining the changes that occur in the spectrum near 1740 cm^{-1}, which shows the formation of the ester carbonyl bond, as well as changes to the keto carbonyl near 1715 cm^{-1} (Balasubramanian et al., 2010). The second method involves observing the changes to the crystallinity of the polymer, which shows whether the structure of the polymer was changing over time (Restrepo-Flórez et al., 2014). This was established by comparing the absorbance of the peaks at 1470 and 1460 cm^{-1} using Eqn 3.1 (Balasubramanian et al., 2010)

$$Degree\ of\ Crystallinity = 100 - \left(\frac{1-(A_{1470}/1.233\ A_{1460})}{1+(\frac{A_{1470}}{A_{1460}})}\right) x\ 100\% \quad \textbf{Eqn 3.1}$$

where A1470 was the area of the band near 1470 cm-1 and A1460 was the area of the band near 1460 cm-1

3.5.1.2 Analysis of IR Band Ratios - Results

Examination of the IR spectra of PE over the 2-year period indicated that there were no changes that occurred in any of the regions associated with the appearance of the carbonyl bonds of PE. This was confirmed by Figure 3.24, which depicts the second deriative spectra of the PE specimens over 24 months of soil burial. The second derivative enables any subtle changes to be enhanced but indicate that none of the soil environments in the given time frame were able to oxidise the polymer. Another area to investigate to identify possible oxidation of PE was the vinyl and terminal double bonds, which occur at 1640 and 910 cm^{-1}, respectively (Albertsson et al., 1987). It can be seen that there are no changes occurring in either of these bands in the spectra for the specimens from the majority of environments. The exception was for the spectrum for the specimen from the clay environment, which shows a slight increase in the peak at 910 cm^{-1}. However, this increase may be attributed to the residual clay soil left on the polymer surface instead of changes in the polymer itself given the presence of the peaks that appear at 1113, 1031 and 1007 cm^{-1} previously attributed to the clay environment with the increase of the band at 910 cm^{-1} been due to the OH groups attached to the Al^{3+} present in the clay soil (Vaculíkovà and Plevovà, 2005). This lack of change to PE in the soil environments within the 2-year period was supported by previous research as the oxidation of PE occurs best in photo-oxidative or thermal conditions neither which were present in the soil environments been investigated (Colin et al., 1981).

The crystallinity of PE was examined by comparing the absorbance of the bands at 1470 and 1460 cm^{-1} using Eqn 3.1. The results obtained from Eqn 3.1 can be observed in Table 3-1. It can be observed from Table 3-1 and Figure 3.25 that the crystallinity of the PE specimens decreased in all of the environments over the 24 months of burial. It can also be observed from Figure 3.25, that this decrease to the polymer's crystallinity tended to decrease following a linear trend.

It has been found in previous studies that a decrease in the crystallinity of PE was most likely due to biotic as opposed to abiotic degradation, so the degradation that has occurred was not due to chemical effect on the polymer (Albertsson et al., 1995; Balasubramanian et al., 2010). Since the crystallinity of the PE specimens in the current study decreased during burial, this also indicates that the polymer did not take up water. The crystallinity of PE was known to increase when water absorption occurs (Albertsson et al., 1987). This also indicates, along with the noticeable lack of carbonyl bonds present in the spectra, that oxidation of PE has not occurred

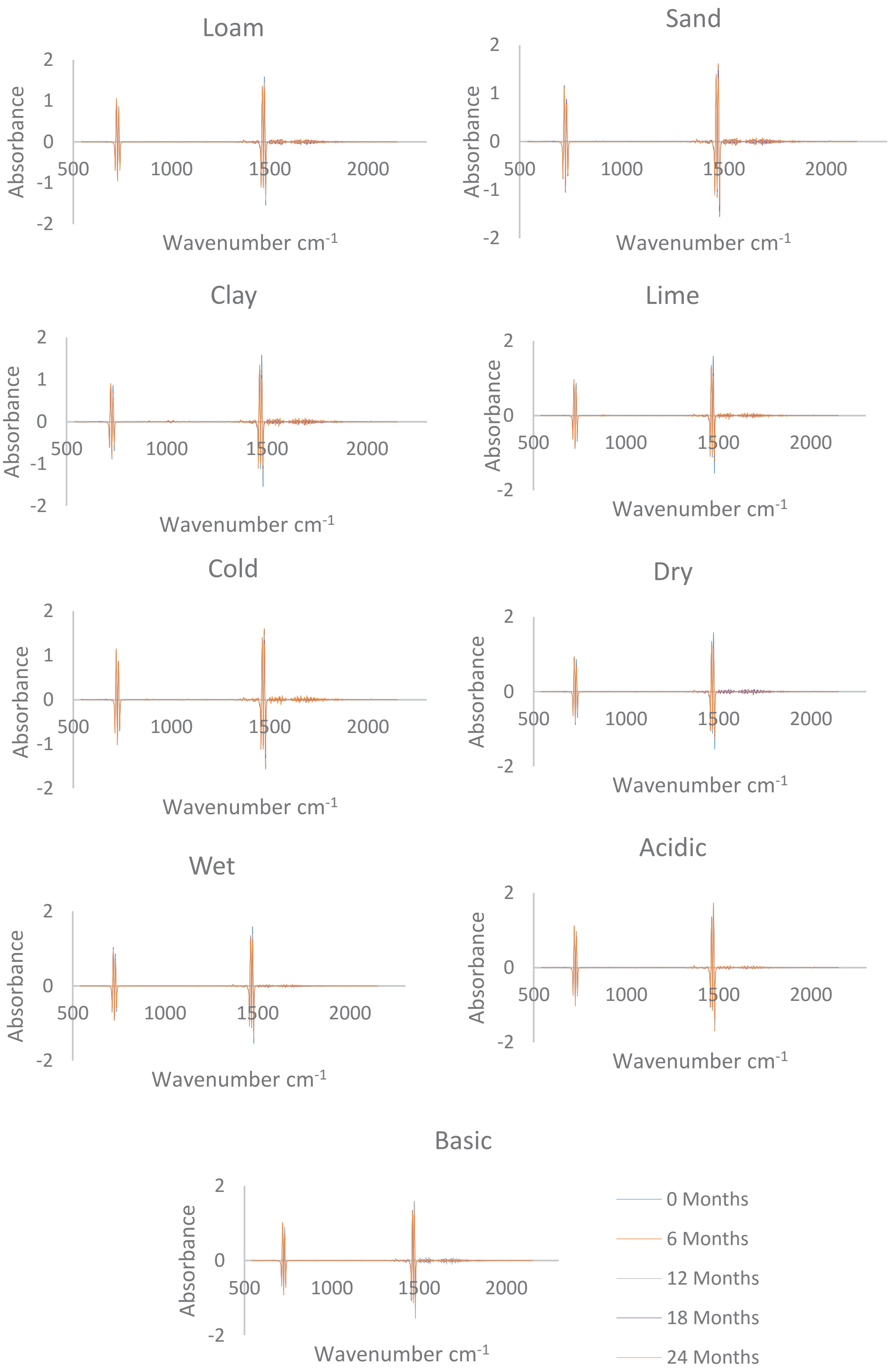


Figure 3.24 Comparison of 2nd derivative IR spectra of PE in the 9 soil environments in the 2200-550 cm^{-1} region

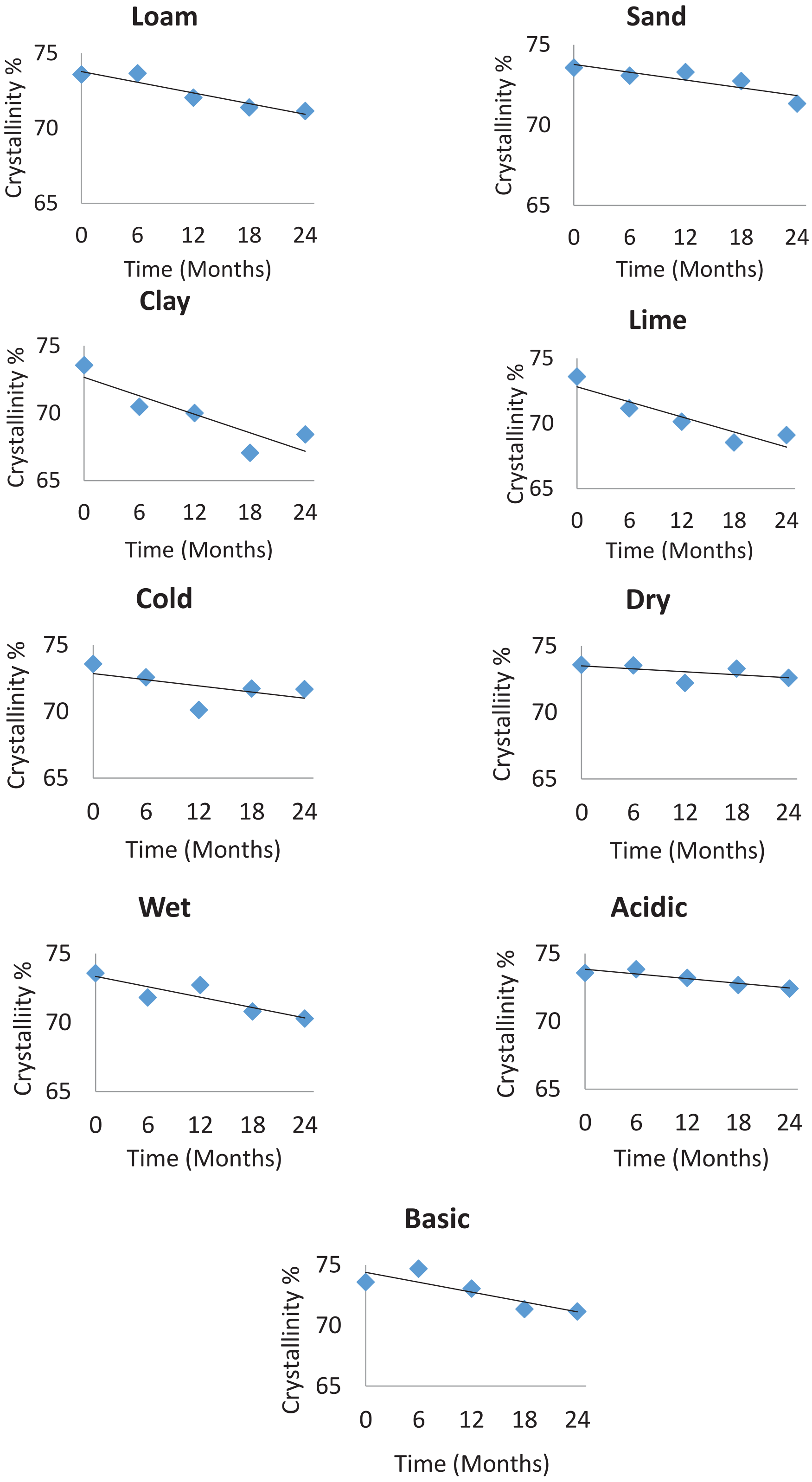


Figure 3.25 Graphical depiction of changes to mean % crystallinity in the 9 soil environments

Table 3-1 Slope of changes to the crystallinity % of PE in the 9 environments

Environment	Slope ± Standard Error
Loam	$-1.2 \pm 0.2 \times 10^{-1}$
Sand	$-8 \pm 3 \times 10^{-2}$
Clay	$-2 \pm 1 \times 10^{-1}$
Lime	$-2 \pm 1 \times 10^{-1}$
Cold	$-8 \pm 6 \times 10^{-2}$
Dry	$-4 \pm 3 \times 10^{-2}$
Wet	$-1.3 \pm 0.4 \times 10^{-1}$
Acidic	$-6 \pm 1 \times 10^{-2}$
Basic	$-1 \pm 1 \times 10^{-1}$

3.5.1.3 Analysis of IR Bands - Discussion

Due to the evidence provided by the IR spectra, microbes are likely to be the cause of the decrease noticed in PE over time. This means that the environments that have the higher microbe biomass are expected to be the environments that effect PE the most. There was a noticeable difference among the environments, with the clay and lime environments producing comparatively large changes to the crystallinity to the polymer when compared to the less reactive environments.

The results listed in from Table 3-1 show that there was a noticeable difference between the specimens from the loam, clay, lime and sand environments. The clay and lime environment specimens showing approximately double the rate of change in the crystallinity when compared to the PE from the loam environment. The specimens from the sand environment show about half the rate of change compared to that observed to the specimen from the loam soil. As the results demonstrate that the changes that have occurred are due to microbial degradation of the polymer, the potential of the different soil types and properties to promote microbial growth will have an effect on the changes to the crystallinity of the polymer.

From previous studies it has been found that both clay and lime present within an environment can promote microbial growth while a sandy environment does not, which supports the observations in this study (Dalal and Mayer, 1987; Xue et al., 2010). It has been found that high levels of clay present in soil help to increase the level of microbial life. This was due to the properties of clay such as high moisture retention, small particle size (offers protection from predators) and the high level of available nutrients present (Brennan et al., 2014). Sand, having a larger average particle size and a lower moisture retention capacity, has the opposite effect by allowing microbes to dry out easily as well as provide less protection from predators such as protozoa (Conklin, 2005b). Lime was found to have a positive effect on the microbial biomass by influencing the pH of the soil indicating that a basic pH promotes microbial growth as opposed to an acidic one (Spiegelberger et al., 2006). This finding can also be seen in the acidic and basic environments of this study, where the acidic soil showed a slower rate in the decrease in crystallinity when compared to the basic environment.

The wet environment also showed a higher rate in the decrease of the crystallinity of PE when compared to the loam soil environment, while the dry soil was observed to produce less change. Dry soil was known to be a deterrent to microbial growth due to the lack of moisture present in the soil, while the wet environment being saturated with water promotes microbial growth (Schnürer et al., 1986). However, it can be seen that while the lack of moisture in an environment has a predicted large impact on the level of microbes present and therefore the rate of degradation, the absolute amount of moisture present was not significant, but rather the pH and the moisture retention capacity of the soil does. Since the lime and clay environments have a greater capacity for retaining moisture than the loam soil, these environments will hold the water around the PE for longer increasing the amount of microbes present near the polymer (Brennan et al., 2014; Sébaïbi et al., 2003). Although the wet environment may have more water present, this water was not held around the polymer but instead drains away and carries many of the microbes away from the polymer (Abu-Ashour et al., 1994). The cold environment has a similar effect to the dry environment. The number of microbes present in the soil was reduced by the cooler temperature as the optimum temperature range for microbiological activity has being observed to be between 25-30°C (Pietikäinen et al., 2005). A warmer environment was expected to have the opposite effect on the crystallinity of PE due to the warmer environment encouraging microbial growth (Yao et al., 2011).

3.5.1.4 Multivariate Analysis of IR Spectra

Multivariate analysis was conducted on the IR results of PE within the different environments. The PCA plots obtained from the data analysis are shown in The PCA obtained from the data shows a generally in agreement with the ratio data for the changes that occur to the PE in the soil (Table 3-1). It can be seen from the first PCA graph in Figure 3.26 that there was a general shift for all of the environments towards the negative on the x axis, with the clay and lime environments show the most change when compared to the before burial PE. The exception to this was the dry environment, which indicates a larger shift than that previously seen in the results where the dry environment was one of the least reactive. The dry environment was observed to be grouping together indicating that there was not much change occurring within the 24-month period, unlike the clay and lime environments which show a gradual shift.

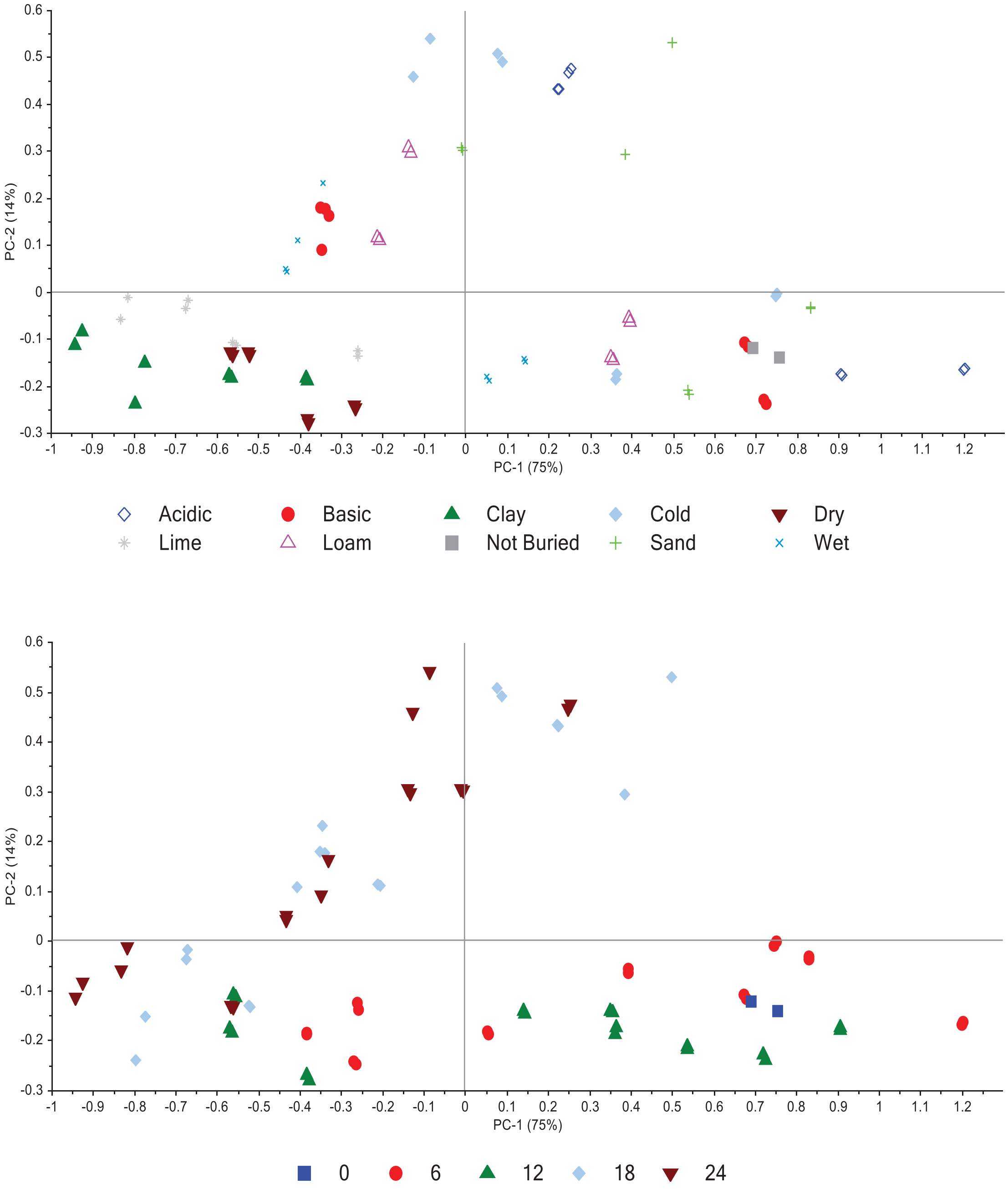


Figure 3.26 PCA plots depicting scores of PE in 9 soil environments with a focus on the environment (top) and time (bottom)

Using the pre-treated IR data from the PE samples, a PLS-R graph was created with the loam environment used as a reference. In order to decide which model would be the most useful for PE both the loadings (Figure 3.27) and the explained variance (Figure 3.28) for each factor were investigated to see which bands were prominent in each factor. The factors that feature the bands of interest at 1460, 1470, 720 and 730 cm^{-1} were used to create the model for PE. Most of the factors were observed to show the peaks of interest, but the explained variance showed some variation between the different factors. It was observed in Figure 3.28 that the explained variance between the calibration and validation improve by factor 5 when compared to the lower numbered factors. Factors 6-7, which also show a good explained variance, were observed to not show any distinguishable peaks. This indicates that factor 5 will be the most appropriate to use in this model.

The PLS-R of the loam soil environment (acting as a reference) was shown in Figure 3.29. It can be seen that the total R^2 for this model was 0.97 indicating a good fit for a degradation model. It can also be seen in Figure 3.29 that the data from 0 to 24 months closely fits the model suggested by the reference environment. This suggests that the model predicted by using the reference data was a good approximation for the degradation of PE in soil.

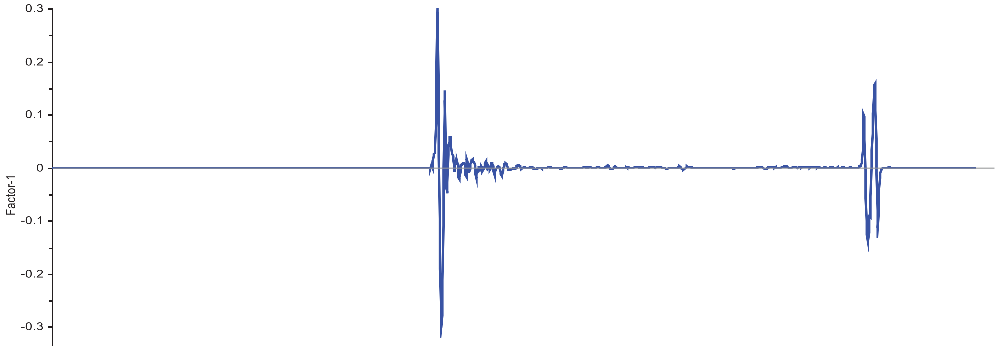


Figure 3.27 Factor 5 loadings showing peaks of interest at 1470, 1460, 720, 730 cm^{-1}

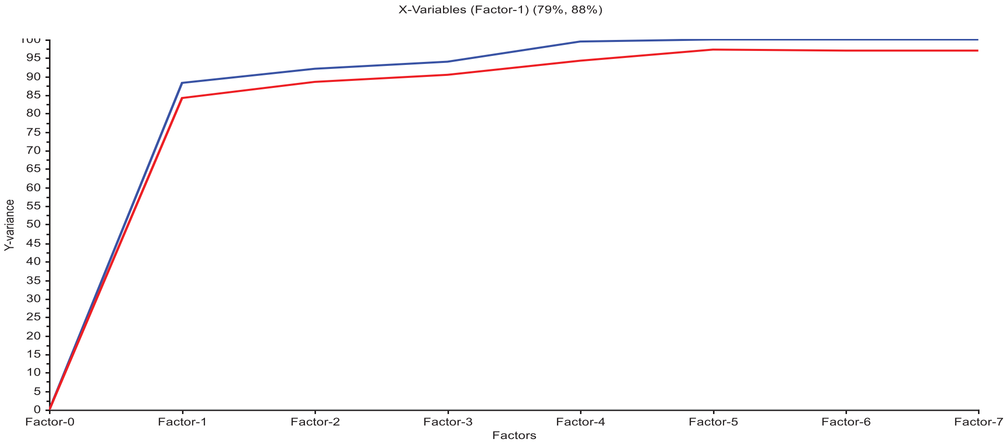


Figure 3.28 Graph showing the explained variance between the calibration and validation of the PLS-R

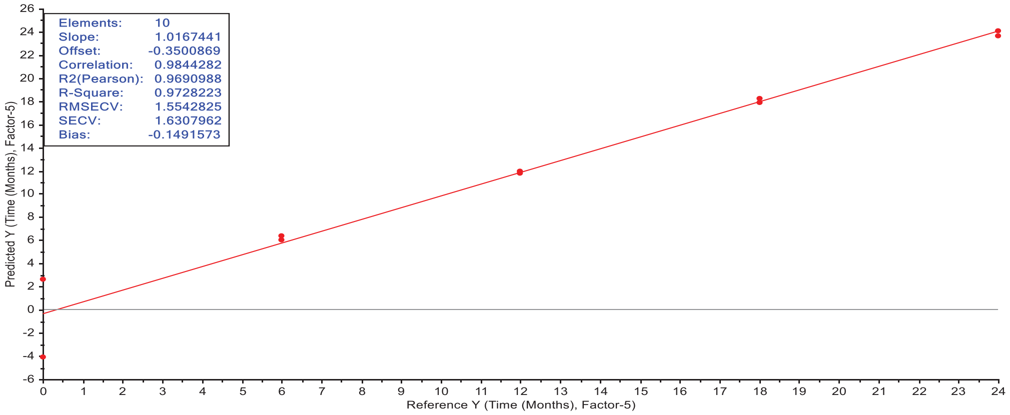


Figure 3.29 PLS-R Calibration graph showing predicted versus reference for IR data

3.5.2 Raman Spectroscopy

3.5.2.1 Analysis of Raman Spectra - Method

The PE specimens were also analysed using Raman spectroscopy. Figure 3.30 shows an example of the Raman spectra of PE before burial within the soil environments. The main bands associated with PE that can be observed in this spectrum are in the CH_2 bending region located within 1390-1490 cm^{-1}, which also includes the band at 1416 cm^{-1} associated with the crystalline region of the polymer (Dothée et al., 1988). Other bands of interest include the CH_2 twisting region that occurs within 1295-1303 cm^{-1} with 1303 cm^{-1} associated with the amorphous region of the polymer and the 1295 cm^{-1} band associated with both the crystalline and the interfacial phase. There was also the C-C stretching band located at 1000-1200 cm^{-1} with 1080 cm^{-1} band associated with the amorphous region of the polymer (Dothée et al., 1988; Rull et al., 1995; Szép et al., 2004).

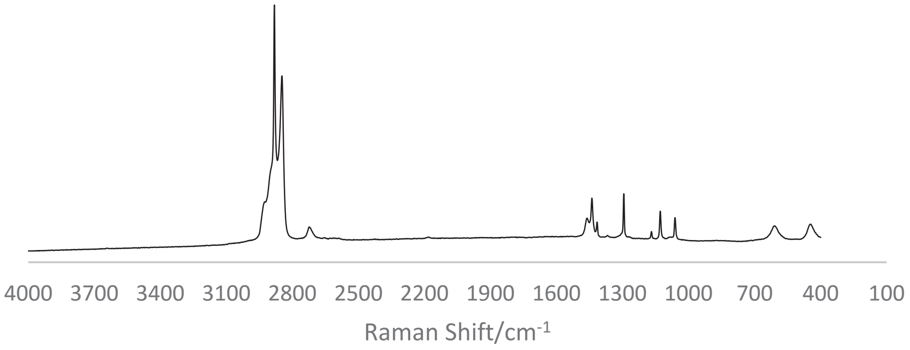


Figure 3.30 Raman Spectrum of PE before burial

Figure 3.31 displays the second derivative Raman spectra of PE in the 9 soil environments for the 1500-1000 cm^{-1}, where the bands that relate to changes in the crystallinity of PE are located. It can be seen from these that there was very little noticeable change occurring to the peaks within these spectra. None of the environments show any visual indication of changes to either the band located at 1416 cm^{-1} or the bands within 1000-1200 cm^{-1} region. Since these bands are associated with the crystalline and amorphous, this shows that there are no significant changes occurring to the crystallinity of the polymer (Szép et al., 2004).

Another way to investigate any smaller changes to the crystallinity of was to examine the ratios of the peaks of interest. In previous studies this has been achieved by comparing the bands at 1080, 1416, 1295 and 1303 cm^{-1} by using Equations 3.2, 3.3 and 3.4, which enable the peak ratios to be determined and used to identify the degree of crystalline and amorphous phases (Dothée et al., 1988; Rull et al., 1995).

$$I_t = I_{1295} + I_{1303} \qquad \textbf{Eqn 3.2}$$

where I_{1295} was the intensity of the band at 1295 cm^{-1}, I_{1303} was the intensity of the band at 1303 cm^{-1} and I_t was the total intensity of these two bands.

$$a_c = \frac{I_{1416}}{\mathrm{I}_t\ x\ 0.46} \qquad \textbf{Eqn 3.3}$$

where a_c was the degree of crystallinity in the PE specimens and I1416 was the intensity of the band at 1416 cm^{-1}.

$a_{as} = \frac{I_{1080}}{\mathrm{I}_t \ x \ 0.79}$ **Eqn 3.4**

where a_{as} was the degree of the amorphous phase present in the polymer specimens and I_{1080} was the intensity of the band located at 1080 cm^{-1}.

3.5.2.2 Analysis of Raman Spectra - Results

In Figures 3.32 and 3.33, the graphs depicting the changes over time to the crystalline and amorphous phases are shown and the corresponding slopes from the plots are listed in Table 3-2. From Figure 3.32, it can be observed that changes to the crystallinity of the polymer was occurring in all environments with most indicating a decrease in the crystallinity of PE over time. The exceptions to this trend are the specimens from the dry and acidic environments, which both show an increasing trend. In Figure 3.33, it can be seen that in most of the environments there was a general increasing trend for the amorphous phase occurring over the 24-month period. The exceptions to this are the specimens from the dry and cold environments, both which show a decrease to the amorphous phase over time.

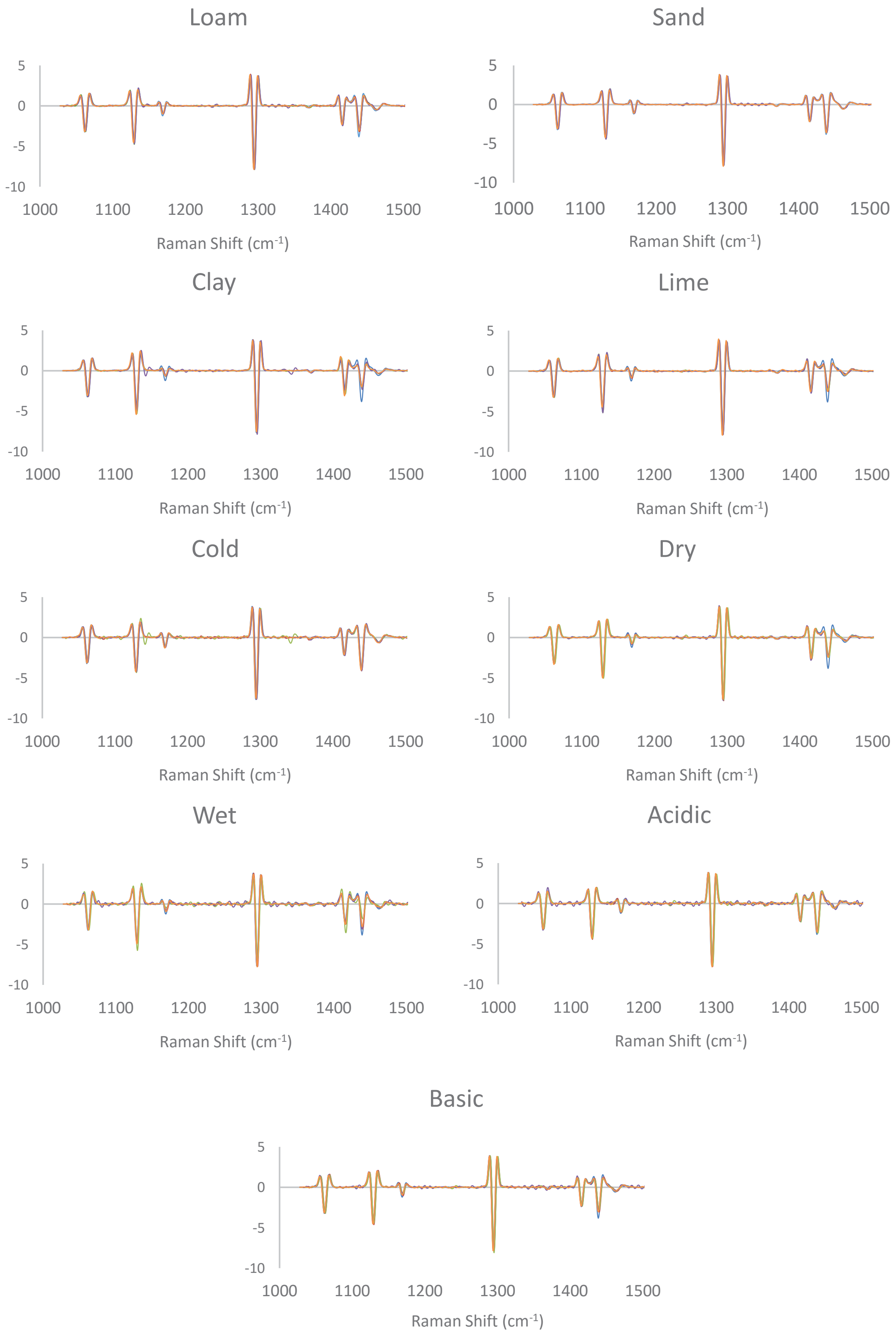


Figure 3.31 Second derivative Raman spectra of PE in 9 soil environments

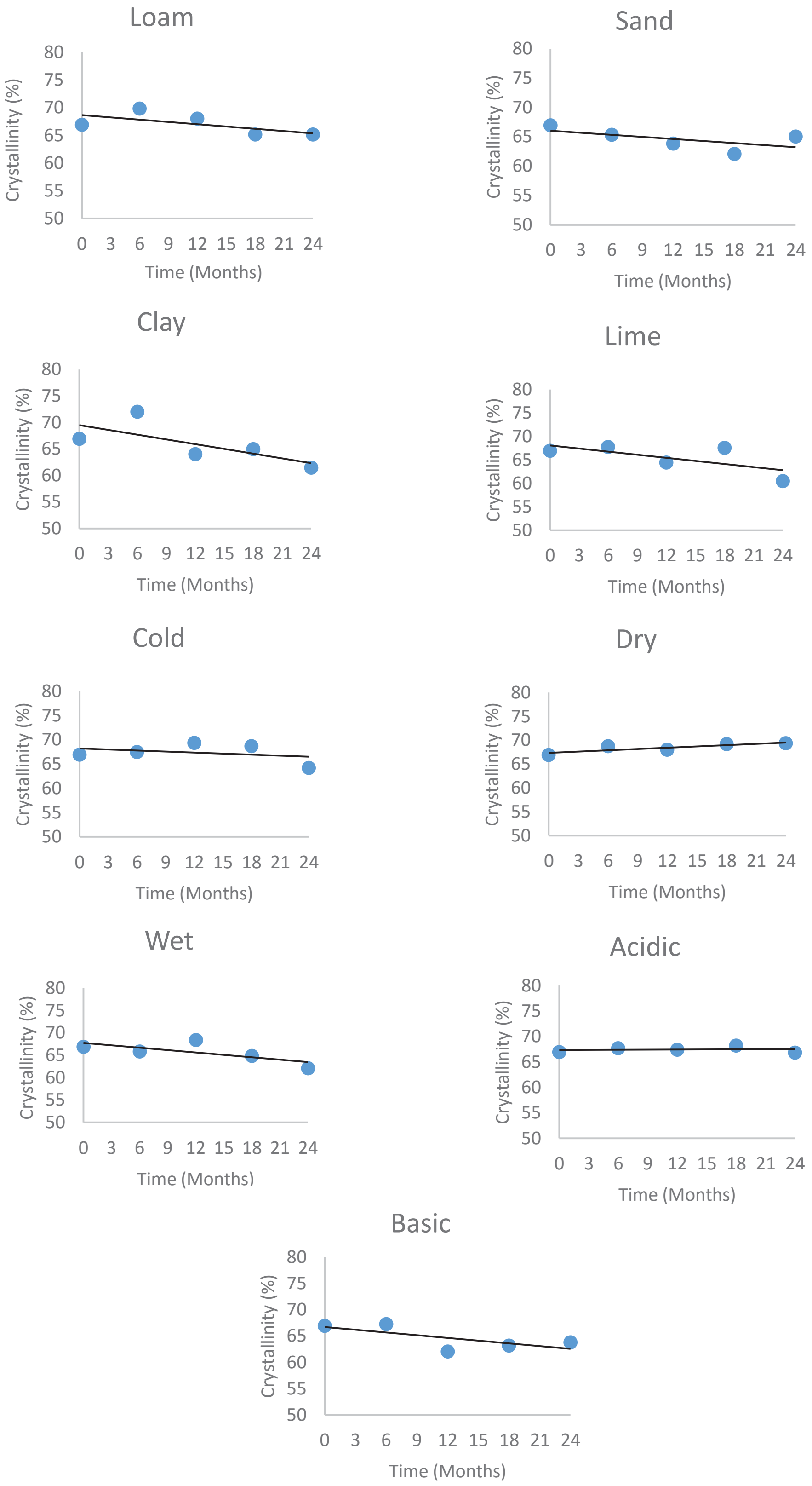


Figure 3.32 Graphs depicting changes to the mean degree of crystallinity in the 9 soil environments

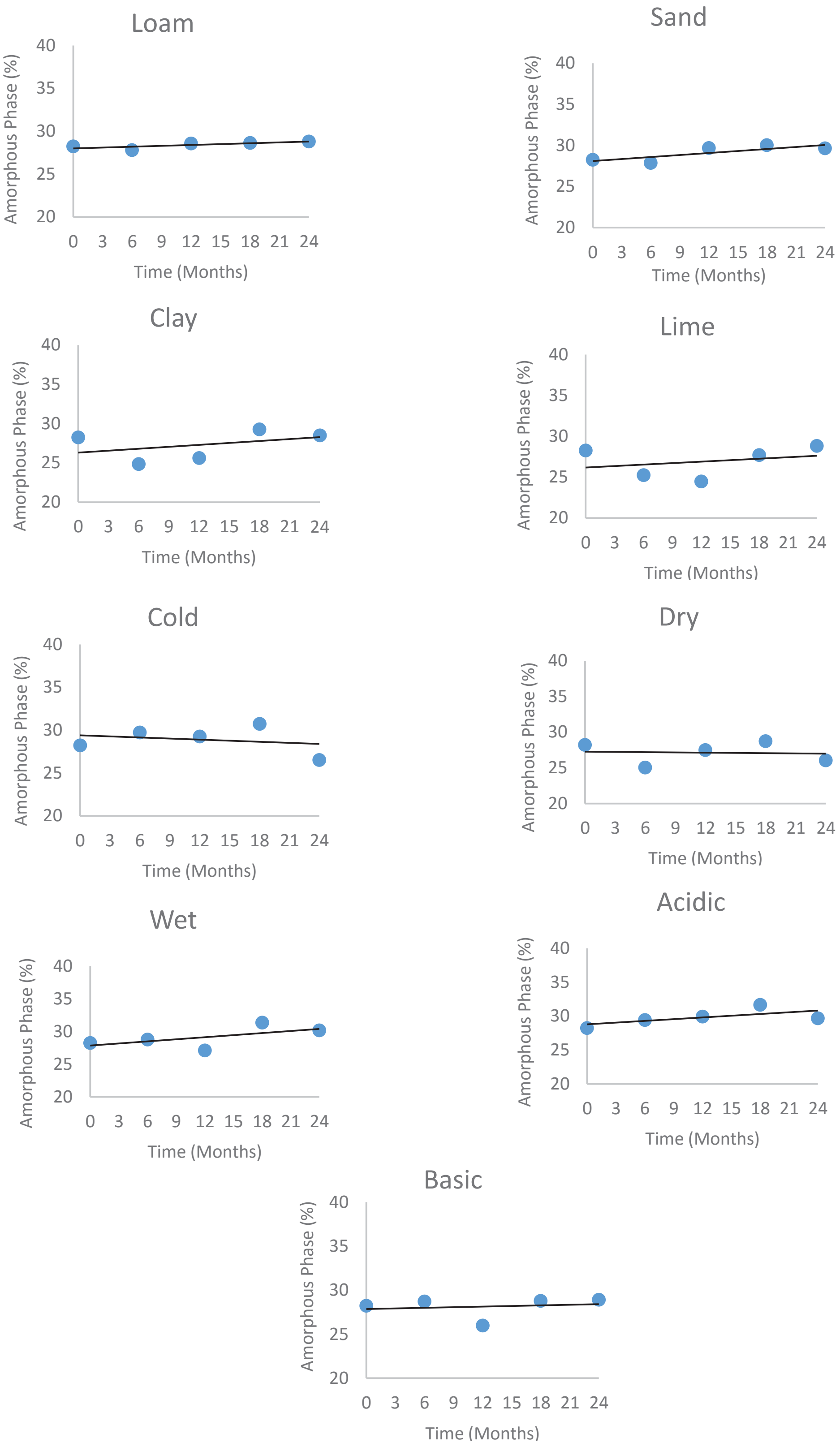


Figure 3.33 Graphs depicting changes in the amorphous phase in the 9 soil environments

Table 3-2 Comparison of the slopes for the degree of the crystalline and amorphous phases with the standard error to a linear trend line

Environment	Degree of Crystalline Phase Slope ± Standard Error	Degree of Amorphous Phase Slope ± Standard Error
Loam	$-1 \pm 1 \times 10^{-1}$	$3 \pm 2 \times 10^{-2}$
Sand	$-1 \pm 1 \times 10^{-1}$	$8 \pm 3 \times 10^{-2}$
Clay	$-3 \pm 2 \times 10^{-1}$	$8 \pm 10 \times 10^{-2}$
Lime	$-2 \pm 1 \times 10^{-1}$	$6 \pm 10 \times 10^{-2}$
Cold	$-7\pm 10 \times 10^{-2}$	$-4 \pm 10 \times 10^{-2}$
Dry	$9 \pm 3 \times 10^{-2}$	$-1 \pm 9 \times 10^{-2}$
Wet	$2 \pm 1 \times 10^{-1}$	$1 \pm 1 \times 10^{-1}$
Acidic	$6 \pm 40 \times 10^{-3}$	$9 \pm 6 \times 10^{-2}$
Basic	$-2 \pm 1 \times 10^{-1}$	$2 \pm 7 \times 10^{-2}$

3.5.2.3 Analysis of Raman Spectra - Discussion

From the Raman data, the environments that have the most impact on the crystalline phase were the clay, lime and wet environments, while the environments with the least impact were the acidic, cold and dry. This does not apply to the amorphous phase, however, with the specimens from the wet, acidic and sand environments producing the greater increases to the amorphous phase while the specimens from the cold, dry and basic environments show the least.

The environments that appear to have the greater impact on the amorphous phase were environments that had little impact on the crystalline phase of the polymer including the sand and acidic environments. Previous studies have shown that the amorphous phase was easier for microbial life to attack than the crystalline phase since the nutrients are more easily accessible in the amorphous phase as opposed to the crystalline phase where it was locked up in hard to access crystals (Restrepo-Flórez et al., 2014). Since more energy was required from the microbes to access the nutrients present in the crystalline phase, the amorphous phases was degraded instead. The environments that were indicated to have the greater impact on the crystalline phase of the polymer, are environments that promote microbial growth. Since there was predicted to be a higher microbial biomass in these environments, there are more microbes available to attack the small crystals in the crystalline phase allowing for the decrease in the degree of crystallinity. This was supported by the small increase in the crystalline phase that was noticeable for the specimens from the clay, lime, loam, cold and wet environments that occurs around 6 to 12 months. Most of these environments were noted to have at least a moderate impact on the crystalline phase, with cold environment being the exception. It can be observed in Figure 3.32 that, while like the more reactive environments, the cold environment produces an increase to the crystallinity. It was also noted that unlike the other environments that show such an increase, the cold environment takes longer to produce a decrease to the degree of crystallinity, with the decrease occurring over a 12-month period as opposed to the 6 months observed for the other environments. This could be due to the lower levels of microbial life present within this environment taking longer to start attacking the crystalline phase.

3.5.2.4 Multivariate Analysis of Raman Spectra

Multivariate analysis was also conducted on the Raman results for PE within the different environments. From the first PCA plot, investigating the environments shown in Figure 3.34, it was observed that there was little change to be occurring based on the observation that the environments appear on both positive and negative ends of the PCA plot. In the time score, however, there are noticeable groups of different time periods that have formed. The 6 and 12 months data appears above 0, while the data from 24 months and the before burial data appears in the negative with the 18 months been split between the two sides of the plot. It was also observed that the duplicates for each environment in the different time periods are close to each other in the PCA plots. The PCA results for the Raman spectra show that there was a distinction between the PE structural properties from different time periods. There appears to be little correlation with the ratio data that depicted certain environments been more reactive than others. With both reactive and less reactive environments appearing scatted around the PCA plots.

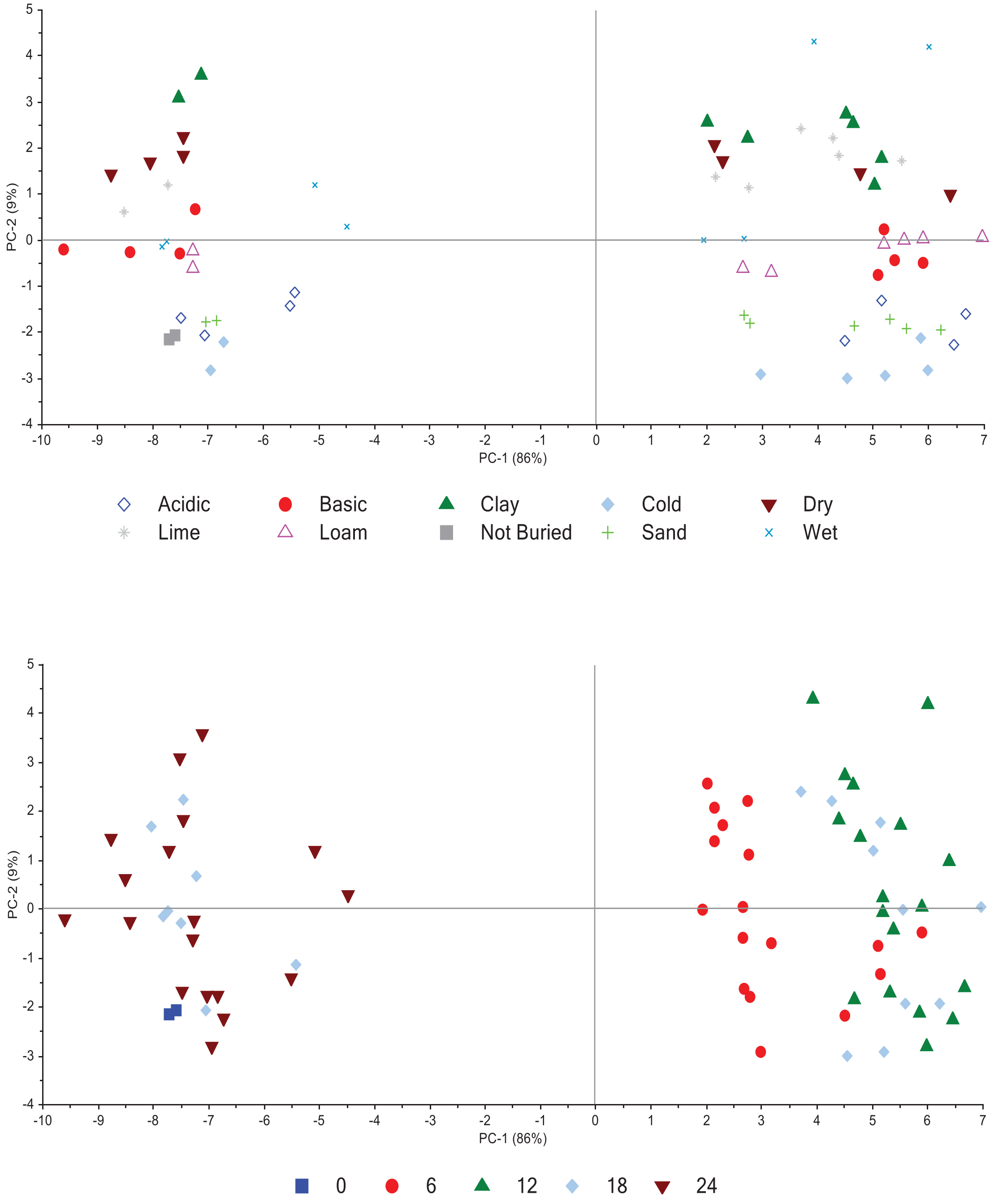


Figure 3.34 Raman spectra PCA environment (top) and time (bottom) score plots

Using the pre-treated Raman spectra data from the PE samples, a PLS-R graph was created, with the loam environment used as a reference. In order to decide which model would be the most useful for PE, both the loadings (Figure 3.35) and the explained variance (Figure 3.36) for each factor were investigated to determine which bands were prominent in each factor. The factors that feature the bands of interest at 1416, 1295 and 1080 cm^{-1}, as well as having a good variance, were used to create the model for PE. Factor 3 was observed to have the best combination of variance and the peaks of interest that appear in the loadings as the factor 1 shows the peaks of interest, it can be seen from Figure 3.36 that the variance for this factor was much lower than factor 2-3, which still shows these peaks of interest. The later factors 4-6 while showing good variance, demonstrate mostly noise when the loadings of these factors were investigated. Both factors 2 and 3 have a relatively low variance between the calibration and validation plots, with the peaks been investigated included, however, factor 3 was found to give a slighter better model than factor 2 as it showed a better prediction of the data.

The PLS-R calibration plot of the loam soil environment (acting as a reference) was shown in Figure 3.37. It can be seen that the total R^2 for this model was 0.77 indicating a good fit. It can also be seen in Figure 3.37 that the data up to and including 12 months generally shows a good match with the model. From 18-24 months the model shows a poor prediction of the data indicating that this model was breaking down by this stage.

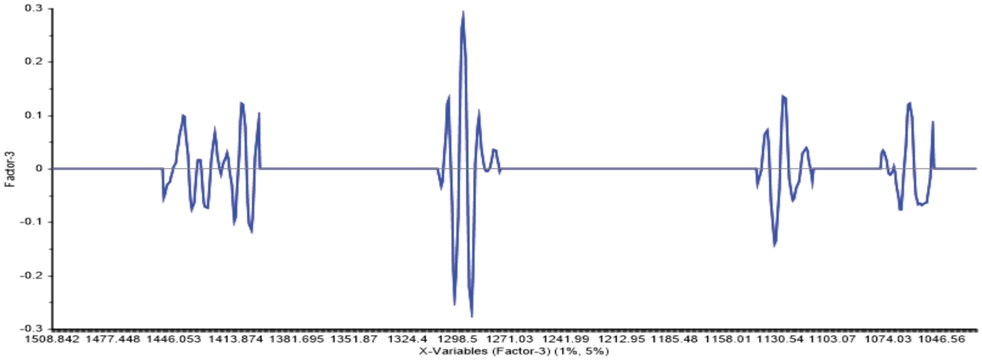


Figure 3.35 Factor 3 loadings showing peaks of interest at 1416, 1295, 1080 cm^{-1}

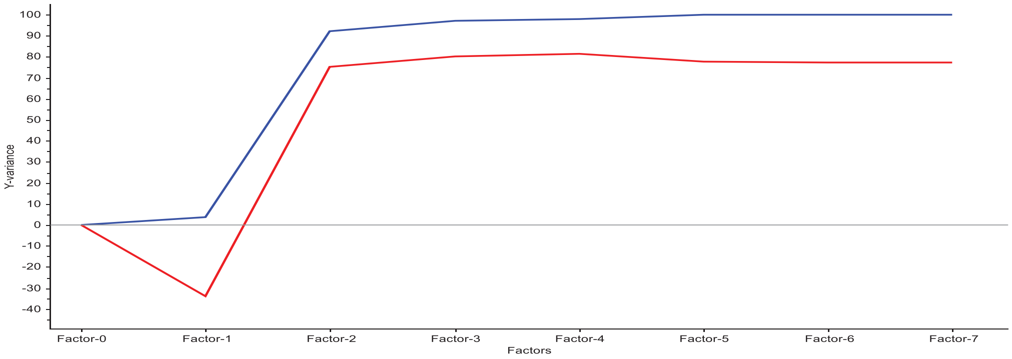


Figure 3.36 Graph showing the explained variance between the calibration and validation of the PLS-R

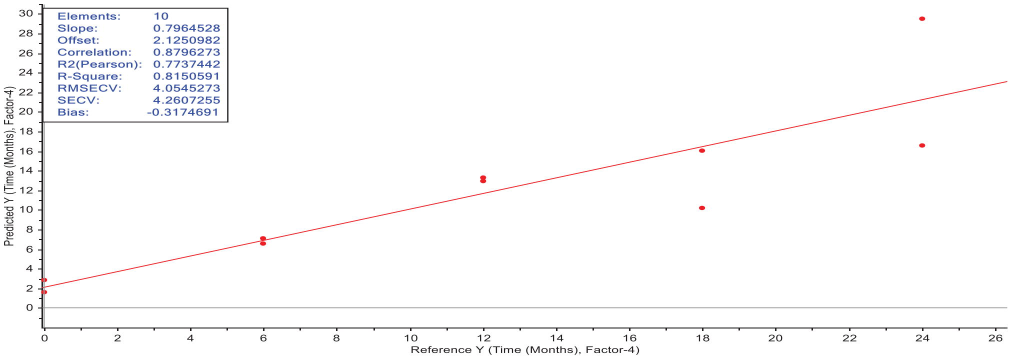

Elements: 10
Slope: 0.7964528
Offset: 2.1250982
Correlation: 0.8796273
R2(Pearson): 0.7737442
R-Square: 0.8150591
RMSECV: 4.0545273
SECV: 4.2607255
Bias: -0.3174691

Figure 3.37 Calibration graph showing predicted versus reference for Raman data

3.5.3 Comparison of IR and Raman spectral data

From the IR results, the degree of crystallinity determined in the before burial PE was found to be 73%, while the crystallinity found in the Raman spectra was found to be 67%. Although these values vary, it has been previously noted that Raman spectroscopy tended to be more appropriate for use as a quantitative technique. This was due to Raman spectroscopy providing more selective information about the polymer structure as well as the higher reproducibility of the Raman data when compared to IR (Kim et al., 2009). The mean of the two crystallinities obtained from these techniques gives an approximate degree of crystallinity for PE of 70%. This value was at the upper limit of the degree of crystallinity that can be commonly found for LLDPE (Edward, 1986).

A comparison of the IR and Raman spectra showing the effect the nine soil environments have on the polymer show many similarities. It was observed that both techniques depicted the clay and lime environments to have the greater impact on the crystallinity of the polymer while the cold, acidic and dry environments had less impact. The other environments that showed moderate change to the degree of crystallinity were observed to have a similar impact on the degradation of the polymer in both techniques.

There was conflicting findings for the IR and Raman spectra collected for the dry environment. This environment produced a slight decrease in the crystallinity as measured by IR, but depicts a slight increase in the Raman spectra. It was noted by both techniques that the dry environment was observed to have very little effect on the crystallinity of the polymer. This difference noted in the trend between the two techniques would most likely be due to the effect of this environment on the polymer been very close to zero.

From observation of the multivariate analysis obtained for PE using both IR and Raman, it can be determined which data provides the best model for use. The data obtained from the IR spectra produced a model with a better fit than the Raman spectra with the R^2 obtained for the IR being 0.96, while the R^2 from the Raman spectra was 0.80. It was also seen that the IR data provided the best prediction model for the data with the model been able to accurately predict all data points. The Raman data however, showed that the model could only reasonable predict up to 12 months after this point the model starts to break down and shows poor prediction of the data.

3.6 Thermogravimetric analysis

A preliminary study of the changes due to the degradation of the polymer was conducted using TGA. Figure 3.38 shows the TG and DTG curves obtained for PE before burial in the soil environments. Figure 3.38 shows that PE follows a single step decomposition process that starts at approximately 300°C and finishes at 500°C when run in a nitrogen environment. By the end of the decomposition process approximately 95% of the mass of the polymer was lost leaving 5% as white residue. From the DTG curve in Figure 3.38, it can be seen that the maximum mass loss rate for the decomposition process occurs at 475°C.

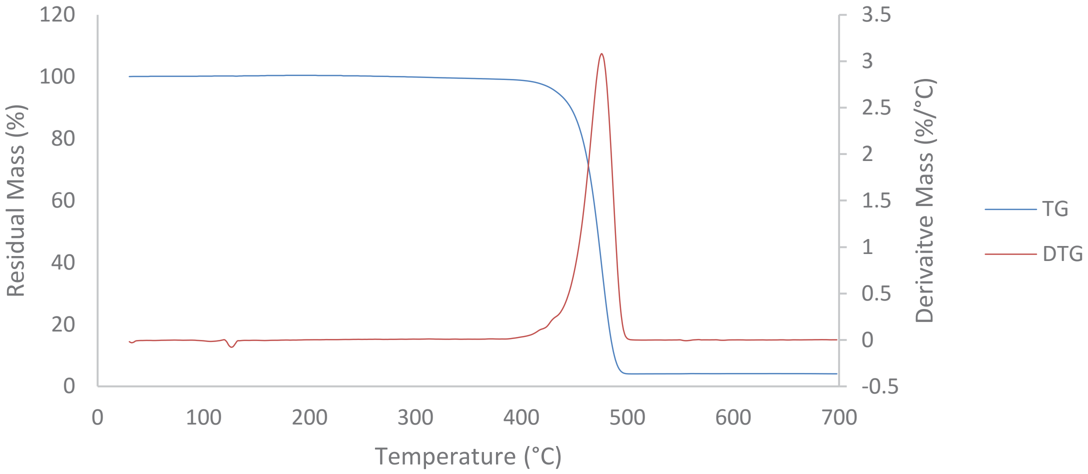


Figure 3.38 TG traces of PE before burial in the soil environments

Due to low level of degradation determined to be occurring in this polymer using the previous techniques, a preliminary analysis of PE that compared the polymer before burial to PE buried for 24 months was conducted. This was carried out to determine if the small changes that had been seen in previous techniques could be observed in a bulk technique such as TGA. Figure 3.39 shows the TG and DTG traces obtained from the analysis of PE before burial and after 24 months burial in the 9 soil environments. It can be observed from the TG traces in Figure 3.39 that there was very little noticeable difference in all of the specimens for each of the environments between the 0 and 24 months. However, there was some variation in the quantity of the remaining residue among the environments, with an increase in the residue occurring between 0 and 24 months for most environments except for the sand (which shows a decrease) and the basic (shows no change). This change was more likely to be due to the low sample size used that was due to low density of the polymer (Gabbott, 2008).

Figure 3.39, which shows the DTG data for the nine environments shows that a decrease in the height of the DTG peak was observed in all of the environments, with the lime and wet environments producing the largest changes while the sand and acidic environments show the least. The changes to the DTG trace peak height are in Table 3-3. This decrease in the DTG peak height along with the slight widening of the DTG peak, could indicate that there was a decrease in the purity of the PE sample. One possible source of change to the purity of the polymer was the formation of degradation products from PE and of any potential additives (Albertsson et al., 1995).

From the DTG curves seen in Figure 3.39, it can be observed that most of the soil environments degrade PE following the same trends observed in the previously described techniques. The exceptions are the specimens from the clay and dry environments. The specimen from the clay environment showed a relatively high amount of degradation compared to the specimens from the other environments, usually approximately the same as the lime environment specimen, while the dry environment which had little effect on the polymer, shows a greater level of change than has been seen in other techniques. These results may be due to the low amount of sample available for the analysis of PE on the TGA leading to greater errors, as well as potential soil contamination (Stawski, 2009).

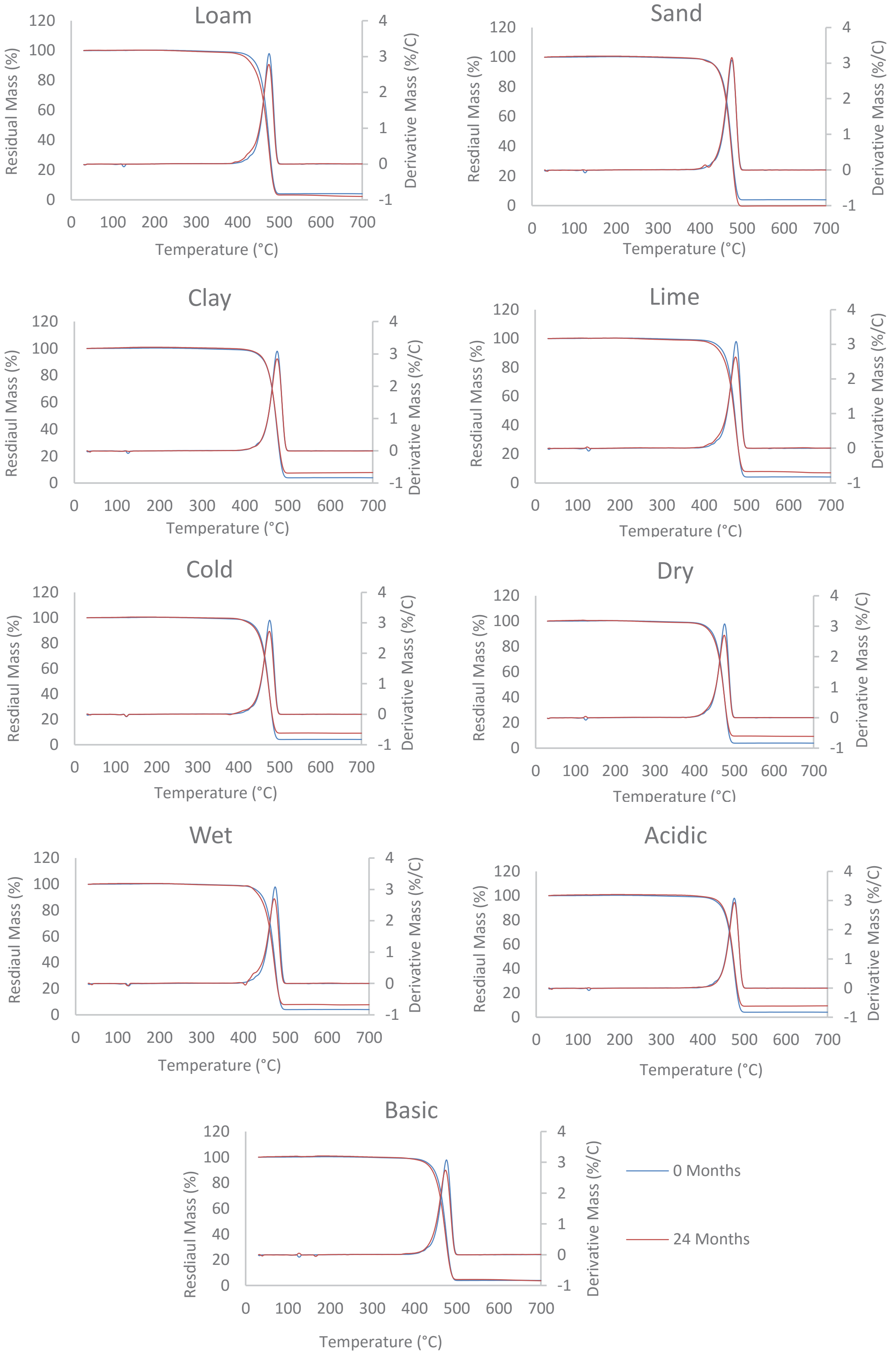


Figure 3.39 TG traces comparing PE before burial to PE after soil burial for 24 months

Table 3-3 Changes observed to the DTG trace maximum peak height

Environment	Changes observed to DTG maximum peak height ± Standard Error
Loam	$-3 \pm 1 \times 10^{-1}$
Sand	$-7.3 \pm 0.3 \times 10^{-2}$
Clay	$-2.3 \pm 0.1 \times 10^{-1}$
Lime	$-5 \pm 1 \times 10^{-1}$
Cold	$-4 \pm 1 \times 10^{-1}$
Dry	$-4 \pm 1 \times 10^{-1}$
Wet	$-4 \pm 0.3 \times 10^{-1}$
Acidic	$-2 \pm 0.3 \times 10^{-1}$
Basic	$-3 \pm 0.3 \times 10^{-1}$

3.7 Discussion

A number of different techniques were used in this investigation in order to analyse the potential degradation of PE in the 9 soil environments. The techniques used indicated that the soil environments affected the polymer by causing a change in the crystalline phase of PE as well as changes to the appearance and roughness of the polymer surface.

From the IR and Raman spectroscopy results, it was observed that most of the specimens buried in the soil environments show a decrease in the crystalline phase. A decrease in the crystallinity of PE was associated with degradation of the polymer due to microbial activity (Albertsson et al., 1995; Balasubramanian et al., 2010). This decrease also indicates that the polymer was not absorbing water so no changes are occurring to the hydrophobic nature of PE (Albertsson et al., 1987). It was also observed in the IR data, that no carbonyl bands were formed during the 24 month period, normally an indication that oxidation of PE was occurring (Sudhakar et al., 2008).

The AFM results indicated certain environments including the clay, lime, basic and wet environments had a greater effect on PE, manifested by an increase to the roughness of the polymer surface over time. This was also seen in the SEM findings, where these environments were also more likely to show surface changes compared to the other environments, with the exception of the acidic soil that showed some unusual surface changes. TGA indicated that there were changes occurring to PE between 0 to 24 months in most of the environments, however more work was needed to develop this technique in order to reduce the effect error has on the data.

The environments that consistently showed the greater decrease to the crystallinity of the polymer were the clay, lime, wet and basic environments. The environments that generally showed little change were the acidic, cold, dry and sand environments, with the loam reference environment showing values in within these two groups. There were a number of factors that allowed some environments to degrade the polymer more than others. The main factors were the moisture content, moisture retention and the basicity of the soil.

The lime and basic environments were both shown to have a large effect on the degradation of PE, with the lime environment showing a greater tendency to degrade the polymer. This was most likely due to the basicity of these two environments, which has been observed to have a positive influence on the microbial biomass in the soil environment (Spiegelberger et al., 2006). This means that in these two environments there are more microbes available to degrade the polymer allowing for more degradation to occur. The opposite occurs in the acidic environment, which has a negative impact on the microbial biomass and was observed in the data to preserve the polymer rather than cause degradation (Spiegelberger et al., 2006).

The clay environment, unlike the lime and basic environments, degraded the polymer due to the high moisture retention of the environment, as well as the small particle size and high nutrient content (Brennan et al., 2014). These factors together allow for the predicted microbes that are then unable to easily move through the environment due to the water retention producing greater degradation of the polymer. The sand environment with a larger particle size and relatively low water retention does not allow for much microbial growth, which preserves the PE rather than degrades. The wet environment, which has a high moisture content showed degradation of the polymer occurring, although not to the same extent as the clay environment. This was most likely due to the wet environment being comprised of loam soil, which has a lower moisture retention ability compared to the clay environments. This allows for greater movement of microbes through the soil and does not allow as much time around the polymer for degradation to occur (Brennan et al., 2014; Sébaïbi et al., 2003). The dry environment having neither high moisture content or high water retention was generally shown to have little impact on the degradation of PE.

Low temperatures are a known microbe deterrent, which explains the ability of the cold soil to preserve rather than degrade the PE at the lower temperature (Chavant et al., 2002). The loam environment, which was at room temperature, showed some ability to degrade the PE when compared to the cold environment. This indicates that temperature has an effect on the degradation of PE by affecting the growth of microbes in the environment.

3.8 Summary

This investigation into the degradation of PE has found that when buried within a soil environment the main change that occurs over 24 months was a decrease in the crystalline phase. The techniques used were generally consistent with each other indicating that these were suitable for examining the effect that the environments have on the polymer. There were no signs of oxidation occurring to the polymer over the burial period.

The environments that tended to degrade were environments that contained soils that promoted microbial growth such as the clay, lime, wet and basic soils. These environments enhanced microbial growth due to a number of factors such as pH, the moisture retention and moisture content of the soil. Environments that were cold or dry preserved the polymer as microbial activity would be reduced in these environments. It was observed that an environment with an acidic pH also preserved the polymer. This would be due to the soil acidity limiting microbial growth.

Overall, PE was observed to be preserved by the soil environments with some of the environments having the capacity to cause some degradation of the polymer within 24 months.

Chapter 4

Poly Vinyl Chloride Film Analysis

4.1 Introduction

PVC was one of the most common polymers in use today and was a popular for film production. PVC films are used in packaging and household goods, such as shower curtains and plastic tablecloths. In this chapter, a commercial PVC shower curtain has been used to model how soil burial will influence the properties of this polymer in a burial context. In order to study the effect that the laboratory controlled burial environments have on the polymer, a variety of different techniques were used.

The PVC specimens were exhumed from the nine different soil environments over a 24-month period and the effects that these environments had on the polymer were examined using a number of techniques including SEM, AFM, ATR-IR spectroscopy, TGA and UV-Vis spectroscopy. These techniques were found to be the most useful in obtaining information about the degradation of the PVC material during the burial process. SEM and AFM were utilised to examine changes to the PVC surface including the formation of scars, pits and variations in the surface roughness. The formation of polyenes was an indication that PVC was degrading and these were observed by ATR-IR and UV-Vis spectroscopy. These techniques also investigated the changes to plasticiser content. TGA examined the thermal changes to the polymer as well as observing the changes to the polymer's composition such as plasticiser loss.

4.2 Characterisation of PVC specimens

4.2.1 Introduction

In order to confirm that the polymer that was been examined was PVC, two tests were employed. ATR-IR spectroscopy was used to identify both the polymer and the plasticiser. DSC revealed information such as the boiling point of the plasticiser and allows for further characterisation of the plasticiser present in the PVC. Characterising the plasticiser, which was added to the PVC in order to make it flexible enough to be used as a shower curtain, was important as there are a number of potential plasticisers that could have been used in the polymer (Krauskoff and Godwin, 2005).

4.2.2 Poly Vinyl Chloride

The sample obtained from the shower curtain was examined in order to confirm the identity of the polymer as PVC. An example spectrum obtained for this sample can be observed in Figure 4.1, which shows the IR spectra of the polymer sample before burial in the soil environments. The spectrum confirms that the polymer used to produce the shower curtain was PVC. The characteristic bands associated with pure PVC that can be observed in Figure 4.1 are 2890-2958 and 1427 cm^{-1} associated with CH_2 stretch and bend vibrations, 1255 cm^{-1} with CH rocking, 961 cm^{-1} associated with trans C-H wagging and 844 cm^{-1} that was assigned to the C-Cl stretch (Ramesh et al., 2007). There are also extra bands that are not associated with pure PVC that can be observed in Figure 4.1. The band at 1720 cm^{-1}, that was assigned to C=O stretching was indicative of a plasticiser. In addition to the characteristic bands associated with PVC, there were weak bands observed near 2300 cm^{-1} that only occur in the PVC sheeting before burial that may be attributed to a phosphate ester that are commonly used as flame retardants in PVC, these bands are not present after burial of the samples (Krauskoff and Godwin, 2005). There was also an extra set of bands that were only observed in the clay samples that occurs around approximately 3600 cm^{-1} as well as an increase in the strength of the band that occur at 1250 cm^{-1}. These bands have been found to be clay soil contamination from the environment that resisted the cleaning process (Vaculíkovà and Plevovà,2005).

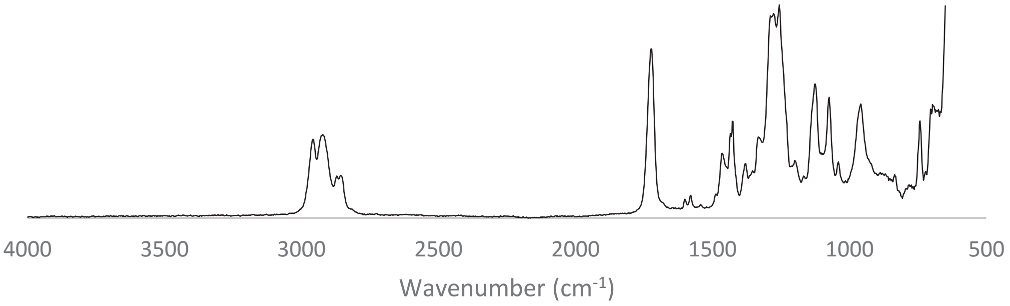


Figure 4.1 Plasticised PVC before burial

4.2.3 Plasticiser

An infrared spectrum of the additive extracted from PVC can be observed in Figure 4.2. This identifies the additive as a plasticiser known as bis(2-ethylhexyl) phthalate (DEHP). DEHP was a common phthalate ester plasticiser that accounts for 25% of plasticisers found in PVC (Patrick, 2005). The characteristic bands associated with DEHP are observed at 1070, 1120, 1465, 1578 and

1595 and 1720 cm^{-1} (Marcilla et al., 2008). The spectrum obtained for the extract also matches with previous spectra associated with this plasticiser in other studies as illustrated in Figure 4.2.

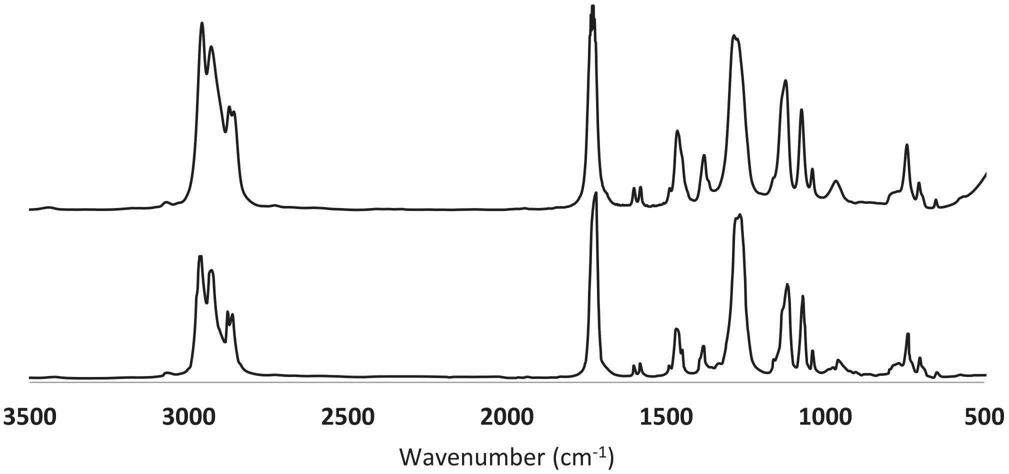


Figure 4.2 IR spectra of plasticiser obtain from PVC samples (top) and reference spectra of plasticiser obtained from NIST (bottom)

4.3 Scanning Electron Microscopy

4.3.1 Results

Changes to the surface morphology of the polymer surface over the 24-month period were examined using SEM. It was previously noted that the degradation of PVC as detected by SEM, was observed by the formation of cracks and changes in the surface roughness (Shi et al., 2008). It was observed that the degradation of the PVC progresses by the eventual disintegration of the polymer from any cracks formed. A typical micrograph of the PVC prior to burial was shown in Figure 4.3. The surface appears smooth with minimal variation in texture across the surface. The morphology of the surface of PVC was examined every 3 months to look for signs of degradation. Over the 24-month period, changes were observed on the surface of PVC in all of the environments to varying extents.

It was observed that by 3 months evidence of changes to the surface of PVC were occurring in some of the environments, particularly the specimens from the lime and clay environments, which show an increase in the roughness of the PVC. Figure 4.4 illustrates the micrograph of PVC after burial in the clay soil for 3 months. Generally, however, most of the specimens by this point retain the smooth surface that was observed before burial as illustrated by the micrograph obtained for the dry environment sample at 3 months (Figure 4.5). The unusual bright spots that can be seen in the micrographs can be attributed to soil particles that resisted the cleaning process and remained attached to the polymer surface.

Between 6-9 months it was noted that some of the specimens, particularly the specimens from the wet environment (and to a much lesser extent the loam environment specimens) show the formation of small pits on the PVC surface (Figure 4.6). These pits may be an early indication of the formation of cracks in the polymer surface. By 9 months most of the specimens show a change from the smooth surface first observed before burial with the formation of darker patches being visible on the PVC, indicating a loss of plasticiser from PVC (Figure 4.7). These dark patches may indicate an increase in the roughness of the surface that has been suggested to be related to possible degradation of the PVC in these environments (Achim, 1996; Škvarla et al., 2010). The specimens that show this roughness variation on the surface of the PVC vary when and how much of roughness variation could be seen. The specimen from the sand environment first showed these changes at 6 months while other specimens, such as the specimens from the cold, dry, loam and wet environments, only show this feature from 9 months with the specimen from the dry environment showing less of these dark areas when compared to the other specimens. The specimens from the clay and lime environments show an increase in roughness observed during this time period (Figure 4.8). However, no unusual features developed in these environments by this point, while the specimens from the acidic and basic environments appear to be still very similar to the before burial micrographs showing no visible sign of degradation by this time period.

At 12 months most of the specimens were very similar in appearance to the 9 months micrographs. However, there were noticeable changes to both the specimens from the acidic and basic environments by this point, with the acidic environment specimen showing a rougher surface (Figure 4.9) indicating that degradation was occurring to the PVC in the acidic environment. While the PVC in the basic environment was similar in appearance as was noted in the specimens from the loam, cold, dry and sand environments (Figure 4.10).

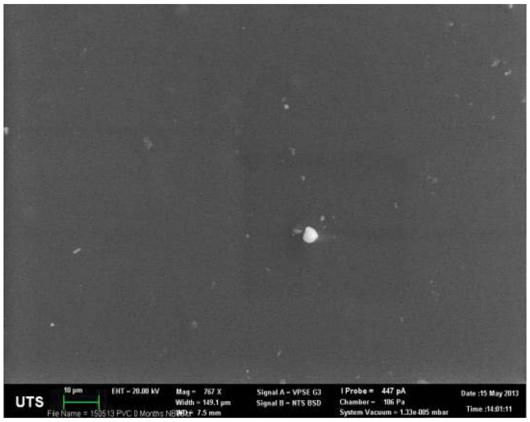


Figure 4.3 SEM micrograph of PVC before burial at a HFW of 149.1µm

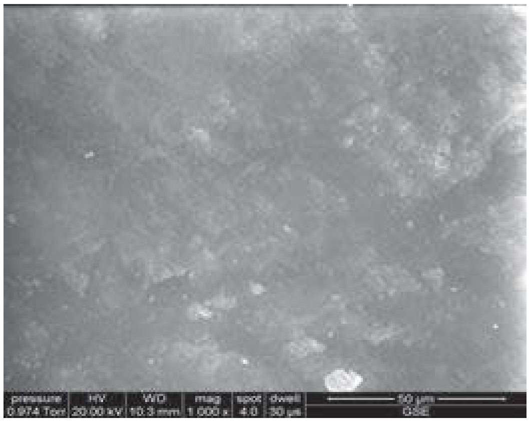


Figure 4.4 SEM micrographs of PVC after burial in the clay environment for 3 months

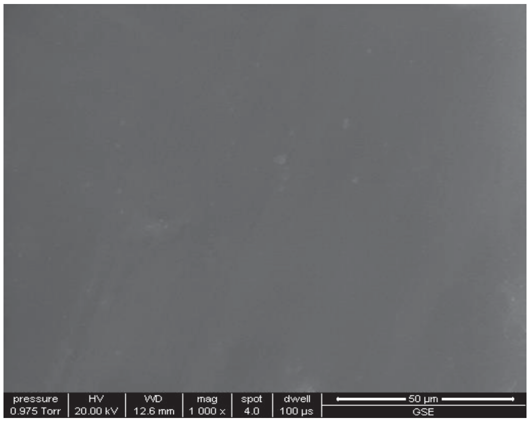


Figure 4.5 SEM micrograph of PVC after burial in the dry environment for 3 months

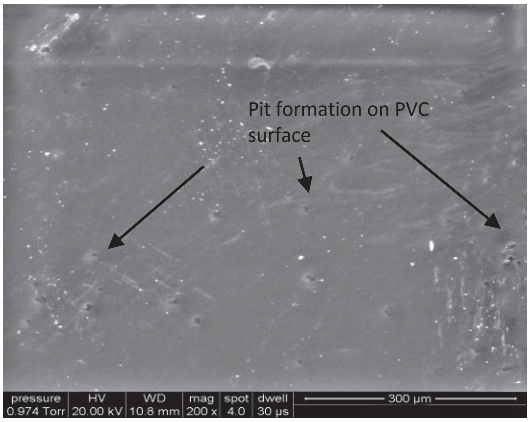


Figure 4.6 SEM micrograph of PVC after burial in the wet environment for 6 months showing possible pit formation

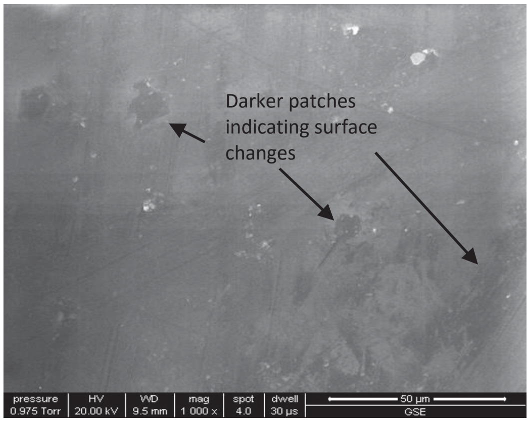


Figure 4.7 SEM micrograph of PVC after burial in the sand environment for 9 months

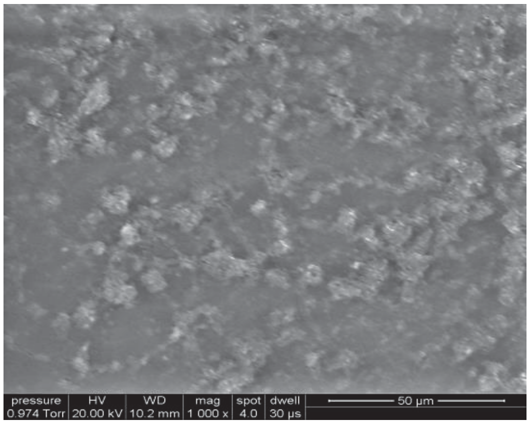


Figure 4.8 SEM Micrograph of PVC after burial in the clay environment for 9 months

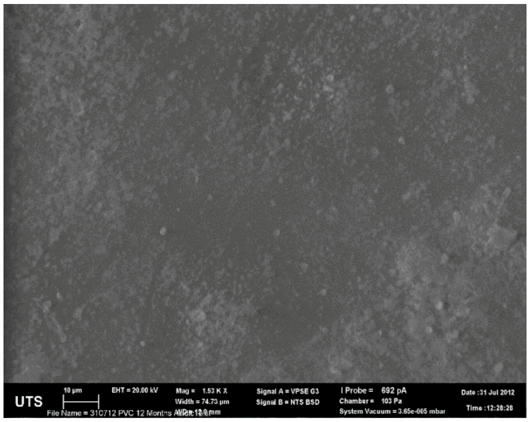


Figure 4.9 SEM micrograph of PVC after burial in the acidic environment for 12 months

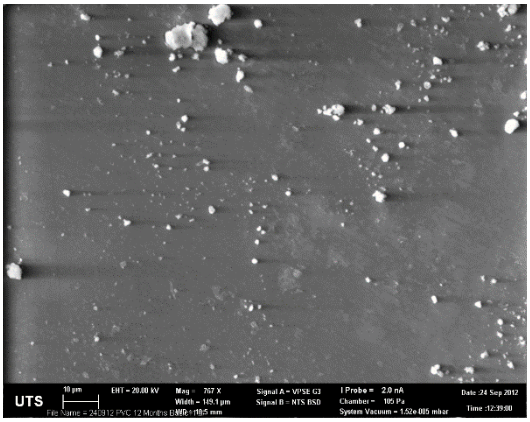


Figure 4.10 SEM micrograph of PVC after burial in the basic environment for 12 months

Between 15-18 months many of the environment specimens showed significant change. Many of the environments have shown the development of pits on the surface of the PVC as well changes in the surface texture been noticeable in most of the specimens by 18 months. Specimens that were more likely to show change in earlier months, including the clay environment specimen (Figure 4.11) tended to have more prominent variations on the surface of PVC with larger and more commonly observed light patches that contrast against the darker PVC surface in these environments, as opposed to the specimens from environments, including the cold environment, that tended to slow degradation of the PVC (Figure 4.12). There was also variation in the formation of pits within the polymer samples, including the cold environment specimen, which only shows evidence of pit formation in small areas while the other regions of the micrograph indicate that the remainder of the polymer has a smooth surface. Specimens from such environments were showing possible signs of plasticiser loss in earlier months with noticeable variation in the surface texture on the surface declining over time. The pit formation may be due to the plasticiser being lost by this stage, which has subsequently stabilised, which would explain why there are few changes seen in the surface texture of the polymer at a later stage.

By the end of the 24-month period, all environment specimens showed that pit formation had occurred with some specimens, including the clay soil specimen, having pits fairly evenly dispersed throughout the PVC surface while specimens from the dry, cold and loam environments have pits only localised in some areas on the surface (Figure 4.13, 4.14 and 4.15). In addition, the pits look somewhat larger and deeper in specimens from environments similar to the clay environment when compared to the slower degrading environments of the loam soil. When compared to the before burial micrograph there was also a visible increase in the appearance of roughness on the PVC surface particularly in the clay, acidic, lime and sand environments (Figure 4.15). The PVC from the clay, sand and lime environments, also showed evidence of scarring and cracking appearing on the polymer surface, which has been seen in previous studies to be an indication of the earlier stages of degradation on the polymer surface (Colin et al., 1981; Monney et al., 2001; Shi et al., 2008).

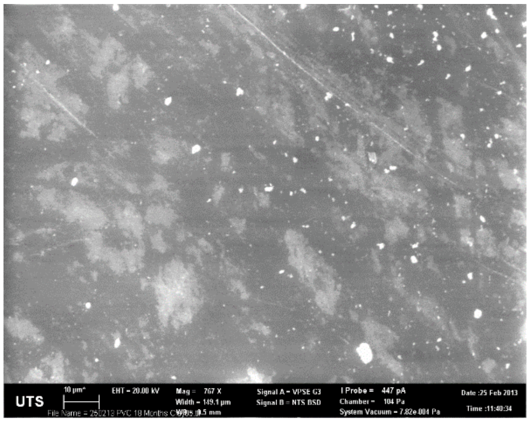


Figure 4.11 SEM Micrograph of PVC after burial in the clay soil for 18 months

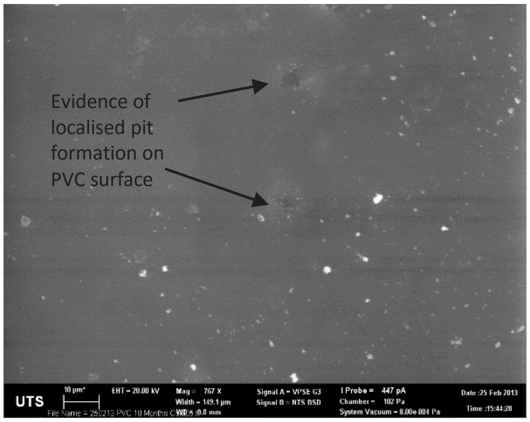

Evidence of localised pit formation on PVC surface

Figure 4.12 SEM Micrograph of PVC after burial in the cold soil for 18 months

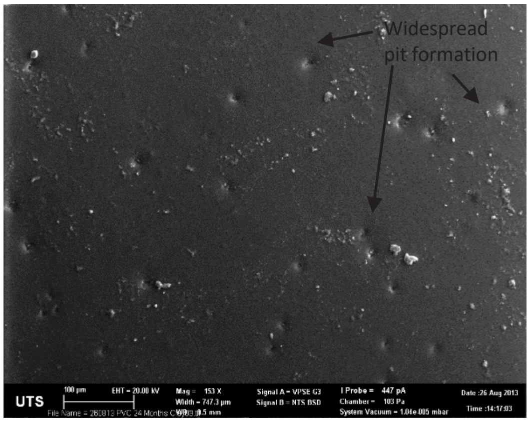


Figure 4.13 SEM micrographs of PVC after burial in the clay environment for 24 months

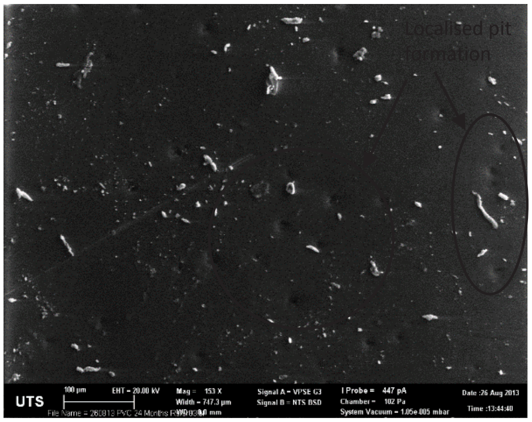


Figure 4.14 SEM micrographs of PVC after burial in the loam environment for 24 months

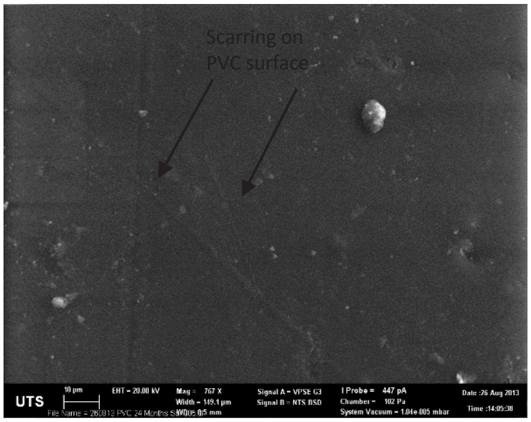


Figure 4.15 SEM micrograph of PVC after burial in the sand environment for 24 months, showing scarring on the PVC surface

4.3.2 Discussion

From an examination of the micrographs obtained from the SEM, it can be seen that there are surface changes occurring to the surface of the PVC to all of the environments, particularly in the lime, sand and clay environments, which had the tendency to produce change earlier and showed these changes occurring across the polymer surface. While the wet environment specimen generally did not show many changes until the end of the 24-month period, it was unusual in demonstrating the early widespread formation of pits occurring throughout the PVC buried within this environment, which an indication of possible degradation was occurring. This may be due to the chemical interaction of the PVC or additives including the plasticiser, with the water present within this environment (Kastner et al., 2012). It was also possible that the fungi and bacteria that were noted throughout the 24 months' periods to grow periodically on the surface of this environment, may be degrading either the PVC or the plasticiser. Previous studies have noted that there are a variety of microbial life, particularly various fungi, are able to degrade both the PVC and the DEHP plasticiser (Coulthwaite et al., 2005; Xu et al., 2008). The specimens from the cold, dry and loam environments tended to show changes throughout the 24 months' period. These environments produced these changes in localised areas as opposed to environments, including the clay soil, which indicated that the changes to the PVC surface were widespread throughout the polymer. The basic environment tended to preserve the polymer with very little change occurring to the PVC in this environment until about 12 months after burial and by 24 months showed less change occurring to the polymer surface when compared to the other environments. While the acidic environment also showed very little change up to 12 months, changes such as a noticeable variation in surface texture were evident after this point. It has been previously noted that PVC has a good chemical resistance to sulfuric acid especially at low concentrations (Titow, 1984). The delayed reaction with the surface of the PVC as observed from the micrographs was most likely be due to this chemical resistance to sulfuric acid.

4.4 Atomic Force Microscopy

4.4.1 Analysis of Changes to the Roughness of PVC due to Soil Burial

The changes to the microstructure of the PVC film as a result of burial in the different environments was investigated using AFM. Figure 4.16 shows an AFM micrograph of PVC before soil burial It can be seen from Figure 4.16 that the topography of the surface of the PVC film was a fairly smooth heterogeneous structure with some peaks and pits been observed, as well as some markings that are most likely due to the manufacturing process and the interaction of the PVC with the plasticiser (Määttä et al., 2007). The peaks and valleys that can be seen in Figure 4.16 correspond to a black to white scale with the darker areas been pits found on the surface and lighter areas been the peaks. It has been seen in previous studies of various polymers that an indication of degradation occurring can be seen by an increase in the roughness of the film, changes in the appearance of more and deeper pits as well as smoother peaks and waves appearing in the sections taken from the image (Gu et al., 2001; Sudhakar et al., 2008; Szép et al., 2004). Over the 24-month period changes were seen to varying extents and were dependent on the environment type. The bright spots that appear as very high peaks on the surface are due to residual contamination from the soil particles that resisted the cleaning process.

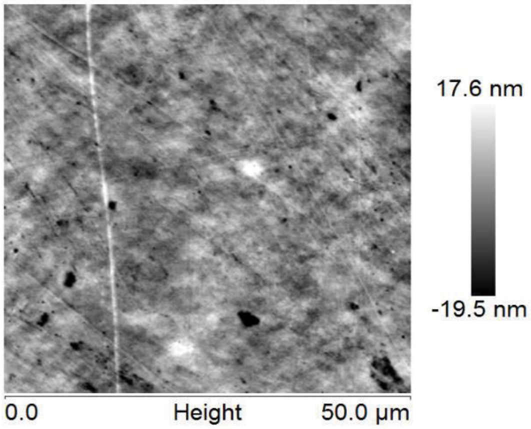


Figure 4.16 2D topography image of PVC before burial from AFM

The roughness of the PVC film in the soil environments was analysed by taking 6 sections from each image and finding the mean value of the roughness using the standard deviation of the Z values (rms) (Gu et al., 2001). Observations show that the rms of the PVC surface varied according to the environment, with the clay, sand and lime environments showing the most change and the dry and basic environments showing the least (Figure 4.17). It can be seen from Figure 4.17 that the greatest change in roughness happens between burial and removal at 12 months rather than the later months. The standard deviation of the 6 sections analysed also varied with different environments. The clay, sand and lime environments that showed the greatest changes in the roughness of the PVC surface also showed a much larger variation in the standard deviation then the less reactive environments. This indicates that the degradation of the PVC sample was not consistent throughout the entire sample with some sections degrading more easily than others giving the larger standard deviation. The cause of this standard variation can be seen in where the pits form within the samples (Gu et al., 2001).

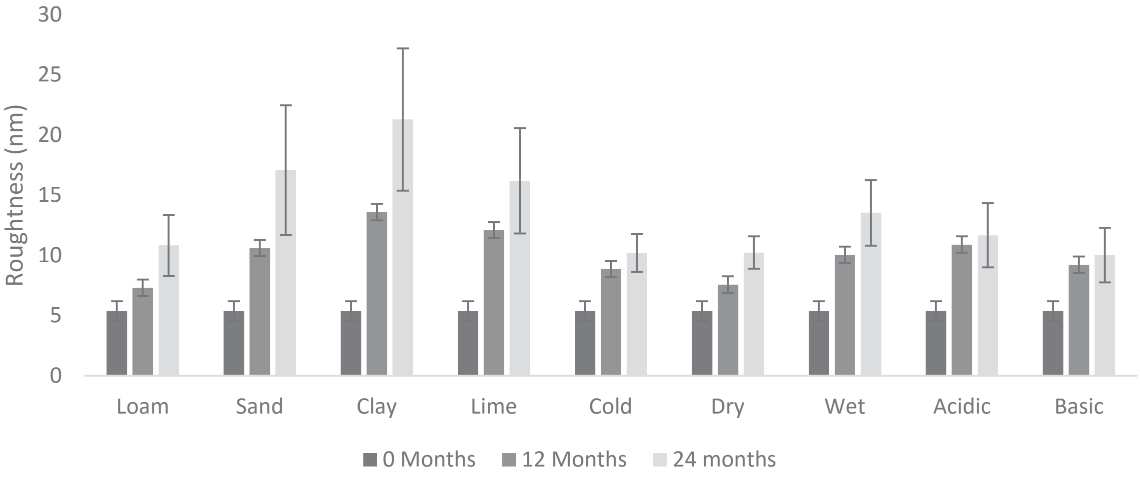


Figure 4.17 Graph showing the mean changes (with standard error) in RMS occurring in the 9 environments

It was observed that most of the environments produced some pits in the surface of the film especially by 24 months, however, it appeared that the pit formation was not consistent over the three 50µm images for each environment specimen. For example, the first image in Figure 4.18 showing a high number of pits and smaller depressions on the surface of the polymer, while the second image has what appears to be some slight depressions, but no clearly defined pits as seen in the first image. Both of these images are from the clay environment specimen after 24 months, which has the tendency to produce the greatest changes out of the 9 environments. This variation in pit formation across the surface of the PVC has previously being noted in earlier studies, to be most likely due to differences that can occur during the manufacturing process such as variations in plasticiser concentration (Behnisch and Zimmermann, 1989; Coulthwaite et al., 2005). This results in weaknesses been introduced across the surface of the polymer. It was noted however, that the specimens from environments such as the clay soil that showed the tendency to change the most as observed in AFM, were more likely to develop new and larger pits on the surface of the film when compared to specimens from environments, such as the cold environment (Figure 4.19) that shows the least tendency to degrade PVC.

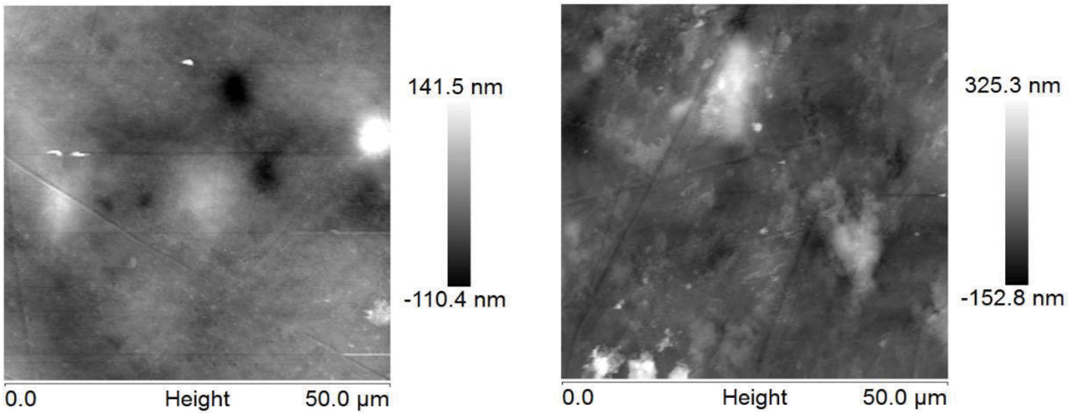


Figure 4.18 Topography image of PVC after burial in the clay environment for 24 months

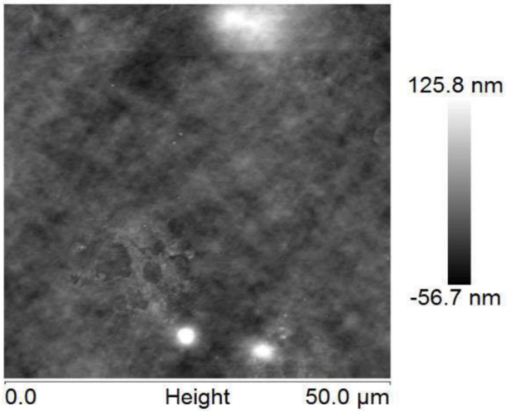


Figure 4.19 Topography image of PVC after burial in the cold environment for 24 months

4.4.2 Section Analysis of PVC Surface

Another method that has been used by previous studies to look for degradation on the surface of the polymers was by the examination of the changes that occur to section waves. It has been noted that degradation can be seen using this method by observations to the changes to both the heights and the smoothness of the section curves (Szép et al., 2004). In Figure 4.20, an example of the section analysis from the PVC before burial can be seen. It shows variations occurring on the surface of PVC that are within 10nm of the centre line on a 'wavy' surface that has two different types of waves. A longer one that has a wavelength range of approximately 5µm and a shorter one with a higher frequency that has a wavelength of approximately 1µm. This wavy characteristic of the surface has previously been attributed to the manufacturing process (Szép et al., 2004).

By comparison, Figure 4.21 shows example specimens from two different environments, the clay and dry soils, which showed different levels of change to the roughness of the surface. The clay environment specimen demonstrated the most change, while the dry environment shows the least. In both of these environments, there was an increase to the amplitude of peaks with the clay, lime and sand environments producing both an increase in depth of surface features such as pits as well an increase in the bumps on the surface of the PVC. By contrast, the specimens from the dry, loam, cold and basic environments, while they show evidence of increase in the depth of the surface features (although not to the same extent as the more reactive clay environment) there was not a significant increase in the corresponding peaks in the section analysis data. There appears to be a change in the length of the longer wave in both example environment specimens with the dry samples showing a wavelength of about 10µm and the clay samples showing about

15-20µm as well as a slight smoothing of the shorter waves. As noted before the degradation of the samples was not consistent across the whole sample and that can be also seen here where in both environments there was a degree of variability in how smooth the wavelengths are in each of the 3 sections looked at as well as the variability in the amplitudes of the different sections.

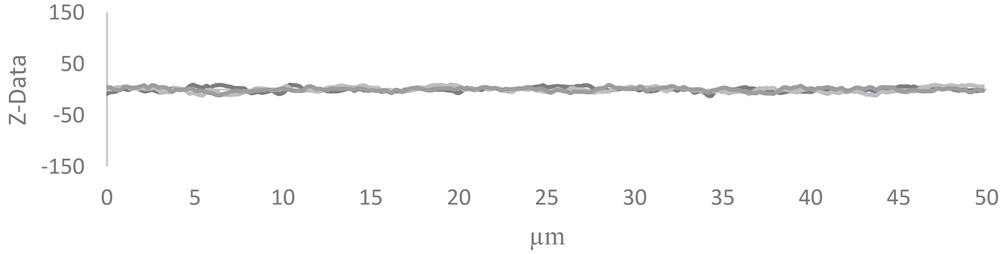


Figure 4.20 Section analysis of PVC before soil burial

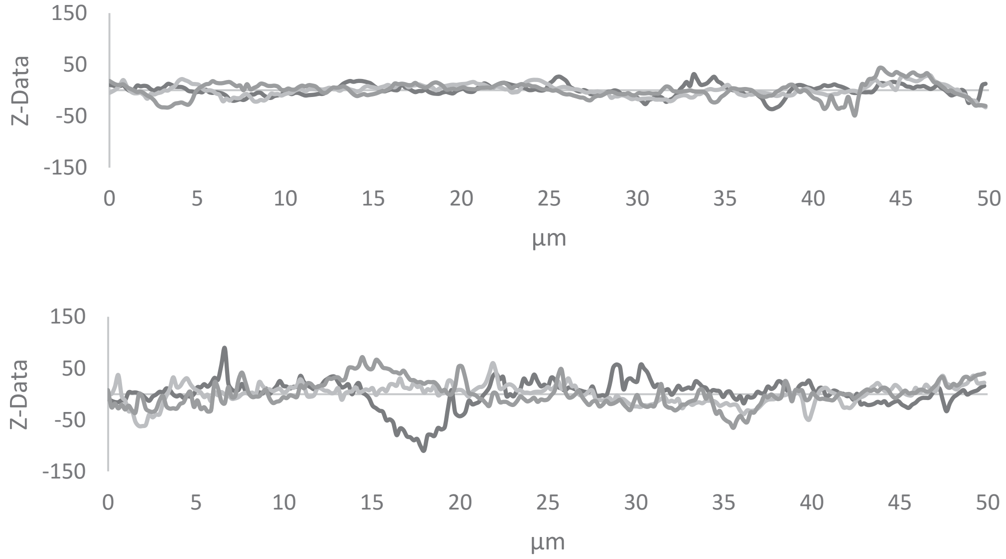


Figure 4.21 Section analysis of PVC after burial in the dry (top) and clay (bottom) environments for 24 months

4.4.3 Summary of Changes Observed by AFM

It can be observed from the data obtained that there have been noticeable changes that have occurred in the PVC. Visually there were changes that occurred in the different environments with the formation and increase to the depth of the pits occurring as well as other features appearing more often on the surface of the specimens from the more reactive environments such as the clay, sand and lime environments as opposed to the specimens from the less reactive environments such as the dry, cold and basic ones. Additionally, changes over time to the mean roughness of the surface of the PVC and to the wavy feature of the surface also indicated degradation occurring in the 9 environments. As the changes that were observed to occur were seen to vary across the different environments, this would indicate that it was the environments themselves that influenced the degradation of the PVC as opposed to been only due to the burial time of the PVC.

4.5 Fourier Transform Infrared Spectroscopy

4.5.1 Analysis of Infrared Band Ratios - Results

ATR-IR spectroscopy was carried out on the PVC films in order to determine the impact the 9 soil environments had on the polymer structure. Inspection of the spectra collected from the specimens in the different burial environments reveals changes to the plasticiser bands as a function of burial duration. The 2^{nd} derivative spectra of PVC buried from 0 to 24 months in the nine soil environments are illustrated in Figure 4.22. From this data, it was observed that the specimens from the clay, lime, sand, wet and acidic environments show a decrease in many of the plasticiser bands within the burial period while the specimens from the dry, cold, loam and basic environments do not. It can also be observed from Figure 4.22 that there was little to no change to PVC in any of the environments in both of the bands at 692 and 1650 cm^{-1} that are associated with the formation of polyenes. This would indicate that the loss of plasticiser that was occurring in the PVC samples was not due to the dehydrochlorination of PVC and the subsequent formation of polyenes, which are incompatible with the phthalate plasticiser as was observed when PVC was degraded under thermal conditions (Gumargalieva et al., 1996; Williams and Gerrard, 1990). Since the rate of loss of plasticiser tends to not be linear in most environments this can exclude the loss of plasticiser though evaporation (Singh et al., 2008). There was also an extra set of bands that were only observed in the clay samples that occurs around approximately 3600 cm^{-1} as well as an increase in the strength of the band that occur at 1250 cm^{-1}. These bands have been found to be clay soil contamination from the environment that resisted the cleaning process (Vaculíkovà and Plevovà, 2005)

The ratio of the absorbance of the 1720 cm^{-1} plasticiser band relative to the 1425 cm^{-1} PVC band decreases with burial time in each environment as shown in Figure 4.23. The principal plasticiser bands at 1720 and 1465 cm^{-1} have been referenced to a 1425 cm^{-1} polymer band as these bands are relatively clear of overlap with adjacent bands and have been used in previous studies as a reference band (Marcilla et al., 2008; Shi et al., 2008). However, the slopes obtained for each plot do vary according to environment and the results are summarised in Table 4-1. The slopes for the 1720/1425 ratio plots for the specimens from the clay, lime and sand environments indicate a sharper decline in plasticiser content compared to the cold, basic and dry environments. The specimens from the wet, acidic and reference environments while not showing as sharp a decline as the clay, lime and sand environment specimens, shows some change compared to the specimens from the less active dry, cold and basic environments. It was observed in Figure 4.24 that most of the specimens from the more reactive environments, such as the clay, lime, wet and acidic, that the decline of the plasticiser tends to leach out of the PVC at the fastest rate in the first 6 -9 months with the rate of decline slowing down greatly in the later months. The sand environment was an exception to this as the rate of plasticiser loss seems to be more linear. The less reactive environments do not show this trend.

In Figure 4.23 examples of the 1465/1425 cm^{-1} ratio plots are also seen and the slopes calculated for each plot are listed in Table 4-1. There was also an indication that the 1465/1425 cm^{-1} ratios decrease with burial time and are similarly dependent on soil environment, although the changes to this ratio are less distinct than those observed for the 1720/1425 cm^{-1} ratio as it also does not show the same steeper decline for the first 6-9 months that occurs in the 1720/1425 cm^{-1} plots.

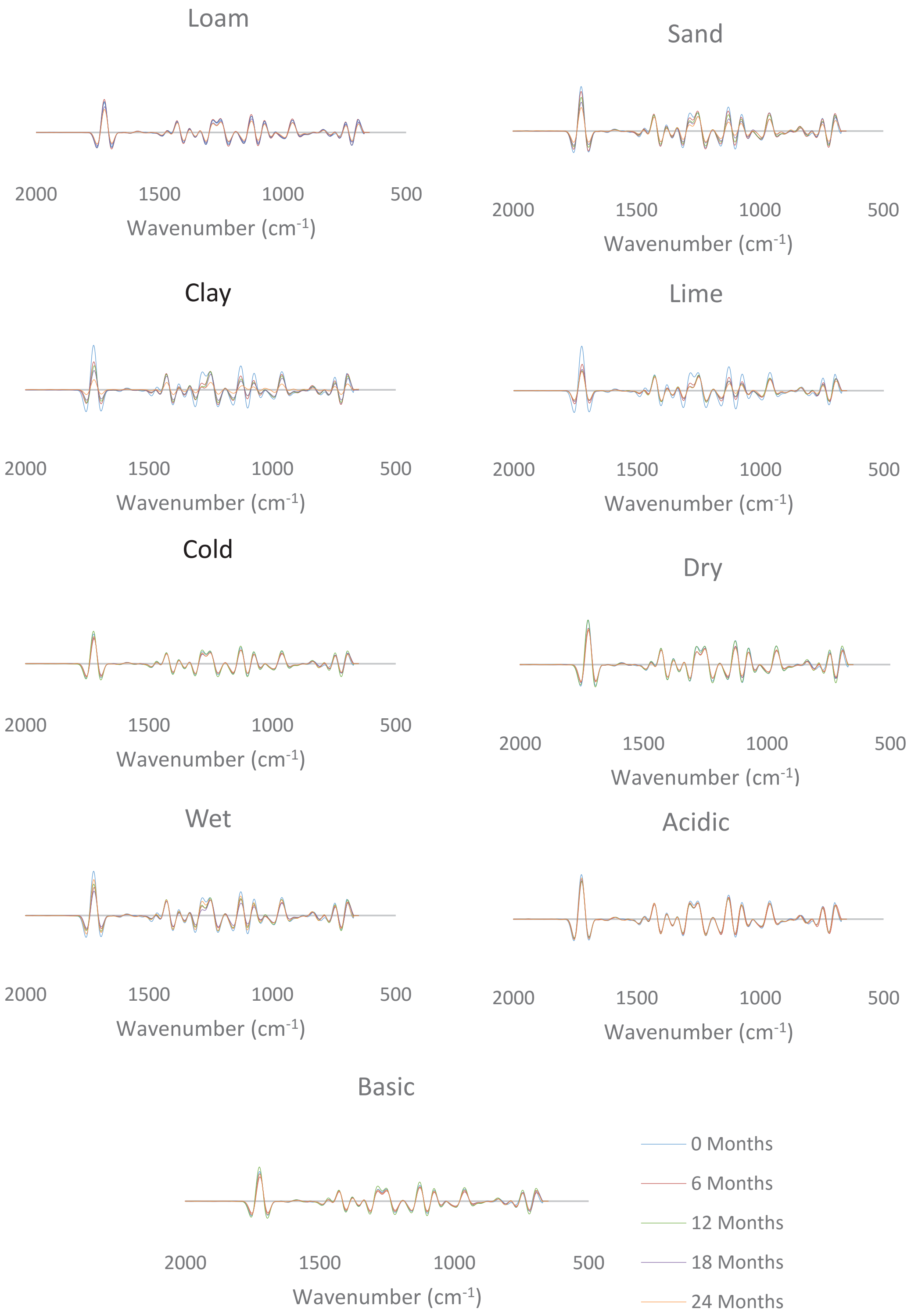


Figure 4.22 2nd derivative spectra of PVC samples buried in the soil environments

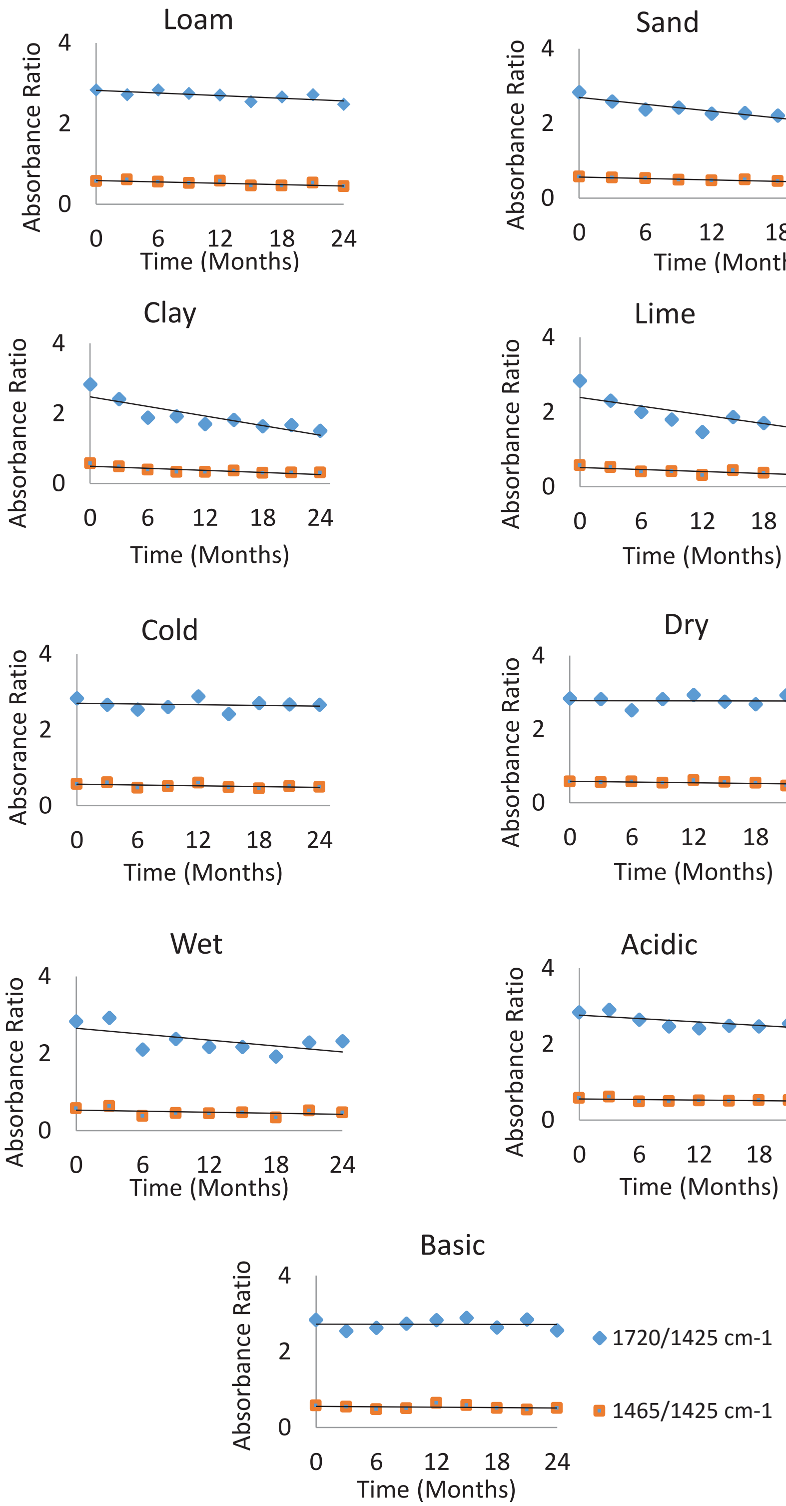


Figure 4.23 Mean FTIR absorbance ratio plots for PVC burials

Table 4-1 Summary of the overall linear trend found when 1720 and 1465 cm^{-1}were compared with 1425 cm^{-1}

Environment	1720/1425 cm^{-1} slope	1465/1425 cm^{-1} slope
Loam	$-1 \pm 1 \times 10^{-2}$	$-6 \pm 2 \times 10^{-3}$
Sand	$-3 \pm 1 \times 10^{-2}$	$-6 \pm 1 \times 10^{-3}$
Clay	$-5 \pm 1 \times 10^{-2}$	$-10 \pm 2 \times 10^{-3}$
Lime	$-4 \pm 1 \times 10^{-2}$	$-9 \pm 3 \times 10^{-3}$
Cold	$-3 \pm 1 \times 10^{-2}$	$-4 \pm 2 \times 10^{-3}$
Dry	$-2 \pm 1 \times 10^{-2}$	$-3 \pm 2 \times 10^{-3}$
Wet	$-3 \pm 1 \times 10^{-2}$	$-5 \pm 4 \times 10^{-3}$
Acidic	$-2 \pm 1 \times 10^{-2}$	$-3 \pm 2 \times 10^{-3}$
Basic	$-1 \pm 1 \times 10^{-2}$	$-2 \pm 3 \times 10^{-3}$

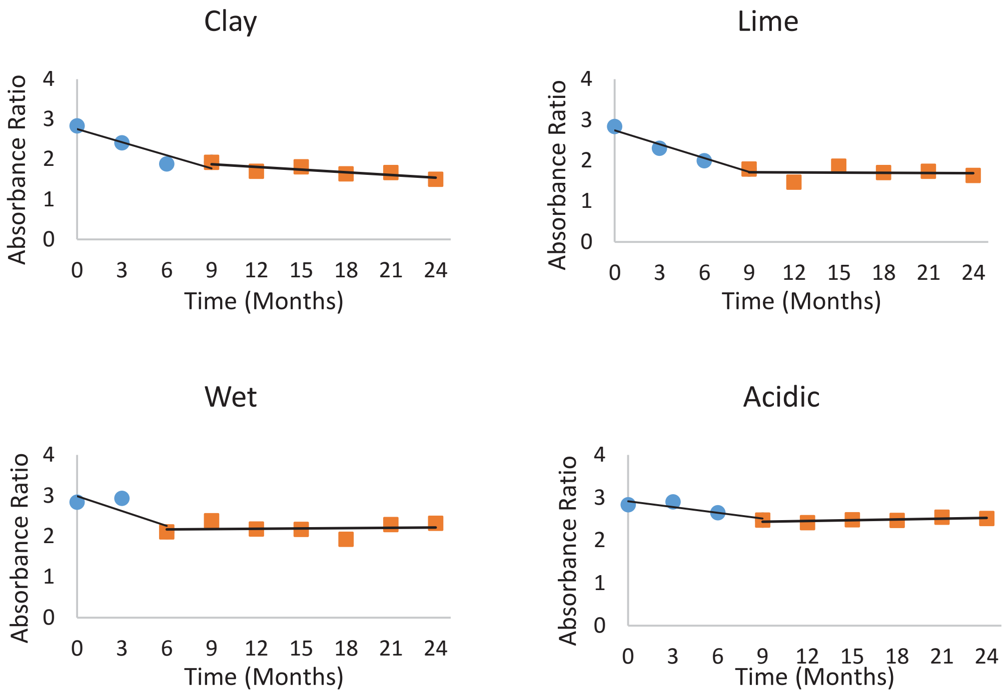


Figure 4.24 Mean FTIR absorbance plots showing 2 step process seen in 1720/1425 cm^{-1}

4.5.2 Analysis of Infrared Band Ratios - Discussion

The presence of water in the soil appears responsible for the loss of at least surface plasticiser (ATR spectroscopy samples to a micrometre level), with the rate of removal more than tripled when compared to the reference loam soil environment as determined from the relative slopes of the decrease in the 1720 cm^{-1} band with time. It has been found in a previous study that although the plasticiser was not water soluble, in an aqueous environment DEHP has a relatively high tendency when compared to other similar phthalate plasticisers to leach into an aqueous environment (Kastner et al., 2012). It was suggested that this can occur due to there been a polar component within the plasticiser molecule that was needed in order for it to interact with PVC (Senichev and Tereshativ, 2013). This allows the plasticiser to also have some interaction with water and it to leach out of the PVC and into the surrounding environment.

It can be seen from Table 4-1 that while the wet environment, which had higher levels of moisture contained within the environment, had less of an effect on the decline of plasticiser than the much drier clay environment. It was possible that the difference in reactivity was due to the clay environments tendency to both absorb and hold water (Nguyen and Marschner, 2014). This would mean that the clay environment, although it was a drier environment than the wet environment, the water molecules in the clay environment are able to stay with the PVC longer than in the wet environment where the water drains to the bottom of the container. This draining was observed throughout the experiments as the layer of soil under the samples could be seen to be wetter than the soil above the samples forming a compacted layer of water and soil under the samples. This would also apply to the lime environment as pure lime has been shown to have to have to ability in previous studies to retain significant amounts of water as well as the sand environment to a much lesser extent (Sébaïbi et al., 2003).

While the lime environment showed significant changes to the plasticiser content of PVC, the basic environment with a similar pH was seen to be one of the least reactive environments. This would indicate that the effect of moisture been held around the PVC has a greater impact on the degradation of the polymer than the pH of the environment. This can also be seen with the acidic environment, which had a similar impact on the degradation of the PVC to the basic environment. The level of plasticiser present in the PVC was preserved rather than degraded. PVC was considered to have a good resistance to both acids and bases at room temperature, explaining why the changes in the pH of the environment had little effect on the degradation of the PVC (Louie, 2005).

Previous studies show that there was also evidence that the DEHP plasticiser was also resistant to reactions with acids and have shown that the removal of the plasticiser from both an aqueous and soil environment was slowed down when the plasticiser was treated with an acidic solution (Hammad Khan and Jung, 2008; Magdouli et al., 2013). It was noted in these previous studies that treating both the aqueous and soil environments with a basic solution tended to have more of an effect on the removal of plasticiser from the environment. However, the pH of the solution used in these studies was approximately 11, which was much more basic then the soil pH 8 environment used in the current study (Hammad Khan and Jung, 2008; Magdouli et al., 2013). Since the basic environment had very little effect on the removal of plasticiser from the PVC, this could mean that only a strongly basic environment will have an impact on the plasticiser content giving the low plasticiser loss rate encountered in the soil environment.

The loam, cold and dry environments all showed a tendency towards preserving the PVC. The loam environment while having some degree of moisture present within the soil did not have the moisture retaining capacities of the more reactive clay and lime environments, thus not allowing for moisture to be held around the samples for greater plasticiser removal nor the high levels of moisture that are present in the wet environment. The dry and cold environments have been found in previous studies to have a preserving effect on many synthetic materials (Janaway, 2008). In the case of the dry environment this was most likely due to the lack of moisture that was present as it appears that the moisture content of the soil has some impact on the plasticiser removal. While the cold environment at a much lower temperature (4°C) indicates that high temperature as well could possibly play a role in the removal of the plasticiser from the PVC. However, this would need to be confirmed by a study of a high temperature environment (Gumargalieva et al., 1996). This may be due to the inhibition of microbial activity that occurs in reduced temperatures as previous studies have shown, that the presence of microbes can have a large influence on the amount of plasticiser removed from the PVC (Nakamiya et al., 2005; Pradeep and Benjamin, 2012).

4.5.3 Multivariate Analysis

Multivariate analysis was conducted on the IR results of PVC within the different environments in order to determine the validity of the band ratio data as well as to investigate the strength of the data. The PCA results obtained shows agreement with the ratio data for the changes that occur to the PVC in the soil. It can be seen from the first PCA plot in Figure 4.25 that there was a general shift for all of the environments towards the negative with the clay, lime and sand environments showing the most change when compared to the before burial PVC. This agrees with the previous data seen in Table 4-1, indicating a reduction in various peaks causing this negative shift. This was confirmed by the second PCA plot that presents the shift that occurs over time, by the later months generally have shifted away from the before burial PVC when compared to the earlier months.

Using the pre-treated IR data from the PVC samples, a PLS-R plot was created with the loam environment used as a reference. In order to decide which model would be the most useful for PVC both the loadings (Figure 4.26) and the explained variance (Figure 4.27) for each factor were investigated to see which bands were prominent in each factor. The factors that feature the bands of interest at 1720, 1465 and 1425 cm^{-1} as well as having a good variance were used to create the model for PVC. Factor 3 was observed to have the best combination of variance (once noise peaks were removed) and the peaks of interest that appear in the loadings as the factors 1 and 2 show the peaks of interest, it can be seen from Figure 4.27 that the variances for these two are much lower than factor 3, which still shows these peaks of interest. The later factors 4-6, while showing good variance, demonstrate mostly noise when the loadings of these factors were investigated. The PLS-R of the loam soil environment (acting as a reference) was shown in Figure 4.28. It can be seen that the total R^2 for this model was 0.89 indicating a fairly good fit. It can also be seen in

Figure 4.28 that the data up to and including 18 months generally shows a good match with the model. However, the 21 and 24 month samples are shown to be a lot further away from the regression line indicating that the model breaks down the longer the burial time of the sample.

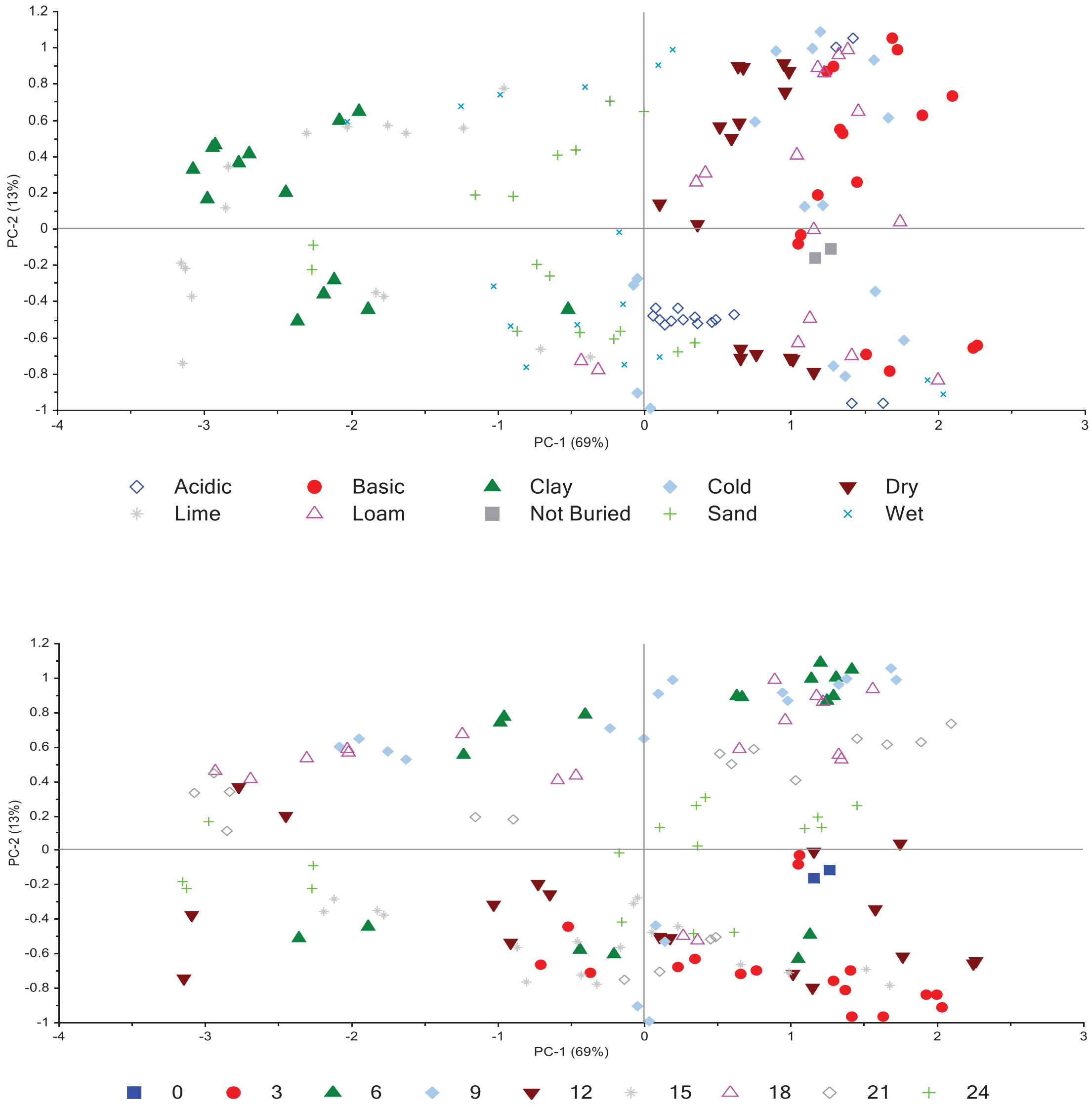


Figure 4.25 PCA environment (top) and time (bottom) score plots

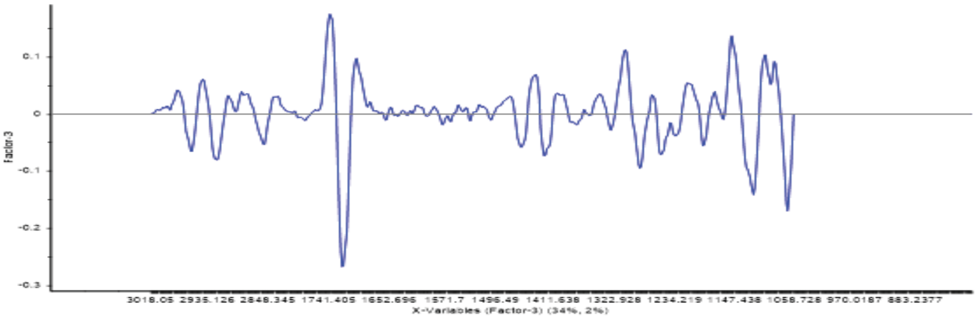


Figure 4.26 Factor 3 loadings showing peaks of interest at 1720, 1465 and 1425 cm^{-1}

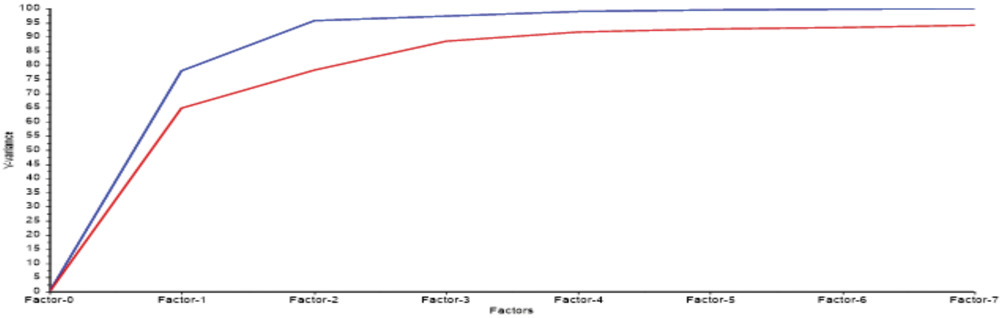


Figure 4.27 Graph showing the explained variance between the calibration and validation of the PLS-R

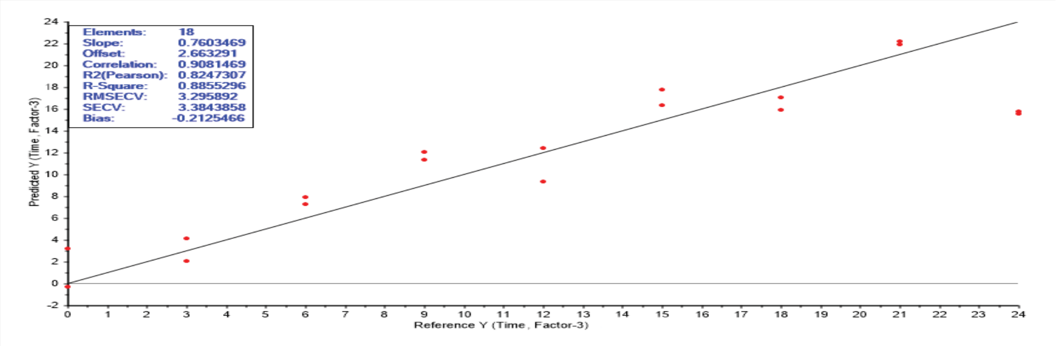


Figure 4.28 PLS-R Calibration graph showing predicted vs reference

4.6 Thermogravimetric Analysis

4.6.1 Results

TGA was carried out on the PVC specimens in order to determine whether this technique was viable for use in the analysis of the PVC degradation in the different soils. Figure 4.29 shows a TG curve for PVC in the clay environment from 0 to 24 months. It can be seen from Figure 4.29 that the PVC samples follow a 2 step decomposition process that starts at approximately 50°C and finishes at 500°C when run in a nitrogen environment. The first stage accounts for the greatest mass loss (approximately 60%) and starts at 50°C and continues to 380°C. The second stage accounts for about 25% of the mass lost and proceeds from 380°C to 500°C. After the decomposition has occurred there was about 10-15% left as a carbon residue. This two stage process was also visible in the DTG curves as can be seen in Figure 4.30 with the peak maximum for the first stage appearing at around 290°C and the maximum for the second stage at approximately 450°C.

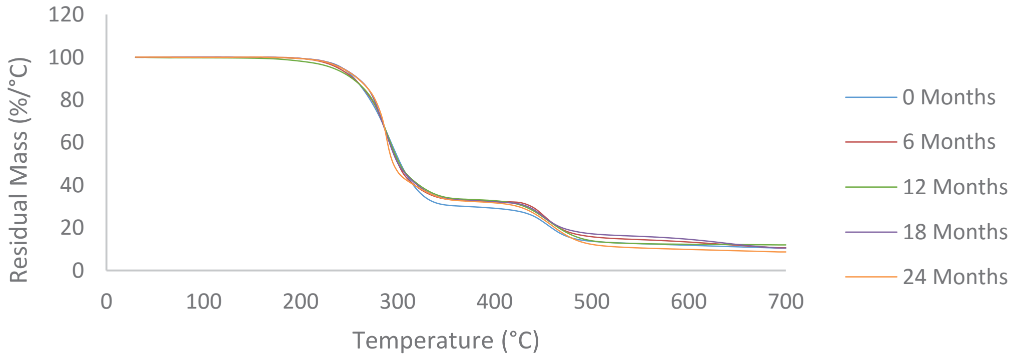
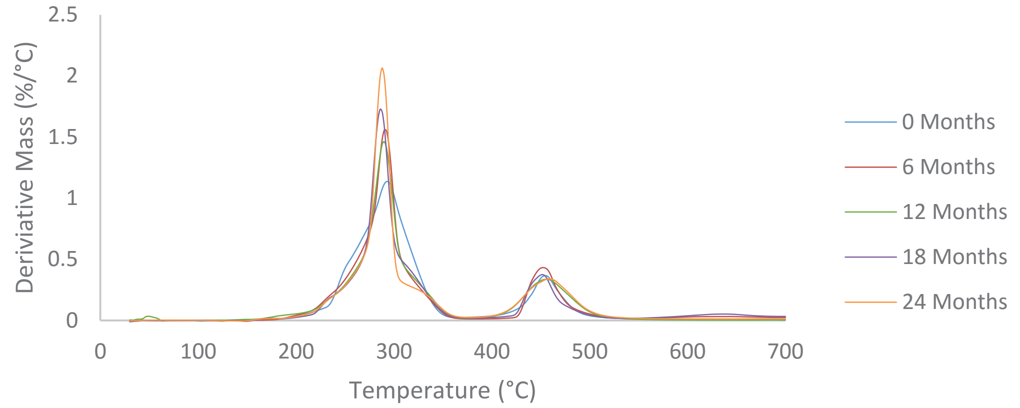


Figure 4.29 TG curve of PVC buried in a clay environment



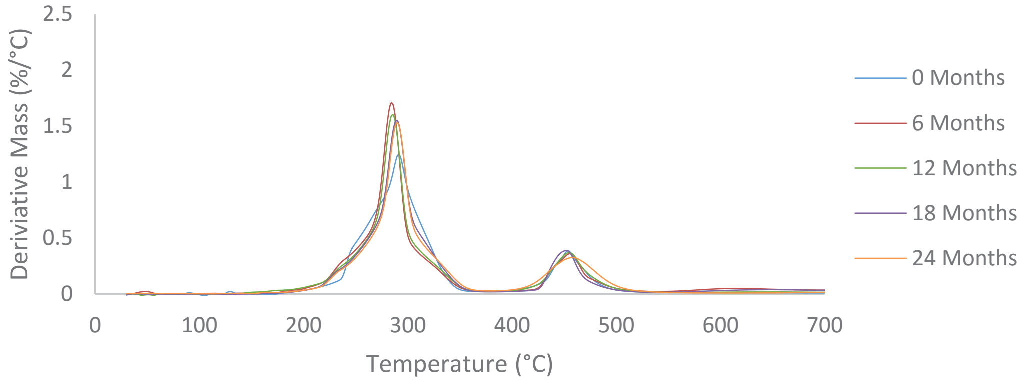


Figure 4.30 DTG curve of PVC after burial in clay (top) and loam (bottom) environment

The first stage peak in the DTG has been found in previous studies to be due to the dehydrochlorination of the PVC followed by the formation of polyenes and other hydrocarbons and point where the plasticiser was evaporated from the sample (Latorre et al., 2012; Shi et al., 2008). This showed consistent changes in the specimens from the sand, clay, lime, cold and basic environments similar to that observed in Figure 4.30 with a gradual increase in the height of the peaks as well as a corresponding reduction in the width of the peak (Kim, 2001; Latorre et al., 2012; Shi et al., 2008; Slapak et al., 2000). This increase in height and narrowing of the peak has been found to be due to the changes in the composition of the PVC (Karayildirim et al., 2006). When the PVC was more of a mixture, it forms a broader peak in the first stage due to the number of different reactions that are occurring. As the composition of the PVC changes, which in the case of this study would indicate plasticiser loss, the sample becomes more of a pure polymer sample leading to the peaks becoming sharper and with a height increase, since the number of the various reactions that occur at this stage have decreased. The specimens from the loam, wet and acidic environments show a different pattern in Figure 4.30. The peak at 0 months was much smaller and broader than the 6 month sample, which then decreases over time to 24 months. The dry environment specimen showed no consistent changes over the 24 month period in these peaks. From Table 4-2, the environments that produce the greatest changes in the polymer specimens during the first stage are observed to be the clay and lime environments followed by the cold, basic, acidic and wet environments. The environments that produce the least change are the dry, sand and loam environments.

The second stage of decomposition, which shows very little consistent change over time in all of the different environments, was attributed to various oxidative reactions that occur to the polyene chains formed in the first stage that leads to these undergoing scission (Shi et al., 2008).

Table 4-2 Changes in maximum of 1st stage peaks in %/°C

Environment	Slope ± standard error
Loam	$1 \pm 1 \times 10^{-2}$
Sand	$5 \pm 4 \times 10^{-3}$
Clay	$3 \pm 1 \times 10^{-2}$
Lime	$2 \pm 1 \times 10^{-2}$
Cold	$2 \pm 1 \times 10^{-2}$
Dry	$5 \pm 5 \times 10^{-3}$
Wet	$1\pm 1 \times 10^{-2}$
Acidic	$1 \pm 1 \times 10^{-2}$
Basic	$1 \pm 1 \times 10^{-2}$

4.6.2 Discussion

There was little change that could be seen in the TG curves when the environments were compared. In all of the environments there was a tendency that can be seen towards a decrease in the carbon residue left after the thermal decomposition of the PVC sample has occurred, however, the changes were found to be mostly consistent across all of the environments when the error of the samples was taken into account, with the exception of the dry environment which showed very little change to the residue level left.

Since TGA was a technique that looks at overall changes that can occur throughout the polymer as opposed to a surface technique that looks at change that occurs on the surface, it can be used to examine bulk changes (Prime et al., 2014). Any changes that occur to the 1st stage decomposition peak are attributed to plasticiser loss that has occurred throughout the whole sample (Latorre et al., 2012). Since the clay and lime environments produce the most change in the polymer when compared to the other environments this would indicate that these environments have lost the most plasticiser of the environment specimens investigated. This was consistent with the findings of the other techniques used in this study. However, the sand environment specimen, which generally shows changes in plasticiser content was found by TGA to show very little change. This was most likely due to the plasticiser loss in the sand environment only occurring on the surface of the polymer rather than through the polymer structure. This would allow these changes to be detect techniques more sensitive to surface changes such as IR spectroscopy but not by TGA, which was a technique that examine changes throughout the entire polymer (Sidwell, 2008). This would also indicate that the loss of plasticiser that was occurring to the specimens from the cold and basic environments was not only a surface process but was throughout the entire PVC samples within these environments (which although has been observed by TGA as well as other techniques to have low levels of plasticiser loss).

The specimens from the loam, wet and acidic environments show a different pattern when compared to the rest of the environments, with a large increase from 0 to 6 months in terms of the peak height and a corresponding decrease in the peak width and a subsequent decrease over time in peak height. It has been noted in the other techniques used that these particular environments show only low levels of change in plasticiser content. As seen in Figure 4.31 (showing the changes in the height of the first stage peak) after the initial change has occurred from 0 to 6 months there was very little change that occurs, although a slight decrease in the peak height can be seen in later months. This may be indicative of low levels of change in the plasticiser content of the PVC in these environments.

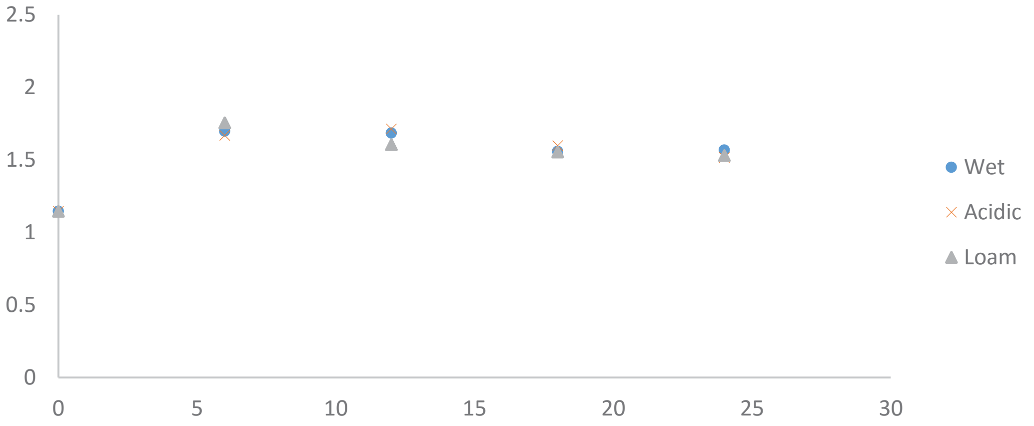


Figure 4.31 Peak height changes in the 1st stage of the DTG traces from PVC after burial in the wet, acidic and loam environments

While collecting data for the PVC samples using TGA, it was observed that there was variation that occurred among the duplicates for the DTG of these samples. It was noted that there could be up to 15% difference among the duplicates with most of them having values within 10%. This difference usually occurred in the 1st stage peak, while for the second stage peak usually there was good reproduction of the data as seen in the example in Figure 4.32. While this potentially can be caused by how well the instrument approximates the temperature of the sample, since this only affects one peak of the DTG it was more likely to be due to variations within the PVC mixture, particularly the plasticiser content, created during the manufacturing process (Kelsey and Foreman, 2000; Krauskoff and Godwin, 2005). While the variability of the plasticiser content throughout the polymer does not affect the degree of flexibility required to perform the assigned function, it can, however, affect where plasticiser loss could occur. Due to the inherent variability of the plasticiser within the PVC, only an approximation of changes that occur to this polymer can be seen and any small scale changes may not be due to plasticiser loss in the PVC samples but rather due to inbuilt variability of the PVC gel during manufacturing.

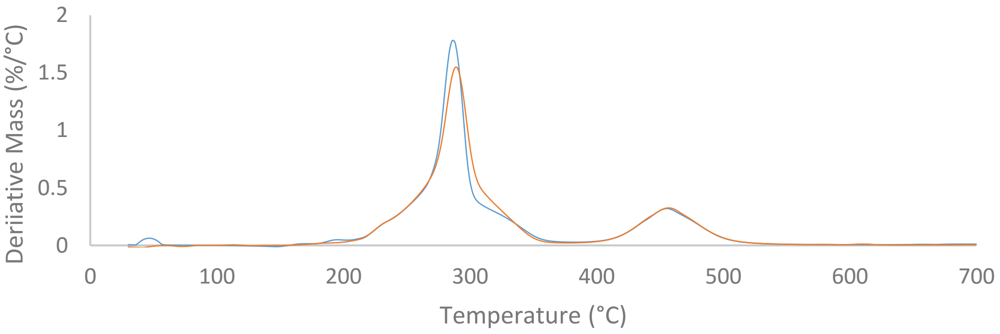


Figure 4.32 A comparison of PVC duplicates in the acidic environment at 6 months

4.7 UV/Vis Spectroscopy

4.7.1 Results

UV/Vis spectroscopy was used to analyse changes that occurred to the PVC, particularly changes to the plasticiser content and the formation of polyenes. Figure 4.33 shows an example of the UV-Vis spectrum obtained for pre-burial PVC with 3 peaks identified at 275, 221 and 210 nm. In order to see which of these peaks was due to the plasticiser, the plasticiser was extracted from the PVC and the spectrum of the extract was illustrated in Figure 4.34. This figure shows that the peaks that are due to the plasticiser only occur at 275 and 221 nm with the peak at 210 nm was due to a combination of the PVC and the plasticiser. This observation has been reported in a previous study that investigated the UV/Vis spectra of PVC showing that PVC in the plasticiser free state does not have any UV/Vis absorbing peak apart from 210nm (Hollande and Laurent, 1997).

In all of the PVC specimens, changes can be seen to occur to these spectra, with the clay environment specimen showing the most change overall. The greatest decrease was observed to occur to most of the specimens from the environments from 0-12 months with a noticeable change in the rate of the decrease between 12-24 months and with the specimens from the less reactive environments showing very little change from 12 to 24 months. The exception to this was the loam soil environment specimen, which shows very little change from 0-12 months and then a slight decrease in peak height occurring within 12-24 months.

Figure 4.35 shows a comparison of the 9 environments to the starting PVC in the 300-700 nm range. There was very little change seen to occur to the PVC from 300 - 700nm except for slight shift to the start of the first main peak in the spectra that can be observed in all of the environments as shown in Figure 4.35. There are some slight differences in absorbance that occur in most of the polymer specimens, however, there does not seem to be any correlation among the environments that otherwise show a tendency to remove the plasticiser from PVC and the changes in absorbance that occurs here. Since this region of the UV-Vis spectrum has been associated with changes to the polyene content of the PVC, it appears that there has been no degradation of the PVC itself and any changes that occur will be due to changes in the plasticiser content (Kip et al., 1992; Martinez et al., 1979).

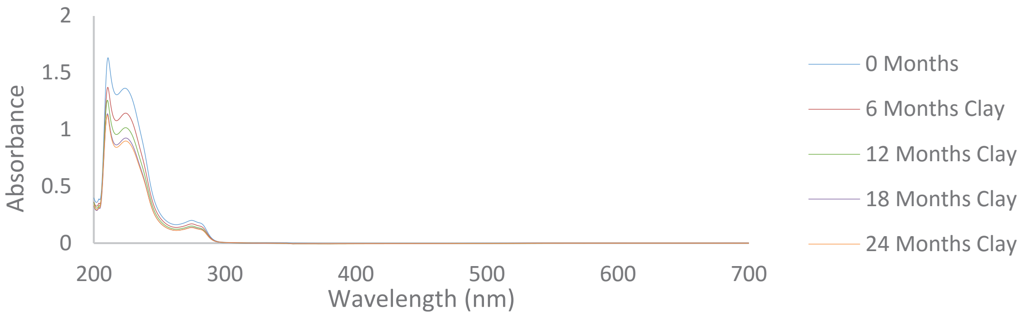


Figure 4.33 UV-Vis spectra of PVC in the clay environment from 0-24 months

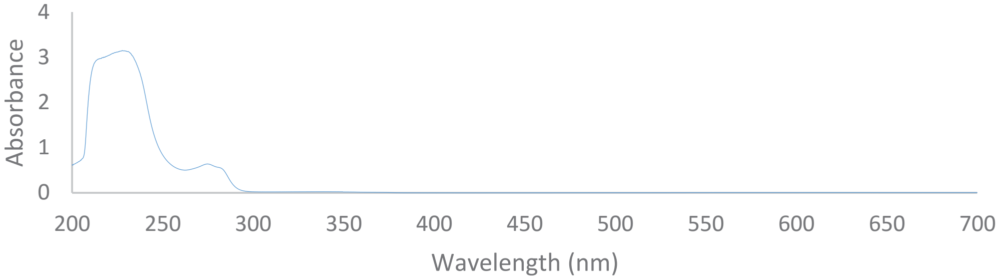


Figure 4.34 UV-Vis spectra of DEHP

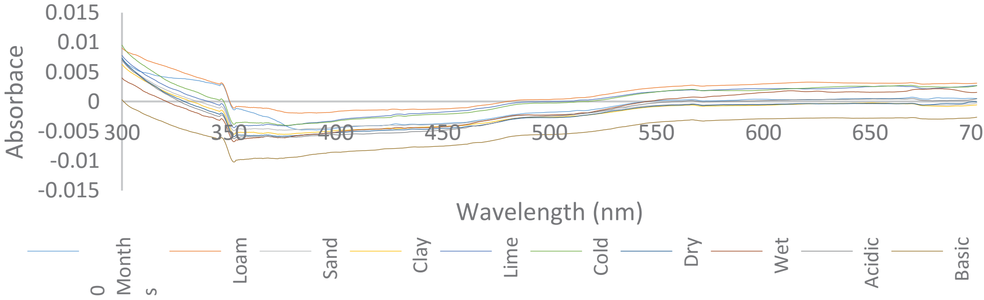


Figure 4.35 Comparison of the 9 environments at 24 months to PVC before burial using UV-Vis spectra (300 – 700nm)

The peak at 275nm was chosen for analysis as the peak at 221nm was too intense in the plasticiser only sample (Figure 4.34). The molar absorptivity of the DEHP at 275nm was found to be 1157 $Lmol^{-1}cm^{-1}$. This allows for the changes in plasticiser concentration over the 24 month periods to be examined as shown in Table 4-3.

Table 4-3 Changes in plasticiser concentrations in PVC as determined by UV-Vis Spectroscopy

Environment	Slope of Plasticiser ± Standard Error
Loam	$-5 \pm 3 \times 10^{-4}$
Sand	$-2 \pm 1 \times 10^{-3}$
Clay	$-3 \pm 1 \times 10^{-3}$
Lime	$-3 \pm 1 \times 10^{-3}$
Cold	$-2 \pm 4 \times 10^{-4}$
Dry	$-7 \pm 6 \times 10^{-4}$
Wet	$-1 \pm 1 \times 10^{-3}$
Acidic	$-5 \pm 4 \times 10^{-4}$
Basic	$-8 \pm 4 \times 10^{-4}$

4.7.2 Discussion

The results found from the UV/Vis indicate that the clay, lime and sand environments were the environments that leached the most plasticiser from the PVC with the wet and cold environments leaching the least. The acidic and loam environments produced very similar rates in terms of plasticiser loss. The dry environment produced similar levels of plasticiser loss in the polymer to the basic environment.

It can be seen from the standard error of the samples (taken from the standard error when compared to the linear trend line), that the environments that produced less change tend to have comparatively high levels of standard error when compared to the more reactive environments.

This variation was also observed for the other techniques used to investigate the degradation of PVC and explains why there can be variation in the order of the less reactive environments in how much plasticiser that was leached out. This large standard error was due to properties of the PVC itself, which includes variation in the plasticiser content of the PVC as well error found due to fitting fairly non-linear data to a linear trend line as the general trend of the plasticiser loss particularly in the less reactive environments, tends to not be linear with the R^2 values for a lot of the less reactive environments been below 0.5 as seen in Table 4-4.

Table 4-4 Comparison of R^2 values for the trend line of the changes in plasticiser in the PVC over 24 months

Environment	Linear trend line R^2 values
Loam	0.55
Sand	0.65
Clay	0.91
Lime	0.81
Cold	0.13
Dry	0.31
Wet	0.60
Acidic	0.39
Basic	0.53

The loam soil type environment with the most plasticiser loss was the wet environment indicating the slight tendency of the DEHP plasticiser to leach into water as has been seen by previous studies (Kastner et al., 2012). This, which mostly agrees with the data found on the other techniques, indicates that the presence of water in the environment has an effect on the desorption of the plasticiser from the PVC. However, it can be seen that the most reactive environments are actually the considerably drier lime and clay environments (which have higher levels of moisture present than the much drier sand environment) rather than the wet environment. This indicates that water content on its own was not the only factor affecting plasticiser loss. Another important factor to consider was also the ability of the environment to retain water around the PVC and it has been observed throughout this study that in the loam soil environments that moisture was lost to the atmosphere over the 24-month period. Previous studies have shown that the clay and lime soils have a tendency to absorb and hold water when compared to the loam soil indicating that the soil's ability to hold water was an important factor in the effect of soil on the amount of plasticiser lost (Nguyen and Marschner, 2014; Sébaïbi et al., 2003).

The spectrum for the basic environment shows a greater loss of the plasticiser when compared to the acidic environment. It has been seen in other studies that the DEHP plasticiser has a tendency to leach out of PVC in a basic environment while being preserved in an acidic environment (Hammad Khan and Jung, 2008; Magdouli et al., 2013). The spectrum of the dry environment was unusual as it seems to be indicating a higher loss of plasticiser than expected considering the moisture content and the ability to retain moisture seems to have a large effect on plasticiser loss. As it can be seen from both the R^2 and the standard error values that the dry environment does not fit the trend line so the possible variation in the data could be relatively large. This can also be seen with the cold sample and could indicate that when the plasticiser loss was too small that the variation of the plasticiser content in the PVC could have a greater effect on the amount of plasticiser observed then the actual amount lost.

4.8 Discussion

From the different techniques used to investigate the degradation of PVC in the various soil environments it can be seen that similar patterns occur indicating that the soil type has an effect on the loss of plasticiser for this polymer material.

From the UV/Vis and ATR spectra it was observed that there was no noticeable formation of polyenes occurring throughout this study. This was observed by investigating the polyene peaks in the ATR and the UV/Vis spectra between the 300-700nm where the polyene absorbance was known to occur. Neither of these spectral regions showed a change over time. This shows that the plasticiser loss was not due to the incompatibility of the plasticiser with polyenes but due to the interaction of the plasticiser with the environment. It can also be seen from the non-linear nature of the plasticiser loss with a greater rate of loss occurring towards the beginning of the 2-year burial period that the plasticiser loss was not due to an evaporation process (Singh and Sharma, 2008).

The environments that consistently produced plasticiser loss in the PVC are the clay and lime environments while the sand environment, which generally showed relatively high plasticiser loss when compared to many of the other environments showed very little change when examined using the TGA. This may be due to TGA been a bulk technique (Prime et al., 2014). This indicates that the plasticiser loss was only occurring on the surface of the PVC in the sand environment as opposed to the lime and clay environments, which lose plasticiser from throughout the entire sample.

In the loam soil environments, it was noted that the wet environment was generally observed to produce the higher rates of plasticiser loss in the polymer than the other environments that are variations on the loam soil one especially when compared to the dry environment. This indicates that water was an important factor in the loss of plasticiser from PVC. This could due to the removal of the plasticiser due to the water or the increase level of microbial life present in wet soil. The lime and clay soils were noted to have a greater tendency to remove the plasticiser from the polymer even though the amount of water present in these soils was much lower than the wet environment. Both the lime and clay environments have been noted to absorb water more easily than the loam soil used the in wet environment (Nguyen and Marschner, 2014; Sébaïbi et al., 2003). This allows water to be available for microbes in the lime and clay soil, which increases the microbial growth in these soils. The wet soil was also a good environment for enhancing microbial growth, however, due to the loam soil not being able to absorb water as well, the water in this environment moves to the bottom of the container. This movement of water removes the microbes from the polymer, reducing the ability of the microbes to degrade the PVC.

The acidic and basic environments observed different relative levels of plasticiser loss depending on the technique used. The ATR and the AFM shows the acidic environment having a greater loss of plasticiser than the basic environment, while the basic showed greater plasticiser loss in the TGA and the UV/Vis data. Both of these techniques are considered bulk techniques while the ATR and AFM are regarded as surface techniques. This may indicate the loss of plasticiser in the acidic environment was higher on the surface of the polymer allowing for greater changes than were observed in both the ATR and AFM, however, the plasticiser loss throughout the PVC must have been greater in the basic environment allowing for the greater loss of plasticiser to be observed in this environment. Previous studies have also shown that DEHP will be more likely to leave the PVC in a basic environment as opposed to an acidic one (Hammad Khan and Jung, 2008; Magdouli et al., 2013).

The cold environment generally showed very little change throughout the 2-year period, the only exception was observed for the TGA data, which showed the cold environment having similar levels of change as the basic environment. This indicates that temperature has a possibly reduces the removal of the DEHP from the PVC perhaps due to the reduced microbial action within this environment (Nakamiya et al., 2005; Pradeep and Benjamin, 2012). Since a warm environment was not examined however, this could be investigated in a future study.

Another important factor to investigate was the amount of error present in the data. It has been seen throughout the different techniques that the less reactive environments such as the dry, cold and acidic tended to show relatively high levels of error when compared to the more reactive environments such as the clay and lime. This was most likely due to the variation of the plasticiser present within the PVC itself. Since in the less reactive environments, the actual amount of plasticiser lost could be partially masked by the changes in plasticiser due to manufacturing rather than actual plasticiser loss occurring. This was noticed in most of the techniques particularly the infrared and UV-Vis spectroscopies and TGA.

4.9 Summary

This investigation into the degradation of PVC has found that when buried within a soil environment the main change that occurs over 24 months was the loss of plasticiser. There was no evidence of the formation of polyenes in the 24 months of soil burial. This indicates that the loss of plasticiser from PVC was due to the plasticiser interacting with the soil environments.

The environments that were observed to cause the greatest removal of the plasticiser from PVC were the clay and lime environments. This was due to these environments having the ability to absorb greater amounts of water from the atmosphere compared to the other soil environments. The wet environment generally had a greater impact on the plasticiser loss than the other loam soil environments, however, this environment had less of an impact than the clay and lime soils. This was most likely due to the movement of water through the soil. The dry and cold environments tended to preserve the plasticiser content indicating the importance of both temperature and water in the removal of the plasticiser. It was also observed that the basic environment caused greater plasticiser loss throughout the polymer while the acidic soil had a greater effect only on the surface plasticiser rather than the plasticiser content throughout the PVC. This effect was also observed in the sand environment where there was a considerable level of plasticiser loss detected on the surface of the polymer but little loss of the plasticiser occurred throughout the bulk of the polymer.

Chapter 5

Nylon Fibre Analysis

5.1 Introduction

Carpets are a likely source of material for the disposal or disguise of human remains. The most common carpet fibre type was nylon and its popularity was due to its excellent wear resistance (Yang, 2006). In this chapter commercial nylon carpet commonly used for residential purposes has been used as a model for the burial of nylon carpet in a clandestine burial situation.

Nylon was exhumed from the nine different soil environments over a 24-month period and the effects that these environments had on the polymer were examined using a number of techniques including SEM, ATR-IR spectroscopy and TGA. These techniques were found to be the most useful in obtaining information about the potential degradation of the nylon material during the burial process. SEM provides information about changes to the surface of the nylon fibres such as formation of cracks and pits. Other possible changes caused by degradation to the structure of the fibre include fraying and thinning of the polymer fibre. ATR-IR spectroscopy has been used to observe the changes to the various amide bonds within the chemical structure of nylon and the formation of imide bonds, which indicates that the degradation of nylon was occurring. TGA has been utilised to perform a preliminary study on examining the changes to the thermal stability and the polymer composition of the nylon fibres.

5.2 Characterisation

Infrared spectroscopy and DSC were used to confirm that the fibres obtained from commercially labelled nylon carpet were, in fact, made of nylon. IR spectroscopy confirms that the polymer used in this study was a type of nylon. Figure 5.1 illustrates the IR spectrum of the fibres before burial in the soil environments. The distinctive nylon bands are observed at 3294 cm^{-1} assigned to N-H stretching, 1633 cm^{-1} predominantly associated with C=O and also known as the amide I band and 1534 cm^{-1}mainly assigned to N-H deformation and also known as the amide II band (Nishikida and Coates, 2003; Vasanthan and Salem, 2001).

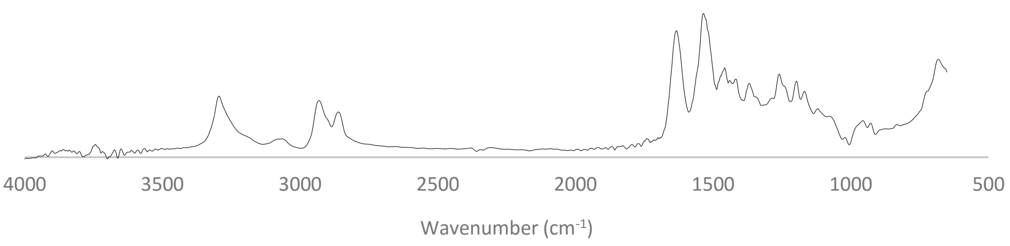


Figure 5.1 Infrared spectrum of nylon carpet fibres before burial in soil environments

There are many different types of nylon available with the most common nylons used in carpets being nylon 6 and nylon 6,6 (chemical structures are illustrated in Figure 5.2) (Burkinshaw, 2013). It was possible to distinguish between nylon 6 and nylon 6,6 with IR spectroscopy. The simplest means of distinguishing the two nylons was to examine at the band at 930 cm^{-1}, in nylon 6 this was a single band while in nylon 6,6 this band has a shoulder (Vasanthan and Salem, 2000, 2001). Figure 5.1 shows a single band in this region indicating that the polymer been analysed was nylon 6 as opposed to nylon 6,6.

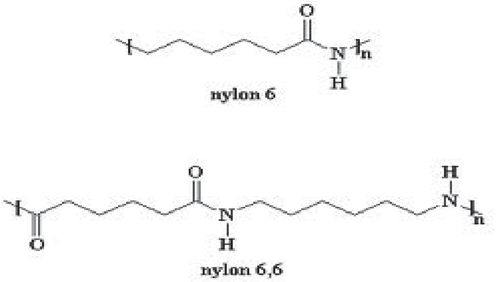


Figure 5.2 Chemical structures of nylon 6 (top) and nylon 6,6 (bottom)

In order to confirm the use nylon 6 fibres, DSC was used to provide the MP of the fibres. The DSC trace that was depicted in Figure 5.3 shows the MP of the nylon fibres to be 218.8°C, which correlates with the MP of nylon 6 at 220°C (Friedrich et al., 2007; Weber, 2011).

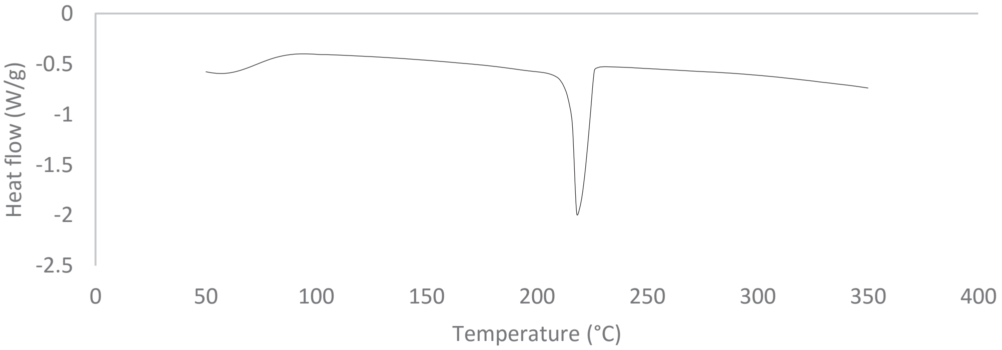


Figure 5.3 DSC trace of nylon before burial in soil environments

5.3 Scanning Electron Microscopy

5.3.1 Results

Changes to the surface morphology of the polymer surface over the 24-month period were examined using SEM. Signs of degradation in nylon fibres that are detectable by SEM include surface stripping, the formation of grooves and increased surface roughness (Friedrich et al., 2007; Parvinzadeh et al., 2009; Sudhakar et al., 2007). A typical micrograph of a nylon fibre prior to burial was shown in Figure 5.4. The surface appears smooth with minimal variation in texture across the surface. The morphology of the surface of nylon was examined every 3 months to look for signs of degradation.

Examination of the fibres after 3 and 6 months showed no significant changes occurring to the polymer surface in most of the soil environments, as illustrated in the examples given in Figure 5.5, which shows nylon in the sand environment at 3 and 6 months. The wet and acidic environments produced some fraying on the edges of some of the fibres in the nylon bundle, as seen in Figure 5.6, which depicts the nylon fibres in the acidic environment at 6 months. This, however, was not widespread throughout the polymer bundle with only a few fibres showing fraying occurring as also seen in Figure 5.6. By 9 months most of the specimens recovered from the soil environments show no change from 6 months, as seen in the example in Figure 5.7 that shows the nylon in the sand environment at 9 months. The specimens from the acidic and wet environments showed increased levels of fraying occurring to the nylon fibres when compared to the nylon at 6 months, as seen in Figure 5.8 showing the nylon in the wet environment at 9 months. The loam environment specimen also produced signs of degradation with minor fraying occurring to some of the fibres in the nylon bundle as shown in Figure 5.9, which depicts nylon fibres in the loam environment at 9 months. Like the acidic and wet environment specimens at 6 months, this fraying was not widespread throughout the polymer bundle with only a few fibres been affected.

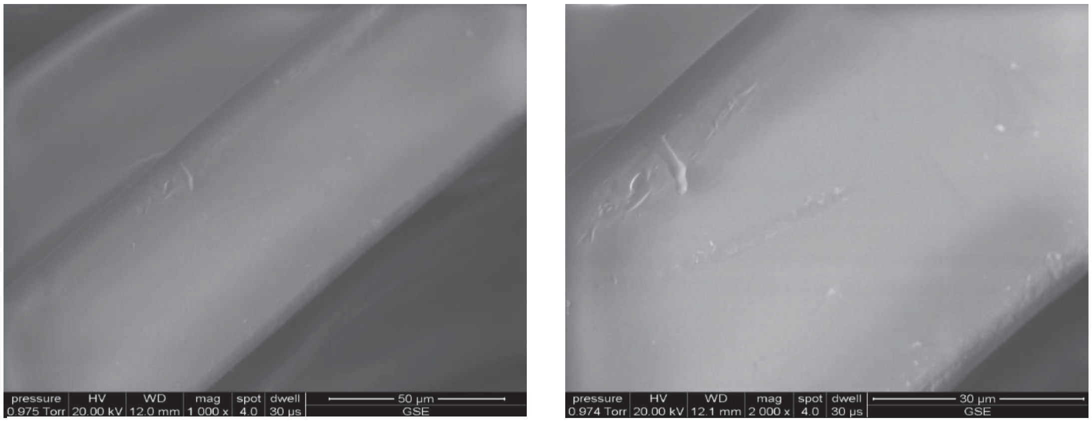


Figure 5.4 SEM micrograph of nylon before soil burial at a HFW of 149.1 µm (left) and 76 µm (right)

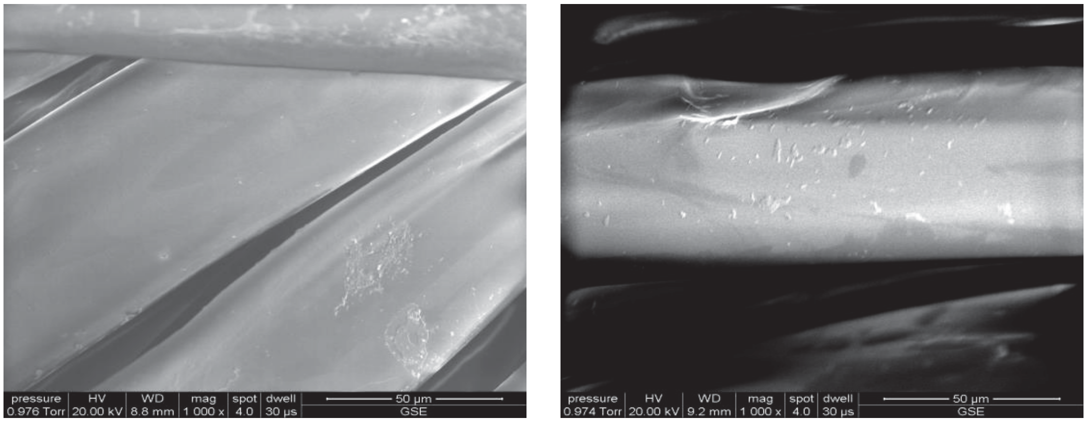


Figure 5.5 SEM micrograph of nylon after burial in the sand environment for 3 (left) and 6 months (right)

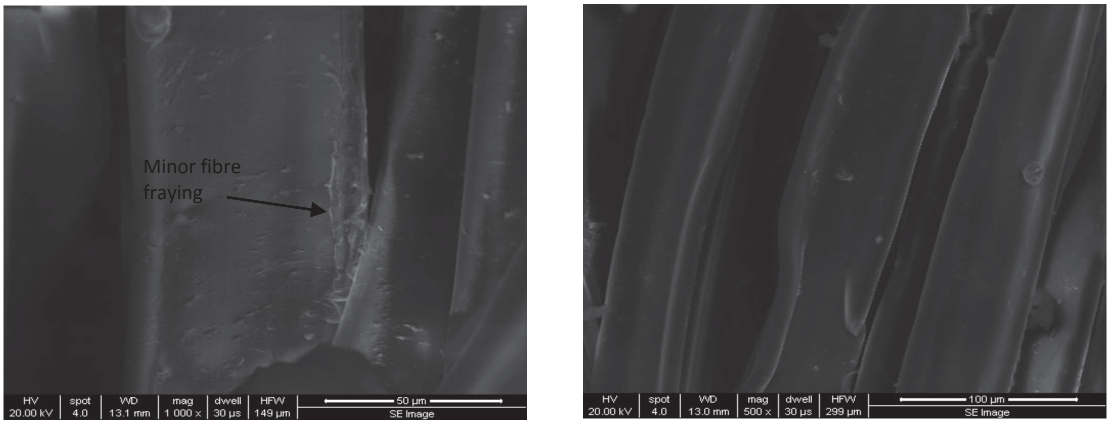


Figure 5.6 SEM micrograph of nylon after burial in the acidic environment for 6 months at a HFW of 149.1 µm (left) and 297 µm (right)

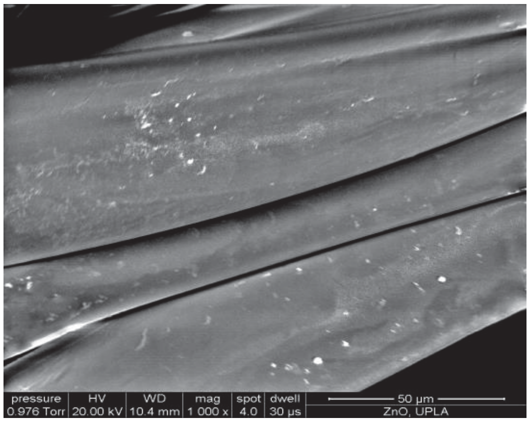


Figure 5.7 SEM micrograph of nylon after burial in the sand environment for 9 months

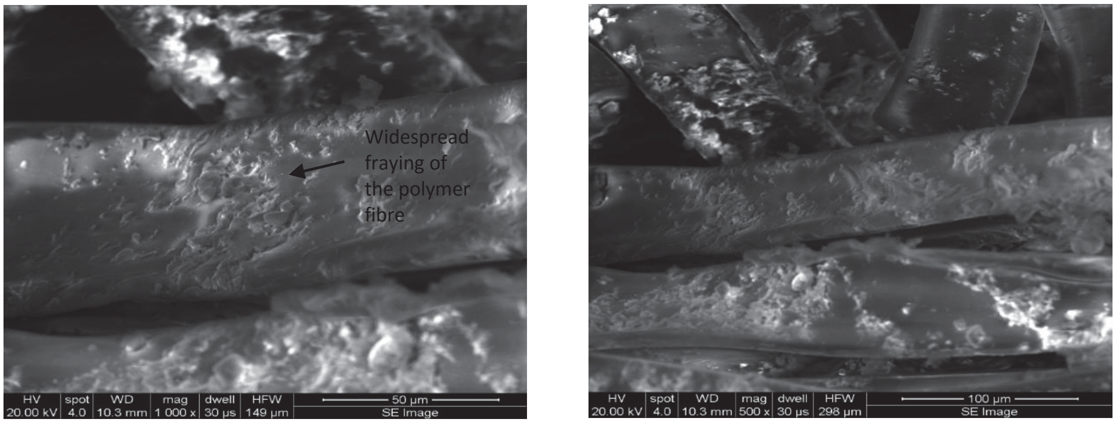


Figure 5.8 SEM micrograph of nylon after burial in the wet environment for 9 months with a HFW of 149.1 µm (left) and 297 µm (right)

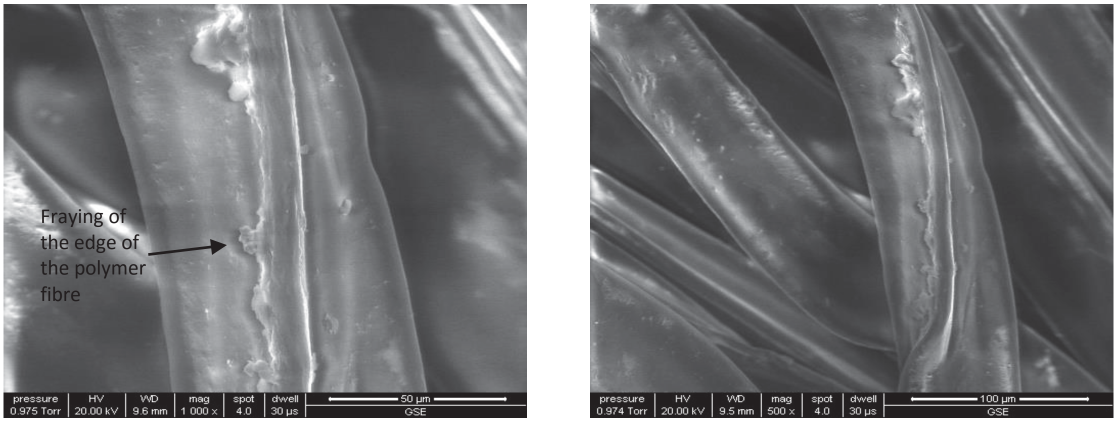


Figure 5.9 SEM micrograph of nylon after burial in the loam environment for 9 months with a HFW of 149.1 µm (left) and 297 µm (right)

By 12 months most of the specimens in the soil environments showed some indication of fraying with the wet, acidic, loam, sand and dry environments only showing minimal fraying occurring to a few fibres. Most fibres in these environments do not show significant change when compared to the fibres before burial, as seen in the example illustrated in Figure 5.10, which shows nylon in the loam environment at 12 months. The clay environment specimen also shows some evidence of minor fraying occurring throughout the nylon bundle as well as a built up layer that was mostly concentrated on the fibre edge as seen in Figure 5.11, which shows nylon in the clay environment at 12 months. The lime environment specimen does not show any signs of fraying, however, it can be seen on some of the fibres that some scale formation of the polymer surface was occurring, which can be seen in Figure 5.12 showing this formation on the nylon fibres in the lime environment at 12 months. The specimens from the cold and basic environments show no change from the polymer before soil burial.

The nylon fibres at 15 months are similar to the fibres observed at 12 months except for the specimens from the basic, cold and wet environments. The cold environment specimen still shows no indication of producing fraying, but there was evidence of colonies of microbial life forming on the fibre surface, as shown in the example given in Figure 5.13 for nylon in the cold environment at 15 months. The basic environment specimens show some minor fraying occurring while the wet environment specimens, along with fibre fraying, also indicates evidence of microbial colonies forming on the fibres. This can be observed in Figure 5.14, where the nylon fibres at 15 months in the basic and wet environments are shown. At 18 months most of the other environments also show evidence of microbial colonies on the polymer surface. Between 18-24 months, there was no evidence of an increase in the fraying of the nylon fibres or any other changes that have been associated with the degradation of nylon. The only noticeable change was the gradual disappearance of the microbial colonies on the nylon fibres that were noticed at 15 months on some of the fibres. Examples of the wet environment showing this change are provided in Figure 5.15, which shows the fibres in the wet soil at 24 months.

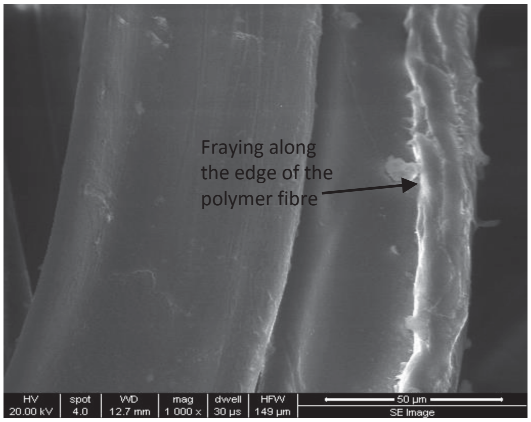

Fraying along the edge of the polymer fibre

Figure 5.10 SEM micrograph of nylon after burial in the loam environment for 12 months

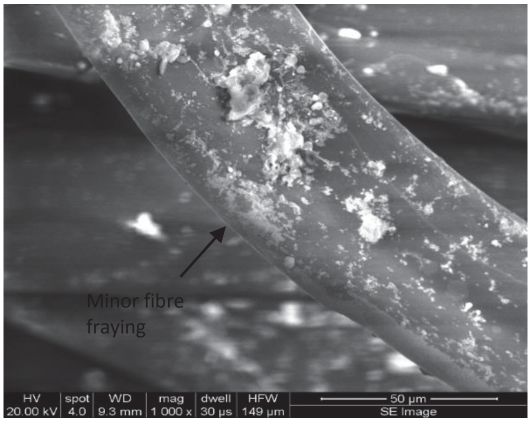

Minor fibre fraying

Figure 5.11 SEM micrograph of nylon after burial in the clay environment for 12 months

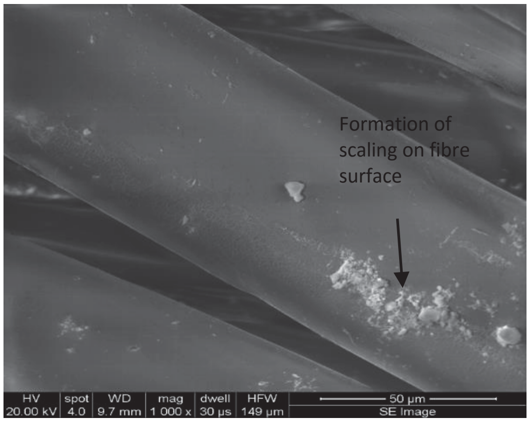


Figure 5.12 SEM micrograph of nylon after burial in the lime environment for 12 months

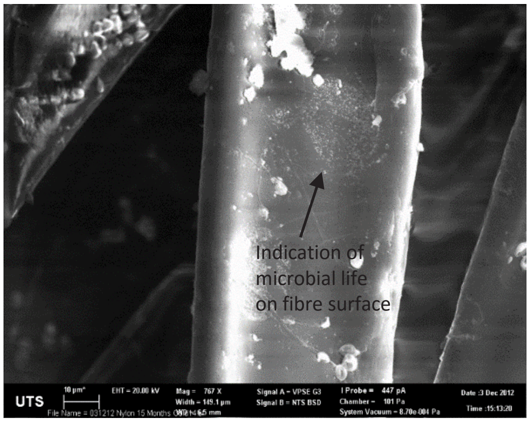


Figure 5.13 SEM micrograph of nylon after burial in the cold environment for 15 months

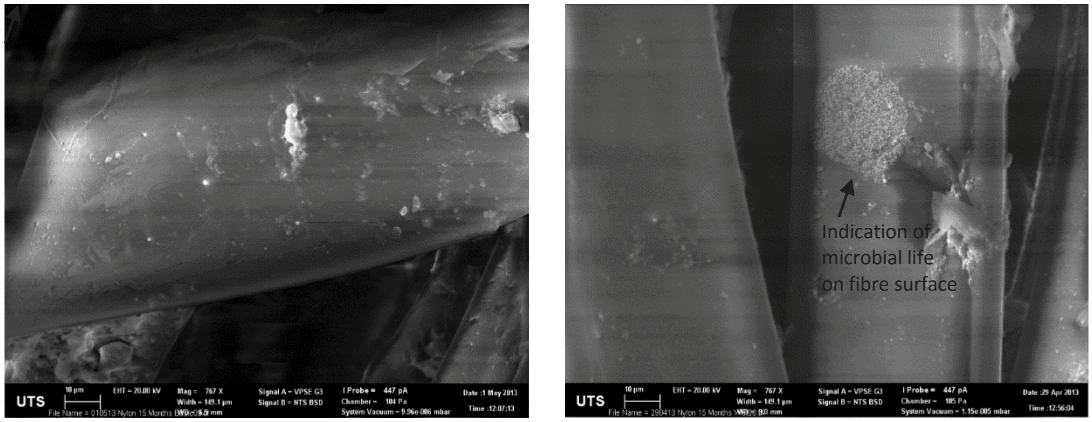

Indication of microbial life on fibre surface

Figure 5.14 SEM Micrograph of nylon after burial in the basic (left) and wet (right) environments for 15 months

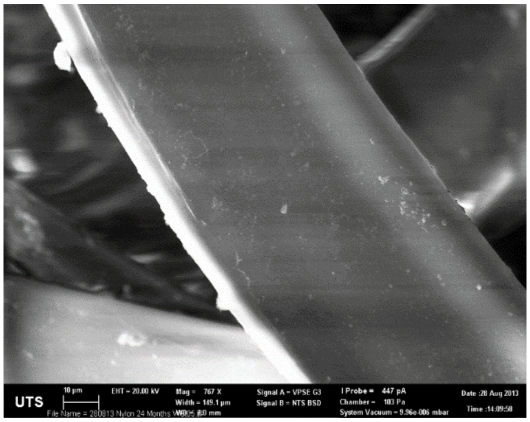


Figure 5.15 SEM micrograph of nylon after burial in the wet environment for 24 months

5.3.2 Discussion

The SEM micrographs of nylon have indicated that the early stages of the degradation of nylon can be observed. Fibre fraying was observed in most of the environments and this has previously been seen to indicate the first stages of nylon fibre degradation (Parvinzadeh et al., 2009). Since none of the other signs, such as the formation of horizontal grooves, were observed during the 24 months, this indicates that the degradation of the fibre did not progress to beyond the early stages. Towards the later months, microbial colonies were observed to have formed on the nylon fibres. Since the fraying of the fibres were noticed before the formation of these microbial colonies, this may indicate that the microbes did not cause the degradation of the fibre, but were able to extract resources from the fibre once degradation via chemical means had begun. This could lead to an increase in the degradation of the nylon fibres if given more time, but no further changes were observed in the 24 months of this study. It was noted that the fibre fraying that was observed was limited to only small sections of the sample with small clusters of fibres in each bundle fraying. This shows that the degradation of the nylon fibres was not widespread with most of the fibres in each bundle been observed to show little change from the polymer before burial.

The specimens that showed the greatest changes were the specimens from the wet and the acidic environments, both of these environments provided evidence of degradation occurring earlier in the polymer than all of the other environments. This agrees with previous research that has indicated that acidic and wet environments generally have the greatest impact on nylon (Lyu and Untereker, 2009; Scheirs, 2000). This was due to hydrolysis of nylon being accelerated in acidic and wet conditions. The basic, cold and dry environments were observed to have the least effect on nylon while all the other environments showed some change to nylon over time.

The nylon fibres were observed to have started degradation to varying degrees in all of the environments, but this degradation was very limited. This shows that nylon even in the most reactive environments was generally preserved in the soil environments with only minor changes being seen.

5.4 Fourier Transform Infrared Spectroscopy

5.4.1 Analysis of Infrared Band Ratios - Results

An analysis of the nylon fibres was carried out using ATR-IR spectroscopy. Several bands were investigated to see if the soil environments degraded the nylon fibres during the 24-month burial. The bands of interest were the amide I, II and A (located at approximately 3300 cm^{-1}) bands as changes occurring to these bands were previously noted to be a good indication of degradation that was occurring to nylon (Kiumarsi and Parvinzadeh, 2010; Wang et al., 2014). These bands were compared to the band at 1460 cm^{-1}, which has previously been identified as a suitable reference band (Arrieta et al., 2013; Bianchi et al., 2002).

Figure 5.16 shows the 2nd derivative spectra of nylon over 24 months in the 9 soil environments. It can be observed in Figure 5.16 that very little consistent noticeable changes can be seen to occur to the polymer in any of the soil environments over the 24 months. The amide I, II and A bands showed little observable change over the 24 months. There were no noticeable changes occurring to other bands that have been previously reported such as the bands within 1690 and 1800 cm^{-1} indicating imide formation or the formation of bands that can be attributed to CHO (2700cm^{-1}) or CH_3 (2022 cm^{-1}) (Sonal. et al., 2010; Thanki and Singh, 1998).

Figure 5.17 depicts the changes occurring to the 3 bands of interest over 24 months. It can be seen from Figure 5.17 that some change was occurring to the nylon in the 9 environments. The specimens from the lime and sand environments show the most change across the three bands while the cold, dry and basic environment specimens show the least. The amide II and amide A bands were generally seen to decrease over the 24-month period. The exceptions to this are the acidic and basic environment specimens, which both show an increase in the amide A band. In contrast, the amide I band absorbance, was observed to have a general increase in most of the environments except for the lime environment specimen, which showed a decrease. It was also observed in Figure 5.17 that in the specimens from the loam, clay, dry and acidic environments from 9-15 months that there was a noticeable increase that occurs to the amide II band. The basic, wet, cold and sand environment specimens also show a change at approximately 15 months, however, for these environments a decrease was observed rather than an increase. The lime environment also shows this feature, but it did not occur until 18 months.

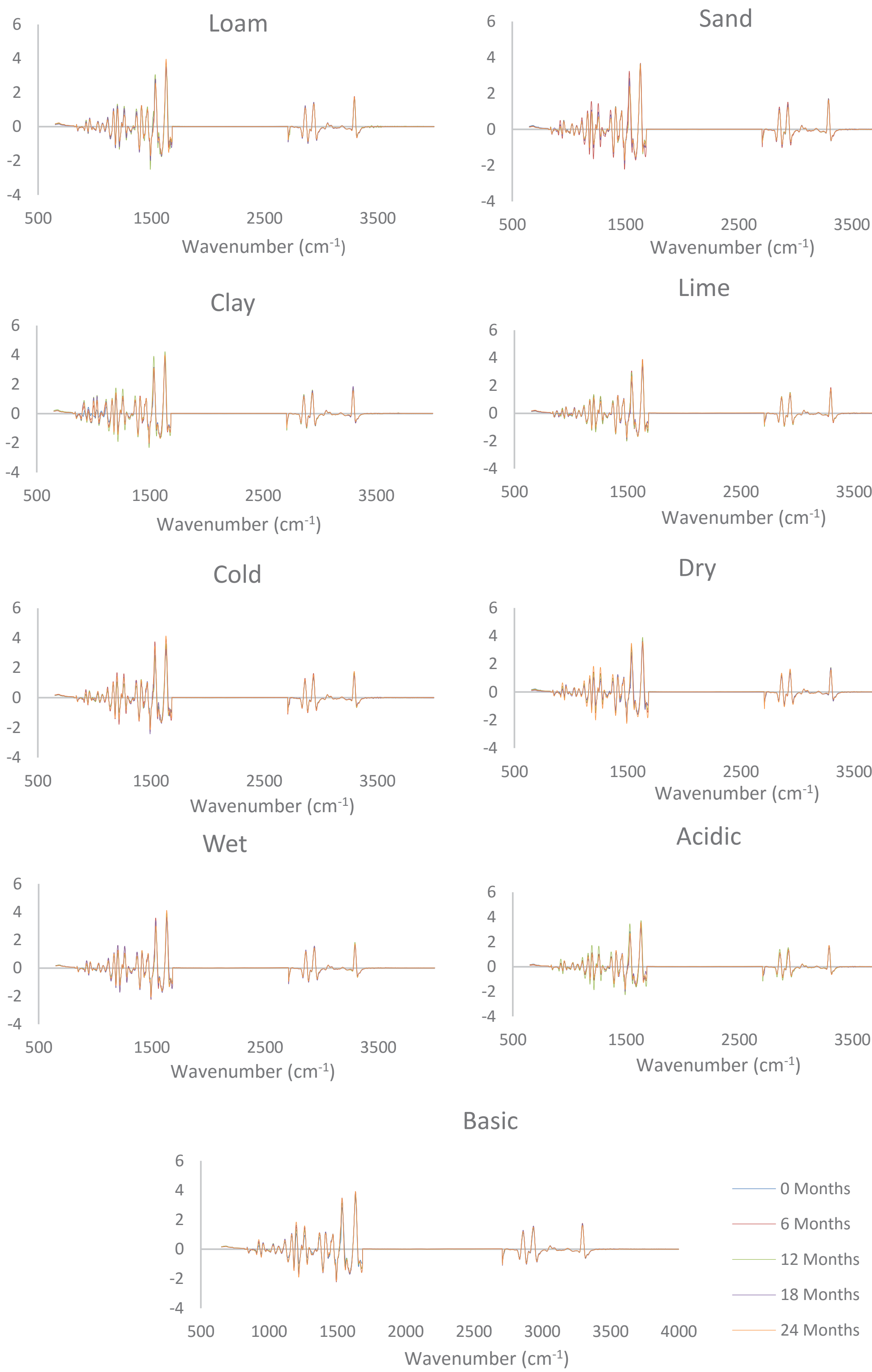


Figure 5.16 2nd derivative spectra of nylon in the 9 soil environments

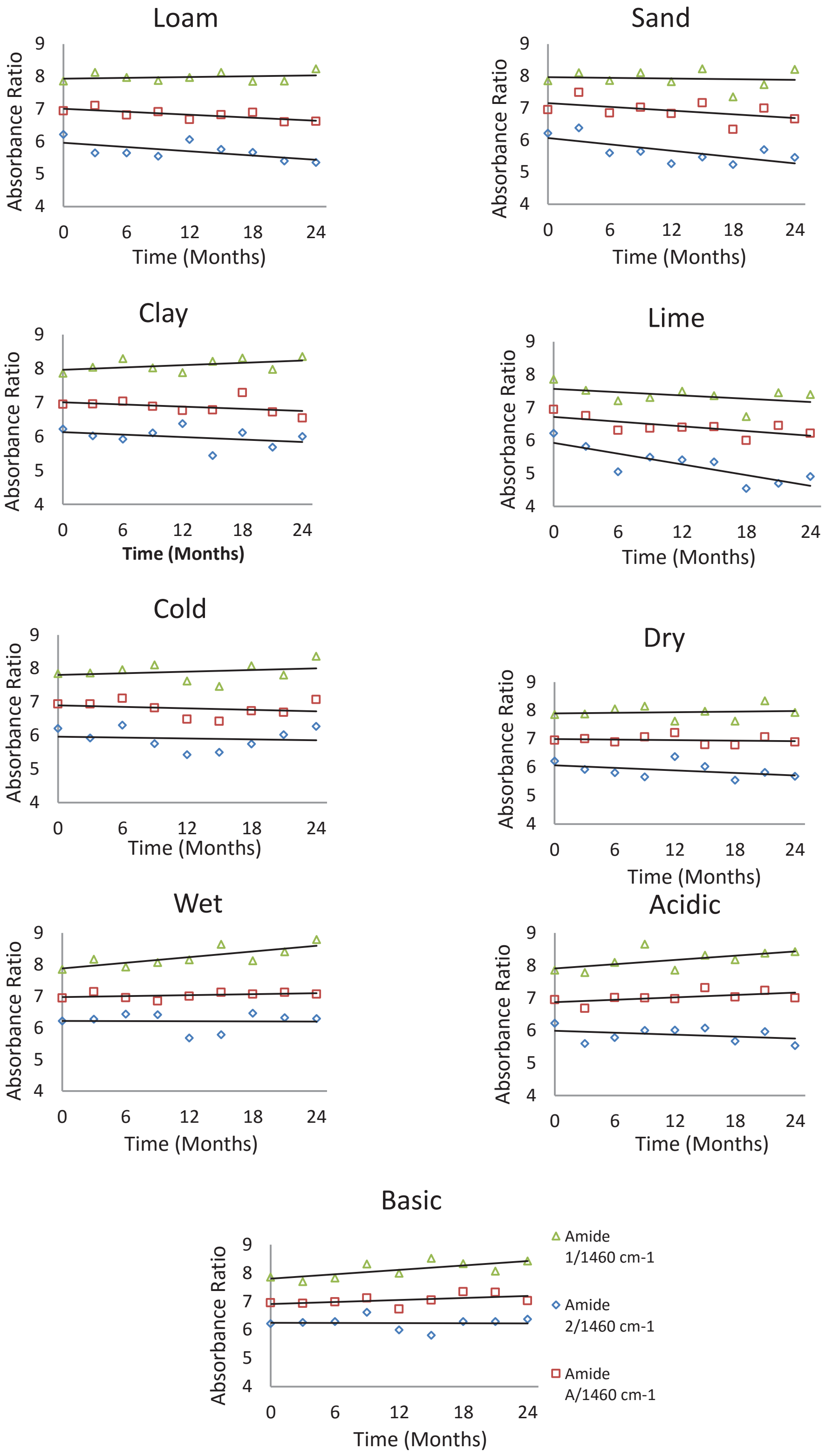


Figure 5.17 Changes to the amide I/1460 cm^{-1}, amide II/1460 cm^{-1} and amide A/1460 cm^{-1} mean band ratios in the 9 soil environments

From Table 5-1 the changes in the slopes of the band ratios can be observed. This confirms the observations made for Figure 5.17 with the specimens from the lime and sand environments producing the most change overall, while the cold, dry and basic environment specimens show the least. It can also be observed from Table 5-1 that the reactivity of the soil environments over the 3 bands of interest were generally not consistent. An example was the sand environment, which was a relatively reactive environment given the behaviour of the amide II and 3300 cm^{-1} bands, but was observed to be much less reactive based on the trend observed for the amide I band. The data from Figure 5.17 and Table 5-1 indicates that the different soil environments had very little impact on nylon, but with some slight changes were observable over the 3 bands of interest in the 9 soil environments.

Table 5-1 Band ratios and standard error (when compared to a linear trend line) for Amide I/1460 cm^{-1}, Amide II/1460 cm^{-1} and Amide A/1460 cm^{-1}

Environment	Amide I/1460 cm^{-1} ± Std Error	Amide II/1460 cm^{-1} ± Std Error	Amide A/1460 cm^{-1} ± Std Error
Loam	4 ± 6 x 10^{-3}	-2 ± 1 x 10^{-2}	-2 ± 1 x 10^{-2}
Sand	4 ± 10 x 10^{-3}	-3 ± 1 x 10^{-2}	-2 ± 1 x 10^{-2}
Clay	1 ± 1 x 10^{-2}	-1 ± 1 x 10^{-2}	-1 ± 1 x 10^{-2}
Lime	-2 ± 1 x 10^{-2}	-2 ± 0.9 x 10^{-2}	-5 ± 1 x 10^{-2}
Cold	8 ± 10 x 10^{-3}	-8 ± 10 x 10^{-3}	-5 ± 10 x 10^{-3}
Dry	4 ± 10 x 10^{-3}	-1 ± 1 x 10^{-2}	-3 ± 6 x 10^{-3}
Wet	3 ± 1 x 10^{-2}	-6 ± 10 x 10^{-4}	-5 ± 4 x 10^{-3}
Acidic	2 ± 1 x 10^{-2}	-1 ± 1 x 10^{-2}	1 ± 1 x 10^{-2}
Basic	3 ± 1 x 10^{-3}	-5 ± 10 x 10^{-4}	1 ± 1 x 10^{-2}

5.4.2 Analysis of Infrared Band Ratios - Discussion

It was observed for the amide I bands that there was a general increase in the intensity of these bands over the 24-month burial, except for the lime and dry environment specimens, which were observed to decrease in this time period. An increase in the relative amide I band intensity can occur during the degradation of nylon due to the breakage of the polyamide chains via hydrolysis, leading to an increase in the C=O bonds (Kiumarsi and Parvinzadeh, 2010). Most of the specimens show this increase to varying degrees with the wet environment specimen showing the greatest increase and the specimen from the basic environment showing the least. Since the wet environment has the greatest amount of available water, this environment was expected to have a greater impact on the nylon due to hydrolysis. The other environments are drier than the wet soil and less hydrolysis of the polymer was observed.

The lime soil produced a different trend by a relatively significant decrease in the intensity of the amide I band. Previous studies have indicated a decrease occurring to this band was due to both oxidation and hydrolysis of the polymer and cannot be used to distinguish if a different degradation type occurred in the lime environment (Sonal. et al., 2010; Sudhakar et al., 2007). It was possible that this decrease in the amide I band occurs due to the polymer absorbing water from the environment, forming a $C{=}O{\cdot\cdot}H_2O$ complex (Iwamoto and Murase, 2003). The formation of this complex would be expected to cause a wavenumber shift for the amide I band to a lower value. The ability of lime to retain water would accelerate this process as the extra water held by the lime soil would provide more water for this reaction (Sébaïbi et al., 2003). However, this was not seen in the clay environment, which also easily retains water (Rycroft and Amer, 1995). The basic nature along with the moisture absorption capabilities of the lime soil may be the cause of this trend. Nylon was known to be resistant to basic hydrolysis so the lime environment was expected to have little impact (Burkinshaw, 2013). It was also possible that there are other factors influencing the effect the lime environment has such as the interaction of the acid dyes with the lime soil (Burkinshaw and Son, 2008, 2010). Acid dyes contain carbonyl bonds that could potentially overlap with the amide I bond from nylon (Chakraborty, 2014). The decrease noted in the lime soil could be due to the reaction of the basic lime with the acidic dye causing the dye to leach out of the fibre. This trend was not repeated in the basic soil though indicating that both the acid dye reaction and the formation of the complex could cause the decrease in the amide I band.

The amide II band was observed to decrease over the 24 months in the 9 soil environments with the sand environment specimen showing the greatest change and the specimen from the basic environment showing the least. A decrease to this band has been noted to occur due to the breakage of the peptide bonds reducing the N-H bonds present (Parvinzadeh et al., 2009). The amide A was also observed to generally decrease over the 24 months except for the acidic and basic environment specimens, which showed an increase in the intensity. Since both amide II and amide A are both connected to changes in the N-H bond it would be expected that the changes to both of these bands would be similar. It can be observed in Table 5-1 that there was generally a match between the changes to the amide II and amide A bands with the sand and lime environments showing the greater changes to both bands, while the cold and the wet environments showed the least. The main difference in the two bands can be seen in the dry, acidic and basic environment specimens.

The results from the acidic and basic environments indicated that there was an increase in the intensity of the amide A band that was not observed in the amide II band. This could be for a number of reasons, but was most likely would be the additives commonly used in nylon carpet such as stain blockers and dyes (Burkinshaw and Son, 2008, 2010). The amide II band was mainly associated with N-H deformation, but there was some association of this band with N-H··H-O NH::OH_2 and N-H··O=C. An increase in these bonds could result from a reaction of the environment with the additives, particularly the acid dyes and the stain blockers commonly used in nylon. The acid dyes are likely to react with the basic soil forming products that cause a decrease in these bonds. Many commercial stain blockers are alkaline and would react with the acidic environment (Cooke and Weigmann, 1990)

The dry environment was seen to have a greater effect on the degradation of the polymer based on changes to the amide II band compared to the amide A band, where the dry environment was fairly unreactive. This result for the amide II band was not expected since previous studies have indicated that an environment with low levels of water should have little effect on nylon (Auerbach, 1989). The amide I and amide A bands also indicate that the dry environment had very little effect on the polymer. Since water was at a very low level in the dry environment, hydrolysis was unlikely to occur. This would indicate that the method of degradation that could occur in the dry environment would be oxidation. However, oxidation was extremely slow at room temperature without light to help initiate the oxidation process (Thanki and Singh, 1998).

The wet soil environment also produced an unexpected result as the amide I band trend indicated that the wet soil had a relatively large impact on the polymer, yet the trends for the amide II and amide A bands indicate that the wet soil had very little impact. The data obtained for the amide II and amide A bands may be due to the influence of the stain blockers commonly used in carpets (Burkinshaw and Son, 2008). This increase was due to the absorption of water as the band due to the OH deformation of water occurs at 1650 cm^{-1}. Since this overlaps with the amide I band, any increase to the band at 1650 cm^{-1} would result in an increase to the amide I band. Although there are stain blockers, which prevent the hydrolysis of nylon due to restrict the access of water to the polymer, some of the water in the heavily saturated wet environment would be able to reach the polymer.

As can be observed from the data, nylon showed very little signs of degradation and any degradation that was observed could be due to other factors such as the additives used during the manufacturing process. While the exact process causing the changes to the nylon fibres was not found, it does indicate that the effect of these environments on nylon requires future study, particularly in relation to the effects the various additives may have.

5.4.3 Multivariate analysis of spectra

Multivariate analysis was conducted on the IR results of nylon within the different environments. Both PCA and PLS-R were carried out in order to determine the strength of the data found by the ratio analysis of the IR data.

Figure 5.18 depicts the PCA plots investigating changes as a result of environment and time. The PCA results confirms that there has been very little change occurring to the spectra over time. This can be observed in both the environment and time PCA plots, which show no general change occurring dependent on environment or time. The data points for both are scattered throughout the plots with no trend away from the polymer before burial. This agrees with the ratio data discussed in Section 5.4.1 as it was observed that the changes that occurred to this polymer were minor even for the environments found to be the most reactive.

Using the pre-treated IR data from the nylon samples, a PLS-R graph was created with the loam environment used as a reference. In order to decide which model would be the most useful for the analysis of the nylon samples, the explained variance along with the loadings were investigated for the peaks of interest. The peaks of interest are the same bands investigated for the ratio analysis of the data; the amide A, amide I and amide II bands. The variance was used to investigate the suitability of the factors of interest, while the loadings were examined to determine which factors apply to the peaks of interest. From these observations, it was found that in order to investigate the nylon samples, factors 3 and 4 were useful for the analysis of the data.

It can be observed from Figure 5.19, which shows the variance across the different factors, that the similarity between the calibration and the validation curves was low across the 7 factors. The factors that were observed to show the greatest similarity among these 2 curves are factors 3 and 4. The loadings were then investigated for these factors to determine which of the peaks of interest are prominent in factors 3 and 4. Figure 5.20 shows the loadings for these two factors. It can be observed from Figure 5.20, that the amide I and amide II bands show prominently in factor 3, while the amide A band was more prominent in factor 4. The models for the nylon samples from these factors were used to investigate the strength of the polymer data.

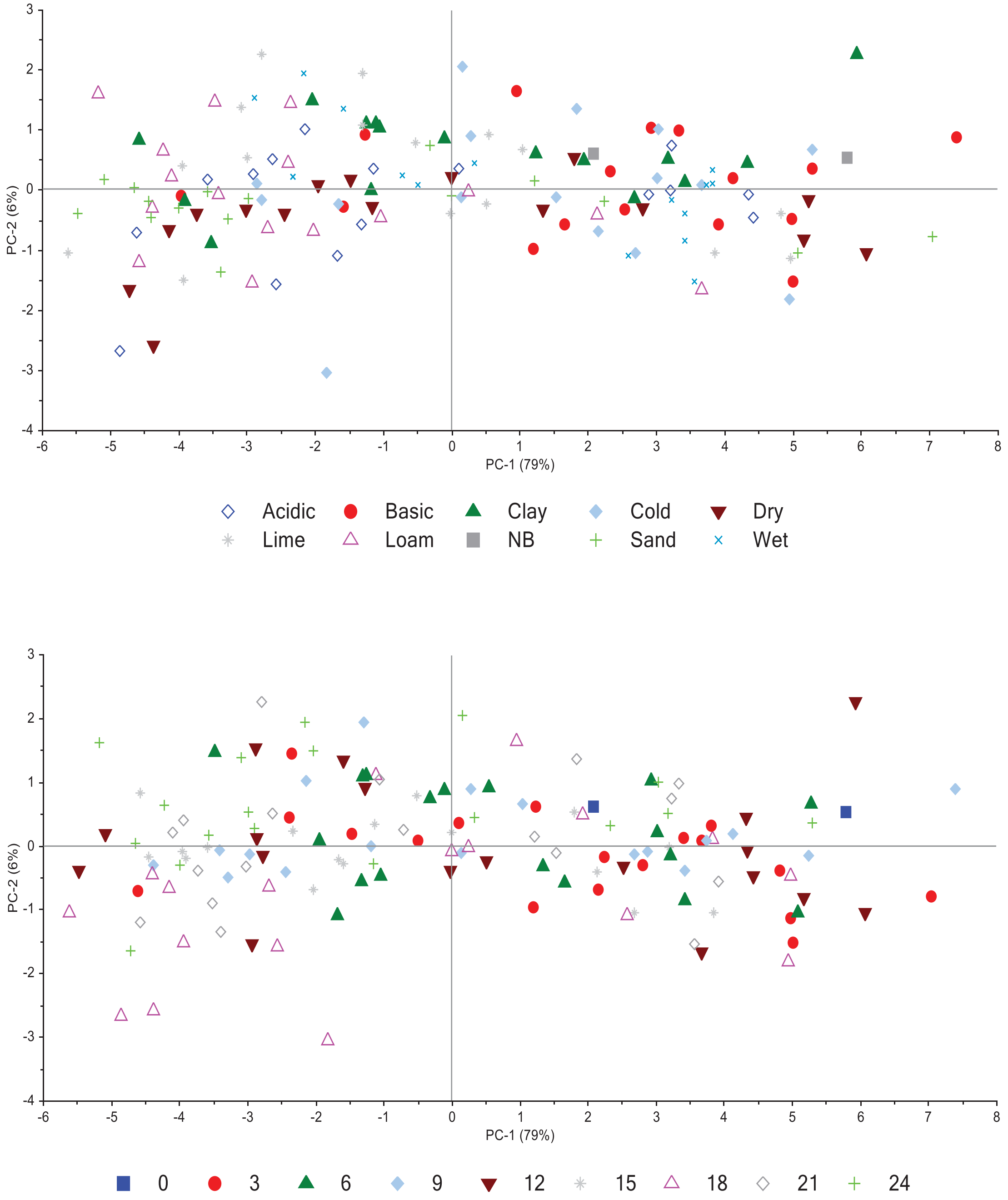


Figure 5.18 PCA plots of IR samples of nylon focusing on environment (top) and time (bottom)

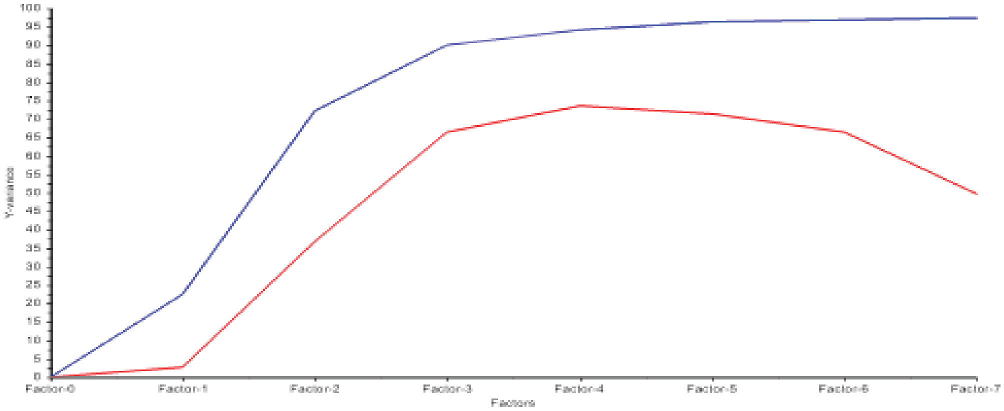


Figure 5.19 Explained variance of the PLS-R factors investigating the IR nylon samples

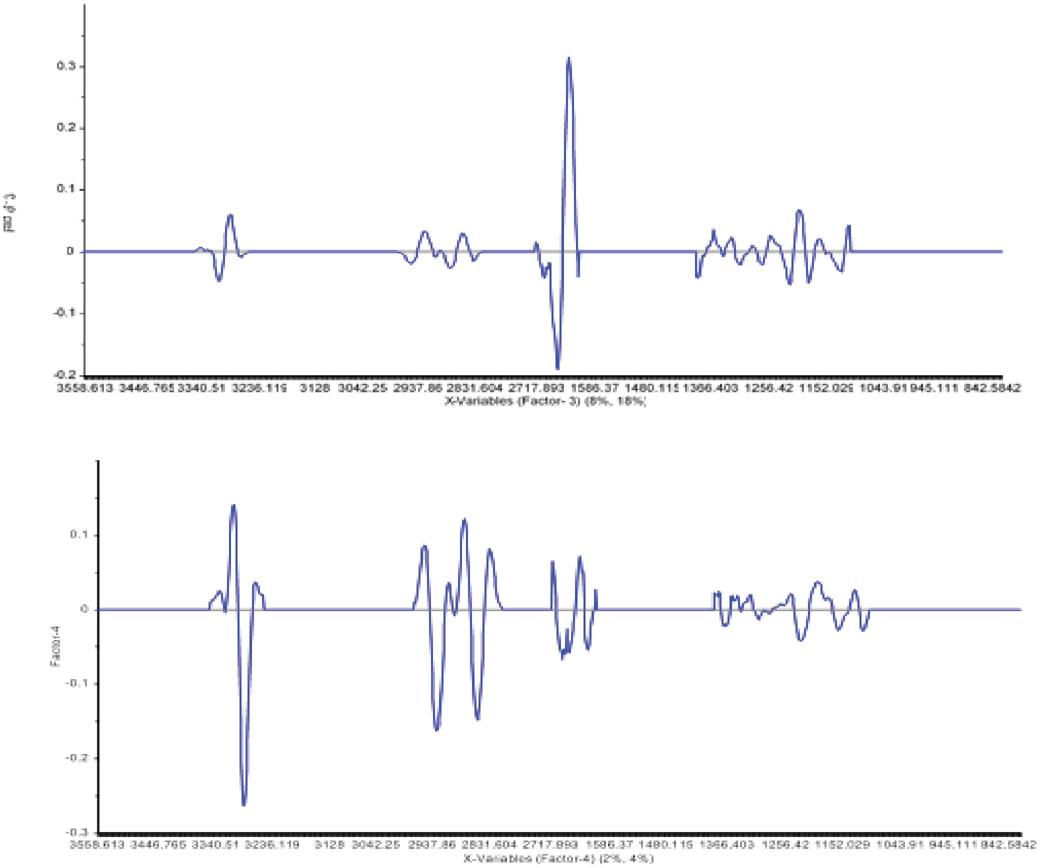


Figure 5.20 Loadings for factor 3 (top) and factor 4 (bottom) for the nylon IR samples

The PLS-R of the loam soil environment (acting as a reference) for both factors 3 and 4 was shown in Figure 5.21. It can be seen that the total R^2 for these models was 0.67 for the amide I and II bands while the R^2 for the amide A band was 0.74. The R^2 for the two models are close to each other and indicate that these models may be used as a satisfactory prediction model for the nylon. From Figure 5.21, it was observed that the models are fairly accurate for the first 9 months. From 15 months onwards, generally the model was a good prediction for nylon. However, it was observed that most of the data points after 9 months (12 months was removed due to large differences been observed among the duplicates) that the duplicates are not as close as the earlier months with larger variation within the duplicates been noticeable. Overall, however, the models indicate a satisfactory prediction for the three peaks of interest.

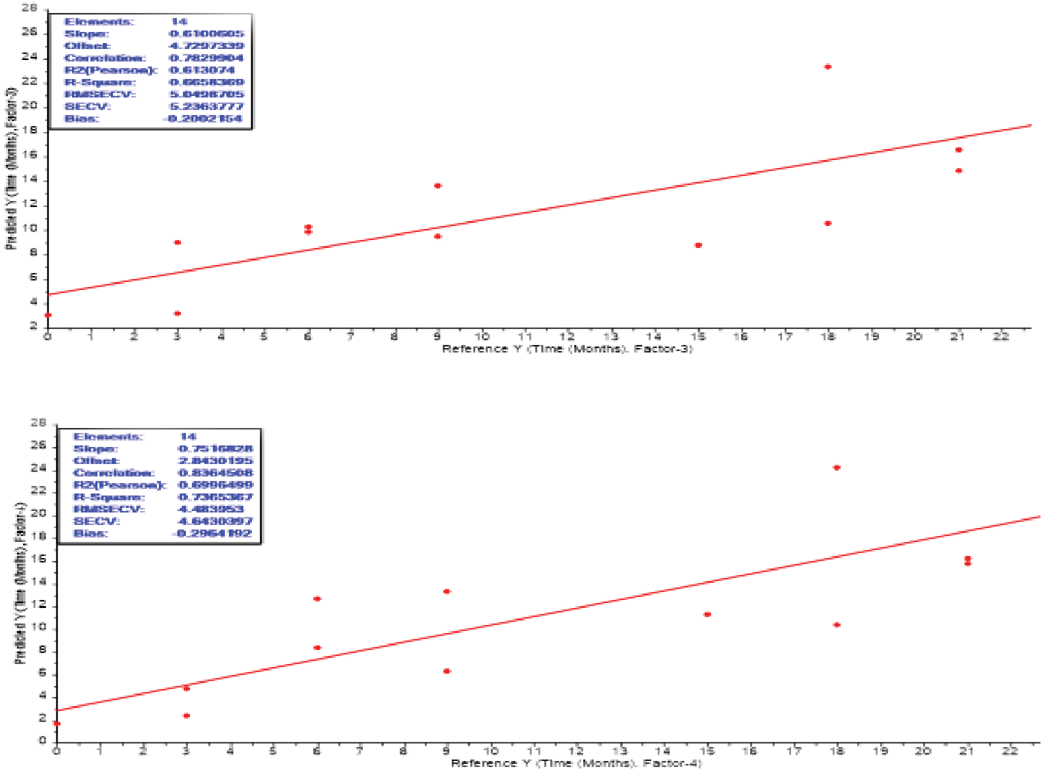


Figure 5.21 PLS-R graphs for the nylon in the loam environments looking at factors 3 (top) and 4 (bottom)

5.5 Thermogravimetric Analysis

5.5.1 Results

A preliminary study on the nylon fibres was run in order to observe whether TGA was a viable technique in the analysis of the degradation of nylon. The polymer before burial was compared to the polymer after been immersed in the soil environments at the completion of the 24 months.

Figure 5.22 shows the TG and DTG curves for nylon before burial in the soil environments. From the TG curve illustrated in Figure 5.22 it can be seen that the polymer follows a single step decomposition process that can be separated into three different regions known as the initial, main and char decomposition regions (Gashti et al., 2013). This decomposition process causes approximately a 97% mass loss leaving about 3% as a carbon residue. The DTG curve indicates that the peak maximum for the greatest mass loss rate occurs at 450°C.

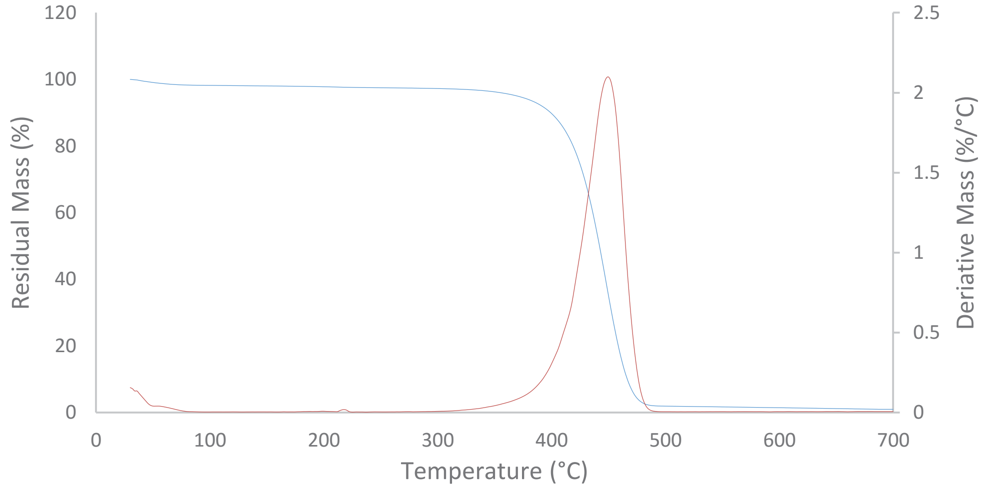


Figure 5.22 TG traces of nylon before soil burial

In Figure 5.23, a comparison of the TG traces before burial and after 24 months in soil for nylon was illustrated. From Figure 5.23, it can be seen that most of the environments show little change in the TG trace. The exception to this was the acidic environment which shows a substantial decrease in the temperature at which the mass loss occurs at 24 months while most of the environment specimens show very little difference from 0 and 24 months. Figure 5.24, which shows the TG traces of the polymer from acidic environment from before burial to after 12 and 24 month soil burial. The nylon specimen after 12 months of burial in the acidic soil was examined so it could be determined whether there was a viable trend. A gradual decrease can be observed to occur over increasing time.

The DTG curves for the nylon fibres in Figure 5.23 also confirm that most of the soil environments had very little impact on the polymer. The exceptions to this were the specimens from the sand, lime, acidic and wet environments, which were observed to have more impact on the nylon fibres, with the lime and acidic environments showing the greatest change over the 24 months. In the specimens from the lime, sand and wet environments, this change was seen as an increase in the height of the DTG peak along with a larger shift towards lower peak maximum temperatures. In order to confirm these changes, the 12 month samples were run for the sand, lime, wet and acidic environments (as observed in Figure 5.25). The acidic environment specimen was the exception, however, as it was observed that a decrease to the height of the DTG peak. Like the specimens from the lime, sand and wet environment, the acidic environment specimen also had a decrease observed in the temperature of the peak maximum.

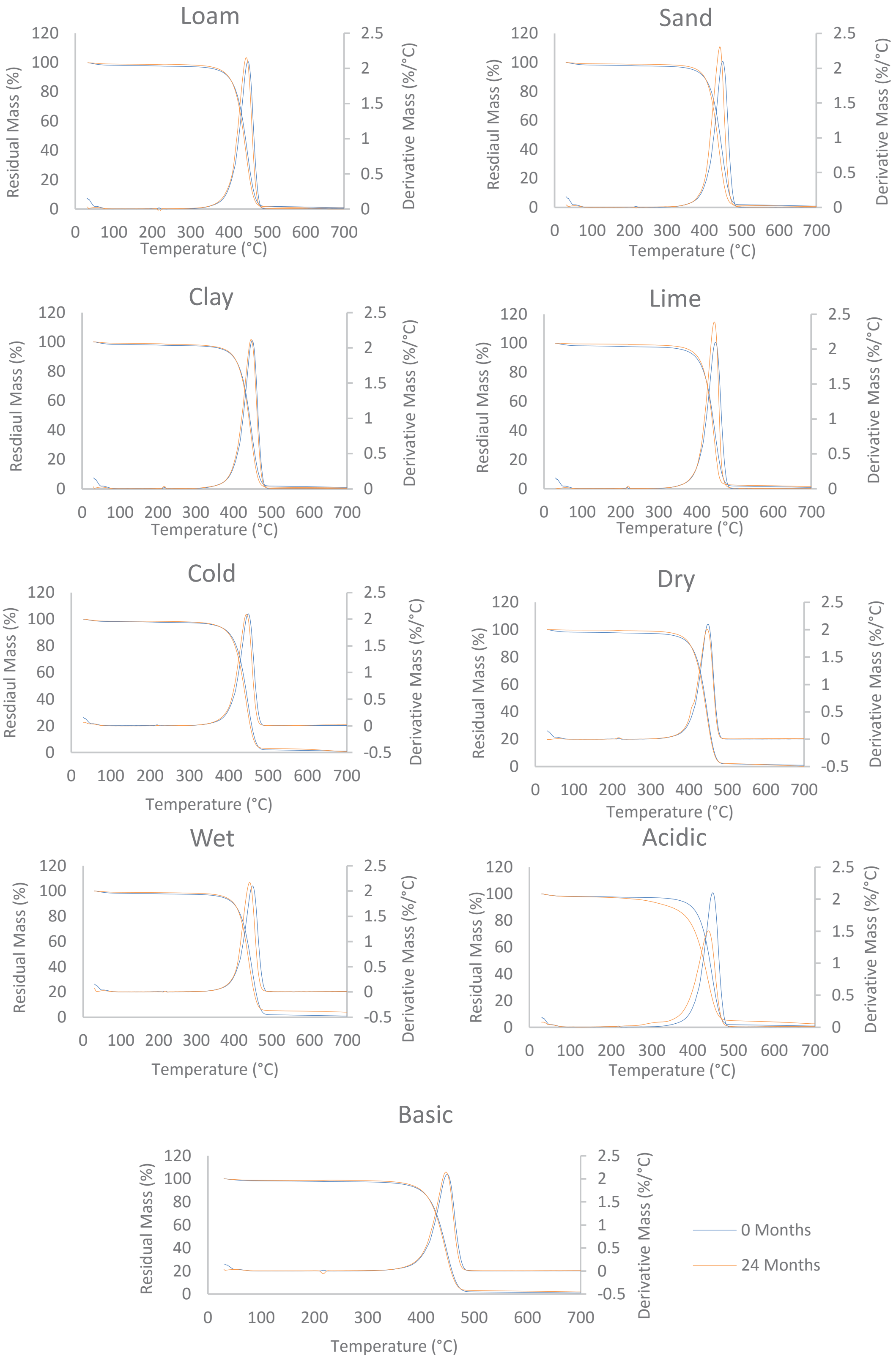


Figure 5.23 TG traces comparing the nylon fibres before burial to fibre burial for 24 months

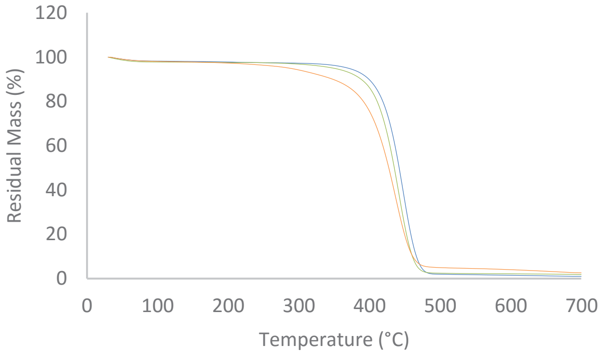


Figure 5.24 TG curve of nylon from the acidic environment comparing 0 and 24 months

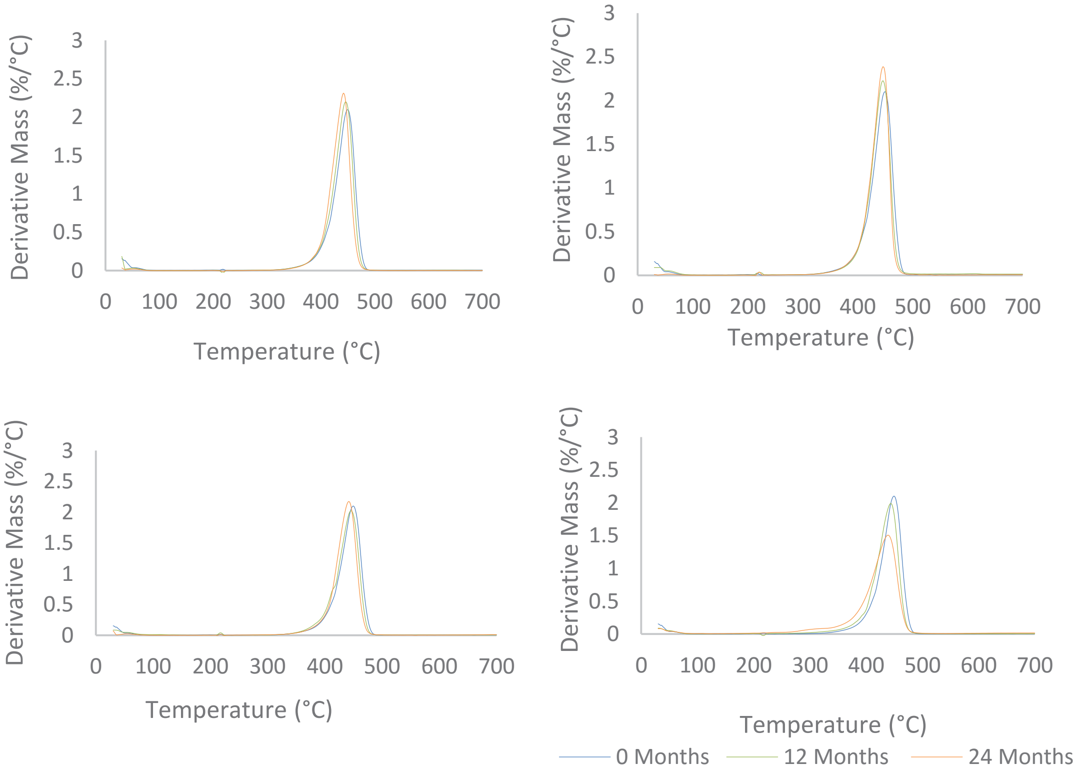


Figure 5.25 DTG curves of nylon in the sand (top left), lime (top right), wet (bottom left) and acidic (bottom right) environments comparing 0, 12 and 24 months

5.5.2 Discussion

The lime, acidic, wet and sand environments were observed to indicate that degradation was occurring over the burial time while the rest of the environments in this preliminary study were observed to show very little change occurring to the polymer. It was observed that in the TG curve of the specimens from the sand and acidic environment showed a shift towards mass loss occurring at lower temperatures that was not observed with either the lime or wet environment. Any shift in temperature has previously been associated with the carbonyl and amide groups present in nylon, particularly the ionic and hydrogen bonds that these groups form (Gashti et al., 2013). The decrease in the onset temperature of the decomposition curve has been previously noted to indicate a reduction in the intermolecular bonds of these groups in the amorphous regions, which in turn shows that the degradation of nylon was occurring (Nam et al., 2011). Since the sand soil was the only environment that produced such changes to the TG curve, this would indicate that this environment was the only one to have changes occurring to these bonds in the amorphous regions throughout the entire polymer. However, his finding does not rule out that these changes are not occurring in any of the other environments. As TGA was a bulk technique and was best suited for detecting changes throughout the whole polymer, it would not show similar changes occurring to the nylon in the other environments if it only occurred in small sections of the polymer such as the polymer surface (Gooch, 2006).

While the TGA indicated that only acidic environment specimen was degrading, it was observed in the DTG curves that all of the environments produced some sign of possible degradation demonstrated by a decrease in the temperature at which the peak maximum occurs. This can be seen in Table 5-2 which shows the difference in the temperatures that the peak maximum occurs with the 0 and 24-month nylon samples. This decrease in the temperature has previously been attributed to a reduction in the amount of hydrogen bonds in nylon indicating possible degradation of the polymer was occurring as the hydrogen bonds break when nylon was degraded (Nam et al., 2011). From Table 5-2, it can be seen that the specimens from most of the environments show similar changes to the temperature except for the sand, acidic and wet environment specimens, which show approximately double the change of the other environments.

Table 5-2 Shows difference in the DTG peak maximum temperature shift between 0 and 24 months

Environment	**Difference in peak maximum temperature (°C) ± Standard Error**
Loam	4 ± 2
Sand	8 ± 3
Clay	3 ± 1
Lime	4 ± 3
Cold	5 ± 3
Dry	3 ± 1
Wet	8 ± 1
Acidic	10 ± 1
Basic	3 ± 1

Another indication of degradation according to the DTG curves was a change to the peak maximum (Burlett et al., 2002). The lime, wet and sand soils were the environments observed to show a significant increase to the peak maximum over the 24 months. Most of the other environments specimens showed a slight increase occurring the peak maximum, but these were found to be very close to each other (except for the clay environment which was significantly lower). This can be observed in Table 5-3, which shows the difference in the peak maximum height of the nylon in the 9 soil environments). It has been previously observed that the presence of other components in nylon such as additives, decreases and widens the decomposition peak when compared to pure nylon (Jha and Bhowmick, 1998). In the nylon used for this study, these other components would most likely include additives used during manufacturing such as stain blockers and dyes (Burkinshaw and Son, 2008, 2010). Since an increase in the decomposition peak height was noted, this would indicate the reduction of other components in the nylon fibres. Since the lime, wet and sand soils produce an increase in the decomposition peak, this indicates that in these environments, the additives in nylon are been lost over burial time. An increase in the DTG curve has also been associated with a decrease in the crystallinity of the polymer indicating possible crystallinity decrease in the lime, sand and wet environments (Hanna, 1984). The exception was noted to be the specimen from the acidic environment, which showed a significant decrease to the decomposition peak. This indicates that the nylon recovered from the acidic environment had an increase to the components present within the fibres as opposed to the decrease noted in the other environments. It appears that in the acidic environment, rather than additives being leached out into the surrounding soil, that a reaction was occurring with the acid in the soil forming a new component on the fibres.

Table 5-3 DTG peak maximum shift between 0 and 24 months for the nylon fibres

Environment	**Difference in DTG peak height (0-24 months) ±Standard Error**
Loam	$-5 \pm 10 \times 10^{-2}$
Sand	$-2 \pm 1 \times 10^{-1}$
Clay	$-2 \pm 10 \times 10^{-2}$
Lime	$-3 \pm 1 \times 10^{-1}$
Cold	$1 \pm 10 \times 10^{-2}$
Dry	$1 \pm 10 \times 10^{-2}$
Wet	$-1 \pm 20 \times 10^{-2}$
Acidic	$6 \pm 2 \times 10^{-1}$
Basic	$-4 \pm 20 \times 10^{-2}$

It has been demonstrated that all of the environments show some slight signs of degradation with changes to the hydrogen bonds present in the nylon fibres decreasing over time. The wet environment showed the greatest indication of the reduction of hydrogen bonding occurring. This agrees with previous studies as the wet environment should make nylon more susceptible to hydrolysis due to the abundance of free water available (Lyu and Untereker, 2009). The clay, lime and loam environments are very similar in the effect that these environments had on the nylon, with the loam having the greater effect on the polymer. The loam soil has been noted previously to have less of a tendency to absorb water when compared to the clay and lime environments thus allowing greater amounts of water to be available for the hydrolysis of the polymer (Nguyen and Marschner, 2014; Sébaïbi et al., 2003). While the basic environment was similar to the loam soil in terms of water absorbance, it has previously been observed that basic environments tend to have a preserving effect on nylon, as the polymer has previously been noted to be resistant to alkaline hydrolysis (Burkinshaw, 2013). The sand environment was unusual as this environment was dry. The increased effect this environment has on these hydrogen bonds may be due to sand being less likely to retain water than the other environments (Conklin, 2005a). This would allow the nylon greater access to most of the water that was present within the soil allowing hydrolysis to occur even though there was less moisture present in the sand soil.

While all of the environments showed some indication of change to the hydrogen bonds present in nylon, only the sand, acidic, lime and wet environments were observed to have a significant effect on the additives present in nylon. There are many possible additives used in the manufacturing of the nylon carpet fibres such as stain blockers, acid dyes, and soil retardants. The number of different additives present within the nylon fibres makes it difficult to investigate which additive was interacting with the soil environment. However, it can be observed from the data that the most of the environments seem to have a similar effect on the hydrogen bonds as can be seen with the additives. It was possible that the hydrolysis of nylon was causing the additives to become incompatible with the polymer causing leaching of the additives. The exceptions to this are the lime, clay and basic environments. From Table 5-3, it can be observed that the lime environment had the greatest effect on the additives and the basic environment was noticed to have an increased effect on the additives then when compared to the effect on the hydrogen bonds. Since both of these environments are alkaline, there may be a reaction with the acid dyes commonly used in nylon (Burkinshaw and Son, 2010). The pH of the clay environment was found to be slightly acidic and if the acid dyes are the additive that was been leeched out, the clay environment would be less likely to react with the additive.

It was seen from the TG data, that the acidic environment had the greatest overall impact on nylon with the sand, lime and wet environments also showing significant levels of change. Most of the environments were found to have little effect on the polymer. The changes seen in this preliminary study indicate that future investigations into the use of this technique for nylon buried in soil could provide further information about the effects these environments have on nylon.

5.6 Discussion

Nylon was observed to be resistant to degradation in the 9 soil environments. This was believed to be due to the additives used for the carpet fibres during the manufacturing process (Burkinshaw et al., 2008). The most reactive environments were found to be the lime and sand environments while the least reactive were found to be basic, cold and dry environments.

There are two mechanisms by which nylon could degrade, either through hydrolysis or oxidation. From the data it was difficult to distinguish between the mechanisms, as both show similar changes in many analytical methods used in previous studies (Sonal. et al., 2010). However, previous studies have indicated that the conditions to oxidise nylon generally require either photochemical light, thermal radiation or good exposure to oxygen, none of which easily occur in soil burial situations (Weber, 2011). There are some microbes that have been noted to be able to degrade nylon by enzymatic oxidation (Friedrich et al., 2007; Sudhakar et al., 2007; Tachibana et al., 2010). While it was possible that there was some degradation of the nylon fibres due to the oxidation of the polymer, this would have minimal effect when compared to the hydrolysis of the polymer. This observation can be made from this study as the environments that were more suitable to the hydrolysis of the polymer such as the wet soil, were generally observed to have a relatively greater impact on the fibres than the drier environments.

From the FTIR and TG data, the environments found to have the greatest effect on nylon were the lime, acidic and sand soils while the least were the basic, cold and dry. The wet, loam and clay environments were generally found to have only a moderate effect on the polymer fibres. However, from the SEM micrographs, the wet and acidic environments were observed to have the greatest changes seen to the fibres over the 24 months. This indicates that the wet and acidic environments were able to have a larger impact on the polymer surface. However, the wet environment compared to some of the other environments, had very little impact to the rest of the polymer, giving the data observed in FTIR and TGA.

While hydrolysis was determined to be the more dominant mechanism for the degradation of the nylon fibres, it was observed that the changes due to the hydrolysis of the fibres was minimal. This resistance to the hydrolysis of the fibres was most likely due to the temperature of the soil environments and the stain blockers commonly used in nylon carpets. Temperature has been observed to have a large impact on the hydrolysis of nylon. A previous study reported that increasing the temperature of the surrounding environment, greatly increases the rate of hydrolysis (Chen et al., 2010). While this study investigated the rate of hydrolysis at high temperature, it was reasonable to assume from this study that room or lower temperatures would help to preserve the polymer. The stain blockers added to the fibres during the manufacturing process would also slow down hydrolysis further. This was due to these additives stopping the water from interacting with the nylon fibres, not allowing hydrolysis to occur. Some additives such as the acid dyes commonly used in nylon, may also interact with the environments instead of the nylon fibres. This was particularly true in the alkaline environments, which were showed to have a greater impact on the polymer. It was unlikely that the nylon fibres were significantly degraded during this study rather the interaction of the additives present in the nylon fibres was the changes observed.

Nylon was generally found to be more resistant to alkaline hydrolysis as opposed to acidic hydrolysis which was seen in the basic and acidic environment comparisons, where the acidic environment was found to have a greater impact on the polymer than the basic. This correlates with observations from previous studies that show the pH of the surrounding environment impacting the polymer in this manner (Burkinshaw, 2013). This can also be seen in the SEM micrographs where the acidic environments caused fraying to occur to the polymer much sooner than the basic environment. The wet environment generally had a slightly less impact to the polymer as the acidic soil, but more than the basic indicating that pH of the soil has a greater impact on the degradation of nylon than the total amount of free water for hydrolysis. The loam and dry soil preserved the polymer more than the wet soil, showing that the amount of water available does have an impact on the hydrolysis of the polymer.

The lime environment had the opposite effect generally showing the greatest impact on the polymer except in the SEM images. As nylon was resistant to alkaline hydrolysis, this indicates that another factor besides the alkalinity of the lime soil may have an impact on the tendency of the soil to degrade the polymer. Lime also has a relatively good tendency to absorb water (Sébaïbi et al., 2003). However, if this was the reason for the lime environment to impact the nylon fibre then the clay soil, which also can absorb relatively high amounts of water would also have a larger impact on the nylon fibres (Nguyen and Marschner, 2014). This was not observed in the data as the clay environment had significantly less impact on the polymer than the lime environment. It may be due to a number of the properties of lime soil causing these changes. It was possible that the lime was interacting with the additives present within the nylon fibres as opposed to the nylon itself causing leaching of the additives to occur. This can be seen in the SEM micrographs of lime, which unlike the wet and acidic environments, do not show much fibre fraying occur, rather scaling of the polymer surface could be seen. This scaling most likely was due to the interaction of the lime soil with the additives, while the fibre fraying indicates degradation of the nylon fibre itself.

The sand environment was also unusual as it had a more significant impact on the nylon compared to the other environments (lime was generally found to have the greatest impact). The reasons for this was unknown as the sand soil was a dry soil, which in previous studies was shown to have a preserving effect on the degradation of nylon (Auerbach, 1989). The possible reasons for this environment to having a greater impact on the polymer may be due to sand being less likely to absorb water (Conklin, 2005a; Nguyen and Marschner, 2014). This could allow any water contained within the soil been available for hydrolysis. Another reason may be due to the polymer being oxidised by another agent present in the soil, but future studies are required for confirmation.

This polymer was found to be generally preserved in soil rather than degraded so the rate of degradation was very low overall indicating the stability of this polymer in soil. The environment that showed the greatest impact on the polymer appeared to affect the additives contained in the polymer rather than the nylon itself. This resistance to hydrolysis was most likely due to the stain blockers commonly added to nylon carpets to prevent staining (Burkinshaw and Son, 2008). Although the oxidation of nylon could possibly occur, the conditions were too mild to allow any significant oxidation of this polymer to occur. This means that this polymer if found in a burial scene would not show much change from at the time of burial to its discovery due to this polymer’s ability to resist degradation. The main changes seen to this polymer seem to be due to the reaction of the additives with the environment such as the dyes used rather than any significant degradation of the nylon fibres with some minor hydrolysis of the nylon been observed (Burkinshaw and Son, 2010).

5.7 Summary

The investigation into the degradation of nylon carpet has found that the polymer was resistant to degradation in soil. This was due to the stain blockers added to the fibres during manufacturing, reducing the rate of hydrolysis of the nylon fibre. It was observed in this investigation that most of the changes observed could be attributed to the reaction of the polymer additives such as the acid dyes and the stain blockers with the soil environment. The low temperature of the polymer specimens also slows down the rate of hydrolysis, as the hydrolysis reaction was faster in warmer temperatures.

The environments that were observed have the greatest impact on the nylon fibres were the lime, acidic and sand environments. The lime environment impact on the polymer was due to the reaction of the alkaline lime soil with the acid dyes contained in the polymer. The mechanism behind the impact of the sand environment on the polymer was not known, however, it may be that an aspect of the sand environment could cause oxidation of the polymer. The basic environment had little impact on the polymer indicating that the lime soil ability to retain water may also help with the reaction with the acid dyes. The wet environments both had a moderate impact on the nylon fibres. It was observed that the acidic environment tended to have a greater effect on the nylon fibre over the wet environment. This indicates that having an acidic pH enhances the hydrolysis of the polymer fibres. However, the loam soil was noted to have less of an impact on the polymer which shows that the amount of water in the soil determines the rate of hydrolysis. The dry and cold environments were observed to have little impact on the polymer.

Chapter 6

Polypropylene Fibre Analysis

6.1 Introduction

PP was an olefin polymer similar in structure to PE except for the methyl groups attached to alternate carbons in the polymer backbone (Lieberman et al., 2000). This type of carpet was mostly used as a cheaper wool carpet substitute commonly used in office spaces and for low maintenance rugs (Maier and Calafut, 2008). The PP carpet obtained for this study will be used as a model to determine the effect the nine soil environments have on the polymer.

In order to study the impact that the 9 soil environments had on the PP carpet, a number of different analytical techniques were used. These were SEM, TG and FTIR spectroscopy. SEM investigates signs of degradation to the polymer surface such as fibre fraying and the formation of pits and cracks on the fibre surface. IR spectroscopy was utilised in this investigation to determine the changes to the methylene/methyl ratio and the apparent isotacticity of the polymer. TGA analysed the changes to the thermal stability and the composition of the polymer.

6.2 Characterisation

IR analysis was carried out on the fibres to confirm the carpet type. Figure 6.1 shows the IR spectrum of the carpet fibres before burial and it confirms the use of PP. This can be seen from the distinctive bands associated with PP present at 1460 cm^{-1} associated with the asymmetrical bending vibration of CH_3 as well as the bending vibration of CH_2, 1370 cm^{-1} that was mostly due to the symmetrical vibration of CH_3, 997 cm^{-1} associated with the rocking vibration of CH_3 as well as the wagging vibration for CH_2 and the bending vibration of CH and 973 cm^{-1} that was due to both the rocking vibration of CH_3 and the stretching vibration of C-C (Andreassen, 2012).

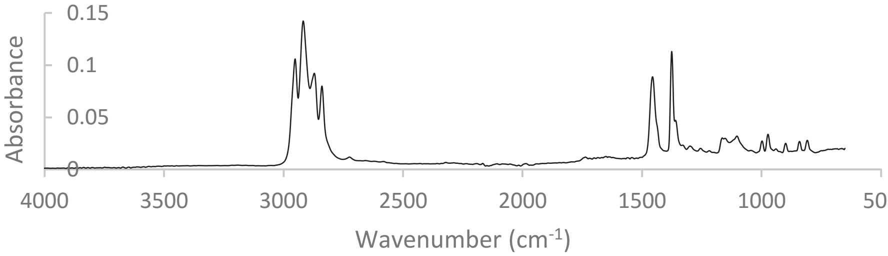


Figure 6.1 Infrared spectrum of PP before soil burial

Different PP stereoisomers result in different physical properties (such as m.p. and crystallinity) and so tacticity needs to be considered when considering degradation mechanisms (Maier and Calafut, 2008). FTIR spectroscopy was used to determine the tacticity of the polymer used in this investigation. The absorbance ratio of the 998 and 973 cm^{-1} bands (A_{998}/A_{973}) was examined (Sundell et al., 1996). The isotacticity of the polymer before burial was determined to be 75% and this indicates predominantly the isotactic form was present. This finding was confirmed by DSC analysis. Figure 6.2 shows the DSC curve of the polymer and the m.p. was determined to be 161-162°C. This m.p. was close to the value for commercial isotactic PP (160-166°C) (Maier and Calafut, 2008).

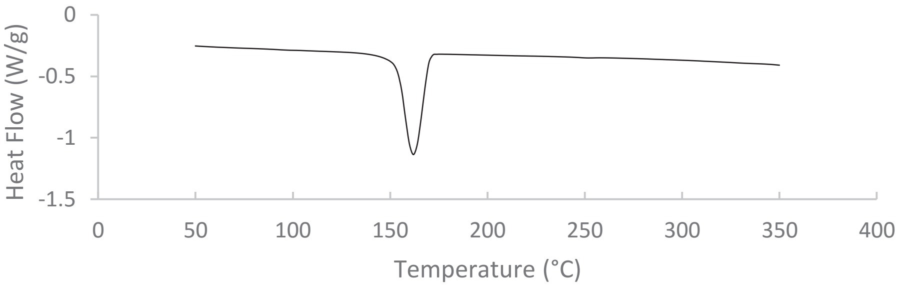


Figure 6.2 DSC curve of PP before soil burial

6.3 Scanning Electron Microscopy

6.3.1 Results

Changes to the surface morphology of the PP fibre surface over the 24 month of study were examined using SEM. PP surface degradation detectable by SEM has been previously reported to include the formation of pits and cracks on the fibre surface (Aslanzadeh and Kish, 2005; Longo et al., 2011). A typical micrograph of an example PP fibre prior to burial was shown in Figure 6.3. The surface appears mostly smooth with minimal variation in texture across the surface. There are some pits that can be observed on the polymer surface before soil burial, particularly along the edges of the fibre. While most of the fibres present in the PP carpet are very similar to the example given in Figure 6.3, there are a noticeable proportion of unusual shaped fibres as seen in Figure 6.4, showing an example of these unusual shaped fibres. The morphology of the surface of the PP fibres were examined every 3 months to look for signs of degradation.

In general, the polymer surface does not change noticeably from the surface observed before burial until 9 months in most of the environments, as seen in the example given in Figure 6.5 showing the polymer in the basic environment at 3 and 6 months. The exceptions to this are for the polymer buried in the acidic and wet environments, which by 6 months, both produce an increase in the surface roughness when compared to the polymer before burial. Figure 6.6 shows an example of the fibres in these environments at 6 months. The fibre in the acidic environment also shows the formation of pits and cracks indicated by the darker areas observed in Figure 6.6.

By 9 months the fibres buried in most of the environments show some change to the surface roughness of the polymer, as seen in the loam environment in Figure 6.7. The extent of the surface roughness changes varies among the environments, with the polymer in the sand and clay soils showing more extensive changes compared to those buried in the loam, lime and basic soils. The fibre surface in the both the clay and sand environments shows the formation of raised structures that give the polymer surface a much rougher appearance. This was observed in the clay environment example shown in Figure 6.8. The polymer from the acidic and wet soils look similar to the fibres at 6 months (the fibres in a wet environment at 9 months was shown in Figure 6.9). The polymer in the cold and dry environments have not changed from the surface seen on the fibres before burial which can be observed in Figure 6.10, which shows a PP fibre in the dry environment at 9 months.

After 12 months of soil burial the fibres in the clay, wet and basic soil environments show cracks similar to the observations of the fibres in the acidic environment at 6 months. This behaviour was observed in the fibres buried in the clay soil after 12 months (Figure 6.11). The PP fibres in the acidic environment appear to have lost many of these features by 12 months with the polymer surface appearing very smooth in comparison to earlier months (Figure 6.11). It can also be observed that the cracking and pit formation was fairly widespread throughout the polymer in these environments, with many of the fibres observed to have these features. This was observed for the polymer in the basic soil at 12 months (Figure 6.12). The polymer specimens from the loam, sand and lime environments show little change based on the observations at 9 months, similar to the fibre buried in the loam environment shown in Figure 6.13. The PP fibres buried in the cold and dry environments were observed to be very similar to the observations before burial however, it was noted that some surface texture changes can be seen. An example of this can be observed in Figure 6.14, which shows a PP fibre exposed to the cold environment for 12 months.

After 15 months of burial, the polymer in the clay, acidic, basic and sand environments have become smooth, losing many of the features noted in previous months with an example in Figure 6.15 showing a fibre buried in the basic soil. Some minor fraying of the fibres buried in these environments was noted. The exceptions to this are the fibres buried in the loam, lime and wet soils, all of which still shows some cracking visible on the polymer surface Figure 6.16 shows an example polymer fibre in the lime soil. The fibres in the cold and dry environments are still fairly smooth, only demonstrating the minor changes that were observed to the polymer surface at 12 months.

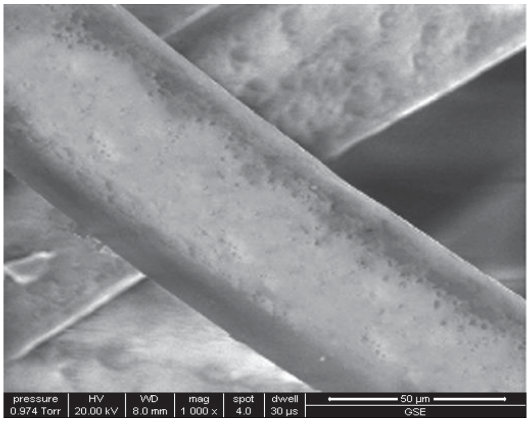


Figure 6.3 SEM micrograph of typical PP fibre before burial in soil environments at a HFW of 149.1 µm

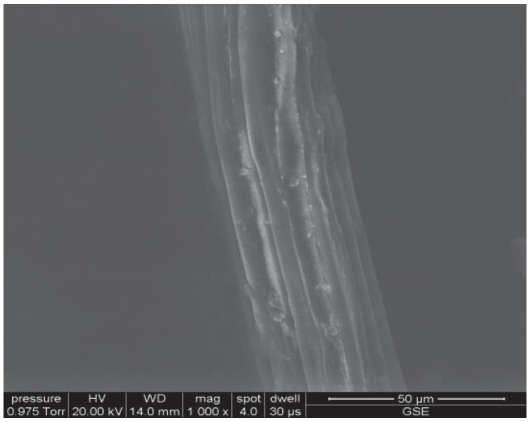


Figure 6.4 SEM micrograph of PP fibre with a different shape and texture to typical fibres at a HFW of 149.1 µm

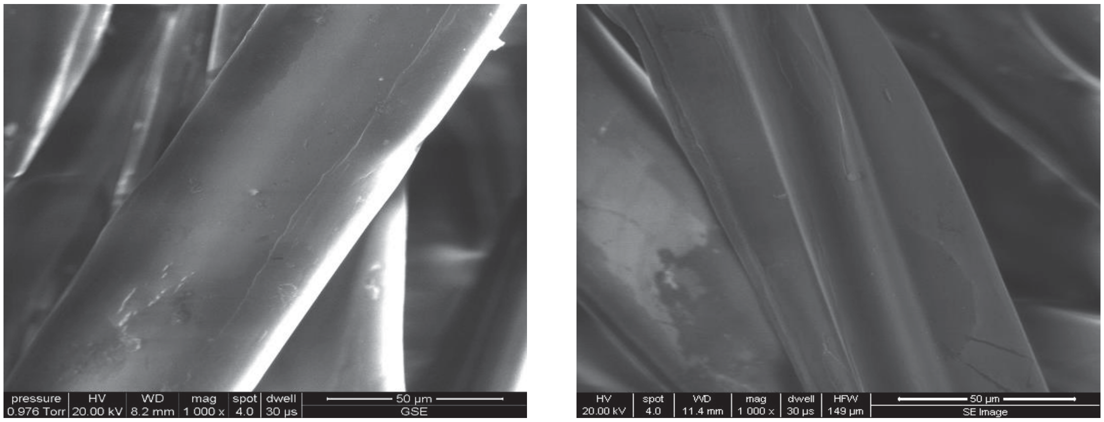


Figure 6.5 SEM micrograph of PP fibres after burial in the basic environment for 3 (left) and 6 (right) months

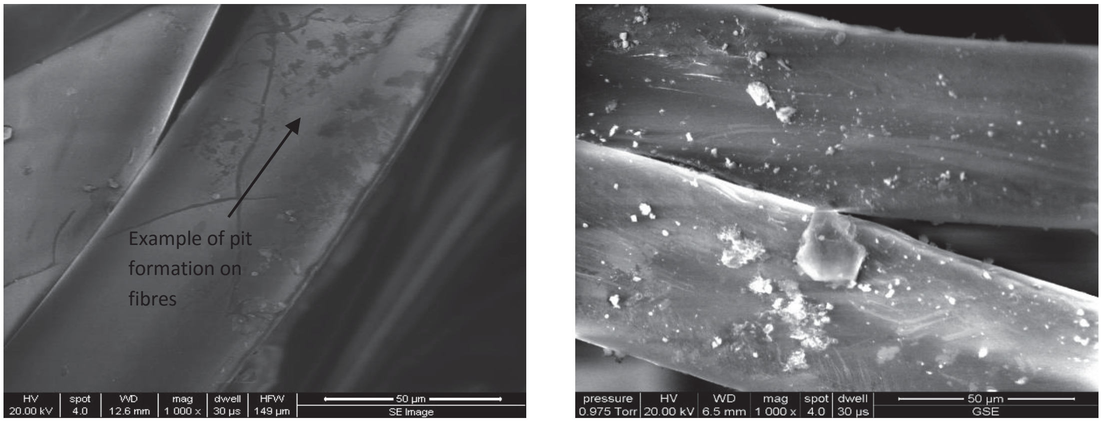


Figure 6.6 SEM micrograph of PP after burial in the acidic (left) and wet (right) soil environments for 6 months

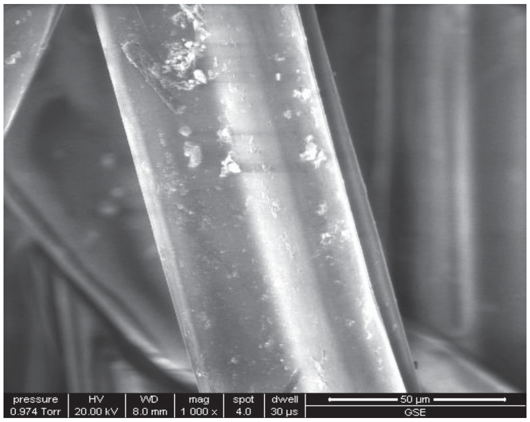


Figure 6.7 SEM micrograph of a PP fibre after burial in the loam soil for 9 months

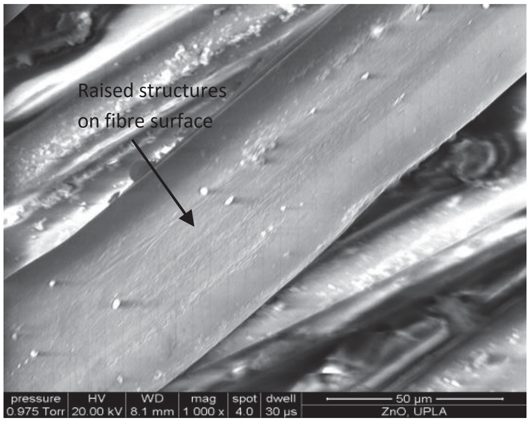


Figure 6.8 SEM micrograph of a PP fibre after burial in the clay soil for 9 months

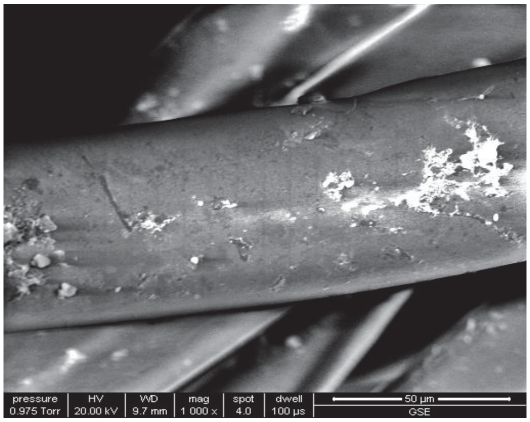


Figure 6.9 SEM micrograph of a PP fibre after burial in the wet soil for 9 months

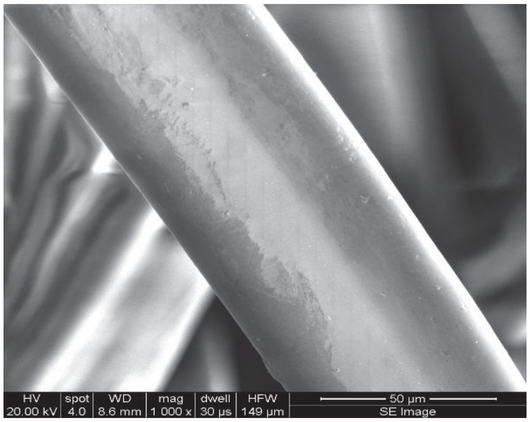


Figure 6.10 SEM micrograph of a PP fibre after burial in the dry soil for 9 months

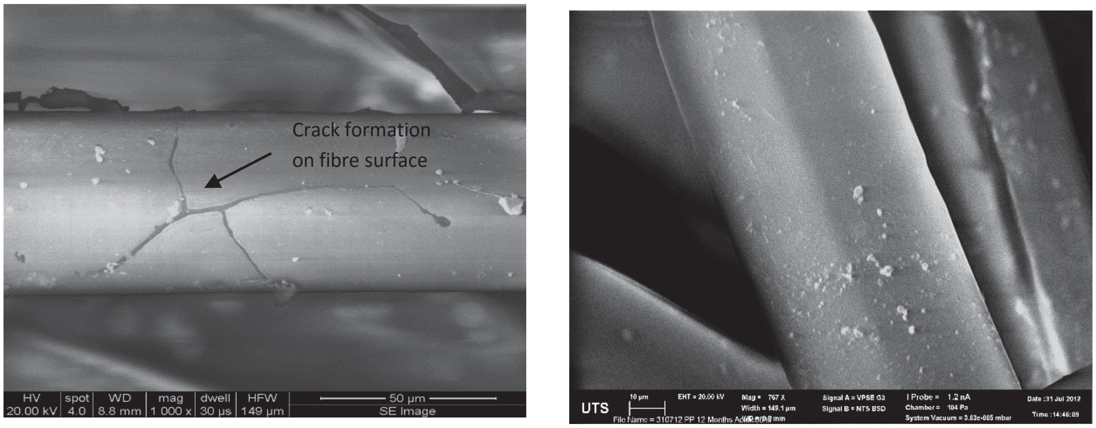


Figure 6.11 SEM micrographs of a PP fibre after burial in the clay (left) and acidic (right) soils for 12 months

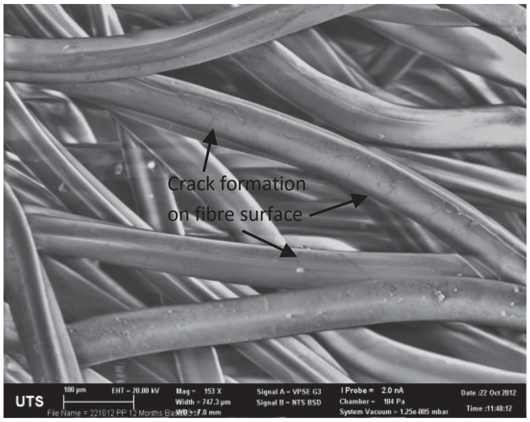


Figure 6.12 SEM micrograph of PP fibres after burial in the basic soil for 12 months

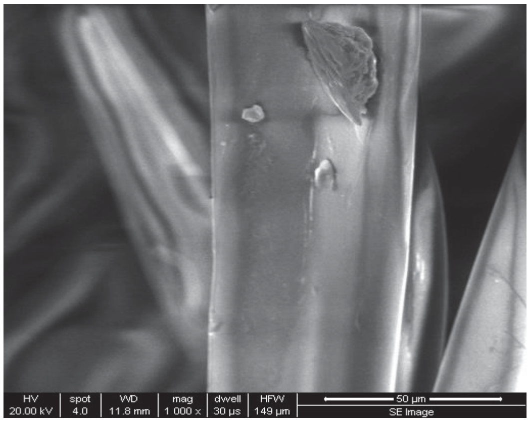


Figure 6.13 SEM micrograph of a PP fibre after burial in the loam environment for 12 months

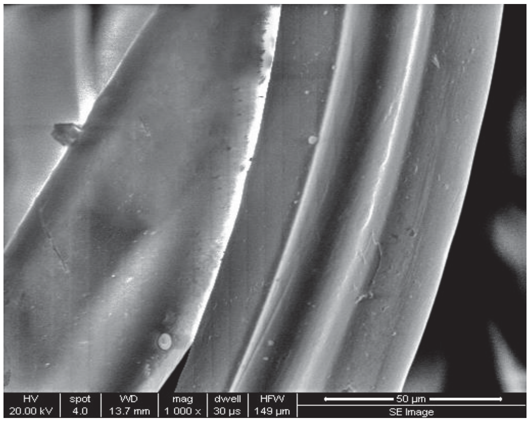


Figure 6.14 SEM micrograph of a PP fibre after burial in the cold environment for 12 months

After 15 months of burial, the polymer in the clay, acidic, basic and sand environments have become smooth, losing many of the features noted in previous months with an example in Figure 6.15 showing a fibre buried in the basic soil. Some minor fraying of the fibres buried in these environments was noted. The exceptions to this are the fibres buried in the loam, lime and wet soils, all of which still shows some cracking visible on the polymer surface. Figure 6.16 shows an example polymer fibre in the lime soil. The fibres in the cold and dry environments are still fairly smooth, only demonstrating the minor changes that were observed to the polymer surface at 12 months.

The fibres buried in the clay, basic and sand soil for 18 months mostly retain the smooth surface that was noted at 15 months. Some minor changes to the surface texture can be observed, possibly due to microbial growth, on the fibre edges as well as some minor fraying. An example of this was illustrated in Figure 6.17, which shows an image of a fibre in the clay soil at 18 months. The polymer in the lime, loam, wet, dry and cold soils have developed more features such as cracking and pits, with the fibres in the wet and lime soils showing a wider distribution of these feature than the fibres buried in the loam, cold and dry soils. This can be seen in Figure 6.18 showing the fibres in both the lime and dry soils after 18 months of burial. The acidic environment, however, showed a growth appearing on the fibre surface. This was very widespread and was visible on most of the fibres as observed in Figure 6.19, which shows the fibres in the acidic soil after 18 months.

The microbial growth noted on the fibres in the acidic environment at 18 months has disappeared by 21 months. This indicates that the microbes were not been sustained by the polymer fibres rather by some other aspect of the environment. If the polymer fibres were sustaining the microbial growth, then these microbes should have been observable in later months. This can be observed in Figure 6.20, showing the polymer in the acidic environment at 21 months. One possible reason for this would be water being added to the soil in order to the keep the moisture levels consistent over the course of the experiment. The other environments show little change from the observations made from the fibre surfaces at 18 months.

By 24 months, most of the fibres in the environments show a smooth surface with the polymer from the dry, cold, lime and loam soils losing the features noted from 15 to 21 months similar to the example given in Figure 6.21, showing a fibre in the cold soil at 24 months. The fibres in the sand, clay, basic and acidic soils have not changed since the observations noted within 18-21 months as observed in the example given in Figure 6.22, showing a fibre after 24-month burial in the clay environment. It was noted that some of the fibres in the basic, clay and cold environments were observed to show similar microbes to those observed on the fibres in the acidic soil at 18 months. These microbial growths are not widespread with only small groups been observed on the fibres. Examples of this are observed in Figures 6.21 and 6.22.

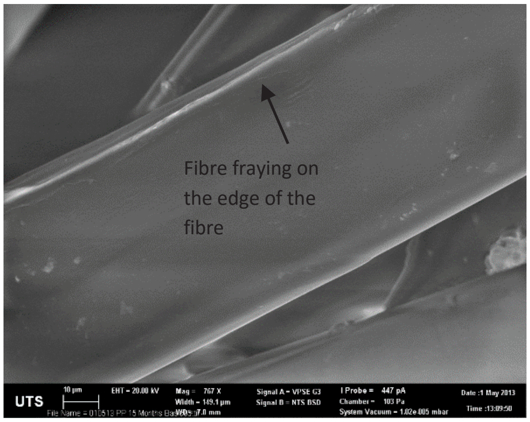


Figure 6.15 SEM micrograph of a PP fibre after burial in the basic environment for 15 months

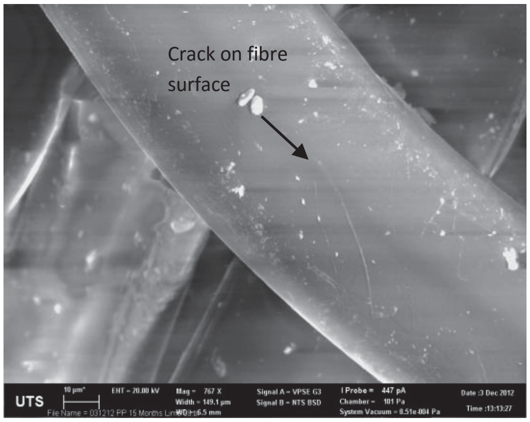


Figure 6.16 SEM micrograph of a PP fibre after burial in the lime environment for 15 months

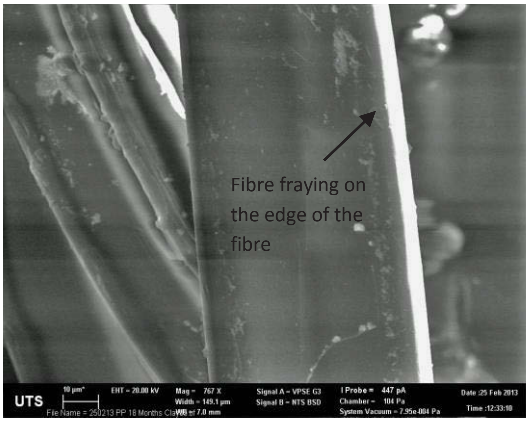


Figure 6.17 SEM Micrograph of two PP fibres after burial in the basic environment for 18 months

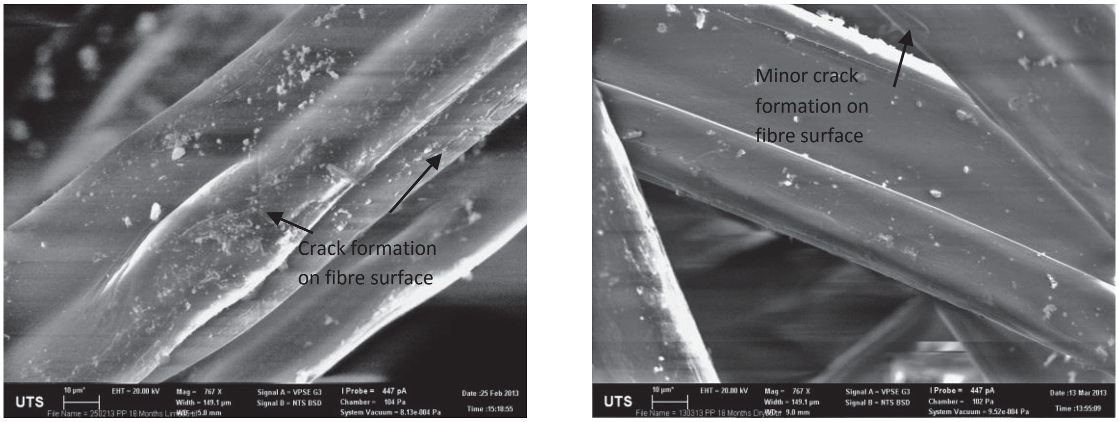


Figure 6.18 SEM micrographs of PP fibres after burial in the lime (left) and dry (right) environments for 18 months

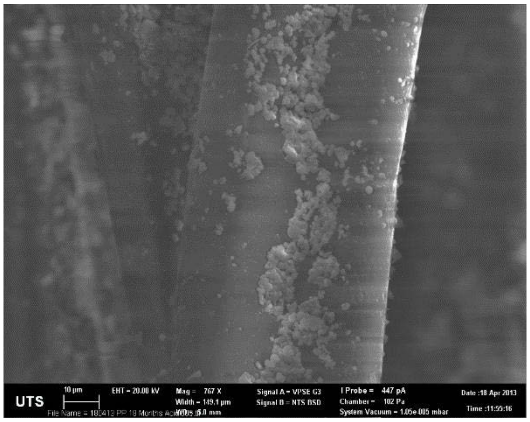


Figure 6.19 SEM micrograph of a PP fibres after 18 months burial in the acidic environment

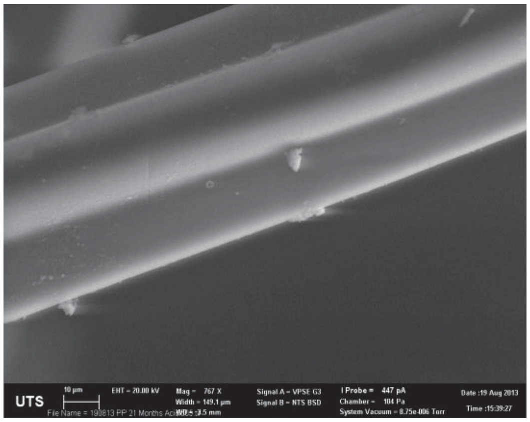


Figure 6.20 SEM micrograph of a PP fibre after 21 months burial in the acidic environment

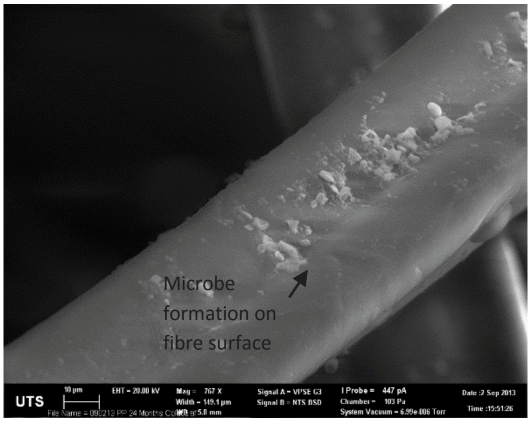


Figure 6.21 SEM micrograph of a PP fibre after burial in the cold environment for 24 months

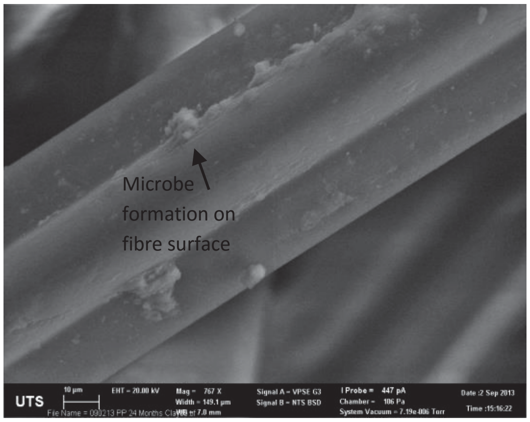


Figure 6.22 SEM micrographs of a PP fibre after burial in the clay environment for 24 months

6.3.2 Discussion

The SEM micrographs of PP have indicated that all of the soil environments were able to, by varying degrees, degrade the polymer. The formation of cracks was seen in the fibres buried in all of the environments as well as some minor fibre fraying at the edges of the polymer fibre in some of the more reactive environments, such as the clay and acidic soils. This has previously been found to indicate that the earlier stages of degradation are occurring in polyolefins (Kijenska et al., 2010). Many of these features were observed to be reversed in later months, with the fibres in all of the environments showing a gradual increase to the smoothness of the polymer surface. Only the edges of the fibres were noted to fray in the later months. There was no fibre breakage observed to occur, which also has previously indicated that the degradation that was observed in the fibres was only in the early stages (Aslanzadeh and Kish, 2005). There was evidence of microbial growth observed in some of the environments, particularly the acidic soil, which showed an explosion of microbial growth at 18 months. It was possible that this microbial growth could have a positive influence on the degradation of the polymer fibres, but this was not observed in the micrographs as these microbes were observed to have disappeared by 21 months except for very small colonies.

The most reactive environments were found to be the clay, acidic and wet soils as these environments were observed to have the earliest and greatest effect on the polymer fibres. These environments tended to show the greatest changes such as more widespread cracking and fibre fraying. All of the fibres buried in the other environments showed the same features as the reactive soils, but the fibres in the other soils generally showed these changes much later with the fibres in the cold and dry soils being the slowest to change.

The clay soil being a reactive environment indicates that microbes have a positive impact on the degradation of the polymer. Clay soil was known to be a soil that promotes microbial growth due to the moisture retention as well as potential nutrients in this soil type (Nguyen and Marschner, 2014). While the lime soil was another environment that has previously being noted to have good water retention properties, it was observed to have less of an impact than the clay soil (Sébaïbi et al., 2003). There are a number of reasons for this including the alkalinity of this soil type assisting to preserve the polymer and the reduced microbe population in the lime soil due to the lower availability of nutrients. PP was known to be resistant to both acidic and basic environments (Wust and Landoll, 2000). This would normally indicate that the acidic soil would not be expected to have a significant impact on the polymer. However, in the micrographs obtained, the acidic soil was found to degrade rather than preserve the polymer. The most likely reason for these observations are the fungi noted in the acidic soil at 18 months. Microbes would also be responsible for the degradation of PP in the wet soil as PP was known to be a very hydrophobic polymer indicating that water should have little impact on the polymer (Wust and Landoll, 2000). Wet soil would promote microbial growth, but due to the movement of water through the soil, this would tend to wash the microbes away from the polymer fibres reducing the potential of the microbes to degrade the polymer (Abu-Ashour et al., 1994). The cold and dry environments both have a negative impact on microbial growth due to the low temperature (cold soil) and lack of moisture (dry soil) (Stolp, 1988). This was observed in the micrographs as these environments where both were very slow to show the changes known to be associated with degradation.

The degradation of PP was found to be influenced by the soil environments. From the micrographs, it was indicated that the microbes and the soil chemistry of the environment had an impact on the degradation of the polymer. This varied throughout the environments, with some environments influencing the degradation via chemical means, such as the wet soil, while others appeared to degrade the PP with microbes.

6.4 Fourier Transform Infrared Spectroscopy

6.4.1 Analysis of Infrared Band Ratios - Results

The PP specimens were analysed using ATR-IR spectroscopy in order to detect any changes to the polymer structure due to degradation. The impact the 9 soil environments had on the PP was investigated by observing the changes to the methyl to methylene ratio as well as a changes to the (A_{998}/A_{973}) band ration of the polymer. The changes to the methyl index can be observed by comparing the absorbance of the band at 1377 cm^{-1} to the band at 1456 cm^{-1} (Arkatkar et al., 2009). Both of these parameters have been observed in previous studies to be good indicators of structural changes to PP (Longo et al., 2011). It has been reported in previous studies that changes to keto and ester carbonyl indexes (comparing the bands at 1715 and 1748 cm^{-1} to the band at 1456 cm^{-1}) was an indication of oxidation of the polymer occurring (Arkatkar et al., 2009; Arkatkar et al., 2010).

Figure 6.23 depicts the 2nd derivative infrared spectra of PP in the 9 soil environments, which were normalised to the band at 1456 cm^{-1}. It can be observed from the spectra in Figure 6.23 that some changes to the spectra over time occurred to PP in most of the environments. The band at 1377 cm^{-1} was noted to show a gradual increase in the acidic, lime and clay environments. This band was not observed to change in any of the other environments. The bands at 997 and 973 cm^{-1} were noted to decrease in the spectra obtained for the polymer buried in acidic, basic, lime, sand and wet environments. The spectra obtained for the PP from the dry, clay and loam environments were noted to have an increase occur to both of the bands, while the cold environment showed very little change to these bands. There were also changes observed to the bands at 1165 and 835 cm^{-1} for the spectra of the polymer buried in all of the environments. The changes to these bands were generally inconsistent and did not show an easily identifiable trend that the soils had on the polymer. In the acidic environment there were also extra bands noted in the spectra at 12 months. Since these bands did not appear in any of the other time periods, these extra bands were predicted to be due to soil contamination from the environment. There was also an unusual increase in intensity of the band at 1017 cm^{-1} in the spectrum for the polymer from the clay environment at 24 months. It was unknown what may have caused this sudden increase, but it was possible that the changes to the band may be due to residual clay soil that resisted the cleaning process (Vaculíkovà and Plevovà, 2005). There are no noticeable changes that can be observed in the spectra for the polymer in any of the environments to the bands at either 1715 or 1748 cm^{-1}. This indicates that oxidation of the polymer in the different soils has not occurred (Arkatkar et al., 2010).

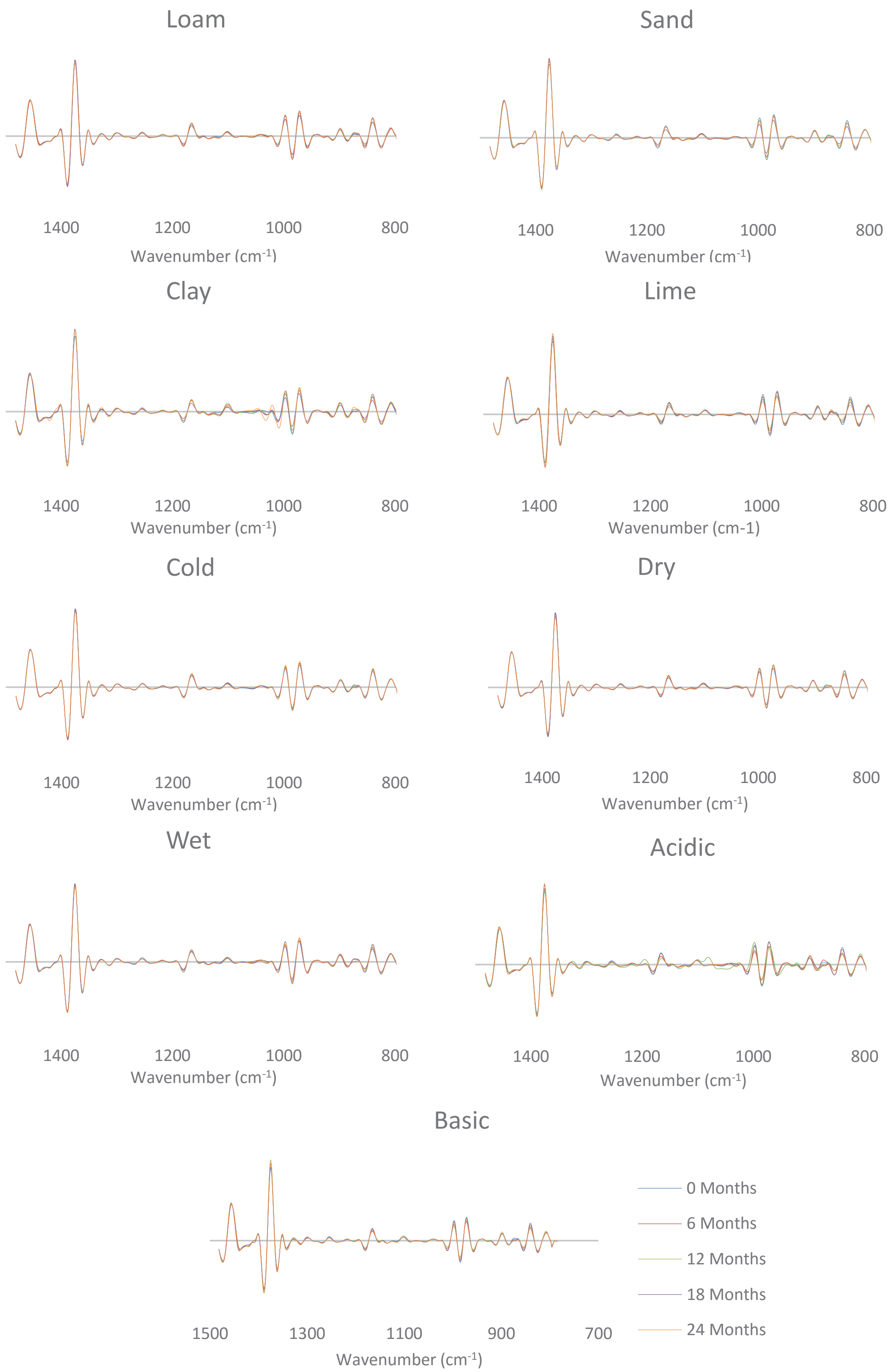


Figure 6.23 2nd derivative IR spectra of PP in the 9 soil environments

Figure 6.24 depicts the changes to the methyl index of PP from the burials over the 24-month period. It can be observed from Figure 6.24 that the polymers in all of the environments show an increase in the methyl index of PP occurring over 24 months. The slopes found from the changes to the methyl to methylene ratio are tabulated in Table 6-1. It can be observed from Table 6-1 that the clay and acidic environments had the greatest impact on the methyl index of the polymer, while the cold and dry environments had the least impact. The changes to the methyl index of PP in the 9 soil environments tended to be linear.

Figure 6.25 shows the changes to the (A_{998}/A_{973}) band ratio of PP over 24 months in the 9 soil environments. It can be observed from Figure 6.25 that this ratio decreased in most of the environments with only the PP in the dry environment been observed to have an increase occur. This change of the polymer tended to be fairly linear for all the environments. The slopes due to the (A_{998}/A_{973}) band ratio of the polymer in the 9 soil environments was in Table 6-1. From Table 6-1, it can be observed that the acidic and clay environments had the greatest effect on this ratio while the loam and cold environments has the least impact.

Table 6-1 Slopes of the methyl/methylene ratio and (A_{998}/A_{973}) band ratio

Environment	**Methyl/Methylene Ratio Slope**	(A_{998}/A_{973})
Loam	$2 \pm 1 \times 10^{-3}$	$-2 \pm 9 \times 10^{-2}$
Sand	$2 \pm 1 \times 10^{-3}$	$-8 \pm 10 \times 10^{-2}$
Clay	$4 \pm 1 \times 10^{-3}$	$-3 \pm 1 \times 10^{-1}$
Lime	$2 \pm 1 \times 10^{-3}$	$-1 \pm 1 \times 10^{-1}$
Cold	$8 \pm 7 \times 10^{-4}$	$-2 \pm 5 \times 10^{-2}$
Dry	$1 \pm 1 \times 10^{-3}$	$9 \pm 7 \times 10^{-2}$
Wet	$2 \pm 1 \times 10^{-3}$	$-2 \pm 1 \times 10^{-1}$
Acidic	$4 \pm 1 \times 10^{-3}$	$-4 \pm 1 \times 10^{-1}$
Basic	$2 \pm 1 \times 10^{-3}$	$-3 \pm 5 \times 10^{-2}$

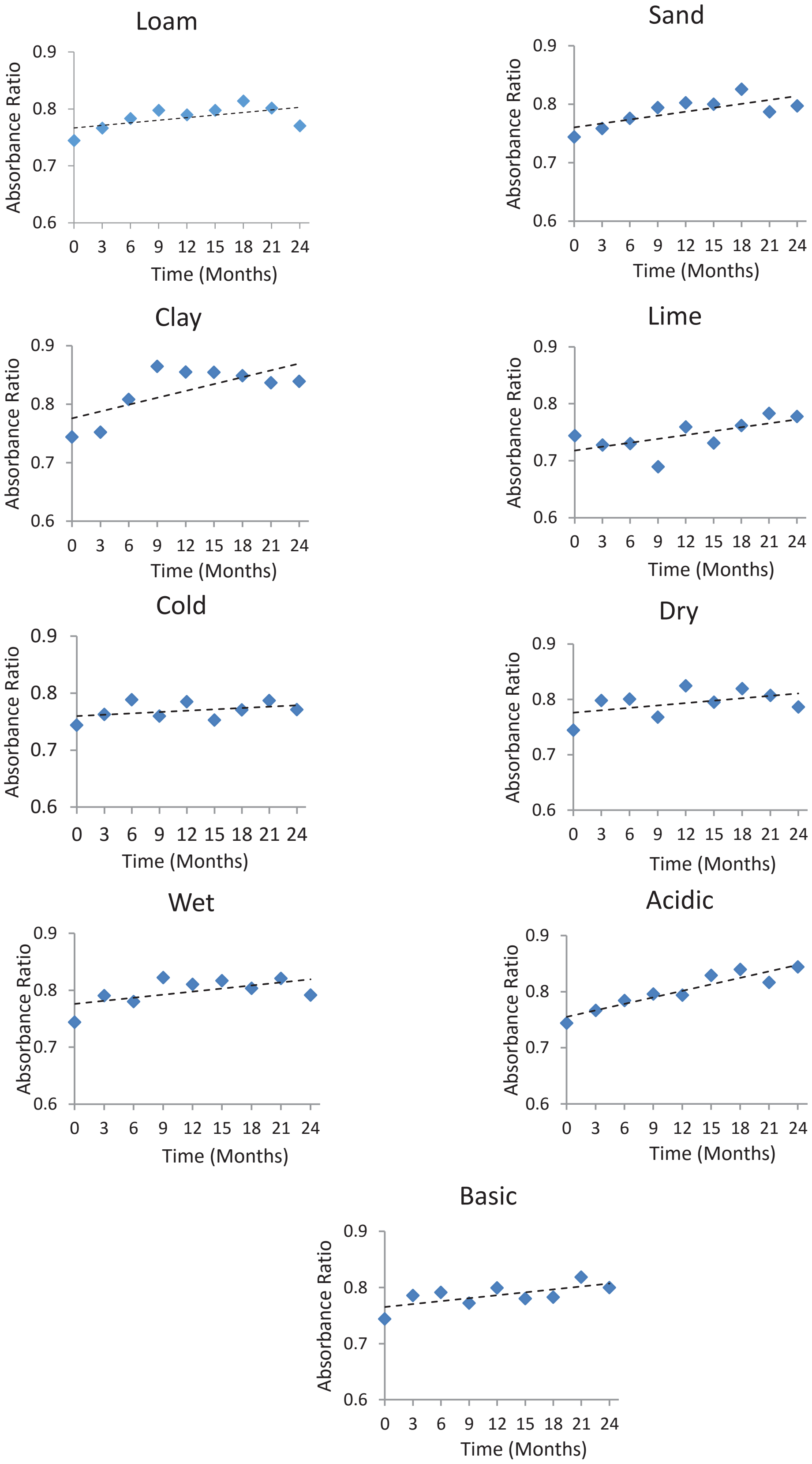


Figure 6.24 Methyl/methylene mean absorbance ratio as a function of burial time

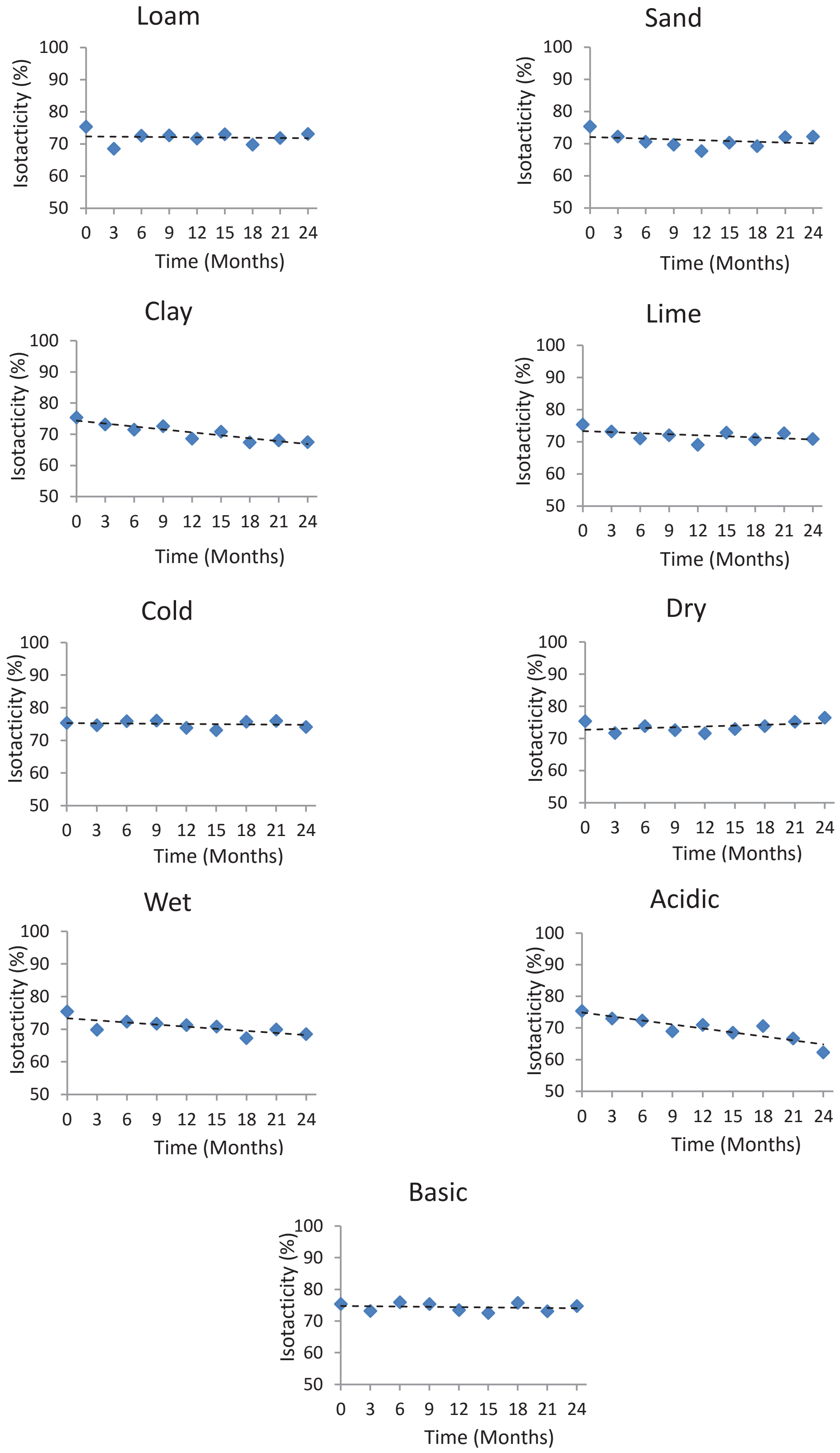


Figure 6.25 Changes to the (A_{998}/A_{973}) mean band ratio as a function of burial time

6.4.2 Analysis of Infrared Band Ratios - Discussion

Changes to the methyl index of PP in the soils was observed in the soil environments. The methyl index for the PP removed from the soil environments was observed to increase over time. This along with the lack of formation of carbonyl bonds indicates the polymer was not being oxidised as the methyl index of the polymer will decrease when the polymer undergoes oxidation (Arkatkar et al., 2009; Longo et al., 2011). Along with the increase noted in the methyl index there was also a corresponding decrease observed in the (A_{998}/A_{973}) band ratio. Due to the lack of oxidation observed in the IR spectra, it was most likely that the changes observed to PP are due to the chain cleavage that occurs during PP degradation before oxidation of the polymer can be observed. Changes to these bands have being observed previously to appear before the distinctive indications of oxidation such as the formation of a band at 1720cm^{-1} (He et al., 2005). This indicates that these changes are early indicators that the degradation of PP was occurring. The bands used to examine the methyl index of the polymer are also associated with various factors of the degradation of PP. The band at 1456 cm^{-1} has been linked to the scission of the polymer main chain while the band at 1377 cm^{-1} are associated with the methyl scission from the main chain. The increase to the methyl band would be due to chain scission occurring faster one area of the polymer over another. Changes to the (A_{998}/A_{973}) band ratio has previously been attributed to reductions in the molar mass of PP due to the chain β-scission of the polymer chain (Chawla et al., 2006; Longo et al., 2011).

From Table 6-1, it can be observed that the clay, acidic, wet and lime environments had the greatest impact on the polymer while the sand, loam, basic, cold and dry environments had the least impact. The environments that had the greatest impact on the polymer were mostly soils that would promote microbial growth. Clay and lime soils both have good moisture retention, allowing this moisture to be available for microbes (Sébaïbi et al., 2003; Nguyen and Marschner, 2014). The clay soil also has increased availability of nutrients for promoting microbial growth (Rycroft and Amer, 1995). The loam soil in the wet environment does not have the same moisture retention capacity as the clay and lime soils, however, the absolute level of moisture present within this environment would assist with the growth of microbes when compared to loam environment. It was observed that the wet soil was observed to have a greater impact on the polymer than the lime soil. This may be due the wet soil promoting the growth of microbes that are able to take nutrients from the polymer while the microbes in the lime soil may be less able to utilise the nutrients present in the polymer. When the lime and basic soils are compared, it can be observed that the lime soil had a much greater impact on the polymer than the basic loam soil environment. This also indicates that the moisture retention of the soil has a large impact on the capacity of the environment to degrade the polymer. The acidic environment also had a large impact on the polymer. It has been noted in previous studies that the pH of the environment was likely to have little impact on PP as neither basic or acidic environments were found to have significant impact on PP (Salvador et al., 2003). This was not found in this study as the acidic soil was found to have a much greater influence on the polymer then both the basic and loam soil environments. This was most likely due to the activity of microbes in the acid environment. While most microbes do not easily survive in an acidic soil, various fungi thrive in acidic soil (Matthies et al., 1997). It has been noted previously that fungi are more efficient in degrading polyolefins than bacteria (Kumar Sen and Raut, 2015). Fungi were also observed in the SEM micrographs of PP from the acidic soil.

The environments that had less of an impact on the polymer all either had less water present or a lower moisture absorbing capacity than the more reactive environments. It can be noted in Table 6-1that the error found in the slope for the less reactive environments was very large in comparison to the change observed in the band ratios of the polymer over time. This indicates that the less reactive environments all had a similar impact on the polymer as the large error makes it impossible to distinguish among the effects these environments had on the polymer.

From the IR spectra, it was observed that the clay and acidic environments have the greatest impact on the polymer and the additives present. Several factors were determined to have an impact on the degradation of PP in the soil environments. These were the moisture absorbing capacity of the soil and the pH of the environment. The soils with the higher moisture absorbing capacity promote microbial growth. The acidic environment also promotes the growth of fungi that are very efficient in degrading PP.

6.4.3 Multivariate analysis

Multivariate analysis was conducted on the IR results for PP specimens from each of the soil environments. The PCA obtained from the data can be observed in Figure 6.26 where the PCA graphs investigating both changes over time and environment can be seen. It can be observed from Figure 6.26 that there are no observable trends for most times and environments, with the data for both been spread throughout the graphs with no easily discernible clusters. The data for the clay environment was an exception to this, where in the later months there was an observable positive movement on the y axis as well as a negative movement on the x axis. This was an indication of change occurring to the fibres buried in this environment. This agrees with the ratio data that was observed for the polymer in this environment, as the fibres in the clay soil were observed to show the greatest change overall.

Using the pre-treated IR data obtained for the PP samples, a PLS-R graph was created with the loam environment used as a reference model for the polymer. In order to decide which model would be the most useful for the analysis of the PP samples, the explained variance along with the loadings were investigated for the bands of interest. In particular, the loadings that included the bands of interest that were used in the ratio analysis of the polymer were used in this model. The variance shows the compatibility between the calibration and validation data for the different factors, with the factors having the closest variance in these factors being the most suitable for use as a model.

The explained variance can be observed in Figure 6.27 and shows that the explained variance between the calibration and validation was fairly poor for most of the factors. The factors where the explained variance between the two was the closest are factors 4-6. This indicates that these factors would be most suitable for use in the loam soil model. The loadings for these factors were investigated for the factor that best covers the bands of interest. This was found to be factor 5, as this factor was shown to represent the bands of interest best. The loadings for factor 5 can be observed in Figure 6.28.

From both the loadings and the variance for the data, it was found that factor 5 was the most suitable for use in the PP loam soil model.

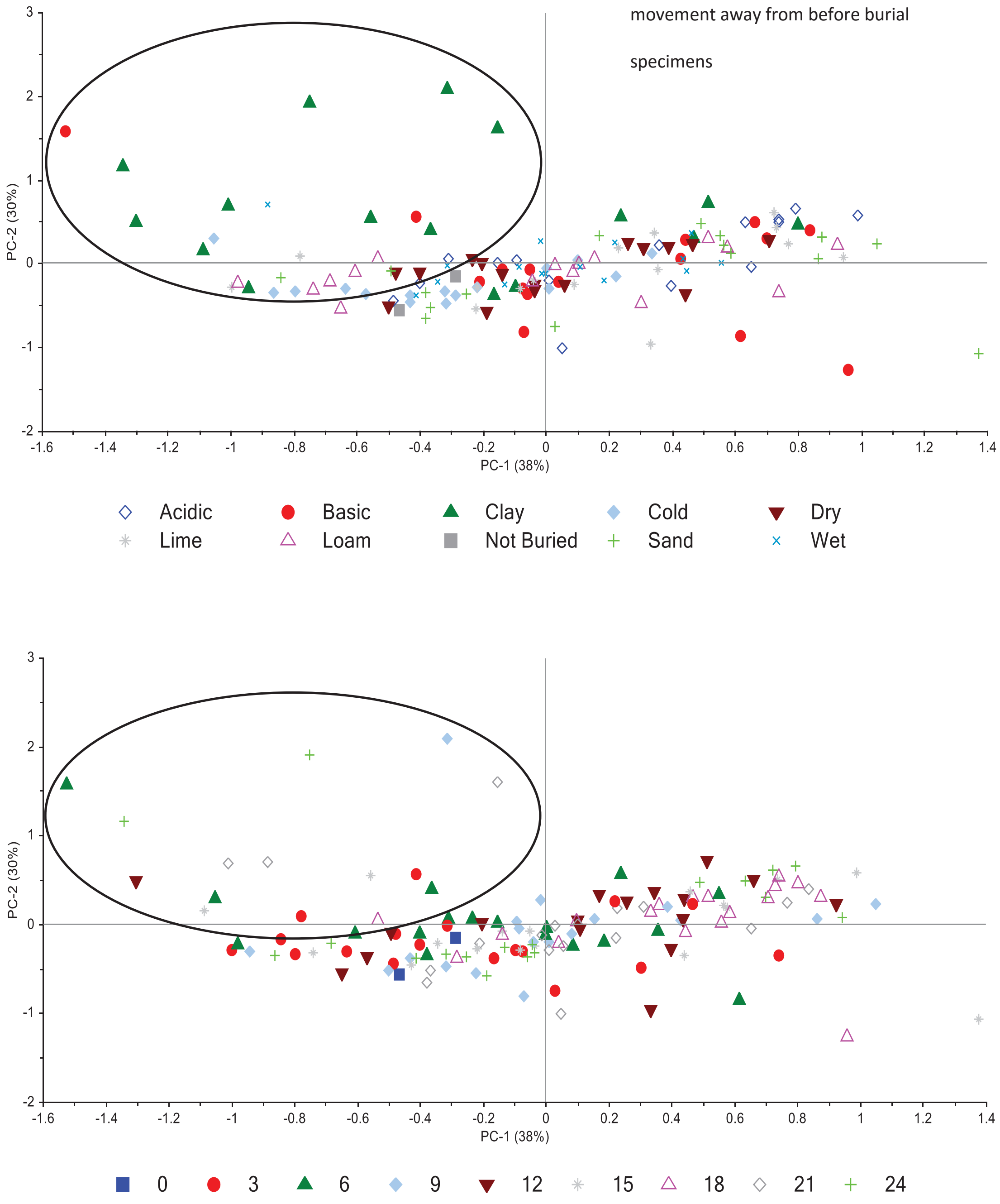

Circle depicts clay environment specimen movement away from before burial specimens

Figure 6.26 PCA graphs of PP IR burial data investigating changes over environment (top) and time (bottom)

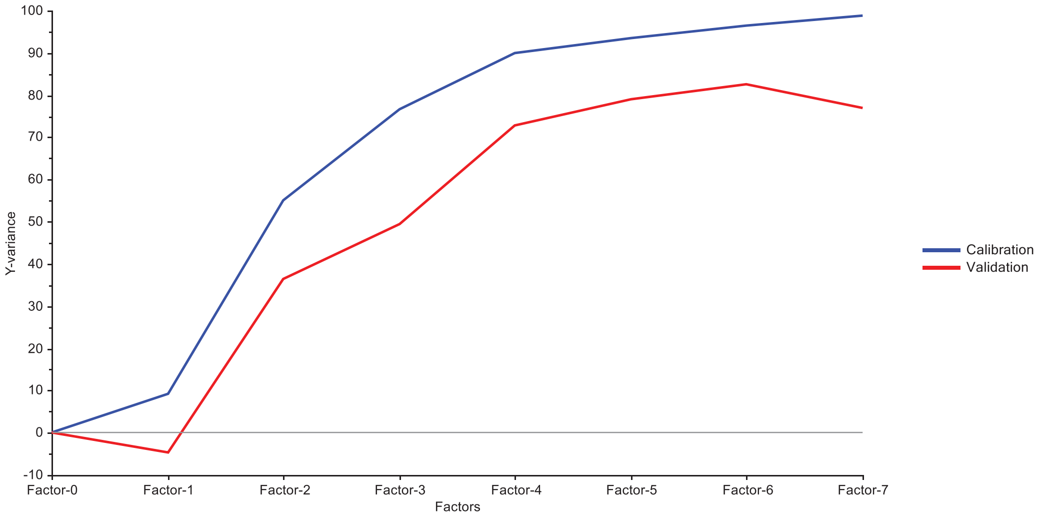


Figure 6.27 Explained variance between the calibration and validation for the PP fibres in the loam environment

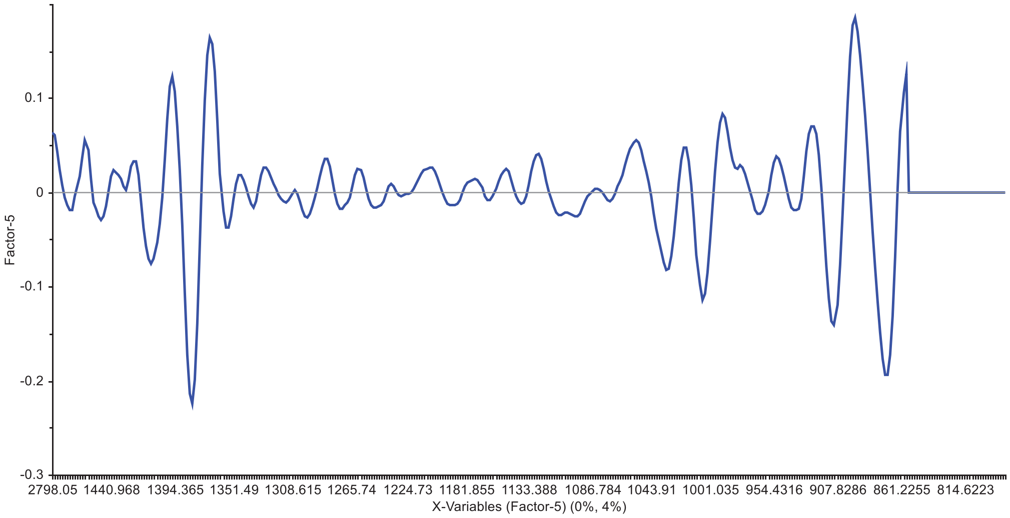


Figure 6.28 Loadings for factor 5 for the PLS-R model for the fibres in the loam environment

The PLS-R of the loam soil environment (acting as a reference) for factor 5 was shown in Figure 6.29. It can be seen that the R^2 for this model was 0.79. This R^2 indicates that the model was a satisfactory representation of the data. From Figure 6.29 it can be observed that the model generally matches the data well throughout the time of interest. Some time periods such as 6 and 15 months appears to not fit the model prediction very well, with the data points for the fibres in these time periods, been located away from the model. Overall, the model determined for the fibres in the loam soil was found to be a good predictor for the data.

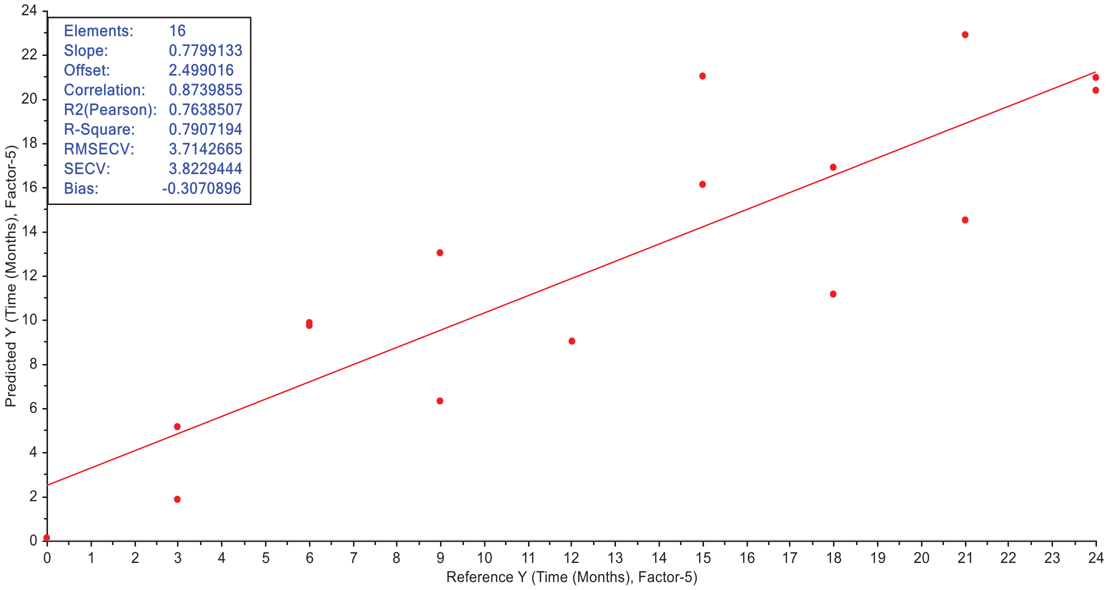


Figure 6.29 PLS-R graph for the PP fibres buried in the loam soil (acting as a reference model)

6.5 Thermogravimetric analysis

6.5.1 Results

The PP carpet fibres were analysed by TGA. The TG data for the polymer before burial in the soil environments are shown in Figure 6.30. It can be observed in the TG trace in Figure 6.30 that PP follows a single step thermal decomposition process that starts at approximately 300°C and was finished by 500°C when decomposed in a nitrogen environment. This one step decomposition removes approximately 97% of the polymer mass leaving 3% as a carbon residue. This was also confirmed by the DTG trace in Figure 6.30, which also show that the maximum mass rate loss occurs at 458°C.

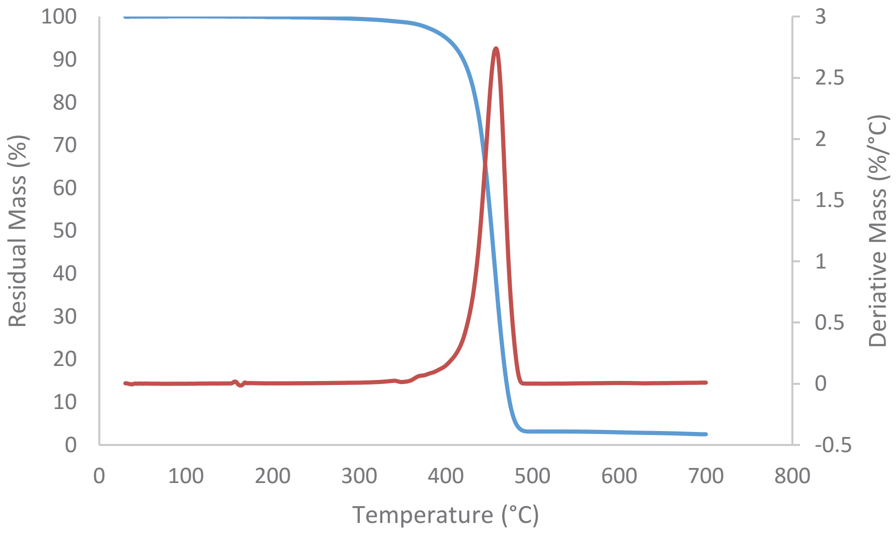
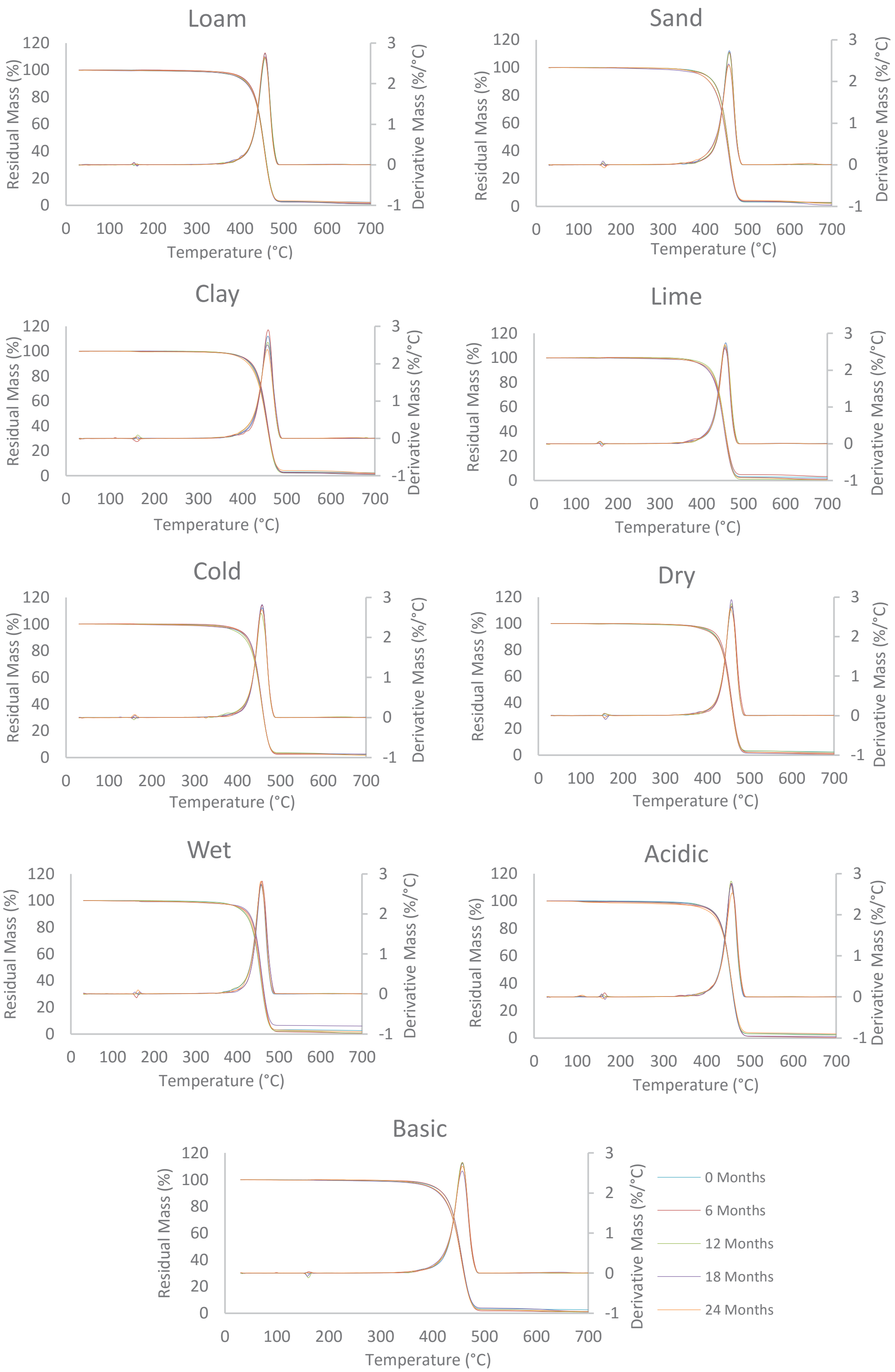


Figure 6.30 TG trace of PP before burial in the soil environments

The TG traces for the polymer in the 9 soil environments are shown in Figure 6.31. There was little consistent observable change occurring to the polymer. While some slight variation to the mass loss curve and the residue can be seen in some of the environments, it was noted that these changes were not consistent across the 24 months of interest indicating that no real change has occurred.

The DTG traces of the polymer in the 9 soil environments can be observed in Figure 6.31. The PP fibres buried in the clay, sand and acidic environments all show a decrease occurring to the maximum rate of mass rate loss of the DTG trace. The other environments, however, show very little consistent change occurring to the polymer. The polymer in the clay environment was seen to have the greatest observable decrease in the rate loss over 24 months, with a significant difference been observed in the polymer before burial and after 24 months in this environment. Both the PP fibres buried in the sand and acidic environments show very little change occurring until the later months were a sudden decrease in the maximum rate can be observed. For the polymer in these environments, there are no observable shift occurring to the temperature at which the maximum mass loss rate occurs. A small peak was noted to occur in the DTG traces at approximately 160°C. This corresponds to the m.p. of the polymer and occurs due to movement of the polymer fibres in the crucible while melting.



Loam

Sand

Clay

Lime

Cold

Dry

Wet

Acidic

Basic

Figure 6.31 TG traces of specimens after removal from the soil environments

The changes to the peak maxima of the DTG traces are depicted in Figure 6.32. The environments that had the greatest impact on the PP fibres were the clay, sand, acidic, basic and loam soils while the wet, lime, dry and cold had the least impact. While most of the environments showed a decrease occurring to the DTG peak maximum, the wet and dry environments showed a slight increase. Since this increase was very small, this would not an indication of a different degradation mechanism occurring to the polymer in these environment instead an indication of the variation in the polymer.

The slopes of DTG maximum peak height changes are depicted in Table 6-2, which shows the slope as well as the standard error of the data to a linear trend line. The error for the polymer in the less reactive environments was much larger than the environments that had the greatest impact on the polymer. This was an indication that the effect these environments had on the polymer was close to zero and any changes that occur to the DTG maximum peak height are more likely due to the variations that occur to polymer fibres during manufacturing.

Table 6-2 The mass loss in the DTG traces over 24 months

Environment	**Slope of mass loss rate ± Standard Error**
Loam	$-4 \pm 2 \times 10^{-3}$
Sand	$-2 \pm 1 \times 10^{-2}$
Clay	$-2 \pm 1 \times 10^{-2}$
Lime	$-8 \pm 30 \times 10^{-4}$
Cold	$-2 \pm 5 \times 10^{-3}$
Dry	$1 \pm 5 \times 10^{-3}$
Wet	$6 \pm 30 \times 10^{-4}$
Acidic	$-7 \pm 5 \times 10^{-3}$
Basic	$-6 \pm 4 \times 10^{-3}$

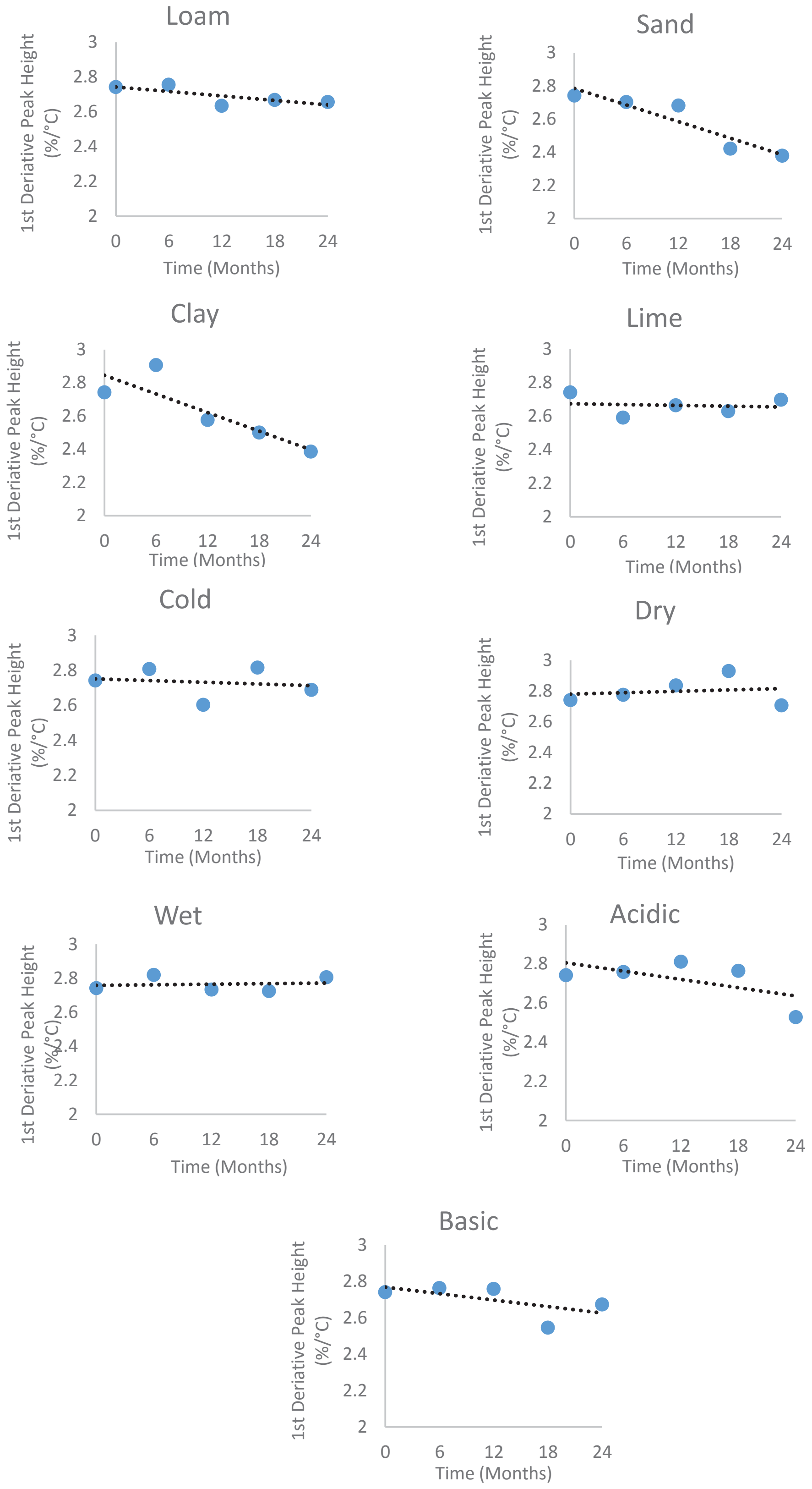


Figure 6.32 DTG peak height as a function of time in the 9 soil environments

6.5.2 Discussion

It can be observed from Figure 6.31 that minimal change had occurred to the PP fibres in the 9 environments according to the TG traces. Degradation of PP can be observed in TG traces by the changes to temperature where 5% and 10% mass loss due to degradation occurs. A reduction in the temperature at these points indicates the loss of thermal stability of the polymer (Krupa and Luyt, 2001). This loss in the thermal stability of the polymer occurs due to degradation. As this was not seen in the fibres buried in the soil environment, this indicates that no widespread degradation has occurred.

The DTG traces have indicated that some change was occurring to the PP fibres in the soil environments, particularly the clay, sand, acidic and basic soils. The polymer in these environments were observed to have a noticeable decrease in the maximum mass loss rate. In Table 6-2, it can be seen that the polymer in most of the environments showed some change however, the changes to the DTG trace was very small in most of the environments. The decrease in the DTG peak maximum has previously being found to be due to the decrease in the purity of the polymer (Canetti et al., 2006). This decrease in the purity of the polymer would be due to the degradation products that are formed while the polymer was degrading in the soil environments. This decrease in the DTG peak maximum could also be possibly due to changes to the additives used in the PP fibres (Broda et al., 2007). Since there were no noticeable changes to the temperature that the DTG peak maximum occurs at, this indicates that there was no change to the thermal stability of the polymer which was another indication of degradation occurring to PP (Chrissafis et al., 2007). It was seen from the TG traces, the environments that had the greatest impact on PP were the clay, sand, acidic and basic environments. Most of the environments were observed to preserve rather than degrade PP, however, some environments like the clay and acidic were noted to degrade the polymer.

6.6 Discussion

PP was found to be resistant to degradation in the soil environments, however some observable changes were found throughout the 24 months. The most reactive environment was consistently found to be the clay soil, while the cold and dry soils had little effect had on the polymer.

The mechanism that PP degrades by in the soil environments has being observed to be oxidation (Arutchelvi et al., 2008). However, fast oxidation of PP requires either heat or UV light, neither of which would be available in a soil burial situation (Maier and Calafut, 2008). This would make PP very resistant to degradation in a soil burial situation. The resistance of PP to degradation in the soil environments are also increased by the additives introduced to the polymer during manufacturing. The additive that would help preserve PP would the UV stabilisers (with the largest group of these stabilisers being HALS) which act as free radical scavengers for the polymer (Tolinski, 2015). This additive would remove any free radicals generated by the initial degradation of the polymer, stopping the propagation step of the degradation process.

The clay and acidic soils were found to have the greatest impact on the degradation of the polymer. All of the techniques used in the analysis of the fibres indicated that the polymer was degraded within these environments. Both the methyl index and the (A_{998}/A_{973}) band ratio were observed to change greatly in these environments in comparison to the other soil environments.

This was an indication of an increased level of chain scission occurring to the polymer in these environments. In the TG data, the fibres buried in the acidic and clay soils showed a relatively large decrease to the height of the DTG traces, which was an indication of changes to the purity of the polymer due to degradation (Canetti et al., 2006). The SEM micrographs also showed the impact that these environments on the polymers. The fibres in the clay soil were observed to undergo changes quickly and to a larger extent than the fibres in most of the other environments. This was also observed in the acidic soil along with the appearance of fungi colonies on the fibres after 18 months of burial. The fungi would be responsible for the enhanced degradation in the soil environment rather than the effect the pH has on the polymer.

Both the basic and lime soil were found by the IR data to have similar changes to the methyl index of the polymer. The lime soil was found to have a greater impact on the band ratios of the polymer over the basic soil. The TG data however, indicates that the fibres in the basic soil had degraded to a greater extent throughout the fibres than the ones buried in the lime soil. This can be observed by the change to the DTG peak maximum, where the fibres in the lime soil showed little change compared to the fibres in the basic soil. The greater impact the lime soil had on the polymer was most likely be due to the moisture retention capacity of this environment, helping to promote microbial growth within this soil type, allowing for more microbes to interact with the polymer (Sébaïbi et al., 2003).

The wet and loam environments were generally found to be very similar in the effect these environments had on the polymer. This was an indication that the amount of water present within the soil environment does not have a direct effect on the polymer degradation. It was noted however, that the SEM images did show that the wet environment showed greater changes to the fibres occurring than the loam soil. Since this was not observed in the other techniques, these changes that were observed must only be minor surface changes that have little impact on the rest of the polymer.

The sand environment was also found to have an impact on the degradation of the polymer. This was most likely due to microbial life present in the sand soil degrading the polymer rather than an aspect of the soil environment itself.

The dry and cold environments were found to generally preserve rather than degrade the polymer. This would be due to the impact that these environments have on microbial growth within the soil. The lack of moisture in the dry soil would cause pressure on any microbial colonies within the soil, slowing down any microbial growth (Yao et al., 2011). The cold environment, being at a lower temperature would slow microbial activity, making it harder the microbes to degrade the polymer.

Overall, it was observed that the PP fibres were preserved rather than degraded with only the early stages of degradation been observed in the most reactive environments. The impact the different environment had on the polymer indicates that a number of factors determine whether the polymer was degraded or preserved. Environments that enhance microbial growth such as the clay soil have a greater impact on the degradation of the polymer. Unusually the acidic soil was also noted to enhance microbial growth with the appearance of fungi being noted on the polymer during the study.

6.7 Summary

The investigation into the degradation of PP carpet in the soil environment found that PP was resistant to degradation in the soil over the 24-month burial period. There were some changes observed to the crystallinity and the methylene/methyl ratio over the 24 months. These changes are most likely due to the degradation of the polymer due to microbes.

It was observed that the clay and acidic environments generally had the greatest tendency to degrade the PP fibres. The clay soil has been noted to have a positive impact on microbial growth and the increased level of microbes present would be increase the degradation rate on the PP fibres. While the acidic environment has been observed to reduce most types microbial life, fungi in particular can survive very well in acidic soils. Fungi colonisation of the PP fibres was observed in the SEM micrographs. The lime and basic environments tended to have less of an impact on the degradation of PP. However, the lime soil was noted to degrade the polymer more than the basic soil. Lime was known to have good water retention properties compared to the loam soil used in the basic environment. It was more likely that the increased microbes present in the lime due to the greater availability of water was responsible for the greater impact on the degradation. This was confirmed by the effect of the wet soil, where the environment was saturated with water but had little impact on the degradation of PP. The sand environment also tended to degrade the polymer more than the other environments, most likely due to microbes present within the sand soil.

Chapter 7

Polyester Fibre Analysis

7.1 Introduction

PET was a very common polymer used for a large variety of different products, such as carpets, clothes and bottles. PET was one of the most common synthetic carpet fibres used mainly due to the stain resistant properties of this polymer (East, 2004).

During this project, PET was observed throughout the 24-month period in order to see if the soil environments degraded or preserved the polymer. In order to study the effect that the laboratory controlled burial environments have on the polymer, a variety of different techniques were used. These were SEM, ATR-IR spectroscopy and TGA. SEM investigated the changes to the polymer surface due to degradation. This includes investigating for evidence of changes to the roughness of the polymer surface, the formation of pores, fibre thinning and cracking. FTIR spectroscopy was used to observe changes to various features of the polymer structure, which includes observing the changes to the carbonyl and ester bonds in PET and the effect degradation has on the crystallinity of the polymer. TGA investigated the changes to the thermal stability and composition of the polymer due to degradation.

7.2 Characterisation

PET was the most common polyester used in textile production. Although non-PET polyester fibres like PBT and PTT, are rare in carpets, there was a growing market for these polymers (East, 2004). In order to confirm the identity of the polyester used in this study ATR-IR spectroscopy and DSC have been employed.

Figure 7.1 shows an IR spectrum of the polyester carpet and confirms that PET was present. The spectrum shows characteristic bands present at 1710 cm^{-1} attributed to C=O stretching, 1410 cm^{-1} attributed to both ring C-C stretching and C-H ring bending, 1247 cm^{-1} assigned to C(=O)-O stretching and 1102 cm^{-1} assigned to C-O stretching (Umamaheswari and Murali, 2013).

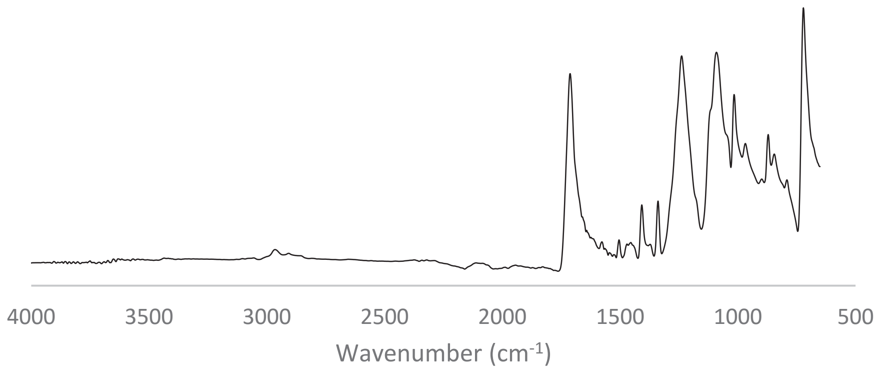


Figure 7.1 IR spectra of PET before soil burial

Figure 7.2 shows the DSC trace of a polyester carpet fibre. The m.p. was 249°C and this value was close to the reported value of approximately 255°C (Hansen and Atwood, 2005).

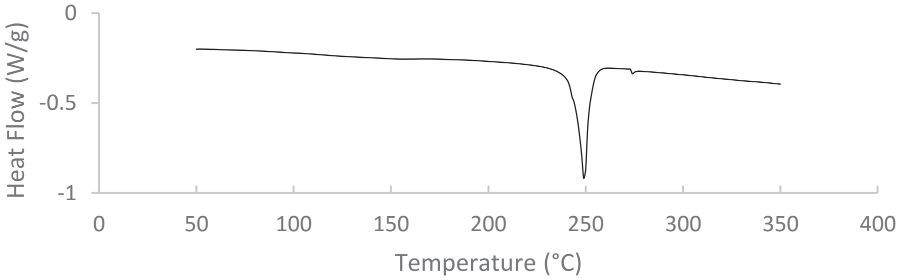


Figure 7.2 DSC graph showing m.p. of PET at 249°C

7.3 Scanning Electron Microscopy

7.3.1 Results

Changes to the morphology of the polymer surface over the 24-month period were examined using SEM. Previous studies have noted that signs of degradation in PET that can be detected by SEM include an increase in the surface roughness, formation of pores, fibre thinning and cracking (Brueckner et al., 2008; Liu et al., 2005b; Rahman, 2012). A typical micrograph of the PET prior to burial was shown in Figure 7.3. The surface appears mostly smooth with some variation in texture across the surface as well as some minor scratches that are attributed to the manufacturing process. The morphology of the surface of PET fibre was examined every 3 months to look for signs of degradation.

Most of the environments showed very little change by 3 months, except for the appearance of soil particles that resisted the cleaning process, as seen in the dry environment specimen example shown in Figure 7.4. The exception to this was the wet environment which showed what appeared to be a film covering some of the surface of the polymer (Figure 7.5). This was still the case for most of the environments up to 9 months, except for the wet environment specimen, which had lost the film covering by 6 months. Instead there were clusters of what may be microbes appearing in a large group attached to the polymer surface as seen in Figure 7.6. However, these do not cover much of the surface of the fibre, but instead are appearing in large clusters that attach to only a small section of the fibre and were not present throughout the entire fibre bundle. The clusters have mostly disappeared by 9 months with only small bundles on the polymer surface. Instead there was an increase in the variation of the surface texture of the fibre, which was observed to be rougher in appearance than before burial in the soil as seen in Figure 7.7.

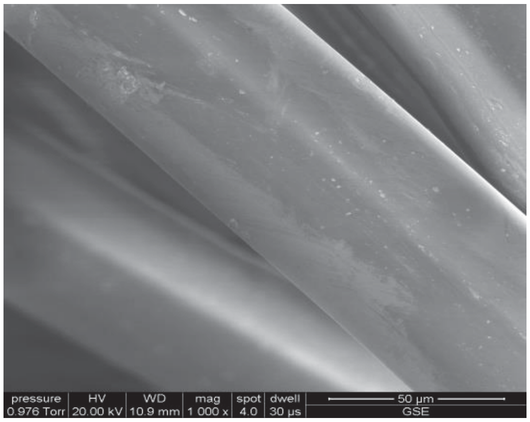


Figure 7.3 SEM micrograph of PET fibre before burial at HFW of 149.1 µm

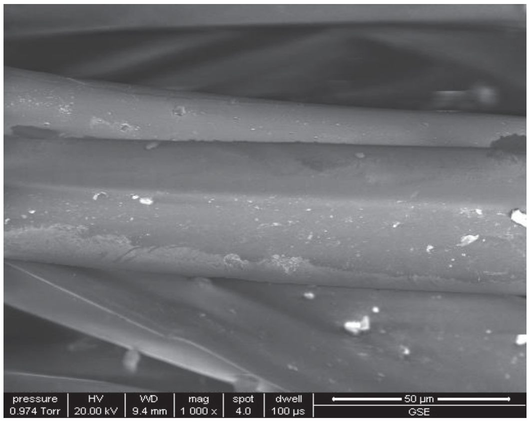


Figure 7.4 SEM micrograph of PET after burial in the dry environment for 3 months

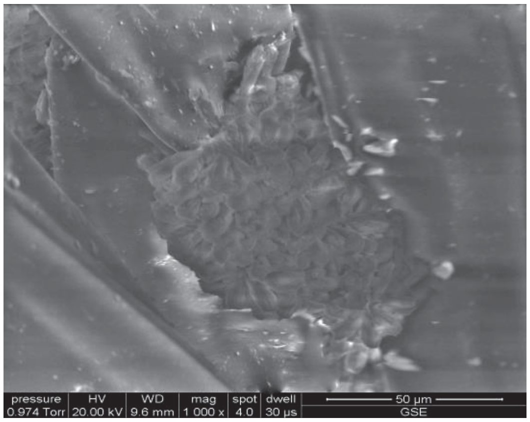


Figure 7.5 SEM Micrograph of PET after burial in the wet environment for 3 months

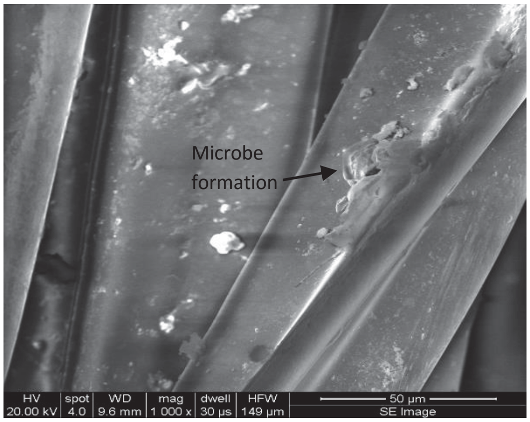


Figure 7.6 SEM Micrograph of PET after burial in the wet environment at 6 months showing mass attached to fibre

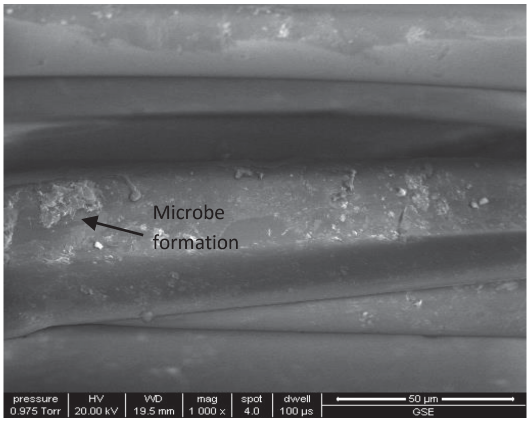


Figure 7.7 SEM micrograph of PET after burial in the wet environment for 9 months

By 12 months more of the buried specimens in the soil environments show some changes occurring to the polymer surface. The loam, clay, lime and acidic environments show an increase in the roughness of the polymer surface, as seen in the example micrograph in Figure 7.8. The clay environment produces a noticeable increase in the number of scratches visible on the polymer surface, as well as a thick film layer appearing on the edges of the fibres (Figure 7.9). The basic environment also produces changes to PET from 9 and 12 months, with the polymer from the basic environment at 12 months appearing similar to the polymer in the wet environment at 9 months (Figure 7.10). The wet environment, however, appears to have become smoother in the periods since 9 months, with the surface generally appearing smoother than the polymer before burial (Figure 7.11). This has been reported to indicate that the early stages of the hydrolysis of PET was occurring (Liu et al., 2005b).

At 15 months most of the environments, except for the dry soil have produced some degree of change to the polymer. The specimens from the lime, cold, acidic, basic and sand environments all show what appear to be microbial colonies in varying amounts. The lime, acidic, cold, clay and sand environments produce fairly widespread small groups of microbial appearing on the fibre surface, as seen in the example in Figure 7.12. The basic environment, however, produces large clusters of microbial life that appear in select areas on the polymer surface, as well as some fraying of the edge of the fibre occurring, as seen in Figure 7.13. The specimen from the wet environment, appears rougher along with the apparent microbial colonies seen in the other environments, as seen in Figure 7.14. The PET in the dry environment does not show any sign of change until 18 months where the small microbial colonies as that were observed in the other environments appear (Figure 7.15).

The loam, sand, clay, lime, cold and dry environments produced very little change to the polymer after 15 months, except for variations in the amount of attached microbial groups which varied depending on the months examined and no general increase or decrease was observed. The specimens in the basic and the acidic environments have both appeared to have become very smooth with the basic environment showing this at 18 months and the acidic at 21 months as seen in the example in Figure 7.16. The wet environment appears to have lost many of the attached colonies, but there was an increase in the fibre fraying and scratches visible on the polymer surface by 24 months, as can be observed in Figure 7.17

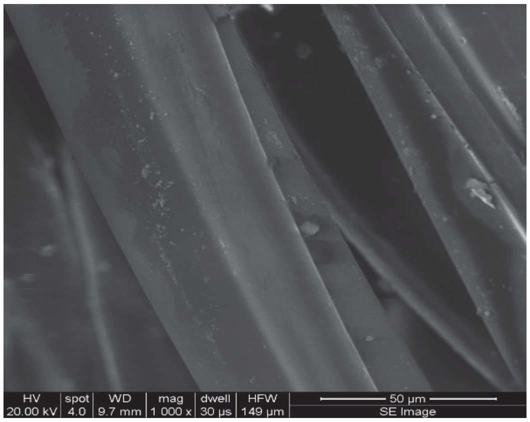


Figure 7.8 SEM micrograph of PET after burial in the lime environment for 12 months

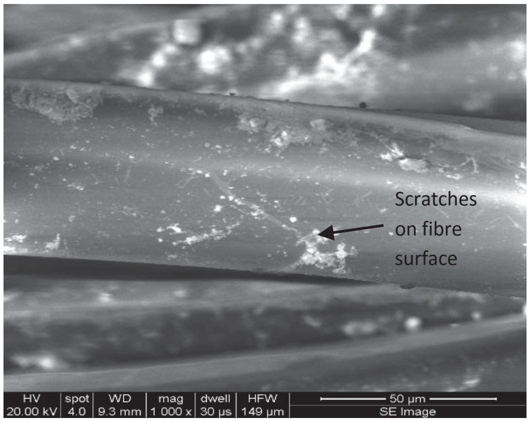

Scratches on fibre surface

Figure 7.9 SEM micrograph of PET after burial in the clay environment for 12 months

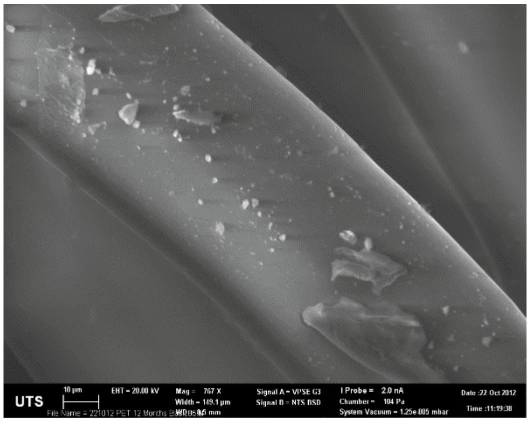


Figure 7.10 SEM micrograph of PET after burial in the basic environment for 12 months

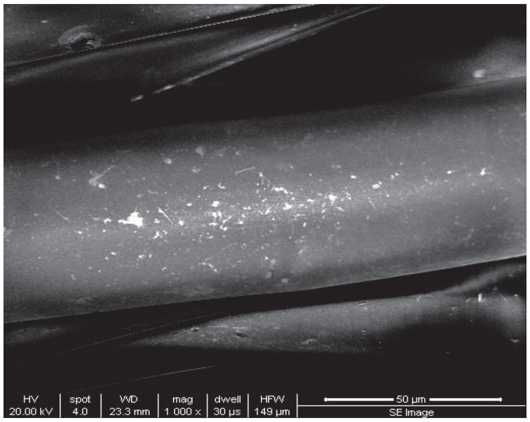


Figure 7.11 SEM micrograph of PET after burial in the wet environment for 12 months


Small groups of microbe formation

Figure 7.12 SEM micrograph of PET after burial in the acidic environment for 15 months

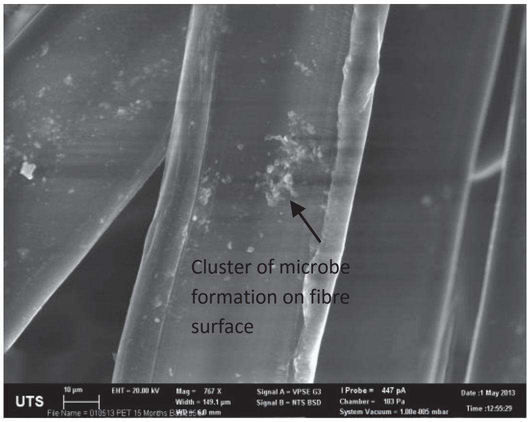

Cluster of microbe formation on fibre surface

Figure 7.13 SEM micrograph of PET after burial in the basic environment for 15 months

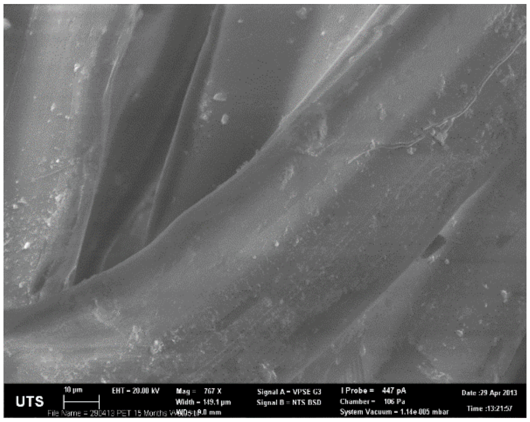


Figure 7.14 SEM micrograph of PET after burial in the wet environment for 15 months

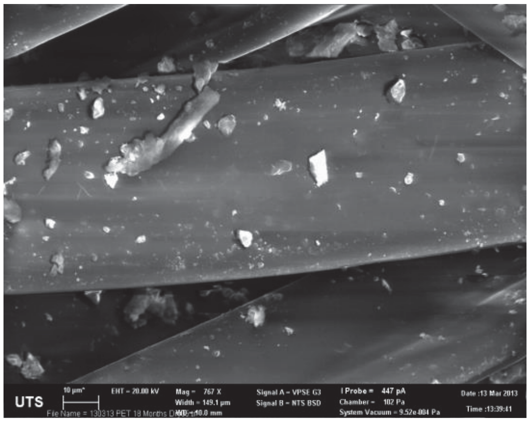


Figure 7.15 SEM micrograph of PET after burial in the dry environment for 18 months

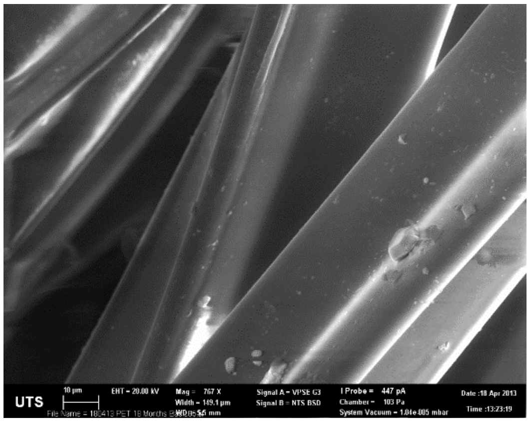


Figure 7.16 SEM Micrograph of PET after burial in the basic environment for 18 months

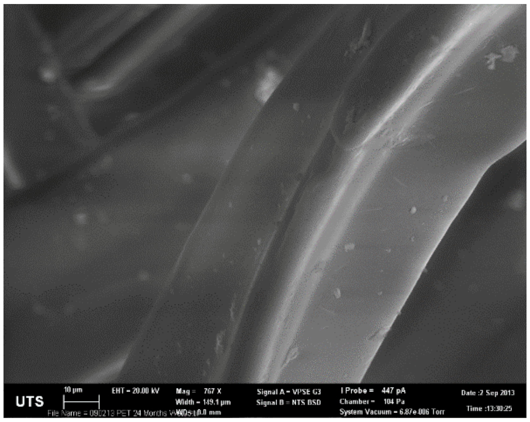


Figure 7.17 SEM micrograph of PET after burial in the wet environment for 24 months

7.3.2 Discussion

Most of the environments show very little change over the 24-month period with the specimens from the loam, sand, clay, lime, cold and dry environments only showing varying increases in microbial colonies on the polymer surface without any noticeable change occurring to the polymer itself. The acidic environment specimen was very similar to these environments throughout most of the 24 months, however, this environment towards the end of the burial period showed signs of hydrolysis occurring in the changes to the surface that occurred. The basic and wet environments specimens were fairly similar in how the changes occurred to the polymer surface, with these changes been more noticeable and the appearance earlier in the wet environment as opposed to the basic environment. The finding that the wet, basic and acidic environments showed the most change to the polymer, agrees with previous research that reported that the as the hydrolysis of PET occurs best in the presence of water or near impurities such as ions from acidic or basic environments (Edge et al., 1991).

Throughout the 24-month period it was observed that there are microbial colonies that appear to be attached to the polymer fibres. While this may lead to the assumption that the hydrolysis of PET was occurring through hydrolytic enzymatic reactions, it was possible that this microbial life may be feeding off another source within the environment as opposed to the fibre itself. The hydrolysis of PET has been observed to occur through either chemical or microbial means (Brueckner et al., 2008). The environment that tends to produce good conditions for microbial activity to degrade a polymer was the clay environment, due to the easily accessible nutrients and the ability of the clay soil to absorb water for microbes to live off (Brennan et al., 2014). However, the clay while it showed high levels of what appeared to be microbial growth on the fibre, did not show any changes that have been previously shown to indicate hydrolysis was occurring i.e. there were no cracks or holes appearing. Comparing this to the wet environment which, although a good environment to promote microbial growth, the excess water present in this environment tends to wash away microbes from the polymer (Abu-Ashour et al., 1994). The wet environment was observed throughout this study to effect the polymer more than the clay environment. This could indicate that the hydrolysis of PET in soil was more likely to be due to chemical means as opposed to microbial.

7.4 Fourier Transform Infrared Spectroscopy

7.4.1 Analysis of Infrared Band Ratios - Results

An analysis of the PET fibres was carried out using ATR-IR spectroscopy. Several factors were investigated to see if the soil environments degraded or preserved the PET fibres during the 24 months covered by this project. These factors included investigating the changes to the degree of crystallinity and changes to the C=O and C(=O)-O bands due to hydrolysis of the polymer in the spectra.

Figure 7.18 shows the 2nd derivative spectra of the PET fibres in the 9 soil environments and little visible consistent change was observed to occur to the PET fibres in the soil environments. There was little change observed to the band at 1340 cm^{-1}, which was a commonly used as an indication that there are changes to the crystallinity of the polymer (Donelli et al., 2010).

In order to check whether there was change to the crystallinity of the polymer, the crystallinity was investigated by using Eqn 6.1 which relies on using the intensities of the bands at 1120 and 1100 cm^{-1} (Donelli et al., 2010).

$$Degree\ of\ Crystallinity = \frac{I_{1120}}{I_{1100}} \qquad \textbf{Eqn 6.1}$$

where I_{1120} was the absorbance of the band at 1120 cm^{-1} and I_{1100} was the absorbance of the band at 1100 cm^{-1}.

Figure 7.19 shows the crystallinity changes to PET determined using Eqn 6.1. It was observed that the overall trend in many of the polymer specimens was a slight decrease in the degree of crystallinity. It can be seen from the loam, wet, dry and acidic environment specimens that there was a slight increase in the crystallinity that occurred before it started to decrease leading to the overall decrease in crystallinity noticed. The specimen from the clay environment shows the opposite trend with a decrease occurring at 6 months followed by an increase over time leading to overall trend showing an increase in the degree of crystallinity. The specimens from the lime and sand environments show a continual decrease to the crystallinity happening over time. The cold environment specimen shows a very small increase overall and little change in crystallinity was indicated.

In order to compare the effect, the environments had on the polymer crystallinity, the slopes were found from Figure 7.19. The slopes are depicted in Table 7-1. It can be seen that there was a slight decrease in the degree of crystallinity occurring to the PET fibres in most of the environments with the wet environment showing the greatest change to the crystallinity of PET, while the cold environment showed the least. Many of the environments show a large standard error when comparing the data to a linear trend line. This indicates that there was very little change occurring to the degree of crystallinity in most of these environments since the standard error found was greater than the changes observed.

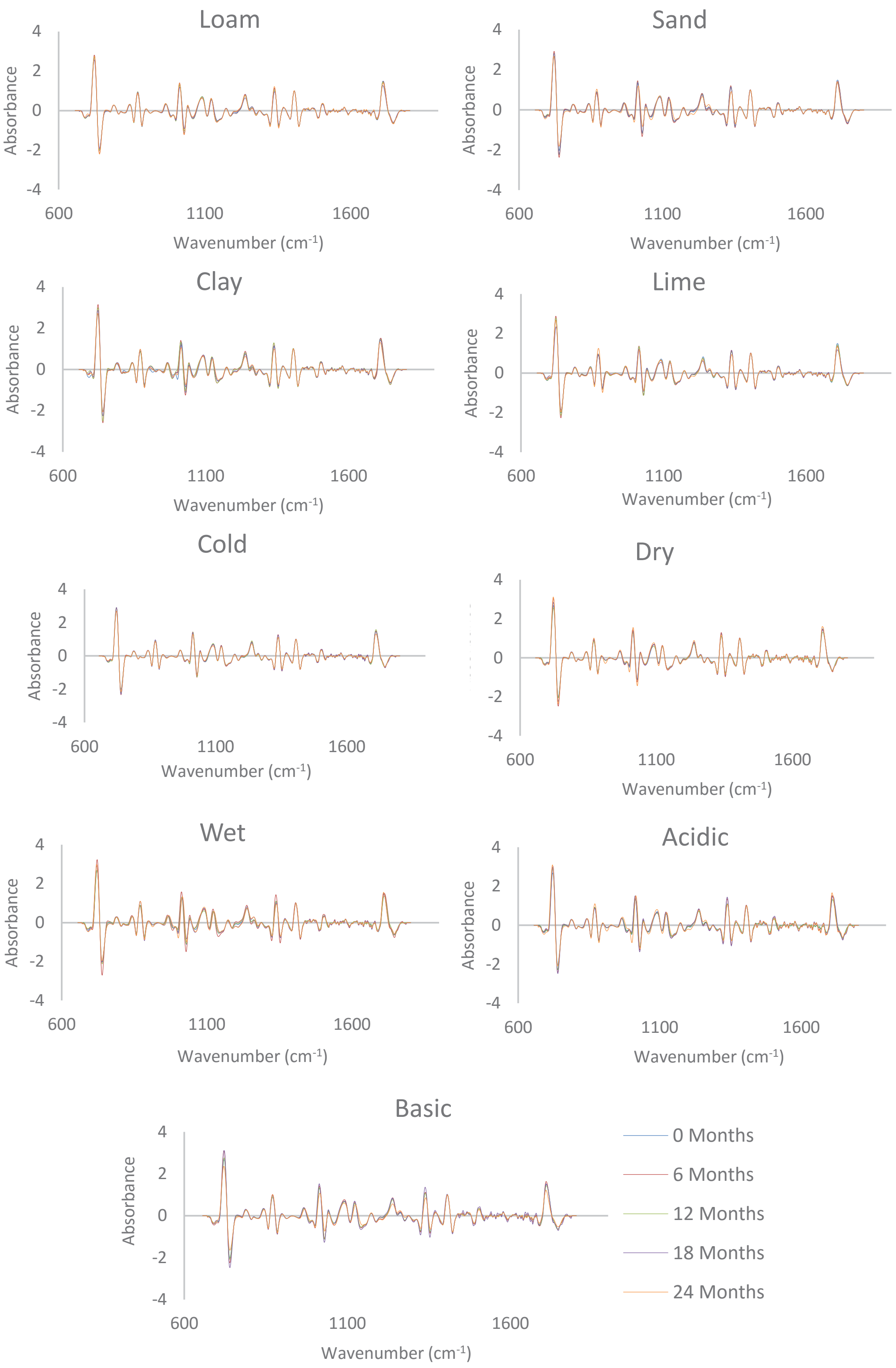


Figure 7.18 2nd derivative IR spectra of PET in the 9 soil environments

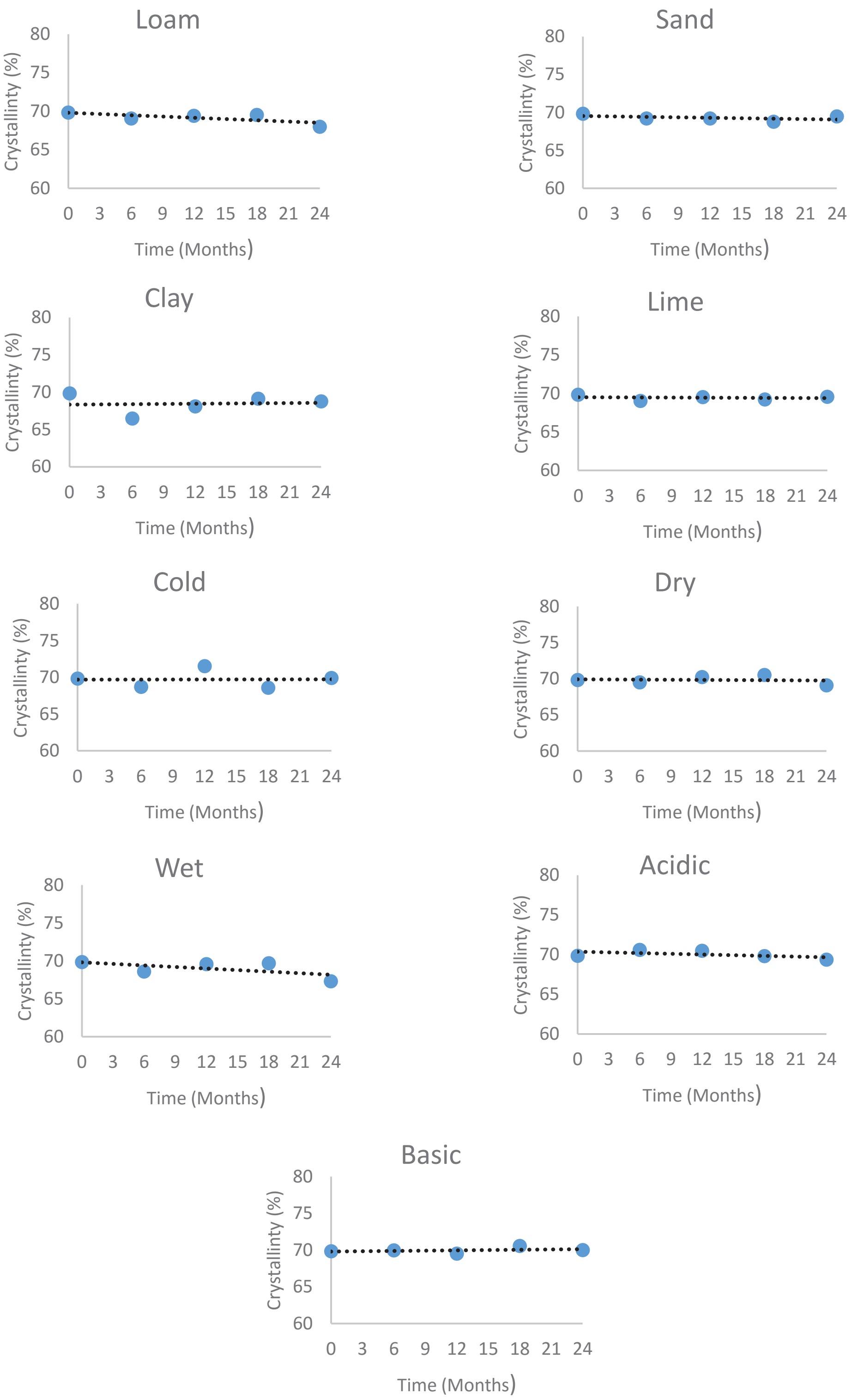


Figure 7.19 Observed changes to the mean crystallinity phase of PET over 24 months in the soil environments

Table 7-1 Degree of crystallinity found using the band absorbance ratio of 1120/1100 cm^{-1}

Environment	Degree of crystallinity ± Standard Error
Loam	$-5 \pm 3. \times 10^{-2}$
Sand	$-2 \pm 2. \times 10^{-2}$
Clay	$9 \pm 80 \times 10^{-3}$
Lime	$-5 \pm 20 \times 10^{-3}$
Cold	$3 \pm 70 \times 10^{-4}$
Dry	$-8 \pm 30 \times 10^{-3}$
Wet	$-7 \pm 5 \times 10^{-2}$
Acidic	$-3 \pm 3 \times 10^{-2}$
Basic	$1 \pm 2 \times 10^{-2}$

Hydrolysis has been found to be the most likely method of degradation that occurs to PET in soil (Colin et al., 1981). The most accepted mechanism for the hydrolysis of PET was that water causes random in chain scission by breaking the C-O bond (located near the carbonyl bond), causing de-esterification of the polymer chain to occur (Sammon et al., 2000). A decrease in the band ratio of 1247 cm^{-1} relative to a reference peak indicates whether hydrolysis of the polymer has occurred. For the current study the reference peak used was the band at 1407 cm^{-1} associated with the benzene ring in plane deformation (Badia et al., 2012; Donelli et al., 2010). This band has been found in previous studies to be not affected by the orientation or conformation of the polymer making it ideal for use as an internal reference. The band at 1710 cm^{-1} was also checked as this band was not expected to show any significant change since hydrolysis has little effect on the carbonyl bond itself and was not expected to be affected by the environment.

Figure 7.20 and Table 7-2 show the changes in the slope of the two bands of interest and small decreases are observed to have occurred to all of the buried PET fibres in all of the bands of interest. The wet environment had the greatest impact on the PET fibres with regards to the 1237 cm^{-1}, while the least was the cold environment. Although the lime environment was observed to have a comparatively small impact on the PET fibres with regards to the 1237 cm^{-1} band ratio, the error for this result was found to be unusually high and this may indicate that there may be greater change occurring within this environment. The 1710 cm^{-1} band ratio was found to be consistent across the 9 soil environments with the observed changes been approximately the same. This indicates that any changes to the C=O bond was not due to the environment. The exception to this was the sand environment which shows a smaller change in slope when compared to the other environment. Due to the large error to result ratio, however, this environment was most likely different due to error sources as opposed to the changes within the environment itself.

Table 7-2 The slope of 1710/1407 and 1237/1407 band ratios versus burial time with standard error.

Environment	1710/1407 ratio ± Standard Error	1237/1407 ratio ± Standard Error
Loam	-2 ± 0.7 x 10^{-2}	-5 ± 1 x 10^{-2}
Sand	-1± 10 x 10^{-3}	-5 ± 2 x 10^{-2}
Clay	-8 ± 10 x 10^{-3}	-3 ± 3 x 10^{-2}
Lime	-9 ± 10 x 10^{-3}	1 ± 20 x 10^{-3}
Cold	-2 ± 0.7 x 10^{-2}	-1 ± 1 x 10^{-2}
Dry	-1 ± 0.8 x 10^{-2}	-4 ± 2 x 10^{-2}
Wet	-1 ± 1 x 10^{-2}	-9 ± 3 x 10^{-2}
Acidic	-1 ± 0.7 x 10^{-2}	-3 ± 3 x 10^{-2}
Basic	-1 ± 0.9 x 10^{-2}	-5 ± 2. x 10^{-2}

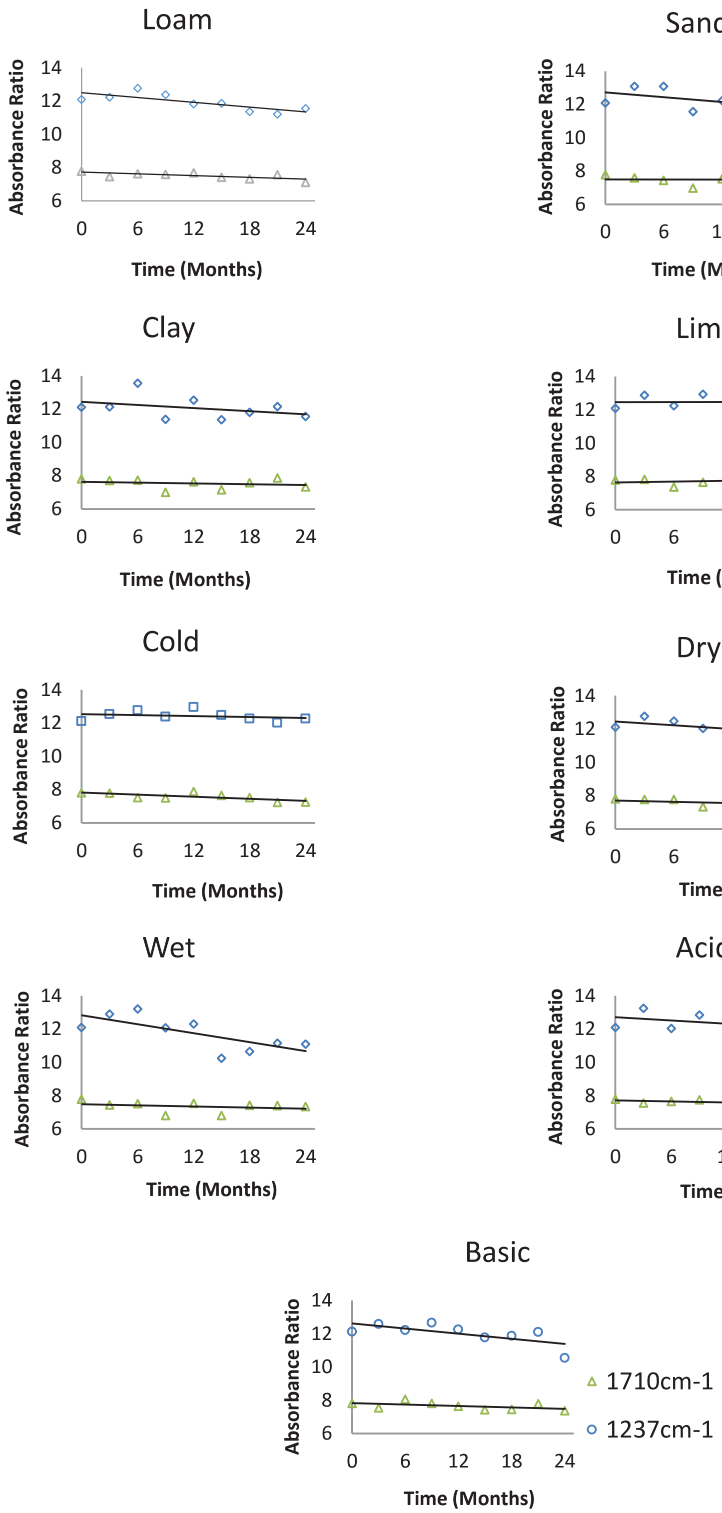


Figure 7.20 Graph showing changes in the slope of 1710 cm^{-1} /1407 cm^{-1} and 1237 cm^{-1} /1407 cm^{-1} ratios

7.4.2 Analysis of Infrared Band Ratios - Discussion

Overall it can be observed from the data that the polymer was mostly preserved over the 24-month burial period in the 9 soil environments. While there was variation that occurred among the 9 soil environments, with the wet environment consistently showing greater change occurring to the polymer than the less reactive cold environment, the changes observed were relatively small. There was a variety of factors that were found to contribute to the preservation of the polymer. The main factors were found to be the temperature of the environment, the amount of water present within the environment itself, pH of the environment and the crystallinity of the PET fibres.

The temperature of the environment has a significant impact on the rate of hydrolysis of PET. It has been found previously that the hydrolysis of PET only readily occurs at temperatures above the T_g of PET (67°C for amorphous PET, 81°C for crystalline PET) (Demirel et al., 2011 Hansen and Atwood, 2005; Pirzadeh et al., 2007; Škvarla et al., 2010). Since most of the environments that were investigated were at room temperature, which was well below the T_g of PET, this would slow down the hydrolysis of the polymer. The cold environment was kept at 4°C, a lower temperature that would be expected to slow down hydrolysis further. This can be seen in the data as the cold environment consistently showed very little degradation compared to the other environments. Although no warm environment was tested in this study, the higher temperature was predicted to have an impact on the hydrolysis of.

The moisture content of the environment had an impact on the degradation of the polymer, with the wet environment showing the greatest change to the polymer specimens overall to the 1237 cm^{-1} band, as well as to the crystallinity of the polymer. The dry environment showed very little change to the polymer when compared to the wet environment. Since hydrolysis was the main mechanism of degradation of PET in soil, the amount of available water present would greatly impact the rate of hydrolysis (Colin et al., 1981; Pirzadeh et al., 2007). The loam environment was also found to have an impact on the fibres when compared to the other environments. This could be due to the need to keep the moisture level of this environment as consistent as possible with the requirement of extra water to be added over time. It was possible that during the times when water was added to the loam environment, the amount of free water present increased, allowing for greater degradation of the polymer to occur (Pirzadeh et al., 2007).

Environments such as the clay soil, which have a high tendency to absorb water when compared to loam soil, tend to preserve rather than degrade PET (Nguyen and Marschner, 2014). For hydrolysis of the polymer to occur, there needs to be freely available water present within the environment (Pirzadeh et al., 2007). While the clay soil water absorption can increase the moisture content of the environment, this water would be locked in the clay soil allowing very little free water to be available for the hydrolysis of PET. While in the loam soil used in the wet environment, this water was not as easily absorbed by the surrounding soil allowing more water to directly interact with the polymer. This was observed in the data as the clay soil consistently showed less degradation than the wet environment. This result was also repeated in the specimens removed from the lime and basic environments. The lime environment, which absorbs water more readily than loam soil, had less of an impact on the polymer than the basic environment even though both environments had a similar pH (Sébaïbi et al., 2003).

The pH of the soil environment has previously been found to have an impact on the degradation of PET with both basic and acidic environments being observed to increase the rate of hydrolysis when compared to a neutral environment (Edge et al., 1991; Sammon et al., 2000). It was observed in this study, however, that while the basic environment was found to have a slightly greater effect on the breakage of the (O=C)-O when compared to the loam soil, the acidic environment had less of an effect. PET carpet fibres usually undergo a pre-treatment process before the fibres are dyed in order to remove undesirable features such as static charge build up and resistant to cleaning (Bendak and Raslan, 2011; Zimmermann and Billig, 2011). There are a variety of methods used to remove these feature including thermal and alkali fibre pre-treatments. Due to the PET used in this study being a commercial product, it was not possible to know the history of the fibres including the pre-treatment. However, it was possible that the pre-treatment of the fibre could have an impact on the way the polymer interacts with the soil allowing for resistances to an acidic environment to occur.

It has been noted that while there were some changes occurring to PET in the 9 soil environments, these changes were found to be minor having little impact on the polymer itself. The PET fibres used in this study were found to have a degree of crystallinity of 69.8% before burial in the soil. This was a high value for the crystallinity of the polymer and has an effect on the ability of water to hydrolyse PET. Crystalline regions of the polymer are not able to be hydrolysed by water. They have also been previously observed to act as a barrier to the water making it harder for water to reach the amorphous regions that can undergo hydrolysis (Guebitz and Cavaco-Paulo, 2008; Pirzadeh et al., 2007). Since the fibres used in this study were highly crystalline, this prevented water reaching the amorphous regions, preserving the polymer rather than allowing hydrolysis to occur. The environments that have greater levels of water, such as the wet soil, have a greater chance of water reaching these amorphous regions allowing some hydrolysis to occur.

It has been observed that the clay, basic and cold soils showed an increase in the crystallinity of the PET fibres while the rest of the environments showed a decrease. It has been noted that many previous studies observed an increase in the crystallinity of the polymer occurring when PET undergoes hydrolysis (Badía et al., 2009; Liu et al., 2005a; Pirzadeh et al., 2007). This increase in crystallinity was believed to occur due to hydrolysis only in the amorphous regions of the polymer (Freure et al., 1999). The polymer chains in the amorphous regions are broken up into smaller segments, which due to increased mobility, are able to realign and crystallise, increasing the overall crystallinity of the polymer (Pirzadeh et al., 2007). While an increase in the crystallinity was observed for the polymer from 3 of the environments, the other 6 environments show a decrease in the crystallinity occurring to PET.

The PET fibres have been found to be a polymer resistant to degradation in soil. This was mainly due to the crystalline nature of the fibres combined with the various properties of the environments. The environments that were found to have an effect on PET were those containing significant quantities of free water, such as the wet environment. Environments that tended to absorb water such as the clay and lime soils were more likely to preserve PET due to the lower levels of water reaching the polymer. While the amount of free water was the greatest factor in determining whether hydrolysis of the polymer would occur, it was found that basic soil also increased the level of hydrolysis that occurred when compared to the loam soil environment. The acidic environment was found to have a preserving effect on the fibres and this may be due to the pre-treatment that occurs to the fibres before been dyed and was worth investigation in a future study as acidic environments usually have a degrading effect on PET (Hansen and Atwood, 2005).

7.4.3 Multivariate analysis

Multivariate analysis was conducted on the IR results of PET within the different environments. The PCA obtained from the data confirms that there has been very little degradation that has occurred to the polymer. It can be seen from the first PCA plot in Figure 7.21 that there was little grouping of the data when looking at the effect the environment has on the polymer, with all the various environments been scattered throughout the plot. The second PCA plot in Figure 7.21 shows some grouping of the different time periods, however, these groups are still located within the same vicinity of the plot as the fibres before burial. This indicates that the environment has had very little effect on the hydrolysis of the polymer with the changes been observed been attributed to the length of burial time as opposed to the environment itself.

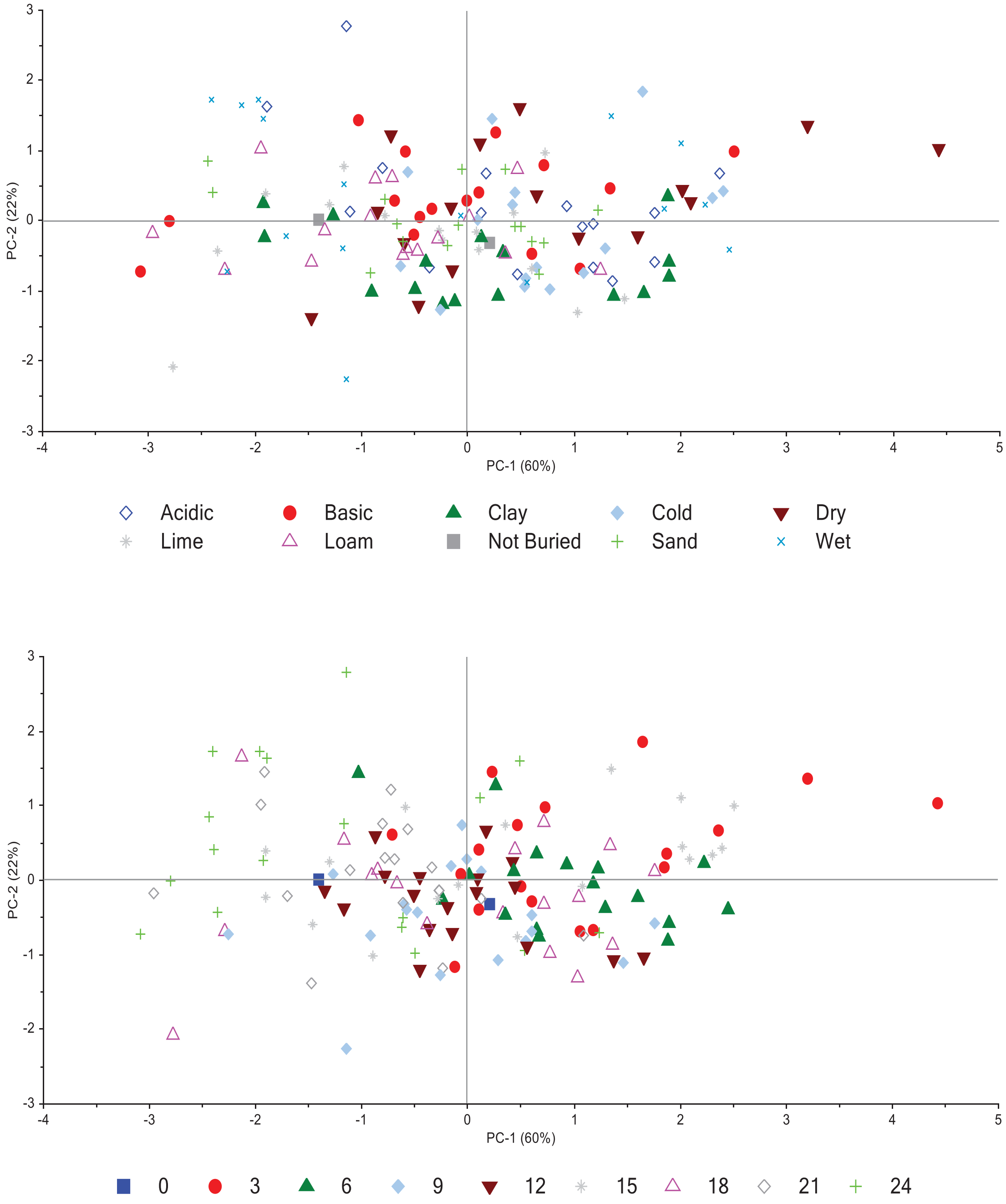


Figure 7.21 PCA plots of PET sorted by environment (top) and time (bottom)

Using the pre-treated IR data from the PET samples, a PLS-R graph was created with the loam environment used as a reference. In order to decide which model would be the most useful for PET, both the loadings (Figure 7.22) and the explained variance (Figure 7.23) for each factor were investigated to see which bands were prominent in each factor. The factors that feature the bands of interest at 1710 and 1237 cm^{-1} as well as having a good variance were used to create the model for PET. Factor 3 was observed to have the best combination of variance (once noise peaks were removed) and the peaks of interest. It can be seen from Figure 7.23 that the variance was poor throughout the different factors with 3 and 4 showing the best match between the calibration and the validation. When comparing factors 3 and 4, factor 3 showed the peaks of interest while factor 4 was showing more noise. Although factors 1 and 2 focused more on the peaks of interest, the variance for these 2 factors was poor meaning that other factor that took these peaks into account had to be used.

The PLS-R of the loam soil environment (acting as a reference) was shown in Figure 7.24 with outliers removed. It can be seen that the total R^2 for this model was 0.59 indicating a poor fit. However, it can also be seen in Figure 7.24 that the data up to and including 15 months generally shows a fairly good match with the model. After 15 months this model breaks down with the 18-24 month period moving away from the model showing a poor fit for this time period. There could be a variety of reasons for this poor fit including factors including the effect fibre orientation has on the infrared spectra as well as any differences between the fibres caused by manufacturing (Hansen and Atwood, 2005).

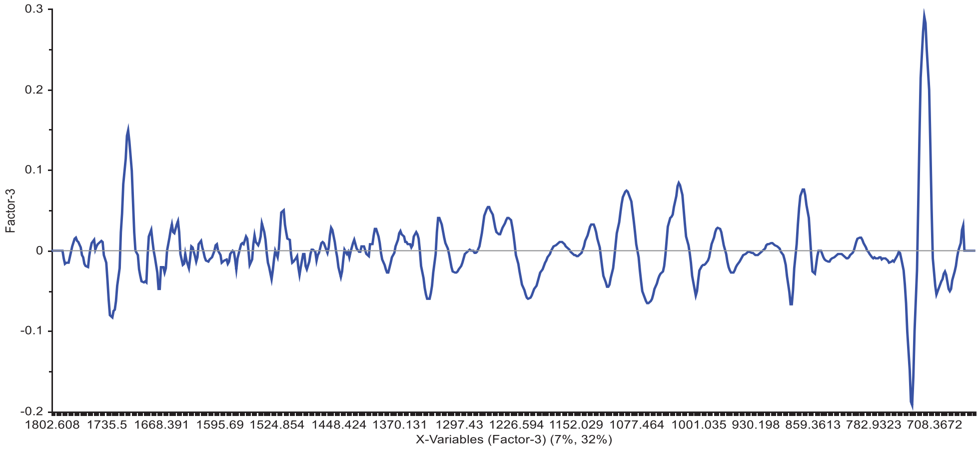


Figure 7.22 Factor 3 loadings showing peaks of interest at 1710 and 1237 cm^{-1}

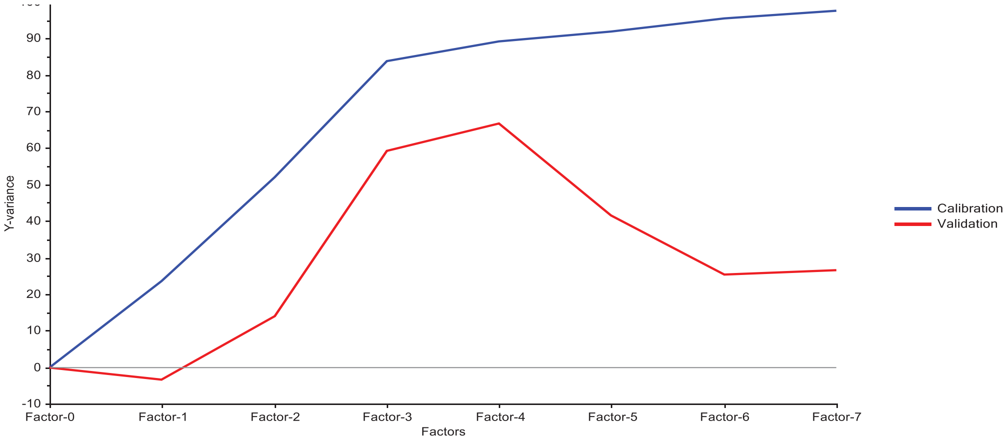


Figure 7.23 The explained variance between the calibration and validation of the PLS-R

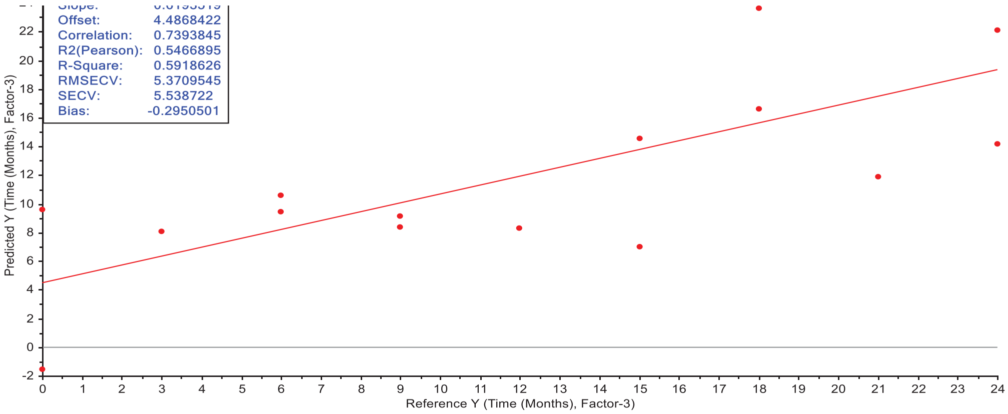


Figure 7.24 Model predicted using the loam environment IR data by PLS-R

7.5 Thermogravimetric Analysis

The PET fibres were analysed using TGA. Figure 7.25 shows the TG and DTG data for the fibres in the wet environment from 0 to 24 months. The PET follows a one-step decomposition process that starts at approximately 300°C and finishes at 550°C when in a nitrogen environment. Approximately 90% of the mass of the polymer was lost during the decomposition process with about 10-15% left as a carbon residue. This mass loss during the decomposition step has been attributed to the random chain scissions that occur when PET was degraded thermally (Dimitrov et al., 2013). This one stage process was also visible in the DTG trace as can also be seen in Figure 7.25 with the peak maximum appearing at around 430°C.

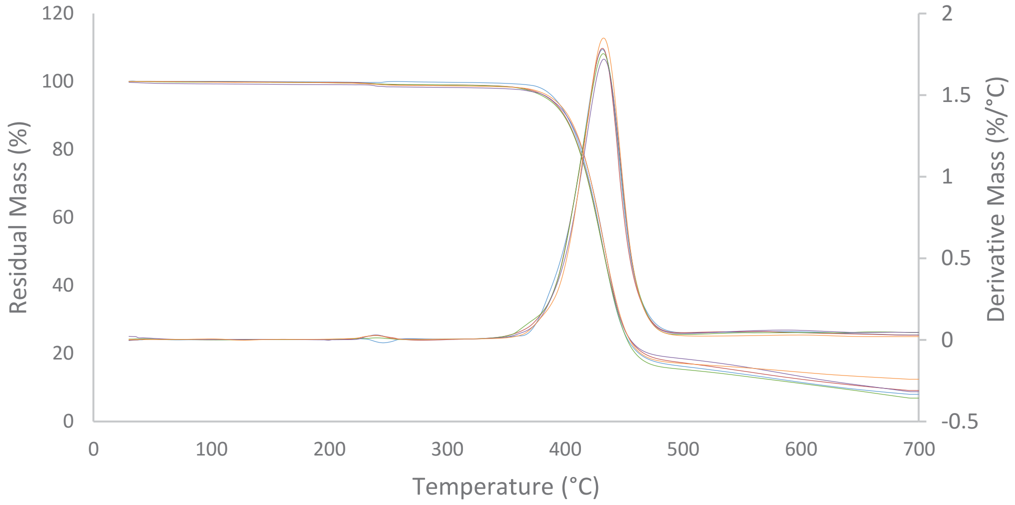


Figure 7.25 TG trace of PET fibre in the wet environment from 0 to 24 months

In the TG plots there was little consistent change that occurs to PET in any of the environments over the 24-month period. There were no observed changes in areas previously associated with the hydrolysis of PET, such as a change in the thermal stability of the polymer (Turnbull et al., 2012). The DTG curves also showed little change occurring to PET over time. The signs that have previously been noted to indicate that the hydrolysis of PET was occurring was a decrease in the peak maximum as well as an increase in the width of the peak in the DTG curve (Dimitrov et al., 2013). It has been put forward that these changes occur due to the products of the hydrolysis process, which breaks up the polymer chain, thus decreasing the purity of the PET fibres (Gu et al., 2001; Pirzadeh et al., 2007). Since the wet environment was predicted to show the greatest degree of hydrolysis, this environment was expected to show the greatest change. However, it can be seen from Figure 7.25 that there was very little consistent change occurring in this environment. There was no change to the width of the peak in the DTG curves and very little change occurring to the height. Figure 7.26 shows the changes in the peak height of PET in all of the environments. There was no consistent change across all of the environments, with half showing a slight increase in height and the other half showing a decrease. It was more likely that the changes noticed are more due to variation that occurs to PET fibres during manufacturing as opposed to any noticeable hydrolysis occurring (Militky, 2009).

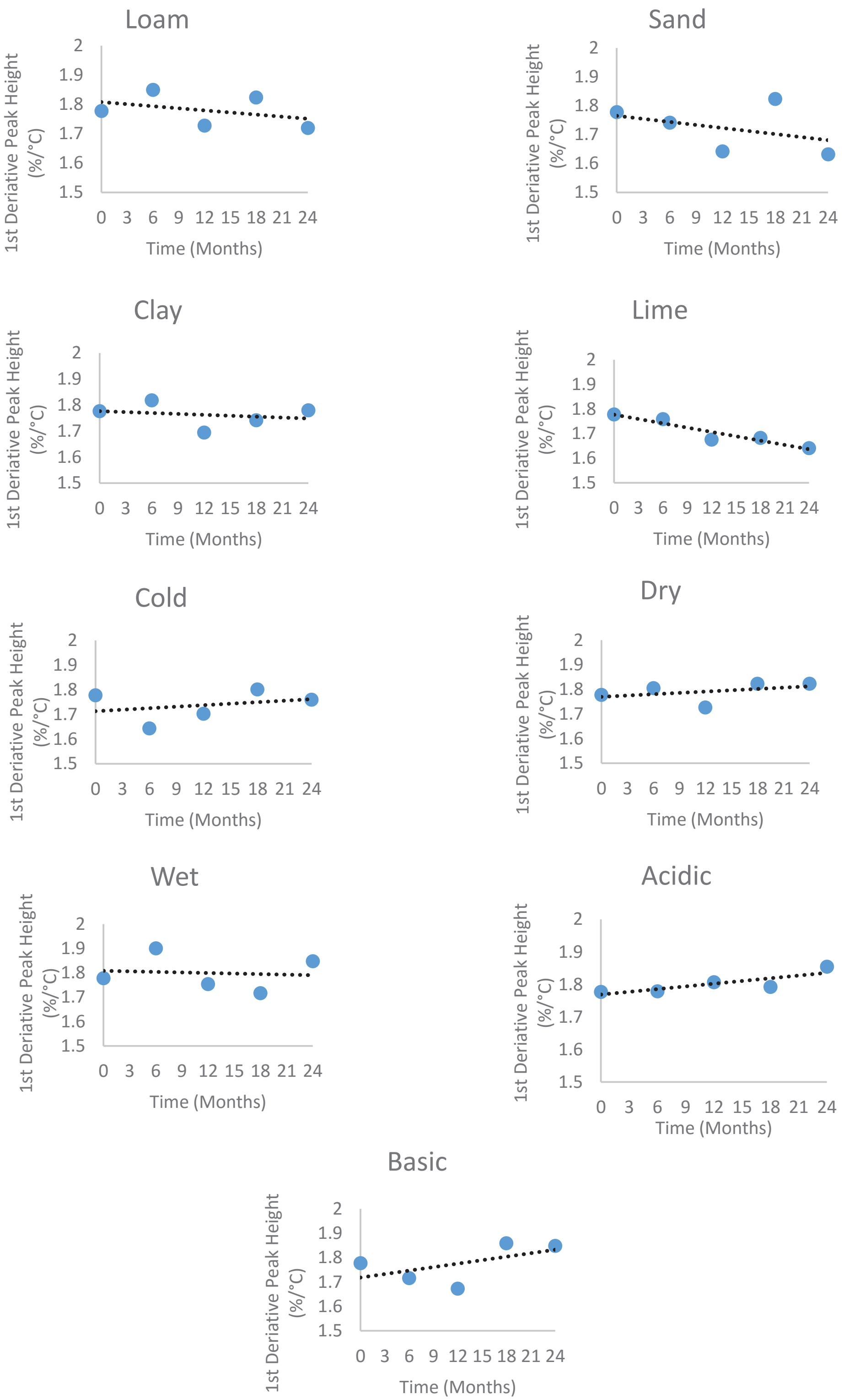


Figure 7.26 DTG peak height for PET as a function of burial time in the 9 soil environments

From the TG data, very little change was occurring to the PET fibres with any change that was observed attributed to variations during manufacturing as opposed to any actual degradation. Since TGA was a technique used for investigating changes throughout the polymer as opposed to surface changes, it would be less likely to detect changes to only the polymer surface such as the low levels of hydrolysis been observed to occur to PET (Prime et al., 2014). This was unlike techniques such as IR which was more likely to detect surface changes (Suëtaka and Yates, 2013). The data from the analysis of PET indicates that TG was not a viable technique for the analysis of degradation of the polymer fibres in soil due to the very minor changes that occur.

7.6 Discussion

PET was found to be preserved rather than degraded in most of the soil environments. This was due to the highly crystalline nature of the polymer fibres investigated in this study. However, some of the environments were observed to have an impact on the rate of hydrolysis of the PET fibres.

The specimens from the dry, cold, sand, clay and lime environments showed very little degradation occurring over the 24-month period in either the SEM micrographs or the IR spectra. There was evidence of microbial growth occurring on the polymer fibres in these environments as seen in the SEM micrographs, however, this may be due to the microbial activity within the environments themselves as opposed to the polymer fibres. The wet environment was found to be the most effective in degrading the polymer through hydrolysis as it was observed to be the most reactive environment with the greatest changes observed, particularly with regards to the 1237/1407 cm^{-1} band ratio that shows changes occurring to the ester bond where the random chain scission occurs as well as showing visible change in SEM micrographs. The basic environment was also seen to be more likely to degrade rather than preserve the polymer however, this was not seen to the same extent as the wet environment indicating that the amount of water present has a greater effect on the hydrolysis of PET than the presence of a weakly basic environment. The loam environment was found to have some impact on the polymer with some changes to the 1237 cm^{-1} band occurring. However, changes to this environment were not very prominent in the SEM micrographs showing that there had been very little visible changes to the polymer surface. The observations in the acidic environment were unusual as previously this environment has been shown to have a similar impact on PET to the basic environment (Arrieta et al., 2013).

From the environments that had caused a greater of degree of hydrolysis to occur, the main factors that impact on a soil environments potential to hydrolyse the polymer can be seen. These are the temperature, pH, soil type and the moisture content with the moisture content having the greatest impact since the wet environment generally hydrolysed the PET fibres more than any of the other environment.

Temperature has been shown both in this and previous studies to have an impact on the hydrolysis of PET, with colder temperature slowing the rate of hydrolysis down (Pirzadeh et al., 2007; Škvarla et al., 2010). A comparison of the specimens from the loam and cold environments demonstrates this process, with the cold environments showing a much slower rate of hydrolysis to the polymer than the room temperature loam soil. In this study it was shown that the basic environment had a much greater effect on the polymer than the acidic one. The reason for this occurring in this study was unknown, but it may be due to the pre-treatment of the PET fibres that occur in order to improve the carpet properties (Bendak and Raslan, 2011; Zimmermann and Billig, 2011). In future studies comparing untreated PET fibres to treated ones may indicate whether this was true. The soil type was found to have an impact on the rate of hydrolysis with the environments such as the clay and lime, which have a tendency to absorb water having a slower rate of hydrolysis to PET than the loam and wet environments (Brennan et al., 2014; Sébaïbi et al., 2003). This was most likely due to the water being absorbed by these soils, leaving very little water for a direct chemical hydrolysis reaction to occur. The moisture content of the environment was extremely important in relation to the rate of hydrolysis since this degradation reaction will not occur without water been available and present within the soil environment.

Even in the most reactive environments, however, the rate of hydrolysis was very low overall indicating the stability of this polymer in soil (Demirel et al., 2011; Hansen and Atwood, 2005). The conditions needed to easily hydrolysed PET would not occur in any soil environment. This means that this polymer if found in a burial scene would not show much change from at the time of burial to its discovery due to this polymer’s ability to resist degradation.

7.7 Summary

PET was observed in this investigation to be preserved in the soil environments. This was due to a number of factors including the highly crystalline PET investigated as well as the low temperatures encountered in this investigation. Hydrolysis was the method by which PET degrades and it requires high temperatures that are unlikely to be encountered in a soil environment. The high crystallinity of this polymer stops hydrolysis from occurring as degradation of the PET fibres can only occur in the amorphous regions. These regions are protected against hydrolysis due to the crystalline regions acting as a barrier to water not allowing hydrolysis to occur.

The environment that had the greatest impact on the degradation of the polymer was the wet soil. This was due to availability of water in this environment allowing a greater rate of hydrolysis. The basic environment also tended to degrade the polymer in comparison to the other environments, which was most likely due to the increased water available in this environment due to the method used to increase the pH of the soil. The other environments had very little impact on the polymer fibres tending to preserve PET. This was due to factors such as reduced temperature and reduced available water.

Chapter 8

Conclusions

8.1 Conclusions

A clandestine burial of a body may be accompanied by covering materials such as textiles and plastic sheeting. Such items can provide valuable information that establishes the identity of a victim or a perpetrator. The nature of a burial environment affects the state of preservation of such grave goods and, therefore, the integrity of the evidence. For this thesis, five synthetic polymer materials were chosen for investigation based on their common usage in plastic film and carpets and therefore the likelihood of these polymers appearing in a forensic investigation. In order to determine the effect a soil burial environment has on the degradation of such polymers of interest were buried in model soil environments over a range of burial periods. These burial environments varied by soil type, temperature, pH and moisture content.

The properties of the soil environments in this study impacted the degradation of the five polymers. It was observed throughout this study that the cold and dry environments preserved the polymers. The lack of moisture in the dry environment preserved PET and nylon, which both require water to degrade. PE, PP and PVC were also preserved in this environment because the lack of moisture reduced the quantity of microbial life in the soil responsible for the degradation of such polymers. The lower temperature of the ‘cold’ environment reduced both the rate of hydrolysis and the microbial life in the soil.

The environments that had the greatest tendency to degrade the polymers varied depending on the mechanism by which the polymer degraded as well as the properties of additives within the polymer. However, some soil environments were observed to degrade the polymers more consistently over the time period investigated. The clay environment caused more significant degradation of PE, PVC and PP compared to the other environments studied. Clay provides a rich nutrient source for microbial life as well as being a good retainer of moisture. Both of these factors allowed this environment to have a greater influence on the polymer structure where a microbial mechanism was responsible for.

Another environment that was consistently observed to degrade the polymers was the lime environment. This environment was observed to have the greatest impact on nylon, PE and PVC. This environment also has good moisture absorption properties allowing it to hold water for use by microbial life. The basic nature of this environment does allow it to interact with polymer additives that are of an acidic nature. Although the pH of the ‘lime’ and ‘basic’ environments was similar, the lime environment was generally observed to be more reactive than the basic soil environment. This was due to the fact that the lime soil holds moisture better than the loam soil used in the basic environment.

Of the loam soil environments, the wet environment generally had the greatest effect on the degradation of the polymers, with the wet environments degrading PE, PVC and PET. The wet environment enhances microbial growth, but due to the movement of the water through the soil, microbes are potentially migrated away from the polymers, reducing the ability of this environment to degrade the polymers. In PET, the overabundance of water allowed for the greater rate of hydrolysis to occur.

The other environments generally were observed to have a moderate effect on the polymers with some exceptions such as the effect the acidic environment had on PP. The sand soil was observed to have a greater effect on nylon and PP than was expected considering the properties of the soil.

There were various analytical techniques used in this study in order to determine the effect the burial environment had on the polymer properties. SEM and AFM were utilised in order to examine the physical changes to the polymer surface. FTIR and Raman spectroscopy were used to examine the microstructural changes due to degradation within the polymer. TGA investigated changes to the composition of the polymer as well the thermal stability. UV/Vis spectroscopy determined changes to the additives within particular polymers. It was determined throughout this study that particular techniques were able to provide information about certain polymers. SEM, FTIR spectroscopy and TGA were determined to provide viable information about all of the polymers of interest. However, AFM was only able to provide information about PVC and PE as these polymers were in the form of film. The use of this technique was problematic for the carpet fibres examined Raman spectroscopy was utilised only for the PE specimens as fluorescence due to the presence of additives caused interference in the analysis of the other polymers. UV-Vis spectroscopy was used to analyse the changes to the plasticiser content of PVC.

This study was successful in examining the effects the soil environments had on the five polymers as well as determining the appropriate analytical methods in order to examine these changes. This adds to the limited forensic study of polymers by broadening the polymer types and soil environments beyond what was commonly examined in these studies. This allows for more information about the nature of a clandestine burial as well as the possible identity of the perpetrator to be gathered.

8.2 Recommendations for Future Studies

While a range of controlled variations of the different soil environments were covered, additional environments have been identified as worthy of study. A study of the processes in a warm environment will provide additional insight into the microbial degradation and hydrolysis mechanisms proposed in the current study. The unusual effect that the sand environment had on polymer degradation warrants further analysis.

An important finding of this study was the influence of additives in polymeric materials on the degradation process in soil environments. There are many different commercial additive products used during manufacture and so the composition of polymer products can significantly vary. Additives of different chemistry have the potential to interact with the soil environments differently to the additives in the polymers investigated in this study. A wide ranging study of polymer additives in burial environments will provide a comprehensive picture of polymer stability in the burial environments of interest.

Although the focus of this study has specifically been on the influence of soil parameters on the preservation or degradation of the synthetic materials of interest, a next step was to investigate how these processes are impacted by interaction with the decomposition products that result from the decay of human remains. A study currently being undertaken at the University of Technology Sydney has shown that body decomposition fluids influences the state of preservation of natural textile materials. This demonstrates the importance of considering the influence of biological agents on the stability of grave goods.

This study investigated various factors commonly found in soil environments and the effect these have on the degradation of five common polymers. This study was successful in determining the effect that the laboratory controlled environments had on the polymers. This has led to a greater understanding of the mechanisms behind polymer degradation in various soil environments and allows forensic investigators to gather more information from the polymers about the burials. It was also established in this study the analytical methods that provide the most useful information about the impact the environment has on buried polymers.

Appendices

Table 8-1 Moisture content of the soil environments over 24 months

	Time (Months)								
Environment	0	3	6	9	12	15	18	21	24
Loam	5	5	5	4	4	6*	6*	5	5
Sand	2	2	2	2	2	2	2	2	2
Clay	2	2	2	3	3	3	3	3	3
Lime	2	2	2	3	3	3	3	3	3
Cold	5	5	4	5*	5	4	6*	5	5
Dry	1	1	1	1	1	1	1	1	1
Wet	10	10	10	9	10	10	10	10*	10
Acidic	7	6	8*	7	7	6	7*	6	6
Basic	7	7	8*	6	8	7	7*	6	6

*Added distilled water

Table 8-2 pH changes to the soil environments over 24 months

	Time (Months)								
Environment	0	3	6	9	12	15	18	21	24
Loam	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Sand	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Clay	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Lime	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Cold	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Dry	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Wet	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Acidic	3.5	3.0	4.0	5.0**	4.0	4.0	4.0	4.0	4.5
Basic	7.5	8.0	7.0*	9.0	7.5*	8.0	8.0	8.0	7.5

*Added lime to increase pH

** Sulfuric Acid added to decrease pH

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